



# Review of materials, functional components, fabrication technologies and assembling characteristics for polymer electrolyte membrane fuel cells (PEMFCs) – An update

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**Abstract**

Fuel cells use electrochemical processes to transform the chemical energy of a fuel into electrical energy, which is a key enabler for the shift to an H<sub>2</sub>-based economy. Because of their high energy conversion efficiency and low pollution emissions, fuel cells with polymer electrolyte membranes (PEMFCs) are regarded as being in frontline of commercialization for the transportation and automotive industries. However, there are two major hurdles to their future commercialization: cost and durability, which promote basic study and development of their components. In this article, we reviewed the materials, functional components, fabrication technologies and assembling characteristics related to PEMFCs. Platinum's significance as a catalyst in PEMFC applications stems from the fact that it beats all other catalysts in three critical parts: stability, selectivity, and activity. In order to create Pt rich surfaces of NPs, Pt metal is alloyed with d-block metals like Cu, Ni, Fe, and Co. PEMFC development is inextricably tied to the benefits and drawbacks of the Nafion membrane under various operating circumstances. Nafion membrane has some drawbacks, including poor performance at high temperatures (over 90°C), low conductivity under low humidification, and high cost. As a result, a variety of nanoscale additives are frequently added to Nafion nanocomposites to enhance the material's properties under fuel cell working conditions. Fiber composite based bipolar plates can deliver best performance. The assembly of PEMFC based on strap approach is being explored. The applications of PEMFC are also projected.

## 1. Introduction

A fuel cell produces electricity in an effective and environmentally friendly way by using the chemical energy of H<sub>2</sub> or other fuels. The only byproducts of using H<sub>2</sub> as a fuel are energy, heat and water. The ability of fuel cells to operate systems as large as a major power plant and as compact as a laptop computer utilising a range of fuels and feedstocks is a special feature of fuel cells. Transportation, industrial, commercial, and residential buildings, as well as long-term grid energy storage in reversible systems, are just a few of the usages for fuel cells. Fuel cells offer a variety of benefits over traditional combustion-based techniques, which are now used in various automobiles and power plants. They may be more effective than combustion engines since they directly transform the energy from chemical reaction to electrical energy in the fuel with conversion efficacy of up to 60% [1]. In contrast to internal combustion machines, fuel cells either produce no or very little pollution. H<sub>2</sub> fuel cells can contribute to the resolution of significant climate challenges because they emit only water and no carbon dioxide [2]. At the location of the operation, there are no major airborne

pollutants that cause smog or endanger human health. Fuel cells run smoothly because they have few moving parts. Alkaline fuel cells (AFCs), solid oxide fuel cells (SOFCs), polymer electrolyte membrane fuel cells (PEMFCs), molten carbonate fuel cells (MCFCs), and phosphoric acid fuel cells (PAFCs) are a few of the fuel cell types that have been developed after extensive research.

Here in this review, we are mainly focusing on PEMFCs and its components. PEMFCs, which are made up of a proton conductor, polymer electrolyte membranes (most prominently Nafion) and a catalyst made of platinum (Pt). PEMFCs are a formidable competitor for the next-generation power sources for fixed, portable, and automotive usages due to their high power density, less working temperature, and simplicity of scaling up. The majority of research on this subject (PEMFC) has been done in a number of different countries throughout the world, with China and the United States yielding the most publications [3]. PEMFC was initially established by General Electric for NASA's Gemini spacecraft [4] in the initial 1960s. Despite their excellent technical demonstration, management difficulties and high costs hampered further development until the 1990s [5,6], when a dependable

PEM was adopted. Low-cost catalysts were employed, and electrode/membrane designs were modified, resulting in a significant reduction in total cost [7]. PEMFCs have a power density of  $0.5 \text{ W}\cdot\text{cm}^{-2}$  to  $0.7 \text{ W}\cdot\text{cm}^{-2}$  at the moment [8,9]. PEMFCs have a phenomenal specific volume power density [10] of  $5190 \text{ W}\cdot\text{L}^{-1}$ . Apart from this, the PEMFCs have lot of advantages than other fuel cells especially which can be operated at low temperatures, smaller in size and lighter in weight. These peculiar properties of PEMFCs make these devices best suitable for automotive and portable applications.

Mehta and Cooper have reviewed the large-scale production of PEMFCs [11]. PEMFC technology holds an advantage over other types of FCs in a number of applications. A comprehensive overview of current developments in PEMFC-powered hybrid systems has been provided by Erdinc and Uzunoglu [12]. Kulikowska *et al.* [13] have focused on several important membrane applications in the area of energy, with an emphasis on electrolytic and fuel cells. Wee has presented and analysed the problems, as well as some of the most recent research on applying PEMFC to everyday systems comprising transport, domestic power making, and laptops [14].

Yonoff *et al.* [15] have found that extreme running temperatures may affect the membrane to dry out and diminish the active part of the catalytic agent, decreasing the efficacy of the cells. So as to have the cell or stack working at a constant temperature and ensure the robustness of the device, proper heat abstraction from the PEMFC via cooling is absolutely essential. Around the world, researchers are examining current developments in chilling techniques and the possibility of the recovery of leftover heat for PEMFC. The primary PEMFC cooling techniques are discussed and assessed in terms of their benefits and drawbacks [16]. PEMFCs have made some encouraging strides and have a lot of potential; however, they still have a long road ahead to go before they can replace the energy sources we now use in an efficient and cost-effective manner. Nguyen *et al.* investigated the essential variables affecting PEMFC long-term robustness and its test methodologies aimed at together PEMFC stationary and transport applications [17]. Fuel pollutants ( $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ , and  $\text{CO}$ ), pollutants in air ( $\text{CO}$ ,  $\text{NO}_x$ ,  $\text{SO}_x$ , and  $\text{CO}_2$ ), and ions of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  produced by corrosion of fuel cell were among the contaminants. The anode, membrane, and cathode are severely poisoned by even minute quantities of contaminations found in fuel/air flows/fuel cell structure constituents, leading to considerable performance losses, especially at low temperatures [18]. The numerous factors that influence the structures, efficacy, robustness, and price of a fuel cell must be studied in a detailed way throughout the development process. The influence of many factors on hydrogen fuel cell durability was investigated by Habib *et al.* [19]. Bipolar plates are a crucial component of proton exchange membrane fuel cells. They are responsible for transporting reactant gases, carrying the current from the membrane electrode assembly to the end plates, providing heat and water management, and separating the individual cells. Many materials are being developed as bipolar plates in PEMFCs. Stainless steel, which is used in metallic bipolar plates, is generally known to have excellent corrosion resistance, which is achieved by forming oxide films [20].

Efforts are being made to produce innovative polymeric materials that will meet consumers' technical and economic requirements. Because Nafion membranes outperform most alternative membranes

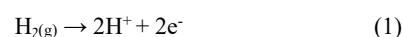
across the board, it may be desirable to compromise on particular aspects in order to produce alternative specialized membranes. Kraysberg and Eli have examined the features of contemporary solid polymer electrolytes (SPEs) for PEMFCs, focusing on conductivity, stability in chemical and mechanical aspects [21]. Although PEMFC and DMFC technologies have been researched for several decades in Europe, the United States, Japan, and Canada other smaller nations may still be able to contribute to their development and commercialization in niche sectors [22]. As alternatives to their per-fluorinated predecessors, many hydrocarbon-based membranes are being investigated. Although these polymers are more susceptible to oxidation, they may allow less peroxide to be formed by gas crossover, leading to appropriate lifetimes. Understanding failure mechanisms can help PEMFC systems function better and last longer [23]. PEMFCs have the ability to convert about 60% of electrical energy into thermal energy or to co-generate roughly 80% of electrical and heat energy with a >90% diminution in main pollutants [24]. Stumper and Stone have provided an outline of few of the major problems and concerns that must be addressed in the areas of functioning and robustness in order to make PEMFC technology commercially viable. While substantial work has been made toward these goals in recent years, a basic knowledge of the mechanisms that cause performance loss and material deterioration is still lacking [25]. Wang and Shih have defined the growth of a HFC technology and its incorporation into the Mingdao hydrogen vehicle automobile (MHV) [26]. Based on the published literature, it was found that still many issues in PEMFC yet to be solved. The aim of this article is to confer the working principle, different ways of fabricating components, role of feed gas, assembly, application of PEMFCs and related parameters in a detailed manner.

## 2. Working principle of PEMFC

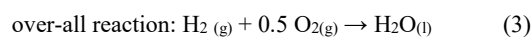
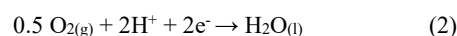
In a PEMFC,  $\text{O}_2$  and  $\text{H}_2$  are transferred through the cathode and anode, respectively. The hydrogen is activated by the catalyst to create proton ions and the  $\text{H}^+$  flows via the membrane and generates electrical energy when the electron is pushed to flow out. When an electron returns to the cathode, it collides with oxygen. Water is formed by the proton ion. The operating temperature of PEMFC is  $120^\circ\text{C}$  to  $140^\circ\text{C}$ .

The catalyst in a PEMFC permits the splitting of  $\text{H}_2$  into  $\text{H}^+$  and electrons on the anode side. When a proton passes through a membrane, it forces an electron to move to an external circuit where it produces electricity. Oxygen will be reached when the electron returns to the cathode with the development of  $\text{H}^+$  ions in water. At each electrode, electrochemical processes are taking place [27,28]. It can be found in Equations (1-3).

Anode: oxidation



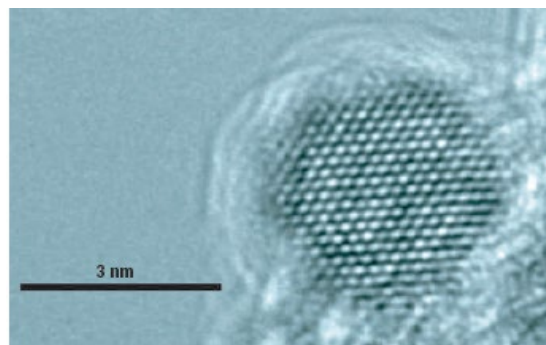
Cathode: reduction



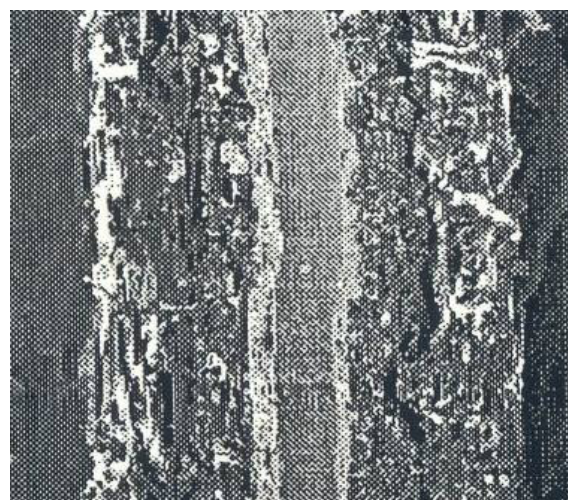
### 3. Electrode components in PEMFC

In PEM fuel cells, each electrode is comprised of a porous, high-surface area material impregnated with an electrocatalyst, typically platinum or a platinum alloy. Platinum's significance as a catalyst in PEMFC applications stems from the fact that it beats all other catalysts in three critical parts: stability, selectivity, and activity. Bulk Pt is often used as a standard for non-Pt systems, especially in terms of activity, although its electrical characteristics can still be honed by alloying with different metals, improving it by an order of scale or more. The function of these modified Pt systems serves as the genuine barometer. The prospect of systems based on less expensive metals is alluring due to the comparative cost of one gram of Pt. Alternative base metal systems, on the other hand, have vital disadvantages such as a deficiency of activity, meagre selectivity proceeding to  $\text{H}_2\text{O}_2$  generation, and catalyst degradation due to meagre stability beneath fuel cell working circumstances, all of which must be addressed [29]. The fundamental downside of these catalysts is that impurities can poison the platinum, lowering its efficiency. Reduced platinum concentration without compromising cell performance, as well as the development of platinum-free catalysts, are essential areas for continued research and development. It's important to note that substantial advancements have been made in this area recently, with catalyst specific power more than doubling from  $2.8 \text{ kW}\cdot\text{g}^{-1}$  of metal from Pt group (PGM) in 2008 to  $5.8 \text{ kW}\cdot\text{g}^{-1}$  in the year 2012. Fuel cells containing Pt have also decreased beyond doubling and the catalyst specific power at this time approaching to  $8.0 \text{ kW}\cdot\text{g}^{-1}$  [30,31]. Pt will continue to be the best significant component of dependable and effective PEMFC oxygen reduction reaction (ORR) electrocatalysts for the time being. The high-resolution transmission electron micrograph (TEM) of a  $\text{Pt}_3\text{Co}$  nanoparticle is shown in Figure 1 [30].

The most costly component of a PEM fuel cell is the catalyst layer made of Pt. Decreasing the quantity of Pt used and improving its performance through composites, morphology, and producing Pt rich surfaces of NPs can significantly reduce the cost of fuel cell stacks. By using less Pt and recycling the membrane electrode assembly (MEA) after use, the effect of Pt in the PEMFC can be decreased to values similar to those of PGMs used in combustion engine accelerators [32]. Although Pt-based catalysts have been developed as the most efficient catalyst towards oxygen reduction reaction (ORR), however, their stability is far from the application requirements, which hinders the large-scale application of PEMFCs to a certain extent. Thus, improving the stability of Pt-based catalysts is urgently desirable to advance the widespread commercialization of fuel cells. In order to create Pt rich surfaces of NPs, Pt metal is alloyed with d-block metals like Cu, Ni, Fe, and Co. Many of these catalysts, including Pt-Co, are currently offered commercially [33], which is utilized in Toyota's fuel cell vehicle; nevertheless, investigation on alternative Pt-Co NP topologies is still on going [34-37]. The creation of Pt-Ni [38,39] alloys is a main goal of current research, and multiple papers have reported the synthesis of octahedral NPs [40,41]. The binary alloys with platinum such as Pt-Fe [42,43], Pt-Se [44], Pt-Ag [45], Pt-Cu [46], Pt-Ir [47,48], Pt-Bi [49] are studied. A number of ternaries [50-52] and quaternary alloys [53,54] have also been studied. Tu *et al.* [55] proposed a Pt-rare earth catalyst, however, due to its limited abundance, such a catalyst is doubtful for large-scale application. The structure of MEA in PEMFC is shown in Figure 2 [56].



**Figure 1.** High-resolution transmission electron micrograph of a  $\text{Pt}_3\text{Co}$  nanoparticle [30].



**Figure 2.** MEA structure in PEMFC [56].

Pure Pt catalysts optimization focuses on shape tuning, activated surface area, optimization, and exposing the most active crystal surfaces, as well as particle size tuning and control. In positions of shape, dodecahedral rhombic nanoparticles have the most perchloric acid activity, while cubic nanoparticles have the least [57-59]. Gouda *et al.* have used rGO/magnetic iron oxide nanocomposite as electrode with more activated surface with great durability for ORR in fuel cells [60]. The enhancement of ORR performance, stability, and low cost are the main concerns of the development of non-precious metals based catalysts in PEMFCs. But, best fabrication conditions to get maximum efficiency yet to be studied. Performance characteristics of Pt based catalysts in PEMFC are indicated in Table 1.

Carbon cloth (CC) and carbon paper (CP) was prepared by hot pressing method and their performance characteristics were studied by polarization technique. The pressing method yields different results based on Gas Diffusion Electrodes (GDE) prepared using CC and CP. Based on the results CP exhibits better performance than CC [61]. rGO and grapheme/magnetic iron oxide nanocomposite with PEO/PVP/PVA was used as anode and cathode in PEMFCs. It was found that performance MEA was enhanced with using GDL more than that of MEA without GDL by 66% at a current density of  $0.8 \text{ A}\cdot\text{cm}^{-2}$  [62]. The performance of MEA with different characteristics of gas diffusion layers was studied at  $70^\circ\text{C}$ . It was found that the maximum power density of  $0.36 \text{ W}$  at  $0.6 \text{ V}$  for MEA having minimum thickness [63].

**Table 1.** Performance characteristics of Pt based catalysts in PEMFC.

Sl. no.	Authors	Electrode	Observation	Concerns	Reference
1.	Oliver <i>et al.</i>	Pt	In the PEMFC system, Pt comes closest to being an excellent catalyst for both the HOR and ORR.	catalyst degradation. Pt anode loadings of 0.05 mg·cm <sup>-2</sup> .	[29]
2.	Mølmen <i>et al.</i>	Pt	Alloying, shape-tuning, and generating NPs with Pt-rich surfaces are all ways to improve its efficiency.	The most important consideration is sufficient durability. Pt loading is reduced below 0.05 mg·cm <sup>-2</sup> at the anode.	[32]
3.	Yoshida <i>et al.</i>	Pt-Co	In comparison to the 2008 FCV model, the MIRAI's oxygen reduction reaction activity has increased by a factor of 1.8.	The catalyst's Pt content is still not low enough.	[33]
4.	Li <i>et al.</i>	L1 <sub>0</sub> -CoPt/Pt nanoparticles with 2-3 atomic layers of strained Pt shell for ORR	This improved ORR correlates to improved MEA performance in fuel cells, with an MA of 0.56 A·mg <sub>pt</sub> <sup>-1</sup> and just 19 percent MA loss after 30,000 ADT cycles at 80C, exceeding DOE 2020 goals.	19% MA loss after 30,000 ADT cycles at 80°C. Stabilizing transition metals (M) in MPt alloy under acidic conditions is challenging.	[34]
5.	Gao <i>et al.</i>	Pt <sub>3</sub> Co/C	Activity of the oxygen reduction process (ORR) appears to have improved (E <sub>1/2</sub> increased by 50 mV).	A minor performance decrease was found after 50 000 potential scanning cycles. In unit-cell tests, the C-spun electrode achieved an excellent performance of 8.207 W·mg <sub>pt</sub> <sup>-1</sup> (H <sub>2</sub> /air, 80°C, 1 bar, 100% RH).	[35]
6.	Hu <i>et al.</i>	Pt/(Co-N)@C	By substituting the non-active XC-72R carbon substrate with active XC-72R, the ORR performance of the Pt-based catalyst was successfully enhanced.	Slight performance degradation after 30,000 ADT cycles and a high intrinsic activity of 0.227 A·mg <sub>pt</sub> <sup>-1</sup> , more than double that of commercial Pt/C (0.105 A·mg <sub>pt</sub> <sup>-1</sup> ). MEA with the Pt/(Co-N)@C cathode could deliver a power density of 1.06 W·cm <sup>-2</sup> at an operation voltage of 0.6 V.	[36]
7.	Sriwannaboot <i>et al.</i>	Pt-Co	Pt-Co with a Pt activity of 58% or greater outperforms Pt, with 77% Pt having the greatest ORR activity.	Oxygen reduction reaction (ORR) of Pt-Co on CC is significantly higher than on GC due to its highly porous structure.	[37]
8.	Tian <i>et al.</i>	Pt-Ni	When compared to a commercial platinum on carbon (Pt/C) catalyst, the bulk activity (3.52 A·mg <sub>pt</sub> <sup>-1</sup> platinum) and specific activity (5.16 mA·cm <sub>pt</sub> <sup>-2</sup> ) are ~ 17 and 14 times greater, respectively.	negligible activity decay after 50,000 cycles	[38]
9.	Mardle <i>et al.</i>	Pt-Ni	improvement in the ORR catalytic activity \is observed for the PtNi	Ni ion contamination at a high temperature. A 2.84-fold improvement in the oxygen reduction reaction catalytic activity is observed for the PtNi NW array GDE.	[39]
10.	Kong <i>et al.</i>	Pt-Ni	Pt's influence on the PEMFC can be decreased to values equivalent to those of PGMs used in internal combustion engine catalysts.	Sufficient durability is the key issue	[40]
11.	Kühl <i>et al.</i>	Pt-Ni	PtNi nanoparticles with a cuboctahedral shape and produced at 400°C provided the best balance of ORR activity, performance stability, and morphological stability.	Cuboctahedral shaped Pt alloy nanoparticles as promising PEM cathode fuel cell catalyst of choice.	[41]
12.	Wang <i>et al.</i>	PtNi/C	MEA constructed with the composite catalyst produces good single-cell power generation.	Compared with the control fabricated with Pt/C (JM), the cell voltage at 1 A·cm <sup>-2</sup> and the maximum power density are increased by 23 mV and 119 mW·cm <sup>-2</sup> , respectively.	[42]
13.	Gong <i>et al.</i>	Pt-Fe	Assists in the development of extremely efficient ORR catalysts for use in fuel cells	The as-prepared O-PtFe delivered enhanced activity (0.68 A·mg <sub>pt</sub> <sup>-1</sup> ) and stability (73% activity retention after 10 000 potential cycles) compared with the corresponding disordered PtFe alloy (D-PtFe) and Pt.	[43]
14.	Choi <i>et al.</i>	Pt	Even after 30,000 cycles in a single cell test, the cBCP-PtFe catalyst carbonized at 900°C demonstrated mass activity of 0.81 A·mg <sub>pt</sub> <sup>-1</sup> at 0.9 V, which is the highest performance recorded to date.	The mass activity measured after 30 000 cycles of single cell tests was 0.81 A·mg <sub>pt</sub> <sup>-1</sup> at 0.9 V.	[44]
15.	Zhao <i>et al.</i>	PtAg/C	In HClO <sub>4</sub> , the PtAg/C catalyst demonstrated outstanding ORR activity and durability.	The final Pt mass percentage of 10.86 wt%	[46]
16.	Zhu <i>et al.</i>	Pt-Ir	The Pd@Pt-Ir icosahedra outperform the commercial Pt/C with a mass activity of 1.88 A·mg <sub>pt</sub> <sup>-1</sup> at 0.9 V, about 15 times that of the commercial Pt/C.	Owing lack of control over their atomic structures at the surface is the hindrance	[48]
17.	Shen <i>et al.</i>	Pt-In-Ni	The improved Pt <sub>2</sub> In <sub>0.2</sub> Ni <sub>1.8</sub> /C catalyst has a mass activity of 0.76 A·mg <sub>pt</sub> <sup>-1</sup> and retains ~97.5% of its original activity following stress testing, according to the results.	Improved ORR activity and catalyst stability by incorporating post-transition-metal indium into Pt-Ni alloy nanoparticles.	[52]

#### 4. Electrolyte components in PEMFC

The three major parts of PEMFC are an electrolyte, an oxidant electrode, and a fuel electrode (also known as an anode). Due to their fast start-up and ability to operate at room temperature PEMFCs are the utmost economically attractive of the competing fuel cell technologies [64-66]. PEMFCs are extremely efficient when operating, produce no pollution, and have specific and volumetric energy. It is now possible to use PEM cells in a variety of settings, including vehicles and aircraft. The electrolyte of a PEMFC is a polymer membrane that may carry charges. The majority of the original fuel cells used Pt electrodes and a fluid electrolyte that was typically an acid (dil. H<sub>2</sub>SO<sub>4</sub>). At the contact between the anode and the electrolyte, the fuel is converted into H<sup>+</sup> and electrons. This is made possible by a catalyst, which is typically Pt-based. Electrons cannot traverse the polymer electrolyte membrane, only protons. Protons move from the anode to the cathode via the membrane, where they mix with oxygen atoms and electrons to produce water. As early as the 1940s, scientists started developing organic ion-exchange membranes for use in fuel cells [67,68]. In 1950s, Grubb and Niedrach [69,70], a General Electric Company scientist, devised the first successful fuel cell for this use, which used an ion exchange [56] resin membrane as the electrolyte. Between 1959 and 1967, varied resins were utilized, but they ranged from membranes made from phenol sulfonic acid-formaldehyde polymers in the past, to polystyrene sulfonic acid variations in the mid-to-late 1960s. The fuel cell, which used a solid-polymer electrolyte, was claimed to be capable of operating at ambient temperature and at atmospheric pressures in a 1959 patent. In the early 1960s, the first PEMFC systems were used as power plants for the Gemini space missions. However, the cells were less durability due to breakdown of the membranes by oxidation, which were made up of a sulfonated polystyrene/divinylbenzene copolymer. Nafion, a perfluoro-sulfonic acid copolymer having a hydrophobic (fluorocarbon) backbone and hydrophilic (sulfonic acid) pendent adjacent chains, was applied by DuPont to make membranes in the late 1960s. As a perm-selective separator, this membrane was mainly used in chlor-alkali electrolyzers. The "zero-gap" cell design idea was made possible by the 1980s introduction of Nafion membrane. The inner resistance of the PEMFCs dropped as a result of the introduction of the zero-gap cell concept, and the total efficacy of the scheme augmented significantly [71].

Nafion related membranes brought in use PEMFCs. Nafion possesses a number of significant characteristics, including stability in terms of mechanical, chemical and thermal, also good water-saturated proton conductivities in longstanding fuel cell process. Nafion is made by polymerizing unsaturated perfluoroalkyl sulfonyl fluoride (PF<sub>6</sub>SF) with tetrafluoro ethylene in various quantities. Nafion is obtainable in a variety of equivalent weights like 900, 1100, 1200, and so on. Due to the strong conductivity of proton and mild enlargement in water, these membranes are commonly employed in PEMFCs [72] (Mauritz and Moore 2004). The current state of PEMFC development is inextricably tied to the benefits and drawbacks of the Nafion membrane under various operating circumstances. Nafion's application in PEMFCs is restricted above 80°C because proton transfer requires that protons separate from the component -SO<sub>3</sub>H groups in the vicinity of H<sub>2</sub>O [73]. Nafion membrane has some drawbacks, including poor performance at high temperatures (over 90°C), low conductivity under low humidification, and high cost. As a result, a variety of nanoscale additives are frequently

added to Nafion nanocomposites to enhance the material's properties under fuel cell working conditions [74,75]. The outcome is, several researchers have sought to create novel polymer nanocomposite materials with improved physicochemical properties by mixing with appropriate polymers and inorganic/organic ingredients. To create polymer blends, a variety of polymers and conducting polymers were utilized, including polyaniline (PA), polyethylene oxide (PEO), polystyrene (PS), polyvinylalcohol (PVC), polypropylene (PP), polyvinylpyrrolidone (PVP), and poly3,4-ethylenedioxythiophene (PEDOT), among others. Additives such as, TiO<sub>2</sub>, SiO<sub>2</sub>, WO<sub>2</sub>, quaternary ammonium salts and others [76,77] as well as silicate and clay minerals layered are employed as catalyst supports and fillers in polymer nanocomposites the application for energy production. Amino clay/Nano-composite Nafion membranes with embedded Pt nanoparticles were made by means of a sol-gel route and a simple chemical reduction method. Pt nanoparticles-embedded Amino clay/Nafion electrocatalytic performance and durability towards ORR were investigated for PEMFC [78,79]. There are many more critical challenges that requirement to be handled afore solid-acid membranes can be employed in PEMFCs in the case of improved-Nafion membranes as electrolytes for PEMFCs. Among these are design difficulties like catalyst compatibility and scale-up as well as common operational parameters like mechanical strength, durability, cyclability, and synthetic circumstances. Several Nafion membrane composites have benefits as well as room for improvement. Several authors conducted research on several Nafion and modified membranes of Nafion for use in PEMFCs and Nafion Modified membranes function better than unmodified Nafion membranes as PEMFC electrolytes. The Nafion-inorganic composite films seem to provide the maximum potential electrolyte for PEMFCs among the many Nafion modified membranes. It is ideal to create thermally unchanging and economical polymer electrolyte membranes to replace Nafion [80]. Nafion/silica exhibits poor conductivity than Nafion in high relative humidity (RH) conditions [81]. In case of Nafion-titania and Nafion-zirconia, in high RH conditions, their conductivity is slightly lower than Nafion, however their conductivity improves at raised temperatures and lesser RH values [82,83]. In high RH conditions, Nafion/ZrP conductivity is similar to Nafion, with enhanced conductivity at raised temperatures and lower RH values [84]. Nafion/Cesium Phosphate composite (Nafion/Cesium Phosphate) shows enhanced conductivity than Nafion at raised temperatures and lesser RH values [85]. Nafion/mordenite composites, in high RH conditions, conductivity is slightly lower than Nafion, while conductivity improves at elevated temperatures and lesser RH values [86]. Nafion/HPA showed improved conductivity, however, HPA leaking occurs [87]. Nafion/imidazole shows excellent conductivity during PEMFC operation; however, imidazole poisons the Pt catalyst [88]. Several research groups have researched the production of novel polymers such as sulfonated aromatic and their functionality as PEMs to produce effective and viable materials in place of presently employed perfluoro sulfonic acid membranes. Recent research in interfacial polymerization, characterisation, and PEM efficiency has placed a significant emphasis on proton conductivity. Non-sulfonated/sulfonated multiblock copolymers include hydrophilic and hydrophobic oligomers strive to create clear, well-associated H<sup>+</sup> passages while retaining good H<sub>2</sub>O steadiness for strong conduction of proton even at low relative humidity and elevated operational



temperatures. Exceptionally valuable materials with well-balanced properties must emerge in the near future as a result of continuing to pursue novel and/or ideal structures of polymers [89].

## 5. Bipolar plates in PEMFC

Bipolar plates are very important part in PEMFC. They were used to feed the gases (fuel and oxidant) uniformly to the device and they can act as effective conductor of electricity between the stacks. They also control the leakage of gases during the operation of PEMFC. The overall volume, weight and rate of PEMFCs are highly dependent on bipolar plates. Different materials, such as, polymer composites, metallic components, graphite, etc. were used as bipolar plates in PEMFC [90]. A thermoset type phenolic resin was used as a matrix to fabricate woven graphite fiber composite based bipolar plates for PEMFCs. The performance characteristics of this bipolar plate with and without carbonization were studied and reported [91]. A simple layer-by-layer method to prepare graphite/ resin composite bipolar plates was proposed recently. The PEMFC assembled with this new bipolar plate exhibited excellent cell performance: the potential of 0.67 V at 1 A·cm<sup>-1</sup> and the optimum power density [92] of 0.99 W·cm<sup>-2</sup>. Graphite-coated SS316L also proposed to be used as an efficient bipolar plate material in the PEMFCs [93].

Carbon-coated 316 L bipolar plates were utilized for long-run PEMFCs with the artificial of conditions of real automotive application. However, during long run, the metals, viz. chromium, nickel and iron present in plates were undergone dissolution from uncoated carbon regions which influenced the cell potential of PEMFC [94]. The corrosion analysis of graphite sinter as bipolar plates in PEMFC simulated environments was carried out and reported. It was found that graphite sinter exhibit good resistivity in anodic and cathodic corrosive environments which makes it to be used efficiently for PEMFC application [95]. Thermo set and thermoplastic resins were combined with graphite, carbon fibers, CNTs, etc. to make bipolar plates in PEMFCs [96]. Conductive composite bipolar plates having natural graphite and expanded graphite as the filler and phenolic resin and epoxy resin as the binder were prepared intercalation mixing, compression molding, and curing for application in PEMFC. These plates have shown better thermal stability under fuel cell working conditions [97]. It was reported that graphite/novolac epoxy (NE) bipolar plates could exhibit good electrical conductivity, mechanical property and corrosion resistance characteristics than that of graphite/ phenol formaldehyde resin based bipolar plates. Also, it was found that graphite/NET composite bipolar plate when utilized in PEMFC exhibited better performance comparable to that of commercial graphite bipolar plates [98].

## 6. Role of feed gas in PEMFC

In PEMFC, hydrogen is used as a fuel in anode compartment and oxygen is used as an oxidant gas in cathode compartment. These gases can be fed into a PEMFC system using proper gas controllers with appropriate pressure at the operating temperature of the fuel cell assembly. The flow rate of the gases should be controlled properly to get better efficiency. Fuel purity, anode fuel supply system setup, and operating procedures all have a part in a PEMFC system's efficiency.

The amount of H<sub>2</sub> that can be utilised in productive reactions and the effects of dissimilar fuel impurities on stack efficacy depend on the anode's operating conditions. The anode fuel delivery system's objective is to uniformly disperse sufficient H<sub>2</sub> across the fuel cell stack's active region whereas eliminating extra gaseous pollutants and liquid H<sub>2</sub>O droplets. Through a series of channels (often incorporated in a conducting plate), hydrogen and oxygen are supplied as fuel to a dynamic zone of a PEMFC where a redox reaction occurs between the fuel and O<sub>2</sub>, generating heat, electricity and water. PEMFCs are superior to traditional fuel cells in a number of ways, including great power density, low working temperature, speedy start-up, good load responsiveness, simple scaling, and high efficiency. Roda *et al.*, have reviewed marketable battery-power-driven pure electric car was converted into a hybrid vehicle by including a PEMFC stack. An inactive recirculation system based on a Venturi-type ejector was included into the stack's hydrogen supply system. Furthermore, a discrete state machine model was explored in the control system of the PEMFC stack in order to ensure optimal functioning [99]. Kurnia *et al.* have presented the results of a computer study of a PEM fuel cell stack's performance through a typical drive cycle with changing inlet flow parameters. The New European Driving Cycle (NEDC) was chosen as the regulatory driving cycle, which consists of four ECE-15 urban driving cycles (UDC) and one extra-urban driving cycle (EUDC) [100]. Dead-end anode operation is desirable to enhance fuel consumption and minimize complexity in polymer electrolyte fuel cells, particularly for automotive applications. The anode outlet is blocked in this mode of operation to obtain approximately 100% fuel consumption. The fuel cell's great potential was hampered by N<sub>2</sub> crossover and liquid H<sub>2</sub>O back dispersion that accumulated in the anode and prevented H<sub>2</sub> fuel from contacting the catalyst, leading to fuel famine [101].

Woo and Benziger have validated that the output power of a PEM fuel cell may be steadfastly synchronised by restricting the H<sub>2</sub> input to the fuel cell. By adjusting the inner resistance of the membrane-electrode assembly, regulation is accomplished in a self-draining fuel cell with pollutants associated to H<sub>2</sub>O reservoirs. H<sub>2</sub>O is intended to flow into and out of the gas flow channel of the fuel cell, which is designed to function as a dead-end system with no gas flowing out of it. The inner resistance of a fuel cell is controlled by the changing the level of water in the flow passage. O<sub>2</sub> (or air) and H<sub>2</sub> supplies are matched to the current stoichiometrically, which controls the water level [102]. For the purpose of evaluating the dynamics of gas configuration in PEMFC anode fuel supply parts with recirculation that are operated dead-ended, Koski *et al.* [103] have supplied the fundamental theory and methods. The approaches are used to analyze measurement statistics from a PEMFC scheme with a 1 kW small stack. The recirculation mode entrainment ratio varied as of 22% to 38%, and was shown to be inversely proportional to the external load. For the recirculation mode, the system efficacy was determined in between 22% and 38%, while the stack efficiency remained constant at around 54 ± 2%. Furthermore, both the dead-end and recirculation modes have nearly the same stack and system efficiencies for stack powers less than 1.2 KW [104]. The sole device that meets the needs for each of the fuel cell's power levels, through 0 to 100%, is an additional hydrogen recirculating mechanism for boosting flow rate inside the fuel cell. Systems for passively recirculating or cascading stacks, on the other hand, must be carefully engineered to satisfy the fuel

cell's needs [105]. Without any noticeable influence from hydrogen recirculation, a cautious purge frequency of 0.92, which corresponds to a fuel utilisation coefficient of 0.92, was adequate to regulate good stack performance in fairly constant settings [106]. Anode contamination, viz., CO, CO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S, and inert diluents such as N<sub>2</sub> can be decreased effectively through pre-treatment of reformat [18]. The effect of CO<sub>2</sub> in a vehicle's anode loop has been investigated by Erbach *et al.* The quantity of adsorbed carbon monoxide from CO<sub>2</sub> in the anode is shown to be concentrated. The measured CO quantities revealed that the ECSA is saturated with adsorbed CO and that the saturation is nonlinear with increasing contaminant concentration [107]. Another mitigating method is to equip a PEM fuel cell with an air filter that captures pollutants before they reach the catalyst layer. To collect sulphur compounds, nitrogen compounds, and aerosol particles, air filters such as MnO<sub>x</sub> (SO<sub>4</sub> route)/Al<sub>2</sub>O<sub>3</sub>, KMnO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>, modified carbon felt, and electro spun nanofibers have been proposed [108]. Figure 3 depicts a liquid-cooled PEM fuel cell stack and a single PEM fuel cell schematically [100].

The manufacturing methods for metallic bipolar plates in order to feed gas into PEMFC were reviewed [109]. The bipolar plate in PEMFC is shown in Figure 4 with two gas diffusion layers (GDL) sandwich an electrolyte membrane with the capacity of conduction of proton in a PEMFC. A second catalyst layer—the MEA—is placed between the GDL and the membrane and can be created in one of two ways. The first technique involves hot pressing a catalyst-coated substrate onto a porous GDL, similar to carbon paper, after placing a catalyst layer on it (CCS). On the other hand, some of the nanostructured catalyst particles might poke through the GDL pores, which would prevent them from being activated catalytically. In the second method, which results in a membrane with a catalyst coating, the multilayer catalyst is directly deposited on the membrane (CCM). MEAs produced using the CCM process offer a number of benefits, including enhanced performance and durability. This is because the catalyst utilisation is increased and there is better interfacial connection between the layers of the catalyst and the membrane. One of the core disadvantages of the CCM technology is the membrane enlargement or crumpling brought on by straight connection with the catalyst ink during the production technique [111]. When compared to MEAs produced by hand brushing, the electrochemical characterization of the MEA revealed a 25% better functional improvement of current density in kinetic region. In comparison to MEAs produced using the traditional technique, the ac impedance tests revealed a 50% reduced interfacial resistance [112]. In comparison with conventional CCM, the advanced CCM has a nearly 20% of greater power density, demonstrating the critical significance of colloidal ink concentration in augmenting the micro-structure in cathode and improving CCM performance. By adjusting the concentration of colloidal catalyst ink, Mehmood *et al.*, were able to create decal CCMs with extremely permeable catalyst layered (CL) cathode. In order to obtain an acceptable pore structure in cathode CL, the hot-pressing temperature must be re-optimized together with a change in the cathode ink composition [113]. Yang *et al.* [114] described a new method for fabricating MEAs that involves employing a doctor blade to apply a direct coating on the anode and cathode CLs with Nafion ionomer, followed by hot pressing. Whenever the electrodes were manufactured by squirting the catalyst ink on a cloth of carbon as GDL, the performance was obtained with around

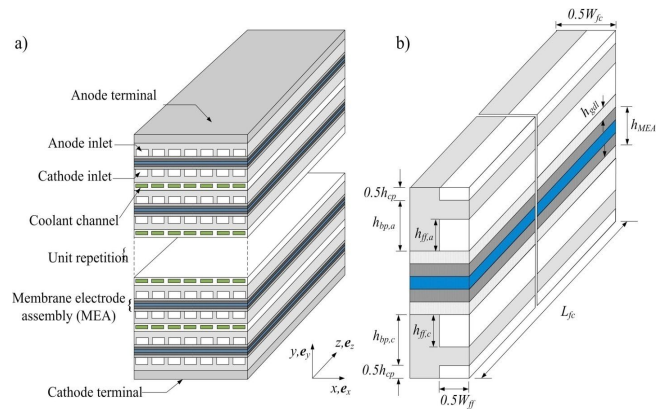


Figure 3. Schematic representation of (a) a liquid-cooled PEM fuel cell stack and (b) single cell PEM fuel cell [100]

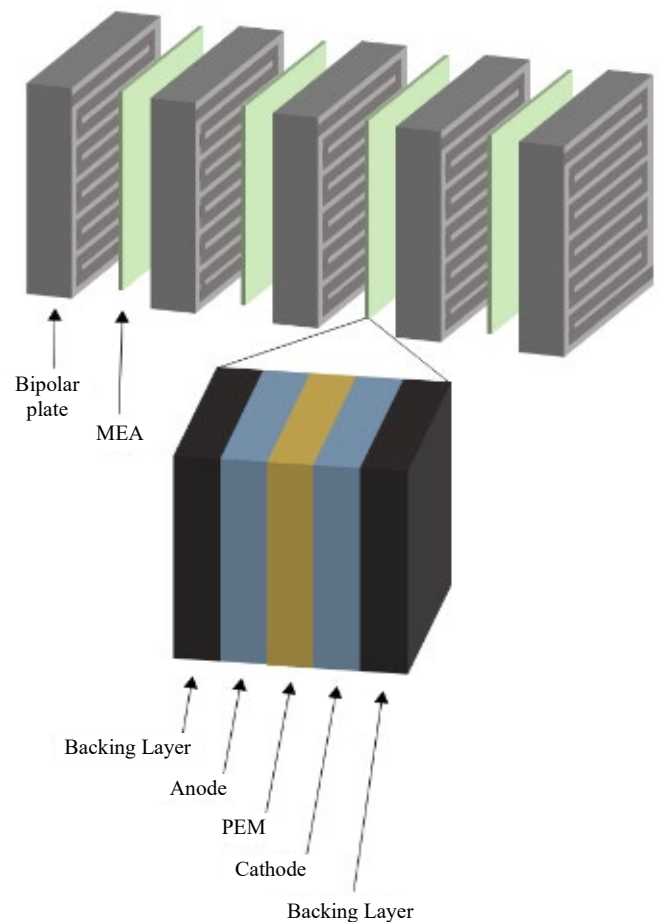


Figure 4. Bipolar plate in PEMFC [110].

830 mA·cm<sup>-2</sup> at 600 mV [110]. Presently, the performance for PEMFC [115] exceeded 1000 mA·cm<sup>-2</sup>. The MEA pressed with carbon cloth is well-studied [110].

Biyikoglu and Oztoprak have reported the enrichment of cell features [116]. In comparison to traditional manufacturing techniques, additive manufacturing techniques are considered as efficient and quick manufacturing processes that create components layer by layer in three dimensions. This lowers overall costs, production time, and waste [117]. Compression Molding (CM), which is ideal for mass

production, and Selective Laser Sintering (SLS), which is suitable for prototyping, were used to create graphite-carbon polymer composite plates [118,119]. A scientific examination into the implications of employing flow field topologies inspired by biological systems on PEMFC performance has just been published. These designs have a lot of potential for effectively transporting reactants and therefore improving fuel cell efficiency [120]. The impacts of GCR and NCR on single cell performance in decal-transferred MEAs were investigated. SEM, DC power cell polarisation, CV, and EIS using the DT at a constant Pt dosage of roughly  $0.20 \text{ mg}\cdot\text{cm}^{-2}$  were used to characterise the resultant MEAs [121]. For mass production of PEMFC electrodes, roll-to-roll (R2R) coating methods were employed. Slot-die and gravure methods were efficiently used to coat the catalyst layers on the carbon fiber gas diffusion media to make gas diffusion electrodes (GDEs). Roll-to-roll (R2R) slot-die coating of PEMFC catalyst layers represents a scalable deposition method for producing  $10 \text{ m}^2\cdot\text{min}^{-1}$  to  $20 \text{ m}^2\cdot\text{min}^{-1}$  of catalyst-coated gas diffusion layers (GDLs). It was reported that R2R process can reduce the cost of PEMFC catalyst layers [122].

Several investigators have run wide simulations to determine the optimum construction technique for various PEMFC devices. Zhou *et al.* [123]. have developed a 2D model of a single cell to investigate the variation in permeability of the Gas diffusion layer (GDL) induced by the assembly stress and the effect of Contact resistance (CR) amongst the Bipolar plate (BPP) and the GDL. The investigators discovered an ideal BPP beam width that results in a truncated CR and excellent GDL permeability. A simplified stacked model was devised by Liu *et al.* in 2007 [124]. To examine the impact of bolt placement and assembly load on the MEA pressure dissemination, a rigorous design approach integrating a Finite element model (FEM) and response surface methodology (RSM) was employed. In order to simulate the uneven stress distribution of the GDL brought on by the assembly load and compare it to the stress distribution seen by a pressure sensor in the experimentation, Lee *et al.* [125] employed a 3D single-cell FEM. Exploring the effect of the assembly force on the GDL, Xing *et al.* [126] had built a 3D model of a PEMFC using the COMSOL software programme. They then applied a stochastic technique to estimate the optimum assembly load at various voltage settings. The findings demonstrate that a 1 MPa to 1.5 MPa assembly load upgraded the fuel cell's potential when the operating voltage was high.

Along with a wide range of PEMFC modelling studies, numerous researchers have carried out several experimentations to explore the impact of the performance in the assembly on fuel cell. A loading device is typically used to apply a particular assembly load in stack assembly experiments. The stack assembly machine also includes a pressure plate, an appropriate calibration rod for assembly, a foundation for evenly spreading air-tightness testing tools and assembly force. Today's automatic stack assembly machinery comes in a wide variety, but the fundamental principles and procedures of assembly remain the same. The methods such as simulation, experimental, and analytical used in the current assembly methodology research when the fuel cell is "off-line," or when it is not operating. But as the fuel cell operates, its parts will deteriorate with time, as evidenced by the thinned seal rings. A fuel cell's assembly condition will be determined while it is operating, and a technique to dynamically change the assembly load will be developed.

## 7. Assembling mechanisms used in PEMFC

The process of building a PEMFC takes a long time. The combination of the assembly load and operating temperature causes some deformation of the components as well as an uneven distribution of stress. The assembly process also frequently includes transfer of load, transporting the material, energy interchange, multi-phase flow, and galvanic reaction. Fuel cell production costs are now quite high, with assembly costs accounting for a substantial share. Manufacturing expenses are increased further by assembly procedures that are inefficient and inaccurate [127]. As a result, further study into stack assembly theory and techniques are urgently needed in order to increase stack assembly efficiency and lower prices. The fuel cell stack is made up of the balance-of-plant subsystem, which includes the power conditioning subsystem, automated programs, and modules for thermal and H<sub>2</sub>O regulation, air provision, and H<sub>2</sub> generation/storage. Currently, the construction of the stack of fuel cells and its constituents is carried out in a scaled-up laboratory environment in simple ways. The establishment of complex manufacturing and assembly methods necessary for the production of reduced cost, elevated volume fuel cell power plants calls for production research and development [128]. The screw assembly is the sort of assembly that is most widely used nowadays. The screw assembly's concept is to transform the screw's point pressure into homogeneous strain over the entire pile via a dense End plate (EP). Although this procedure is easy and useful, the EP has a sizable volume and mass. Another popular assembly structure on the market is the strap assembly. Steel straps that are flexible are widely utilized. By using this technique, the EP can be made lighter and thinner while also being more compact. An extra uniform load distribution is possible due to the greater action area of the associated load. On the other hand, the assembling design process for stacks with only a strap assembly is more challenging [129]. Automatic assembly is becoming increasingly popular, but it also confronts a number of challenges and issues. The accuracy of the manipulator's alignment comes first. The manipulator's multi-joint structure's concerns with flexibility and mobility affect alignment precision. In traditional hand assembly, alignment pins are frequently utilised to limit component interaction. In particular for soft structures like MEAs, the usage of alignment pins during manipulator operation might affect clogging in the constituent insertion method. However, the alignment procedure could suffer from poor alignment precision in the absence of alignment pins. Low alignments precision prevents the desired constraint link between components from being satisfied, which could lead to gas leaks and other issues [130]. The assembly structures such as compliant strap [131], overlapping sheet [132], side spring [133], screw [134] and leaf spring structures [135] were also studied and reported. Various assembling techniques of PEM are presented in Table 2.

Other assembling techniques, such as, tie rod [136], coupling mechanism [137], rigid clamping [138], fastening housing [139] and fixed carriage [140] have also studied and patented recently. Each assembly technique has unique advantages when compared to the other methods. However, proper technique can be chosen for PEMFC application based on simulation, experimental and analytical investigations.



**Table 2.** Assembling techniques used in PEMFC.

Sl.No	Assembling mechanism in PEMFC	Characteristics	References
1.	Strap	Adapt to changes in assembly load during operation.	[131]
2.	Overlapping sheet	Prevent relaxation of assembly load	[132]
3.	Side spring	Keep dynamic assembly load.	[133]
4.	Screw	With assembly load adjusting bolt.	[134]
5.	Leaf spring	With tension members.	[135]
6.	Tie rod	Tie rod connects upper and lower end plates.	[136]
7.	Coupling mechanism	Element that has been preformed and has a known curvature.	[137]
8.	Rigid clamping device	Define the gaps between the end plates.	[138]
9.	Fastening housing	A load-adjusting mechanism is installed in the housing.	[139]
10.	Fixed carriage	Fuel cells can be built directly in the carriage.	[140]

## 8. Applications of PEMFC

PEMFCs employ a platinum-coated solid polymer to generate energy using just H<sub>2</sub> and O<sub>2</sub>. The benefits of a PEMFC are its light weight and large power density. They can also function at low temperatures, generally about 80°C, allowing them to get up and running rapidly (less warm uptime). PEMFC technology has wide range of future aspects and applications. Due to their light weight, PEMFCs are most suited for transportation applications. PEMFCs for buses, which use compressed hydrogen for fuel, can operate at up to 40% efficiency. Generally PEMFCs are implemented on buses over smaller cars because of the available volume to house the system and store the fuel [141]. Chalk *et al.* [142], have presented a status update on the PNGV programme as well as an overview of the Transportation Programs by DOE Fuel Cells for technological accomplishments and future objectives. Systems that cost \$60,000 in 2005 now cost \$10,000 due to advancements in technology and manufacturing. Commercial items are becoming more widely available, and specialized industries such as US forklift trucks and Japanese microgeneration are seeing substantial growth. Due to the difficulties of decarbonizing heat and transportation, a renewed global determination to combat climate change is being accompanied by a growing recognition that clean power alone is insufficient [2]. In the years 2020 to 2025, activity picks up, with the development of systems for converting the gas grid to hydrogen, the usage of hydrogen in a broader diversity of cars, and a number of initiatives delivering regional advantages through hydrogen production and usage. After 2025, a phased conversion of the gas grid with low carbon hydrogen produced through techniques such as CCS would enable broad use of hydrogen in heating, transportation, and industrial [143].

Particularly receiving attention and being quite developed, fuel cell buses have a Technology Adoption Level (TRL) of 7. Due to space limitations, on-board tanks usually transport roughly 40 kg of H<sub>2</sub> under the bus roof at 350 bar, which lowers the costs of compression and tank. By 2030, fuel cell vehicles might cost 10% to 20% more to own than diesel buses, but if widely used, they might be cost-effective [144]. Some fuel cell transportation usages that can be detailed include APUs, light traction vehicles (LTVs), light-duty fuel cell electric vehicles (L-FCEVs), heavy-duty fuel cell electric vehicles (H-FCEVs), aerial propulsion, and maritime propulsion [145]. Basics of fuel cell, history, competing knowhow, categories, opportunities, and constraints, mobile, static, and transit implementations and markets, existing R&D position, targets in the future, design levels,

thermal, and principles of redox reactions, process assessment issues, possibilities, and worldview have all been aptly covered by Sharaf *et al.* [146]. A summary of the steps taken to establish the usage of PEMFC in commercial aircraft was provided by Dyantyi *et al.* [147] The focus of the study is on efficacious field analysis, difficulties, and necessary stack-level experimenting to confirm the viability of a PEMFC-powered APU for marketable airplanes. The majority of FCVs are alike to ICE cars in terms of range, top speed, and acceleration. They have a peak power of about 100 kW, consume H<sub>2</sub> compressed at 35 MPa or 70 MPa (4 kg to 10 kg), and have a sort of about 200 miles. Most of these FCVs have a NiMH or Li-ion battery that boosts efficacy by energy storage all through regenerative braking and deceleration and transferring energy throughout propulsion or idle [148,149].

## 9. Conclusions

This article reviewed the electrodes, electrolyte components and assembly of PEMFC for automotive applications. PEM fuel cells have several advantages over other categories of fuel cells, because they have the ability to convert about 60% of electrical energy into thermal energy or to co-generate roughly 80% of thermal and electrical energy with a >90% decrease in main pollutants. Pt embedded carbon materials are used as electrodes in PEMFC because Pt has excellent activity, selectivity and stability in different operative conditions. Apart from Nafion, a variety of conducting polymers viz., polyaniline, polyethylene oxide, polystyrene, polyvinylalcohol, polypropylene, polyvinylpyrrolidone, and poly(3,4-ethylenedioxythiophene) are used as electrolytes in PEMFCs. The feed gases may be used to directly regulate the output power of a PEMFC. Analysis of feed gases is very important to have a better performance in PEMFC. Membrane electrode assembly (MEA) should be made by appropriate techniques to have excellent electrochemical characteristics during the operation of PEMFC. The PEMFCs can be combined with NiMH or Li-ion battery to obtain better efficiency for application in electric vehicles. Based on the technology development, we can expect that PEMFC based electric vehicles will occupy the roads of every country in nearby future.

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## Declaration of competing interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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