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Research Paper

The Role of Nanotechnology in Proton Exchange Membrane Fuel Cell and Microbial Fuel Cell: The Insight of Nanohybrid

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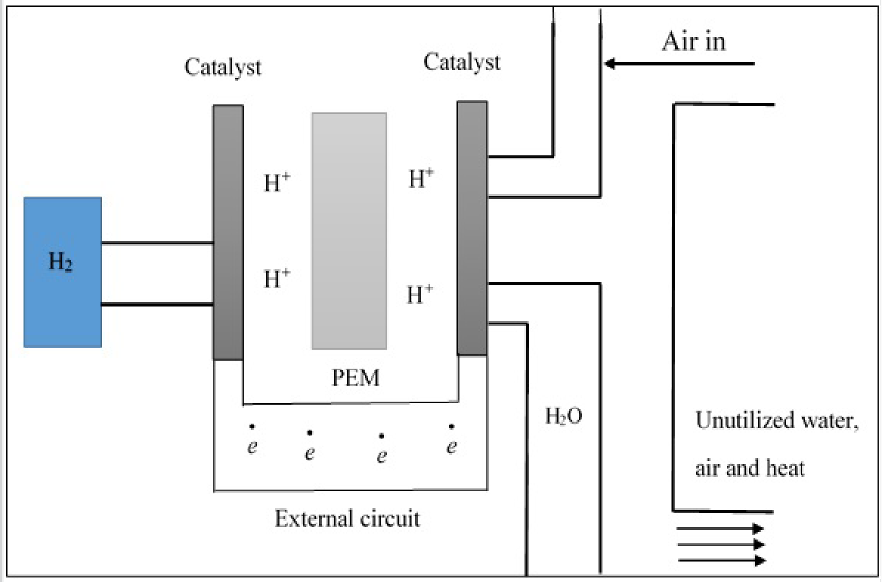
- Proton exchange membrane fuel cells.
- Membrane electrode assembly.
- Microbial fuel cell.
- Nanotechnology in fuel cell technology.
- Enhancement of nanocomposite membrane for fuel cell technology.
- Role of nanotechnology in PEMFC.
- Role of nanotechnology in MFC.
- Future prospect of PEM and MFCs: The Insight of Nanohybrids.

Graphical abstract



Abstract

The utilization of proton exchange membrane (PEM) or polymer electrolyte membrane fuel cell (PEMFC) and microbial fuel cell (MFC) is attaining prominence for the production of energy; however, these technologies come with their challenges like the cost of platinum catalyst, which is fifty percent of the total budget of the technologies. Here, the role of nanotechnology in proton exchange membrane and microbial fuel cells is reviewed. Remarkable exploits have been committed to the use of nano-materials to synthesize catalyst that are earth-abundant as an alternative to -platinum catalyst. The design of these nano-materials must be intentional for the attainment of very large surface areas. In the quest of making fuel cells affordable, researchers have focused their attention on designing nanomaterials that will make fuel cells cost-effective. The outstanding chemical characteristics in addition to the physical characteristics of these nano-materials have resulted in all-encompassing investigations targeted at enhancing the performance and cost-effectiveness of fuel cells. The application of nano-materials has also been extended in areas such as PEMFC and MFC, by incorporating the nanomaterials in the membranes and electrodes for the purpose of enhancing the performance of the fuel cells. The future prospects of proton exchange membrane and microbial fuel cells in the light of nanohybrids discussed showed that nanohybrids yields outstanding mechanical properties together with chemical steadiness; increased selectivity and proton conductivity; increased electron transfer efficiency and the highest capacitance; increased output power density and the transference of charge; and upsurge kinetics of the electrodes which will enhance power production.

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1. Introduction

The consumption of energy worldwide, is anticipated to upsurge by 56% by the year 2040 owing to several factors like swift urbanization and population growth [1]. For the purpose of responding to the ever increasingly universal demand of energy, quite a number of substituted energy technologies have been proposed. Fuel cell (FC) technology is considered one of the substituted energy technologies that has attracted great attention [2]. In this current century, the essential need of this moment is an environmentally protection power generation, this need has stimulated widespread research on the technologies for the conversion of energy like fuel cells [3]. The transformation of chemical energy to electrical energy is facilitated by all fuel cells, given rise to direct current (DC) electricity.

Fuel cells are devices used to generate electricity by means of oxidation-reduction chemistry. A fuel cell is made of an anode and cathode. The site in the cell where the fuel is oxidized, is the anode. The oxidation denotes the loss of electrons, and the released electrons from this substrate are moved onto the anode in the fuel cell. These electrons travel into the cathode via the means of electrical connections. The site where reduction, the gain of electrons, occurs to the oxidant is called the cathode. The generated positive ions in the anode compartment generally travel into the cathode via an ion penetrable membrane which completes the process of electrical circuit [4]. The PEM is a main component in the fuel cell system. This component operates as an electrolyte that involves the transference of protons from the anode to the cathode. The membrane functions as a barricade to the passageway of electrons amid the electrodes. Though, the lack of proton conducting membranes has hindered the breakthroughs for more advanced fuel cell technology. However, the elevated energy density, less corrosion glitches and lesser operational temperature will enable fuel cells to be potential technologies for numerous uses [5].

Fuel cells have the capacity to yield the highest percentage of electricity of any combined heat and power (CHP) technology. They are a pliable, commutable technology that possess the capacity to be upgraded without difficulty from serving different homes, individually to serving huge office blocks and facilities in the industries. Though some systems are exclusively made from a well-drawn plan for the purpose of producing electricity; however, the most constant usual use is CHP, which can offer outstanding high efficacy of about 95%. Furthermore, it has the potential to reduce its reliance on central based produced power, possibly redeemable on the cost of electricity and emissions of carbon [6]. When compared with conventional energy generation technologies which are solely dependent on fossil fuels, fuel cells possess numerous remarkable benefits over orthodox technologies [7]. For example, when compared with combustion engines, fuel cells have the capacity to function at greater efficacies. Furthermore, they have the potential to directly turn the chemical energy in the fuel into electrical energy providing efficacies beyond 60%. In addition, fuel cells possess lesser, sometimes, no emissions. Hydrogen fuel cell only releases water; and this addresses serious climate defiance. Furthermore, air contaminants that generate smog that give rise to well-being glitches at the operational point no longer exist. These technologies are noiseless in the course of operation because they possess lesser parts in motion [8].

It is of the fact that the advancement of green technologies such as fuel cell is needed on account of the zero emission they possess and they are considered effectual technologies used for producing electrical energy [9]. However, in spite of all the advantages of fuel cell technologies, these technologies however, have their own challenges. The budget for a fuel cell construction and sturdiness are the two major challenges that stand as restriction to fuel cell commercialization. Nonetheless, obstacles differ and is dependent on the application in which the technology is employed. For commercialization, the sizes of structure need to be considered for different applications; because the exceptional performance for fuel cell technology application is usually instituted in diverse sizes. These sizes range from minute - scaled grid linked micro joint power heat and power units for household usage, to off - grid backup power systems that provides continuous power supplies to censorious infrastructure, and to major power for structures, even to megawatt - scale installations designed as grid - linked to power stations [10]. Studies have shown that FC systems possess the prospective capability for energy densities of >500 W-hr/kg, >500W/kg and >400 W-hr/liter, >200 W/liter. This magnitude of performance allows FCs to be more striking as high-power density and high-energy density sources for planetary rovers, space science probes and other payloads [11]. Hence, the high energy density is to be considered for a high-quality FC technology. With regards to the weight, PEMFCs are moderately small and they are light-weight which is determined by the power density [12].

Hence, this review is conducted to discuss the role of nanotechnology in proton exchange membrane fuel cell and microbial fuel cell. The future prospects of these fuel cells will also be discussed by looking at the insight of nanohybrids. These two fuel cells are chosen for this review because of their uniqueness over other categories of fuel cells. (1) PEMFC is unique because it is cost effective, it has possessed the advantages of functioning under low temperature, fast start-up, high efficiency, low emissions and environmental pollution [13]; (2) MFC is unique on account of its eco-friendly and self-sustainable technology to generate energy from waste material.

2. Proton exchange membrane fuel cells (PEMFCs)

Currently, PEMFC is a prospective technological advancement that is an upcoming high-tech development with potentials, targeting uses in stationary, automotive, and compact power production employing hydrogen as fuel. In PEMFCs, the main element motivating electrochemical reactions for the production of power is the electrocatalyst [14]. In this technology, the processing of hydrogen fuel takes place at the anode. At the anode, electrons are detached from protons on a platinum catalyst surface. In the cell, the protons are transmitted across the membrane to the direction of the cathode while electrons proceed in an external circuit, producing the electrical output of the cell. An additional valuable metal electrode combines the proton and electrons with oxygen on the cathode side which is employed to produce water, is alone ejected as waste material. Oxygen could be supplied in a decontaminated form or directly eliminated at the electrode from the air [15]. The membrane electrode assembly (MEA) is known as the imperative element of PEMFCs as it is an ordered heap of an anode gas diffusion layer (GDL), a cathode catalyst layer (CL), an electrolyte stratum, an anode CL and a cathode GDL. The thickness of a typical GDL is in the range between 100-400 µm [16, 17], while the distinctive porosity is in the range between 0.6-0.9 [17], and the distinctive pore size of the membrane that is allowed and acceptable to move the protons from anode to the cathode varies around 10-100 µm [17]. Hence, PEMFCs can be viewed as an ordered piling of functioning stratums, in which the GDL portraits an imperative role, physically and electrically joining bipolar plates and catalyst layers, providing a means for the diffusion of gas and drainage and offering the membrane electrode assemblies mechanical support [18]. All the mechanisms describe here are shown in Fig. 1 [19]. The three basic electrochemical reactions that takes place at the same time on the two sides at the membrane electrodes, MEA, of the PEMFCs are represented by equations 1-3 [20].

Equation 1 represents the anode reaction, equation 2 represent the cathode reaction and the all-inclusive equation is given by equation 3.

$$2H_2 + 4nH_2O \rightarrow 4H^+ \cdot nHO_2 + 4e^- \quad (1)$$

$$O_2 + 4H^+ \cdot nH_2O + 4e^- \rightarrow (n+2)H_2O \quad (2)$$

$$2H_2 + O_2 \rightarrow 2HO_2 \quad (3)$$

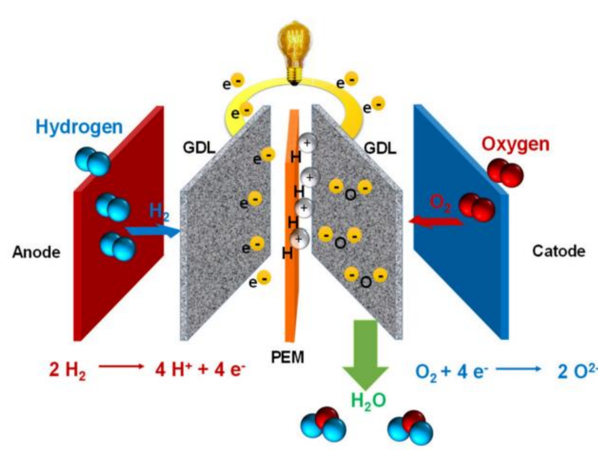

Fig. 1. Diagrammatic illustration of the PEMFC (for single components) [19] (Permission granted by MDPI).

The most frequently utilized catalyst at the cathode and anode for proton electrolyte membrane (PEM) is platinum (Pt); it is an extremely expensive and infrequent element on earth. As a result, its application should be carefully accomplished and more skillfully [21]. Hence, fuel cell technologies (particularly proton electron membrane technology) employ platinum as a catalyst, which an expensive component in the fuel cells [22]. In addition, this catalyst displays the lowest overall potentials for the reaction of oxygen reduction and the reaction of hydrogen oxidation respectively, at the cathode and anode, demonstrating the maximum steadiness [14]; however, it is very expensive. In addition, the superb imperative reaction in PEMFC is the oxygen reduction reaction (ORR) which is dependent on Pt catalyst. As a result, an upsurge in Pt loading subsequently result in an upsurge in ORR rate which in turn provides additional power output. However, should there be a little stacking of Pt, then power output will decline. Nonetheless, literature has documented some studies and some are still on going on how to upsurge the rate of ORR in PEMFC via little Pt catalyst stacking either through the modification of Pt with other metals to synthesize an alloy or totally finding an alternative to Pt with other potential metal [21].

Furthermore, Carbon black is conventionally employed as the bearing material on account of its excellent electrical conductivity and large surface area, which subsequently benefit the swift electron transportation at the electrodes, together with reduction in the dispersal of Pt particles to integrate into its surface. All these advantages of carbon black ensued with the intention of boosting the overall efficacy of fuel cell. However, several investigations have documented the subject of degradation performance over an extended operational space of time of PEMFC which consequently contributed to the reduction in the energetic site density of the catalysts. This problem is connected to the manifestation of Pt migration, Pt dissolution and Otswald development on the surface of the electrode ensued from carbon bearing corrosion in the PEMFC milieu in the course of an extended operations [14]. It is therefore essential to seek an alternative catalyst to platinum such as the ones made from nanomaterials which will subsequently reduce the cost of fuel cell. The size of the structure, weight, thermal and the management of water are other challenges that serve as restriction to the commercialization of fuel cell technology. Due to the size of fuel cell, it is imperative to research on the size reduction and weight for portable applications.

3. Microbial fuel cell (MFC)

MFC is another kind of fuel cell technology that involves the conversion bio-convertible substrates to electricity by using biocatalysts [23]. MFCs possess some benefits when compared to other technologies employed for energy generation from organic material. The primary advantage is that, the straight forward transformation of substrate into electricity enables extraordinary transformation efficiencies. Subsequent advantages are (1) they efficiently function at immediate surroundings temperature; (2) treatment of gases produced in the cell is not required; (3) extra energy to expose the cathode is not required because it has the capacity to be passively aerated; (4) they have the prospect of applying them in unpopulated regions devoid of electrical structure, enabling them to be a supplementary renewable energy choice to fulfil the demand of energy obligations, worldwide [24, 25]. This technology uses bacteria as catalysts to oxidized organic and inorganic material for the generation of energy [26]. It is well used for the treatment of wastewater in parallel with the production of electricity [27]. Several factors such as electrode spacing, bacterial composition, electrodes, media, flow patterns, conductivity of solution and type of membrane are known to have impact on the efficacy of MFCs [23, 28]. In addition, chemical substrate, material employed for proton exchange (or void of this material), permeability of proton exchange membrane, cell interior and exterior resistance, solution ionic strength also affect the performance of MFCs. An electrode material with the capacity to highly performed is the utmost important among these factors. The anode is also an imperative factor that impact on the performance of MFC and it is usually the restraining factor for an elevated power output. Anode material and its structural configuration may influence the bacteria bond, the transference of electron and the oxidation of substrate directly [26]. Hence, the membrane ought to have the protons transmission capacity from the anode to the cathode parallel to the perversion of the transmission of other materials [26].

Recently, there been significant improvement in MFC technology. One of the improvements is to lower sonic pollution as this technology has no mobile parts. With the intention of enhancing the output power efficiency of MFCs, researchers have paid attention to anodic and cathodic materials [28]. In terms of correlating cathode to anode, anode function is imperative in attaining high power efficiency and microorganisms take part in the imperative functions in anode chamber and the electrons produced. The generated electrons are employed to lessen the electron acceptors in cathode as soon as they moved across the exterior circuit. In the same vein, for the circuit produced to be completed, protons have to bore into PEM from anode to the cathode [29]. It is vital to take into consideration that the incorporation of microbial biomass is reliant on the nature and structural configuration of the electrode material to transfer electrons (see Fig. 2). In addition, it also has some short comings like, high mass generation and high cost. Additional challenges it encountered are augmented advancement and real-world application [30].

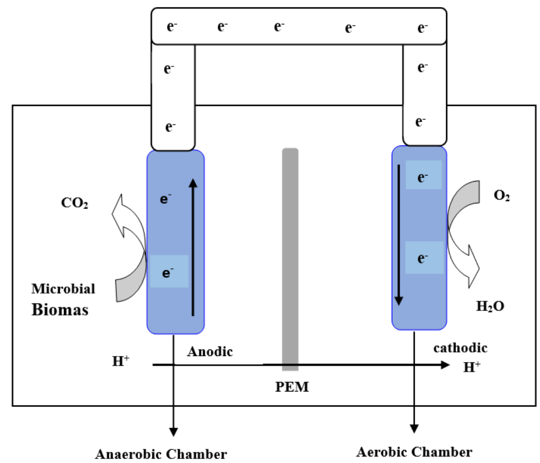

Fig. 2. Diagrammatic illustration of the components of MFC: PEM, a cathode and an anode.

In MFCs, several types of materials like carbon-based materials, Teflon treated carbon fibrous paper, platinum, graphite and polytetrafluoroethylene (PTFE) based composite have been employed for anode electrode. These materials are responsible for steadiness to the inoculums of biomass and improve steadiness of the electrode, which subsequently upsurges the efficacy of MFC [30]. Nonetheless, anode electrode that are supported with carbon materials are connected with some downside such as the fact that the carbon electrode electric conductivity varies, which is lower when compared with metal, despite their significant advantages [31]. The improvement in electrode resistivity leads to the reduction in cell voltage and reduction in the system power, which sequentially have influence on the MFCs electrochemical performance [30]. The modification of anode electrode can aid in stimulating MFCs performance; hence, the use of nanomaterials could help in combating most of the drawbacks of MFCs, if not all. The role of nanotechnology in MFCs will further be discussed.

A classic MFC is usually encompasses of dual chambers, an anode and a cathode, which are parted through the medium of PEM membrane. Electrons are conveyed from the anode section to the cathode section via exterior circuit [32]. At the exterior circuit, they are amalgamated to the formation of water via protons and oxygen as depicted in Fig. 2. Protons made in the anode chamber move into the cathode by means of PEM and it is responsible for completing the electrical circuit. The generated electrons at the anode site travel to cathode chamber and transmit onto oxygen in accordance with Equation 4 [29]. The radical oxygen and the positive ions produced in the anode take part in the reaction as shown in Equation 5 for the formation of water which outspreads through the means of the ion permeable membrane on the cathode with the aid of the catalysts. The cathode is the site where reduction and electrons gain occurs to the oxidant [4].

$$H_2 \rightarrow 2H^+ + 2e^- \quad (4)$$

$$O_2 + 4H^+ + 4e^- 2H_2O \quad (5)$$

Furthermore, the mechanism of reaction plays a significant role on the MFCs performance. The molecular oxygen reduction is considered the vital reaction in life processes, this also includes biological respiration [33]. ORR has dual passageways in acidic and alkaline based aqueous solutions [33, 34]. (i) Decrease through four electrons from O_2 to H_2O and (ii) Decrease of O_2 to hydrogen peroxide (H_2O_2) through dual electrons ORR for the acidic electrolytic solutions. The mechanism of ORR for the electrolytic solutions are represented by equations 6-8 [34].

$$O_2 + 4H^+ + 4e^- \rightarrow H_2O \quad (6)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (7)$$

$$H_2O_2 + H^+ + 2e^- \rightarrow 2H_2O \quad (8)$$

While mechanism of ORR for the non-electrolytic solutions are represented by equations 9-11 [34].

$$O_2 + H_2O + 4e^- \rightarrow 4OH^- \quad (9)$$

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad (10)$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad (11)$$

For fuel cell/MFC application, the four-electron pathway is preferred. When the four-electron pathway occurs in the course of the reaction, the catalytic activity upsurges. The two-electron pathway happens to be uncompleted oxygen reduction resulting in the reduction of the energy conversion efficacy and creation of intermediates and free radicals, which can be damaging [34]. Should carbon electrodes be employed as cathode such as MFCs, two uninterrupted electron reactions prevail with H_2O_2 intermediate production. The mechanism of oxygen reduction is dependent on quite a number of parameters like the nature of electrode material, the current density and pH [35].

The species and the concentration of the oxidant (electron acceptor), the ease of use and accessibility of proton, catalyst efficacy, and the structural configuration of electrode together with its catalytic capacity impact the cathode reaction yield. Hence, catalyst is required in anodic and cathodic reactions. It should be taken into consideration that a suitable catalyst could lessen the activation energy and improve the reaction rate; hence, the employment appropriate catalyst is very vital in this technology [36]. For an often-employed abiotic catalyst, platinum is usually utilized due to the cathodic reaction. However, as a result of its exterminating reactiveness in the direction of some substances in the substrate solution, platinum cannot be considered a suitable catalyst in MFCs [37] and besides, it is very expensive. Oxygen is the utmost frequently utilized electron acceptor in the cathode section as a result of its extraordinary oxidation capability and the certitude of its production of clean water at the end of reduction [32]. Nonetheless, literature have shown that the oxygen bestows to the cathode section consume a lot of energy [38]. Hence, the utilization of substituted electron acceptors might possess the ability to upsurge the power production and lessen the operational expenses; in the same vein, it can however, extends MFCs scope of application. In addition, it is also crucial to find an alternative catalyst to platinum like the ones made from nanomaterials which will subsequently bring down the budget of MFCs.

4. The role of nanotechnology in fuel cell technology

Nanotechnology is regarded as the manipulation of matter close to the atomic scale to bring about novel structures, materials and devices. The employment of materials with diverse structural configuration at the nanoscale ranges between 1 to 100 nm. Several nanomaterials/nanofillers possess diverse diameter size as depicted in Fig. 3 [39]. In addition, the ranges and properties of nanomaterials/nanofillers is shown in Table 1. The properties of these nanomaterials vary depending on their composition, method of synthesis, size, shape, and structure. Nanomaterials properties, particularly nanoparticles, display some form of change as their sizes gains energetic thrust. In view of their nano-sized measurements, nanomaterials like nanoparticles; and carbon nanotubes, nano-sheets, and nanofibers revealed unique chemical and physical characteristics [40]. The utilization of many nano-sized additives like cross-linkers, fillers, carbon-based materials and plasticizers are on the increase because of their imperative role in synthesizing polymer nanocomposite, for exclusively improving the functional behavior, structural configuration, and ultimate efficacy of nanocomposites in a wide-ranging use [41].

The integration of these diverse nano-additives like zirconium dioxide, zirconium phosphate, silica, titanium dioxide and metal-organic frameworks, etc., into the diverse polymer matrix like sulfonated poly (ether etherketone), Nafion, and biopolymers with the inclusion of chitosan and polyvinyl alcohol have been evaluated in the literature having the characteristic of proton conductivity, oxidative steadiness, mechanical steadiness and power density [9]. For example, PEMFCs have greatly fascinated increasing consideration owing to their elevated efficacy when likened to other kinds of fuel cells. The utmost frequently utilized polymer used in synthesizing membranes for PEMFCs is Nafion. Different ranges of nanoparticles with diverse attributes and sizes could be combined with a Nafion matrix to generate a novel categories of nanostructured electrolyte membrane with stimulating physical properties [42]. Hence, this technology (nanotechnology) offers potentials scientific advancement in several sectors like energy, medicine, water treatment, transport, consumer products, materials, and manufacturing.

4.1. Nanotechnology: An enhancement of nanocomposite membrane for FC technology

The mode of FC operation is a single unit mode; hence, every material and component in this technology is very imperative. The reason of the importance of every material and component is to avoid any kind of defect in the material and component which can subsequently impact any of the parameters; and following the 1st law of FC, an alteration in a parameter will at the least impact twofold other parameters negatively. The actions of event taking place in this technology is hinged on both materials and component together with the functioning parameters. Gas diffusion stratums, electrolyte, electrodes, and bipolar flow plates are the focal components of this technological know-how [43]. The electrolyte, electrodes and the gas diffusion stratum are occasionally assembled together; and named the Membrane electrode assembly (MEA) [43, 44]. Hence, the common factors that aid a successful performance of fuel cell like PEMs are elevated proton conductivity, low electronic conductivity and the transportation of water via the means of diffusion and electro-osmosis, low penetrability to fuel and oxidant, oxidative and hydrolytic steadiness, excellent mechanical steadiness, competency for synthesis into MEAs and low cost [3]. As a result of the substantial portion of absorbed water onto the membrane, mechanical steadiness and the transportation of water turn out to be main concerns. Developing systems with conducting proton with slight or devoid of water is possibly the utmost obstacle for making novel membranes [3].

Table 1
Size ranges and properties of nanomaterials/nanofillers.

Nanomaterials	Size range	Properties
Single walled carbon nanotubes	2-3 nm	Nontoxic, outstanding electrical conductivity, exceptional thermal and optical properties,
Multi walled carbon nanotubes	7-100 nm	High electrical conductivity and tensile strength
Graphene nanosheet	1 - 14 nm	Outstanding mechanical flexibility, biocompatibility, high electron mobility, and exceptional plasmon properties
Molybdenum disulfide nanosheet	1 - 100 nm	A low friction coefficient, outstanding thermal stability and high wear resistance
Continuous nylon -4,6 nanofiber	14 -1000 nm	High weariness strength, excellent chemicals resistance and low coefficient of friction
Crystalline nanofiber of polyethylene	30 - 50 nm	Low stiffness and strength
PET nanofiber	35 - 100 nm	Chemical resistance and recyclability
Ultra-fine PVA nanofiber	20 - 2550 nm	Exceptional tensile strength and elongation properties
PANI nanofiber	20 -50 nm	Anti-corrosion, high electrical and exceptional sensing properties
Metal oxide nanoparticles	6 -100 nm	High surface area and excellent optical properties
Metal nanoparticles	1 -100 nm	Exceptional interaction with light, high surface area, outstanding mechanical strengths, Outstanding optical properties and excellent magnetic properties

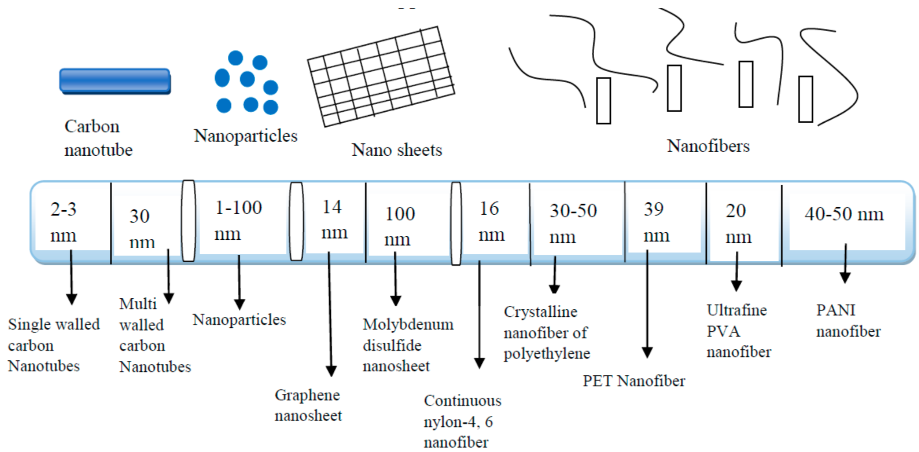

Fig. 3. Schematic illustration of diverse sizes of nanomaterial. There is an alteration in the properties of nanoparticle as it approaches nanoscale [39] (Permission granted by MDPI).

Hence, in this context, membrane is well-thought-out to be the most vital component in the PEM and in FCs, generally. Based on its importance, membrane is employed for classifying fuel cells. By the way of illustration, proton electrolyte membrane is being utilized for PEM fuel cell [45]. Novel membranes with a considerably minimal methanol penetrability and transportation of water (via electroosmotic drag or diffusion) plus satisfactory conductivity and steadiness are needed for direct methanol fuel cells (DMFCs). Diffusion of methanol by the use of the membrane should not drop the efficacy of the voltage and the efficacy of fuel cell. Furthermore, the sophistication and the resistivity of membrane would be boosted, with lessened energy density, by the means of the utilization of methanol in a diluted state the fuel. Conductivity and water uptake of the membrane both hinged on the ionic group concentration. Ionic groups possessing high density should be avoided because of excessive membrane swelling, which will subsequently deteriorate the mechanical stability and durability of the membrane [3]. Thus, the design and synthesis of organic-inorganic nanocomposite PEMs through the integration of nanomaterials appears to be enticing in combating the challenges of membranes employed in FC.

Additionally, the addition of nanofillers into these membranes made the polymer nanocomposite membranes and they are most preferred because their constituent materials are low-cost, ecofriendly highly efficient materials in terms of energy. Polymer nanocomposite is a relatively novel material that provides an alternative to conventional blends of polymers. Hence, polymeric nano-composite membranes are synthesized via the incorporation of nano-sized fillers in the polymer matrix to improve performances like high permselectivity, rigidity, thermal stability promising surface morphology owing to outstanding fouling resistance in comparison with the pure polymeric matrix membranes [45]. A crucial property of polymer nanocomposites lies on the fact that the minute size of the nano fillers resulted in an intense upsurge in interfacial area when compared with conventional composites [3, 46]. Studies have revealed that the area of nanomaterial polymer matrix interphase has extremely upsurge on the account of intrinsic high surface-to-volume ratio that subsequently results in extraordinarily improved features. The application of these novel materials has been extended in several researches like PEMFCs, electroluminescent devices and memory devices, etc. PEMFCs denote a prospective technology for the generation of electrochemical energy in recent times owing to their improved efficacy and their nature of been friendly to the environment. Proton exchange/PEM has an important part to play in the PEMFCs [47].

Hence, the rapid attention in designing and synthesizing novel nanocomposite proton exchange membranes (PEMs) that will offer enhanced functional achievement for high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) and DMFCs. Nanocomposite membranes assists in increasing the mechanical steadiness of the PEMs via the amalgamation of more polymer stratums, most specifically with a firm grip stratum [9]. Nanofillers like graphene, graphene oxide (GO) and carbon nanotubes (CNTs) including the nano-additives are novel fillers used for synthesizing different range of nanocomposite PEMs. The integration of these nanofillers offers exceptional structural configurations possessing high surface areas together with additional passages for proton transference; furthermore, it boosts the mechanical properties and the proton conductivity of the nanocomposite PEMs [48]. In addition, the advancement in developing instinctive, biodegradable polymer-based PEMs possessing an improved proton conducting capacity together with chemical steadiness can only be possible on the account of a well-designed nanocomposite membranes; this will otherwise be impossible. Some particular hygroscopic inorganic additives enhanced the capacity of water uptake of the nanocomposite membranes even at much higher temperatures. Literature have recorded researches on nanocomposite membranes that have the capacity to matched up with the sought-after characteristics of PEMs for fuel cell uses [9], especially for the reduction of cost.

Researchers from numerous laboratories all over the world have put in so much effort into synthesizing an innovative polymer electrolyte membrane that possess high proton conductivity, highly durable, enhanced thermal steadiness, extraordinary peak power density (PPD), and a reduced fuel crossover that is not expensive. In the pursuit of coming-up with cheaper but well-functioning fuel cells, some researchers, that include scientists from Indian, China and the UK, might have discovered a less expensive alternative to Pt catalyst, which is very vital for fuel cells to operate well. These scientists claimed that the catalysts they synthesized from zirconium nitride nanoparticles might possibly be a high-functioning substitute to Pt catalysts for utilization in FCs and metal-air batteries. There might possibly be more less expensive and effectual fuel cells in the market in future should their discoveries in the lab be made to be practically employed into real applications [49]. Another group of scientists in the USA recently developed and studied fuel cell catalysts-chemicals that do not use platinum, but however, speed up important fuel cell reactions. Their research made available a good comprehension of the mechanisms that make these catalysts effective and this novelty provided information on more efficient and cost-effective catalysts. According to these researchers, an extensive, workable profitability of fuel cell electric vehicles needs either much more decrease in the quantity of Pt needed or to find an alternative catalyst that are earth-abundant, inexpensive materials such as iron which will replace platinum catalysts [50]. Apart from the benefit of low-cost obtainable from platinum free catalysts, Platinum nanoparticles have a tendency of losing catalytic efficacy through aggregation into bigger particles in the course of time or through the sticking of carbon monoxide to their surface. CNTs are more solidly built in an extended course of time [51]. The following subsection will discuss the role of nanotechnology in nanocomposite membranes and electrodes for different fuel cells.

4.2 The role of nanotechnology in PEMFC

PEMFC has enticed great attention for application in distributed power generation due to their exceptional efficacies, elevated power density, possessing the benefit of functioning at lower temperatures. PEMFC has contributed so much in sustaining energy; nonetheless, the main challenge encountered with this fuel cell is catalyst degradation and the platinum nanoparticles and carbon black (Pt/C) electrocatalysts that are mercantile obtainable are prone to Pt dissolution and carbon support corrosion [52]. The degradation of catalyst in the ORR electrode is ensued from the poor sturdiness of PEMFC. Catalyst degradation instigated by means of the corrosion of carbon supports and platinum dissolution in the course of fuel cell operation conditions results in an wide-ranging degradation performance FC [53]. Hence, extremely steady electrocatalysts are needed to upsurge PEMFC extended performance period. Hitherto, the electrocatalysts utilized in PEMFCs that are mercantile available were hinged on Pt nanoparticles (Pt) and carbon black supports. However, researchers are working tirelessly to find solutions to all these challenges.

Zeng et al. [54] designed and constructed a nanostructured membrane MEA centered on Pt/Nb_2O_5 nanobelts (NBs). The fastest sturdiness test pointed out that the Pt/Nb_2O_5 NBs-built MEA was considerably highly steady than orthodox Pt/C-built MEA. Ding et at. [55] designed and synthesized even TiN nanotubes which was further modified with Pt nanoparticles. The fastest sturdiness test pointed out that the improved activity was accredited to the robust interaction that exist in-between the Pt nanoparticles and the TiN support. Daudt et al. [52] fabricated a Pt-NbOx catalyst built on TiN nanoparticles as a substitute to electrocatalyst such as platinum catalyst, for the ORR. The utilization of Pt-NbOx resulted in costs reduction of the material via lowering the needed Pt stacking and enhancing catalyst functionality. The TiN support was chosen to enhance support steadiness. The novel electrocatalyst provided highly functional ORR that was equivalent to the futuristic Pt/C electrocatalyst.

Apart from the much more reduction in the quantity of platinum needed PEMFC or to finding an alternative catalyst that are earth-abundant, inexpensive materials, nanocomposite membranes are employed for PEM fuel cells to enhance its performance. The design and synthesis of nanocomposite membranes that are more stable with the integration of nanofillers in them can enhance the stability of existing membranes used in fuel cell; and this could be one of the strategies for PEMFC commercialization. Promising results have ensued from the integration of hydrophilic inorganic metal oxide particles, on account of their tendency to accommodate water and acid in their interlayer area which subsequently result in been more hydrophilic or more permeable to water [56]. For example, investigations have discovered that the integration of inorganic particles, owing to their high surface area, enhances the water uptake and proton conductivity of Polyvinyl acetate (PVA) polymer electrolyte membranes. Wu et al. [57] synthesized Polyvinyl acetate-silicon dioxide (PVA-SiO_2) anion-exchange membranes via through sol-gel process. Membranes cross-linked using 25% poly (GMA-co-γ-MPS), heated at 120℃ exhibited promising hydrophilicity (water uptake, W_R, ranging between 64-151 percent) together with tensile properties. Hooshyari et al. [56] synthesized PVA/ $La_2Ce_2O_7$ (PVA-LC) membranes with elevated proton conductivity for PEMFC. The outcomes obtained demonstrated that the proton conductivity and the membranes water uptake were more when likened with the PVA membrane.

In addition, substantial advancement has been attained in the evolution of nanomaterials for the purpose of enhancing the performance of polymer electrolyte membrane FCs. Nanomaterials are utilized for the improvement of substance behavior through shifting physical properties. FCs with integrated nano/nanocomposite-structured components possess green emissions, extended sturdiness, and higher current density which are cost-effective in comparison to regular commercial fuel cells [58]. Hence, the utilization of nanotechnology has turned out to be a vital trend in PEMFC because nanotechnology is well adapted with outstanding performance in the PEMFC process [59]. Nevertheless, because the structure of PEM fuel cell comprises of four principal parts; bipolar plate (BP), CL, PEM, and GDL; different studies concentrate on either one or two of these principal parts to study the performance of PEMFC. For a certain porous GDL or CL, the saturation levels primarily affects the capillary pressure, which subsequently governs the mass transport resistance and the whole performance of PEMFCs by employing the operating condition of elevated current density [60]. Table 2 depicts recent publications that studied different types of nanomaterials used for different principal parts of PEMFCs for the improvement of their performances.

4.3 The role of nanotechnology in MFC

At the moment, MFCs are less complex and enhanced through the modification and optimization of the designs [68], nor their components like eradicating the cathode chamber using air breathing cathode for producing electricity [68, 69]. Components such as bacterial organisms by improving the bacterial adhesion [70], electrode materials [71] together with the electron transfer along with the electrode surface are modified [70]. Furthermore, electrode spacing [72], and using different novel polymer electrolyte membranes are also used in enhancing MFCs performance [73]. However, the material used in making these membranes still benefits the oxygen crossover, which is a key draw-back [74]. Studies have shown that the existence of oxygen led to a lower production of power [75]. In addition, anode is still the main hindrance for traditional twofold-chamber MFC's extensive applications, especially with inadequate precise surface area, poor biocompatibility and expensive materials [76].

Taking advantages of the exceptional electrical properties of nanomaterials with respect to their biocompatibility, porosity and specific surface area; nanomaterials display incredible prospect in stimulating the power supply of MFCs. The Introduction of innovative anode nanomaterials is usually well thought-out and known to be an effectual means of boosting the efficacy of MFC through the upsurge of bacterial adhesion and expediting extracellular electron transfer (EET) [77]. Hence, with regards to electrode materials, more than a few scholars have recently commenced the modification of anode by utilizing diverse nano engineering methods that are capable of making the electron transfer easier. Lou et al. [76] synthesized a cost-effective material; graphene-like molybdenum disulfide (GL-MoS_2) nanoflowers that possess a crosswise size of 200-300 nm through a non-complicated one-step hydrothermal technique. These new materials were utilized for the modification of MFC anodes. The new materials demonstrated that the adjustment of MFC anodes can provide large specific surface area and an excellent biocompatibility for the advancement of biofilm. The nano materials further make the anode surface more reachable for microbes' colonization and the transference of substrate; hence resulted in a considerably decrease in polarization loss.

Table 2
Different types of nanomaterials used for different principal parts for the improvement of the performance of PEMFCs.

Nanomaterials	Principal structure parts for the study	Performance parameters	References
Gold (Au) and silver (Ag)	Pt-Ru/C catalytic layer	Decrease in performance was experienced with silver nanoparticle while a large gain of net result was experienced with gold nanoparticle.	[58]
-	Nanoscale gas diffusion layers nano	The FC showed that a higher 14% maximum power density was attained with 3-MG nano-GDL sample when compared with commercial Toray GDL devoid of cathode humidification.	[61]
Carbon nanofibers	Carbon nanofibers integrated gas diffusion layer	The microporous structured CNF/carbon paper provided an appropriate hydrophobicity.	[62]
Carbon nanofibers	Cathode catalyst layer integrated with carbon nanofiber	The membrane electrode assembly utilized had the unsurpassed performance through the integration of 1 wt% carbon nanofiber. Furthermore, the voltage upsurges to 74 mV (15.42%) at 2 A cm^{-2}; In addition, carbon nanofiber principally varies the membrane electrode assembly performance via altering the hydrophobicity of CCL, which subsequently impact the mass transport resistance.	[63]
Pt nanoparticles incorporated with vertically aligned carbon nanotubes (VACNTs) growth on Al foil	Catalyst layers	With the deposition of Pt nanoparticles on VACNTs, the cell demonstrated the utmost performance.	[64]
Nanosilica	-	There was an upsurge in exchange capacity with the incorporation of 1 %-wt nanosilica. The integration of 0.5%-wt nanosilica enhances water uptake from 79.2% to 94.9% and proton conductivity of PEM was also enhanced from 0.02 to 0.09 mS/cm.	[65]
Platinum-based nanoparticles integrated with secondary metal (iron, yttrium and cobalt) and functionalized graphene oxide	Gas diffusion layers and catalytic layer	The cathode catalyst, that governs the facilitation of the sluggish oxygen reduction reaction, was enhanced via the synthesis of platinum-based nanoparticles with the integration of the secondary metals.	[66]
Pt nanoparticles into functionalized carbon supports	Catalyst layers and gas diffusion layers	Pt/functionalized-carbon exhibited high performance via optimization of the higher ionomer content.	[67]

There are circumstances where metals like copper have been utilized; however, these metals that could corrode. Bensalah et al. [78] modified Cu anode surfaces with less expensive thin stratum together with a mechanical steady carbon nanofiber-Polydimethylsiloxane coating (CNF-PDMS). The method of modification surface was taken through an optimization technique for enhancing the interfacial electron transference of Cu anodes for utilization in MFCs. The functional capability of Cu anodes coated with diverse stratum thicknesses of CNF-PDMS was assessed in MFC. The authors found that the utmost power density attained with 500 µm CNF-PDMS around 8-times higher and steadier than that attained with unmodified Cu. This subsequently demonstrated that the modification effectively enhances the functional capability of Cu anode for MFC uses. Shetty et al. [79] synthesized a high-Performance magnesium cobalt oxide- poly(3,4-ethylenedioxythiophene) polystyrene sulfonate-nickel ($MgCoO_2$/PEDOT:PSS@Nickel) to create anode for the production of bioelectricity by means of MFCs. The study demonstrated that, by using the improved electrocatalytic activeness and biocompatibility, $MgCoO_2$/PEDOT: PSS@NF anode presented improved steadiness and porosity for the creation of compact biofilm which aided in the effectual production of bioelectricity.

Additionally, design and fabrication approaches and different modification comprising of nanomaterials have been studied for improving the power density and intensifying the competency of electron accepting heterogeneous [80]. By optimizing composition, design and fabrication approaches, structural configuration, and characteristics of the interface, investigators can now fabricate novel high-performance materials with boosted power density, and overall efficiency. For example, silicon electrodes now attracted more attention as a result of having almost ten times the power of a graphite anode. Hence, an insightful configuration designs are targeted at combating unsteadiness created by massive volumetric changes [81]. Jaswal and Nandabalan [82] employed rice husk as a basis of silica to synthesized rice husk silicon nanoparticle and established its capability as an anode modifier in dual chambered H-shaped MFC. The anode modified with silicon nanoparticles of 0.50 mg cm^{-2} respectively documented the supreme current and power density of 1.5 A m^{-2} and 190.5 mW m^{-2}, correlating to 3-fold and 7.6-fold upsurge as likened to the control. The results they obtained served as indication that rice husk resultant silicon nanoparticle are excellent anode modifiers and effectual in improving bioelectricity production.

Silicon nanoparticle have also been utilized for improving the functional capability of membranes in MFC. The membrane, which split-up the cathode chamber from the anode, has a censorious part to play in having controlling influence the mobility of proton in twofold-chambered MFC. Hence, the material used in fabricating the separator must be carefully chosen in a way that the transference of proton could be fully taken advantage of and oxygen and substrate diffusion could be decreased [83]. Angioni et al. [84] synthesized composite Nafion™-based membranes by the means of employing mesoscale silica (SBA-15), and organic-inorganic fillers attained via the functionalization of SBA-15 with SO_3H groups. The membranes were used as substitute separators in MFCs to be utilized in treating wastewater and their operational functionality were likened to standard Nafion™ 117. At the end of three months of operation, MFC depicts that the membrane integrated with 5 wt% of SBA-15 functionalized with 10 mol% of SO_3H provides topmost power density, which is thrice enhanced than the Nafion™ after three months of functioning. Raychaudhuri et al. [83] developed a cost effective MFC by utilizing a clayware ceramic separator modified with silica. The separators properties were assessed with respect to oxygen and proton diffusion. The membrane comprising of 30% silica showed enhanced operational capability when likened to the non-modified membrane. The topmost volumetric power density and coulombic efficacy were attained in MFCS-30, which were respectively 60.4% and 48.5% higher than that of MFC. MFC fabricated with modified ceramic separator gave a good demonstration of topmost power production and erasure of contaminants. Michu and Chaijak [85] integrated silica modified ceramic separator using yeast built MFC for the electricity and treatment of phenol from wastewater. The results obtained depicts the utmost power density of 0.212 Wm^{-2} and 95.05% of the removal of phenol using 0.2 thick ceramic plate integrated MFC. Apart from silicon nanomaterial, several nanomaterials have also been utilized to boost the performance of MFCs. Diverse range of performances have been documented in the literature (See Table 3).

Table 3
Different range of performances in the application of nanomaterials in MFC.

Nanomaterials	Method of synthesis	Types of chamber	Performance parameters	References
PtOx@M-TiO_2 and PtOx@P-TiO_2	Synthesized by means of a modest, green and ecologically genial process employing an electrochemically dynamic biofilm.	-	PtOx@M-TiO_2 displayed a topmost power density when likened to the PtO_x@P-TiO_2 nanocomposite	[86]
Graphite oxide (GO)	Integration of GO sulfonated polystyrene and glutaraldehyde cross-linked PVA membrane	Single chamber	Upsurged proton conductivity and the upsurged capacity of ion exchange were attained	[87]
Chestnut shell	A modest carbonization method, then an activation process followed.	-	Improved charge transference efficacy amid the surface of the anode and microbial biofilm, maximum power density	[88]
Cu-doped iron oxide	Phyto-compounds of *A.blitum* plant.	Dual MFC chamber	Enhanced peak power density, boosted potential and resistance reduction for layered anode	[89]
Carboxylated multiwalled carbon nanotube/carbon nanofibers (CNTs/CNFs)	Synthesized through the technique of electrospinning by employing heat compressing process in order to boost the fiber interconnecting aggregates and mechanical steadiness.	-	Boosted conductivity and outstanding biocompatibility, excellent	[90]
Iron oxide	Facile dip-and-dry methods	Two-chamber MFC	Indicated effectual tannery wastewater biodegradability of and an elevated electron transference rate from sulfate-reducing bacteria to the conductive anode.	[91]
Iron oxide	Iron oxide was incorporated in ceramic membranes and sintered at different temperatures	Single chamber	Increases structural porosity, pore size reduction and improved power output	[92]
Cobalt-nickel nanoparticles supported on Al_2O_3-GO matrix	-	Single chamber	Obtained maximum electrochemical activity, elevated power density, higher stability and electrocatalytic activities and topmost power production.	[93]
Fe_3O_4/Fe@C	Prepared through carbonization in argon atmosphere.	Single chamber	Demonstrated superb maximum power density, high-throughput sequencing that exhibited good biocompatibility.	[94]
Ordered porous carbon foams	Fabricated by the pyrolysis of Fe-MIL-88B-NH_2	H-shaped two-chamber MFC	Boosted bacteria-electrode charge transfer efficiency, enhanced power density of and current density.	[95]
Cobalt and Nickel nanocatalysts built on TiO_2-nanotubes	-	Single chamber	Higher stability, excellent electrocatalytic performance, boosted catalytic action having topmost power output.	[96]
Co_3O_4 nanoflowers	Obtained by calcination	-	Higher conductivity and enhanced power density were attained.	[97]
Iron oxide	-	Dual MFC chamber	Improved electricity generation and cell power.	[98]

Table 3 has shown that nanomaterials have been utilized for the improvement of different working parameters of MFC. One of the main purposes of utilizing nanomaterials for manufacturing anode is for the enhancement of the mechanisms of electron transference amid microorganisms that act as biocatalysts in the anode chamber and the material that makes the anode in order to enhance the power output. In addition, nanomaterials are used to enhance the operational functionality and efficacy of the anode, like to upsurge the surface area, upsurge the electron transference, and upsurge the production of electrical energy [99]. The selection of appropriate materials and the direct development of processing technology for the attainment of new anodes would be advantageous to the growth of microbes and electricity generation. For example, 3-D anodes with micron-scale pores will aid in the preparation of high-performance anodes [100]. Furthermore, the modification of the electrode surface by using functional materials aids in the alteration of morphology and structure [101]. Fig. 4 depicts the demonstration of functional materials used in modifying anode in MFC.

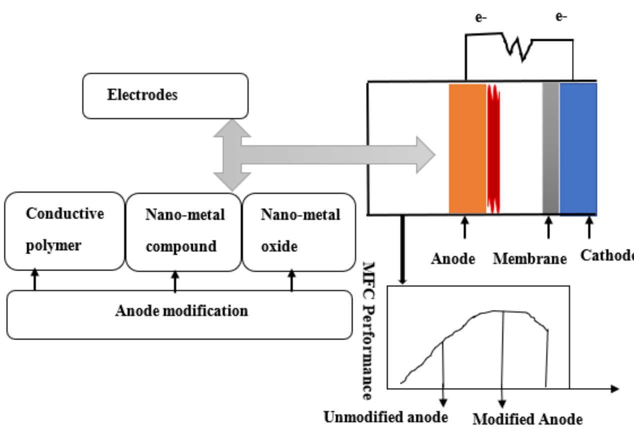

Fig. 4. A Diagrammatic illustration of the modified anode for boosting MFC performance.

The second aim of utilizing nanomaterials is to enhance cathode reactions or ORR. The third aim is the utilization of nanomaterials in the synthesis and the setting up of PEMs and their influence on the transference of proton and averting the transference of oxygen from the cathode to the anode [99]. Hence, the utilization of nanomaterials is to enhance the operational functionality of membranes in addition to their physical and thermal characteristic features via the integration of nanomaterials into membrane structural configurations, which will subsequently aid in attaining the anticipated characteristic features that will enhance the operational functionality of MFC [102].

4.4 The role of the nanomaterials towards the electrocatalyst

The role nanomaterials towards electrocatalysts in fuel cell comprises of a powerful tool in the electrochemical reaction between the oxidation-reduction chemistry; taking advantage of many nanoscale effects, like high surface area, improved conductivity, improved charge transfer kinetics, huge number of low-coordinated surface atomic sites, and favorable structure of PEM fuel cell which comprises of BP, CL, PEM, and GDL. All these advantages of nanoelectrocatalysts necessitates the development of advanced characterization techniques that probe the material at the nanoscale [103]. The advanced characterization techniques are really required because electric current have now been demonstrated to bring about the movement of the atoms in electrocatalyst nanoparticles, resulting in structural configurational alterations and the degradation of performance. This effect must be accounted for in the course of designing nanostructured catalysts for electrochemical devices [104] such as fuel cell. The key factor in altering the structural feature of nanomaterials is to have a good comprehension of the formation of their principal mechanism. This mechanism is defined by the classical Ostwald ripening, where larger nanoparticles outgrow smaller ones for the assurance of a reduction in the surface energy [105]. The description of the formation of spherical nanocrystals usually take place on account of this phenomenon [106].

In a FC technology, employing materials that are naturally porous or materials that attained porosity through modifications, attains the possibility of exerting huge control of the surface area amid the electrode and the electrolyte, subsequently enabling the construction of a quick diffusion pathway for the manoeuvre of the charge and molecules [107]. This is to guarantee that the electrochemical process will turn out to be very efficient. The surfaces of the exterior and interior nanostructured material pores interrelate with the surrounding milieu. Small pores could restrict electrolyte-ion diffusion, leading to a reduction in the kinetics' reaction rate [108, 109]. The electrode's pore structural configuration plays an integral part in its electrocatalysis. Hence, the design of a very porous material is very vital for FCs' electrochemical process for commercial utilizations.

Najja and Safadi [110] designed an experiment for the replacement of Pt particles in the PEMFC catalytic layer with an inexpensive metal like gold (Au) and silver (Ag), to examine the likelihood of fabricating a low-priced and economical PEMFC for commercial application. Although, when the platinum was replaced with Ag, the performance of the cell moderately reduced. Nevertheless, on account of the large variance in cost amid Pt and Ag, the overall outcome was a large gain, particularly in automotive engineering applications (around 10 folds). Choi et al. [111] presented a precise examination of the reactivity of oxide electrodes enhanced via the utilization of metal nanoparticle and all particles partook in the reactive examination. 10 nm in size monodisperse particles such as Pt, Pd, Au and Co, that are steady at high temperature ≨ 600 °C, were distributed evenly onto modified electrodes. The pattern of metal catalysts activation was identified and the upsurge in reaction rate was also quantified. Polagani et al. [112] employed platinum with nickel and supported on carbon (Pt–Ni/C) by means of an ultrasound-assisted route. In the fuel cell operation, the sonochemically made Pt–Ni/C nanoparticles showed high-level electrocatalytic properties when compared to the commercial Pt/C nanoparticles. Outstanding oxygen reduction and higher electrochemical active surface area were attained with Pt–Ni/C electrocatalyst. Therefore, the utilization of nanoelectrocatalysts in FCs improves the complete performance of the system. Nanoelectrocatalysts upsurge the electrode-surface area and offer the assurance of an elevated reaction rate of oxygen- reduction at the electrode [106].

5. The future prospect of PEM and MFCs: The Insight of Nanohybrids

Hybrid materials are made of organic and inorganic components homogeneously blended together [113]. Nanohybrids are materials synthesized from a blend of polymeric organic components and ceramic or inorganic components which are interrelated on a molecular scale [114]. For this reason, nanohybrids have attracted great attention in diverse fields such as adsorptive membranes for dye removal [115], especially in fuel cell technology; on account of the merged effect of the properties from each of the components blended into a single material.

Conducting polymer-supported nanomaterials are regarded as exceptional category of hybrid electrocatalysts employed for the applications of fuel cells that collaboratively offer the advantageous characteristic features of nano-scaled materials and conducting polymers as single materials [116]. Higher surface area and the metal NPs/metal oxide distinctive complementary impacts perform an imperative function in improving the electrocatalytic activity of the catalysts and to make steady the FC effectiveness in the course of operation [117]. Conducting polymers utilized as catalyst supports have shown optimistic applications as a result of their exceptional conjugated structures that offers exceptional electrical conductivity, excellent chemical steadiness, easy preparation, and they are cost effective [118]. Hence, conducting polymer-based nanohybrids (CPNHs) possessing a sequence of metal, metal oxides or metal oxides nanoparticles modified with standard wet chemistry methodologies placed on polymer surface have been utilized for electro-oxidation of small molecules like hydrogen and methanol [116, 119].

Heterogeneous attempts have been channeled to the fabrication of electrode materials through placing the nanostructured metal catalysts directly on conducting polymer surfaces or on polymer nanostructures that are already modified [120, 121]. Nanostructured materials draw attention to researchers due to their ease and precision which enables their utilization in making electrodes. With respect to electrochemical and electrical conductivity, these materials have numerous advantages such as incessant route for electrons flow; which subsequently upsurge the conductivity and kinetics of the electrodes [122].

In MFC, the modification of anode by employing a nanomaterial with multiple functions might be able to make possible bacterial adhesion and electron transference by employing either chemical or physical surface treatments approaches [123]; in addition to the upsurge the conductivity and kinetics of the electrodes which will enhance power production. However, unloaded separate nanostructured materials without support, though not all the time, suffer from a very low surface area. On account of this shortcoming, elimination of pollutants is not effectual for waste bioremediation and power production if unloaded nanostructured is employed on electrode surface as a catalyst, with or without the presence of microbes [124]. Hence, investigation on the integration of a biological unit with efficient metal, metal oxides or modified metal oxides nano-hybrid structured materials enclosed with conducting polymers should be considered in order to combat these drawbacks. For example, Zhong et al. [125] prepared a novel electrode which implanted polyaniline (PANI) in petaline NiO (NiO@PANI-CF). The power density output and the charge transference resistance were greatly increased. NiO@PANI-MFC was able to effectually biodegrade dye wastewater owing to elevated biocompatibility of NiO@PANI-CF. Liu et al. [126] coated carbon felt (CF) with manganese dioxide (MnO_2), this serves as electron intermediary in electroactive biofilm. A covering stratum of conducting Poly 3,4-ethylenedioxythiophene was further made in order to shield the MnO_2 and improve the efficacy of electron transference of MnO_2 intermediary. The hybrid bio-anode provided the topmost electron transference efficacy and capacitance, when compared CF bioanode. Hence, electrochemical reactions in MFCs can effectively gain more improvement by employing nanohybrids materials, especially, from low cost.

For proton exchange membrane, graphene oxide (GO) based nanohybrids are considered favorable for fabricating highly effective materials. GO-Nafion nanohybrids has been communicated in the literature. Nafion chains have been chemically integrated to the surfaces of GO via an atom transference radical addition (ATRA) reaction with the C-F groups of Nafion chains as the energetic locations. When likened to the neat Nafion membrane, the incorporation of GO-Nafion leads to a 1.6-folds of proton conductivity to the resultant nanocomposite PEM. Furthermore, the single cell tests on the PEM nanocomposite depicts approximately 35-40% upsurge in the effectiveness of fuel cell [127]. Carbon nanotube composite membranes have also shown higher oxidative and thermal steadiness, proton conductivity, and mechanical characteristic features in PEM. Ahmed et al. [128] synthesized composite membranes using chitosan (CS) and multi-walled carbon nanotubes (MWCNTs) for FC utilizations. CS/MWCNTs membranes depicted improved thermal and mechanical steadiness when compared to neat CS membrane on account of the robust electrostatic interaction amid the $-SO_3H$ groups of MWCNTs and the $-NH_2$ groups of CS, this possess the capacity to hinder the movement of CS chain. Al and Louis [129] used functionalized carbon nanotubes and exfoliated MoS_2 nanosheets as additives for CS, for the purpose of ameliorating the proton transference alongside the biopolymer membrane via the development of added ion-exchange site attained owing to cross-linking the CS chains by employing citric acid. The CS membrane doped with the highest percentage weight (6%) of carbon nanotubes and exfoliated MoS_2 depicts increased selectivity than other nanohybrids membranes. Covalent organic frameworks (COF) also provide the likelihood opportunity of aiding proton transport as a result of their structural benefits like ordered pore networks and tunable functionalities.

Based on its exceptional structural designability, COFs possess the capability of regulating the operational functionalities of PEMs. Meng et al. [130] uniformly dispersed COFs comprising of diverse groups like sulfoacid, pyridine, and the two groups together, into sulfonated poly (ether ether ketone) (SPEEK). The sulfoacid group significantly enhances proton conductivities. SPEEK, as a prospective PEM material, possess outstanding mechanical characteristic features and a chemical steadiness [131]. Comparable to the Nafion microphase structural configuration, SPEEK is also made of hydrophilic domains and hydrophobic domains. Zhai et al. [132] synthesized phosphotungstic acid functionalized covalent organic framework nanohybrids (P-COF), whereby the phosphotungstic acid was immobilized in the interior of the cavities of COF via the means of the chemical bonds. The novel nanohybrids expedites the swift and effective proton conduction in the Nafion/P-COF membranes, which led to boosted proton conductivity together with exceptional functionality with regards to H_2/O_2 PEMFCs in the state of low humidity. Furthermore, an outstanding operational functionality was observed in a H_2/O_2 FC, attaining the topmost power density.

All these studies have shown that nanohybrids in PEM and MFCs yields outstanding mechanical characteristic features and a chemical stability, increased selectivity and proton conductivity, increased electron transference efficiency and the highest capacitance, increased in output power density and the charge transference; and upsurge kinetics of the electrodes which will enhance power production. In addition, the anode, cathode and membranes in these fuel cells that essentially consists of nanohybrids offer improved water retention and low electron conduction across the membranes. Hence, the main function of nanohybrid membranes is to reduce the flow of electrons and upsurge the rate of ions through the membrane concurrently. Though, the decrease of the membrane resistance at low relative humidity has always caused glitches in polymer electrolyte membranes (PEMs). This challenge can however be solved if the anode, cathode and membranes in fuel cells are made of nanohybrids in order to enhance proton conductivity and a reduction in membrane thickness. Hence, a carefully designed nano hybridized PEM by incorporating nanomaterials in the anode, cathode and membranes in FCs offer a good prospect in combating the challenges of membranes employed in fuel cell.

6. The future prospect of nanotechnology towards power generation and green energy

Fuel cell is a substitute to reduce the utilization of fossil fuel with a high-level efficiency and low/zero emission [133] because of the impact of nanotechnology for high efficiency and which subsequently resulted to green energy. Nanotechnology has evidently become an optimistic frontier in the search for sustainable energy solutions, contributing to the transformative prospects that will address the crucial challenges in the generation of renewable energy, its storage, and conversion [134]. Renewable energy importance outspreads beyond environmental benefits; it further plays an excellent role in improving energy security and sustainability [135]. The incorporation of renewable energy sources into the worldwide energy mix is censorious for attaining sustainability and reducing greenhouse gas emissions. Hence, with its ability of nanotechnology to manipulate nanoscale materials at the atomic and molecular scale, provides groundbreaking advancements in green energy [134]. The surface properties at this scale, control the material's bulk properties. The electrical properties, sturdiness, strength, and activity of the materials are enhanced to bring about the attainment of desired features via nanotechnology [136].

The novelty of nanotechnology towards power generation and green energy is key because it has the capacity to offer the essential solutions to the low efficacy and expensive renewable energy systems; it hence, improve green energy technology, its efficiency, longevity and subsequently facilitating a smoother transition to a green renewable power generation. Uncommon properties and upsurged surface areas of nanomaterials offer huge prospect capable of improving renewable energy applications. For example, CNTs are prospective material for carbon-based PEMs on account of their high aspect ratio, which offers a large surface area for proton exchange. The combination of CNTs and amino groups can improve their proton conductivity and selectivity [137]. In addition, nanomaterials, with their upsurge surface areas and excellent electronic properties, are being employed as effectual catalysts [138]; hence, nanostructured catalysts are employed to upsurge the efficacy of FCs with nanomaterials that possess high porosity which is subsequently being employed for hydrogen storage. Furthermore, nanotechnology aids in the advancement of portable energy systems and large-scale systems with very high efficiency. In addition, over the past decade, notable research studies have been done to design a novel PEM, specifically on the aspect of structures like dense, thin nanocomposite membrane, thick, sandwich, layered together with a pore-filling kind on account of nanotechnology to enhance the performance of PEM [139]. Hence, the growth of cost-effective green energy systems with the incorporation of nanotechnology will provide immense contribution to the crucial energy goals, globally and decrease the damaging consequence of human activities [136].

7. Conclusion

Fuel cells are known to be good sources of green energy offering high conversion efficiency of energy, environment-friendliness, and rapid start-up and they are being employed as a substituted source of energy to fossil fuel. They are hence, considered as an eco-friendly energy conversion device which satisfies the technological requirements for present issues connected to combating environmental challenges and power generation. This review emphasizes the role of nanotechnology in PEMFC and microbial FC. The role of nanotechnology in fuel cell technology as an enhancement of nanocomposite membrane for fuel cell technology had been looked into. Furthermore, the role of nanotechnology in microbial fuel cells and PEMFC have also been discussed.

Systematic and technological efforts in PEMFC technology are tackling several issues pertaining to catalyst degradation and the platinum nanoparticles and carbon black (Pt/C) electrocatalysts that are mercantile obtainable which are prone to Pt dissolution and carbon support corrosion. These efforts have resulted in the advanced progress in making of novel materials that could be used as an alternative catalyst that are earth-abundant and cost effective; which will subsequently allow the continuous contribution to PEMFC in sustaining energy. Furthermore, it will subsequently ensure the maximum performance of PEMFC as highly stable electrocatalysts will be designed to upsurge PEMFC long-term performance. The decline in the membrane resistance at low relative humidity is also known to be the most imperative challenge in polymer electrolyte membranes (PEMs). This challenge will be combated by improving proton conductivity, low electronic conductivity, low transportation of water via diffusion and electro-osmosis, low penetrability to fuel and oxidant and decreasing membrane thickness. Hence, for the future fuel cells, exceptional proton conductivity, gas barrier property, and membrane steadiness are required in high-performance polymer electrolyte membranes.

MFC is a bio-electrochemical hybrid system due to its anaerobic treatment process and it also reduces sludge, possess high nutrients recovery; and their positive energy generation is known as bioelectricity harvesting. Hence, it is dependent on biocatalyst which is some electrochemically active bacteria that without deviation absorbs the organic load of wastewater and yields electricity. Though electrode spacing and the utilization of different novel polymer electrolyte membranes are used in enhancing MFCs performance; nonetheless, the material employed in synthesizing these membranes are still in favor of the oxygen crossover, and this is major draw-back. Furthermore, anode is still considered as another major obstruction for traditional twofold-chamber MFC's extensive use, particularly with insufficient precise surface area, deprived biocompatibility and expensive materials. However, the utilization of nanomaterial has transformed the design and construction of MFC components, which has enhanced the performance and the efficiency of MFC with regards to its power density, electron conductivity, thermal stability, cost, ORR rate and anti-corrosion. This transformation of the utilization of nanomaterials has also aided the modification of both anode and cathode electrodes which subsequently enhance power production. Hence, exploiting the excellent electrical properties of nanomaterials with respect to their biocompatibility, porosity and specific surface area; nanomaterials has shown immense prospect in stimulating the power supply of MFCs. In addition, incorporating a biological component with functional metal, metal oxides or modified metal oxides nano-hybrid structured materials enclosed with conducting polymers should be put into consideration for the purpose of combating these drawbacks.

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The authors declare that there are no any financial and personal relationships with other people or organizations that could inappropriately influence (bias) this review.

Conflicts of Interest

The authors declare no conflict of interest.

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