



The Operating Parameters, Structural Composition, and Fuel Sustainability Aspects of PEM Fuel Cells: A Mini Review

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Abstract: This mini review discusses the sustainability aspects of various fuels for proton exchange membrane fuel cells (PEMFCs). PEMFCs operate by converting the chemical energy in a fuel into electrical energy. The most crucial parameters in the operation process are the temperature, pressure, relative humidity, and air stoichiometry ratio, as presented in this work. The classical structure of a PEMFC consists of a proton exchange membrane, anode electrode, cathode electrode, catalyst layers (CLs), microporous layer (MPLs), gas diffusion layers (GDLs), two bipolar plates (BPs), and gas flow channels (GFCs). The mechanical behavior and the conductivity of the protons are highly dependent on the structure of the MEAs. This review discusses the various fuels and their production paths from sustainable sources. For the fuel production process to be renewable and sustainable, a hydrogen electrolyzer could be powered from solar energy, wind energy, geothermal energy, or hydroelectric energy, to produce hydrogen, which in turn could be fed into the fuel cell. This paper also reviews biomass-based routes for sustainable fuel production.

Keywords: PEM fuel cells; fuels; biomass; proton conduction membranes; sustainability

1. Introduction

Over the past few decades, the enormous energy generation from fossil fuels and dispersion of industrialization have increased greenhouse gas (GHG) emissions, mainly carbon dioxide, which is the major contributor to global warming and climate change [1–3]. Hence, cleaner and more efficient energy sources with low pollutant emissions and noise levels are required [4]. Among the various renewable energy sources, fuel cells are a promising alternative for stationary power stations, transportation, portable electrSonics, backup power systems, and other applications [5,6].

Fuel cells are electrochemical devices that convert the chemical energy stored in fuels directly to electrical power. There are various types of fuel cells, such as proton exchange membrane fuel cells (PEMFCs), solid oxide fuel cells (SOFCs), molten carbonate fuel cells (MCFCs), alkaline fuel cells (AFCs), and phosphoric acid fuel cells (PAFCs) [7–9]. In particular, PEMFCs have recently attracted the attention of the power generation market around the world, due to many advantages that include a high power density, high efficiency, low operating temperature, zero-emissions (depending on the fuel used) [10], a solid structure, and being environmentally friendly [11]. Additional advantages include their rapid start-up and silent operation [12,13]. The by-products of PEMFC are water and heat if a hydrogen fuel is used. The PEMFC components consist of bipolar plates (BPs) and storage tanks, in addition to catalyst layers (CLs), electrodes, membrane, gas diffusion layers (GDLs), and microporous layers (MPLs), which are called the membrane electrode assembly (MEA) [11].



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The most common CLs in PEMFCs are platinum (Pt)-based [14]. Catalysts based on platinum, palladium, and gold have been utilized. Among them, Pt has exhibited a remarkable performance over other metals regarding synergized electrochemical activity, especially oxidation reactions at the anode and oxygen reduction reactions (ORRs) at the cathode in low-temperature PEMFCs [15]. Despite this superior performance, the high-cost factor can be minimized with an optimum size of the platinum catalyst. The electrolyte, in most cases, is made of Nafion material, which has good mechanical properties and provides a high proton conductivity at temperatures around 80 °C [16].

There are many types of fuels used to operate PEMFC, such as hydrogen, hydrocarbons in general, and alcohols (e.g., ethanol and methanol). Hydrogen fuel is considered a promising fuel to operate PEMFC, with water as a byproduct only at a high power density. Usually, around 95% of hydrogen fuel is produced from fossil fuels; however, there are green production methods, such as water electrolysis and gasification of biomass [17]. Even though hydrogen fuel suffers from a high cost for transferring, compressing, and storage, it possesses some features such as burning without toxic emissions and having a gravimetric heating value much higher than hydrocarbon fuel (by three times) [18]. Furthermore, hydrogen fuel is stored/transported efficiently in a tank under a very high compression pressure, as it is ultra-light gas with substantial volume occupation, which can be reduced by applying high-pressure conditions. The PEMFC operates at a temperature range from 60 to 85 °C for low-temperature PEMFC (LT-PEMFC), on the other hand, the temperature operation range varies from 120 to 140 $^\circ$ C in the case of high-temperature PEMFC (HT-PEMFC), with an average power capacity of ≤120 kW and electrical efficiency of 50–60% [19]. Nevertheless, PEMFC technology still faces several technical and economic challenges, which are related to the cost of catalysts, operating temperature conditions, durability/stability [20], the infrastructure of membrane electrode assembly (MEA) corrosion [21], and water management problems [22–24].

The introduction of the infrastructure of hydrogen stations (pipelines, liquefaction/storage facilities, and compressors) requires a robust control system and an optimized design of the fuel cell stack for efficient operation [25]. Degradation affects the expensive membrane and cathode electrode structures. The high cost of PEMFC occurs due to the high price of the platinum and membrane materials [26]. Flooding problems occur because of the reduction reaction at the cathode, and this process leads to water generation in the liquid form at the cathode [27].

The sustainable development of societies should be governed by sustainable energy sources that do not cause environmental pollution. Recently, there have been many efforts aimed at finding a sustainable solution for producing various fuels and reducing carbon footprints. Catalytic hydrogenation of carbon dioxide appears to offer an opportunity and a challenge at the same time. It is directly impacted by the development of novel catalysts and environmentally friendly approaches. This paper aims to review the many sustainable aspects of fuel production. Fuel cell systems are believed to play a key role in achieving sustainability, especially when they operate using hydrogen or other sustainable fuels [28,29]. Fuel cells are receiving attention because they possess a high theoretical efficiency [30], are environmentally friendly [31], and have zero to low emissions (depending on the fuel) [32]. This mini review discusses the potential fuels for proton exchange fuel cells, with a focus on the sustainability aspect of this fuel production.

The performance of a PEMFC is known to be influenced by the various operating parameters, including the pressure, temperature, humidity, and the air stoichiometry ratio. The various effects of these parameters must be first explained in the following sections, because an optimum fuel cell performance is crucial for a direct impact on the macro-level system performance, the environment, and eventually the sustainability of the system.

2. PEMFC Operation

The basic operating system of the PEMFC relies on the main components of it is structure, such as the anode electrode, cathode electrode, CLs, proton exchange membrane,

GDLs, and BPs. The PEMFC system in Figure 1 is supplied with hydrogen fuel at the anode layer [33]. The protons and electrons are formed due to the electro-oxidation reaction of hydrogen at the CL. The generated electrons move through an external circuit to produce a DC electrical current, whereas the protons reach the cathode side by traveling through the electrolyte, which is a proton conductive polymer (e.g., Nafion) [33]. The PEMFC system is provided with oxygen at the cathode layer; thus, the reaction of hydrogen protons and electrons with oxygen generates water and heat [34].



Figure 1. PEMFC operation system [33].

2.1. The Fuel Cell Operation Pressure

The fuel cell pressure has a proportional relationship with the partial pressure of hydrogen and oxygen in the flow channels of the anode and cathode compartments. When the fuel cell pressure increases, the performance of PEMFCs increases at low current densities, as reported by Askaripour in Figure 2 [35]. Askaripour showed that the PEMFC performance improved at 0.4 A/cm² of current density, with different inlet cell pressure values. At current densities larger than 0.4 A/cm², the performance and the open-circuit voltage decrease, and the cathode activation, Ohmic, and concentration losses also increase. Li et al. [36] performed a comparative analysis on thick/thin MEAs for high FCs performances. The low ohmic resistance, low ohmic polarization, and ease of hydration at low humidity offered by thin MEAs/membranes improved the current density, the cathode catalyst O_2 reduction activity, and localized O_2 transport. The maximum performance of the thin MEA was reported with a 50 cm² PEM fuel cell and a peak current density of 2.51 A/cm², at 0.65 V operation under 50% RH (at the cathode and at the anode) and a counter-cross flow pattern. In another study, the enhancement of power density was investigated with a variation in temperature/pressure, RH of anode/cathode, and proton conductivity of the porous gas diffusion electrode (GDE), with the support of the vector machine (SVM) approach [37]. At an optimized temperature of 86.2 K and 3.44 atm fuel cell pressure, a peak power density of 870 mW/cm² and conductivity of 997.7 S/m were reported at a RH of 50% and 64.4% for anode and cathode, respectively. It should be noted in this context that this temperature (86.2 K) is not practical.



Figure 2. The effect of different cell operating pressures on the polarization curve (Reprinted with permission from Ref. [35], license No. 5353090032287).

2.2. The Fuel Cell Operation Temperature

The fuel cell operating temperature is considered a crucial parameter in a fuel cell operating system. The operating temperature influences the membrane conductivity, current density, synthesis of input gas streams, and water vapor pressure. The molar fraction of hydrogen and oxygen relies on the temperature and the inlet pressure. The cell operating temperature affects the kinetics of PEMFC; when the temperature increases, the current density (reaction rate) increases [38]. The operating temperature must be selected in a suitable range, to obtain a constant electrochemical reaction rate, and to avoid corrosion/degradation of the PEMFC materials. At high temperatures, the membrane dehydrates or decomposes (depending on the material); thus, the cell voltage decreases, and hence, the performance and efficiency of the fuel cell will eventually be reduced. The optimum temperature range for LT-PEMFC may be about 65–85 °C and for HT-PEMFC about 120–140 °C [39]. Badduri et al. [40] reported that the performance of a PEMFC was improved when the temperature increased from 45 °C to 75 °C at 100% RH, 1.5 bar of inlet operating pressure, and the back pressure equaled ambient pressure. On the other hand, when the temperature was increased up to $85 \,^{\circ}$ C, the performance of the PEMFC was impacted negatively, because of the membrane dehydration; thus, the Ohmic losses increased, which in turn reduced the ionic conductivity of the membrane. The obtained optimum conditions were a 0.41 W/cm² power density at 0.69 A/cm² of current density, at an optimal operating temperature of 75 $^{\circ}$ C, as shown in Figure 3 [40]. Xia et al. [41] examined the temperature effect on the polarization curve of HT-PEMFC at a temperature range from 101 to 180 °C. The highest ionic conductivity of 7.8 S/m occurred at 160 °C. They noted a reduction in power density when the temperature varied from 160 to 180 $^{\circ}$ C, at a current density of 1.05 A/cm^2 . The reduction happened because of the rising water content. The optimum operating temperature was in the range of 160–180 °C, the HT-PEMFC showed a high performance, with high power densities. Wannek et al. [42] carried out a detailed analysis of the HT-PEMFC system over a temperature range of 140–200 °C and measured current/power density. With the rise in operating temperatures, novel ABPBI membranes showed a decrease in resistance, which ultimately enhanced the power density up to 250 mW/cm^2 , as shown in Figure 4.



Figure 3. The performance of three-channel designs at the optimum temperature of 75 °C(Reprinted with permission from Ref. [40], license No. 5353090612869).



Figure 4. The effect of different operating temperatures on the performance of a H₂-based HT-PEMFC at ambient pressure [42].

2.3. Relative Humidity

The relative humidity (RH) of a cell affects the membrane resistance. Whenever the humidity increases, the Ohmic losses decreases, due to a reduction in membrane resistance and the enhancement in proton conduction paths, by virtue of the available water content. A dehydrated membrane, on the other hand, restricts the movement of the protons because of a lack of water content (necessary for proton hopping); thus, the current density drops. An optimal relative humidity improves the cell voltage, increases the power density, and eventually the fuel cell performance. Li et al. [36] conducted an experimental study on PEMFCs with thin MEA under a low humidity at the anode of 50% and anhydrous conditions at the cathode. Then, under fuel cell operating conditions of 0.65 V, 0% relative humidity at the anode, and thin MEA, the average

current density obtained was 2.51 A/cm². As mentioned earlier, Peng et al. [37] reported that the operation conditions of RH at the anode were 50%, RH at the cathode was 64.4%, with an optimum operating temperature of 86.2 K, 3.44 atm of cell operating pressure, 50% porosity of the gas diffusion electrode (GDE), and 997.7 S/m conductivity of the GDE generated 870 mW/cm^2 of power density of PEMFC. In this context, it should be noted that the temperature of 86.2 K reported in the previous work (Peng et al.) is not practical. Peng et al. compared their results to Cheng et al. [43], where the pressure and temperature were 3 atm and 80 °C (353 K), respectively. Toghyani et al. [38] examined the effect of a fuel recirculation system that contained a compressor and an electrochemical pump in a PEMFC stack operating at temperatures 60-80 °C. An electrochemical pump is a device used to compress hydrogen gas. They noticed that when the relative humidity varied from 20 to 100%, the recirculation ratio increased from 1.18 to 1.5 and the hydrogen stoichiometric ratio was raised from 1.64 to 1.82. The electrochemical pump was assessed and compared with the ejector. Figure 5 shows the PEMFC stack voltage as a function of RH. The results revealed that the voltage was reduced from 17.99 to 17.03 mV with the increase in RH, accompanied by a decrease in power consumption (for the electrochemical pump) from 0.535 to 0.506 W.



Figure 5. Effect of anodic relative humidity of PEMFC on the voltage and power of the pump (Reprinted with permission from Ref. [38], license No. 5353100068143).

2.4. Air Stoichiometry Ratio

The air stoichiometry ratio has a direct effect on the abundance of oxygen and the hydration level of the membrane [44]. Air stoichiometry ratio is defined as the ratio of injected oxygen to the oxygen required by stoichiometry (chemical reaction). At a low stoichiometric ratio of airflow, the rate of water removal is reduced thereafter, and the amount of oxygen that arrives at the membrane decreases; however, the humidity of the membrane increases [45]. Hence, the membrane resistance is also reduced. The availability of more oxygen in the air enhances the kinetics at the cathode.

When the airflow ratio exceeds an optimal value of air stoichiometry ratio at a low current density, the electrical resistance has a slight effect on the fuel cell voltage [46]. At a high value of current density and a high value of the airflow rate, a significant effect on the fuel cell voltage is observed, because increasing the oxygen content enhances the formation

of water at the cathode. To enhance the performance of a PEMFC, a high value of current density and an optimal rate of air stoichiometry should be met [47]. This is because of the water accumulation at the cathode, which imposes mass transfer limitations, preventing more oxygen from reaching the catalyst's surface [48]. Qu et al. [49] mentioned that changing the stoichiometry air ratio affected the cell voltage and the current density. The study indicated that the extent of air dilution/starvation at the end of the flow field channel depended on many factors, including the air stoichiometric flow ratio. The study also showed that the downstream oxygen content in the flow field was depleted progressively during the load change. Under air starvation conditions, a cell voltage undershoot was observed, which could be enhanced by increasing the airflow rates.

Polak et al. [50] examined changing the oxygen stoichiometry ratio from 1.25 to 1.5, and their findings showed that the cell voltage at a 1.5 cathode stoichiometry ratio was higher than the cell voltage at 1.25, by 3 mV, due to the increase in the oxygen flow rate. Below ratios of 1.2 of cathode stoichiometry rate, the researchers noticed a critical variation of the cell voltage, because of imperfect cathode ventilation, due to the flooding in the cell, as seen in Figure 6. Kim et al. [51] reported that the voltage drops increased when the air stoichiometry rate decreased below 2.0, because of the low rate of water removal and a lower concentration of oxygen, high mass transport resistance occurred.



Figure 6. Effect of cathode stoichiometry on cell voltage [50].

3. Materials and Structure of PEMFC

The major components of a PEMFC are the polymer electrolyte membrane, anode electrode, cathode electrode, MPL, and GDL, which together compose the MEA, which is generally sandwiched between two BPs [52]. The structure of a PEMFC is illustrated in Figure 7 [53].



Figure 7. PEMFC structure: (1) bipolar plate; (2) flow channels; (3) sealing; (4) gas diffusion layer; (5) microporous layer; (6) electrolytic membrane; (7) catalyst layer (Reprinted with permission from Ref. [53], license No. 5353101200640).

3.1. Anodes and Cathodes

The anodes and cathodes in the PEMFC are the CLs at which the electrochemical reactions take place. The CLs affect the gas diffusivity and the oxygen diffusion at the cathode side. The water removal process from the CL depends on the pore size distribution (PSD) and the porosity of these layers [54]. The CLs are usually composed of an ionomer, metallic nanoparticles (such as Platinum), and carbon particles [55]. Platinum is one of the most common catalyst materials in PEMFCs, due to its high effectiveness and catalytic activity. However, a Pt catalyst has some drawbacks, such as a high cost and it is poisoned by the adsorption of carbon mono oxide (CO) in hydrogen fuel. This leads to the reduction in the efficiency of the PEMFC because of the occupation of Pt catalyst sites by CO molecules. To eliminate the effect of the CO poisoning phenomenon in a PEMFC, researchers have developed an alloy composed of platinum-ruthenium (Pt-Ru) catalyst [56,57]. Moreover, as a result of the high cost and instability of platinum, studies have aimed to reduce the amount of Pt by mixing it with other cheap transition metallic nanoparticles, such as nickel [58], iron [59], cobalt [60], manganese [61], and chromium [62], for an enhancement of oxygen reduction reactions (ORR) and catalytic performance, leading to water activating ability, excellent durability, and anti-poisoning characteristics [52,63,64]. The MPLs are composed of black carbon powder with a porous structure and are commonly located between the CLs and the GDLs. The MPL has a role in speeding up the rate of water removal from the CL and reinforces the performance and durability of the fuel cell [53] by balancing the reactants and products at the multi-phase interface [65]. The GDL in a PEMFC is usually inserted between the CL and the BP. The common materials used in the GDL are carbon paper and carbon cloth. Studies showed that carbon paper had a better performance in comparison with carbon cloth. However, carbon cloth, in contrast with carbon paper, showed an improvement in the performance of a PEMFC when the current density was greater than $0.5 \,\mathrm{A/cm^2}$ [34]. The GDL influences the current density, power density, performance, and durability of a PEMFC; the GDL also controls the flooding on the cathode side. Usually, the GDL is covered by polytetrafluoroethylene (PTTE), which is considered a hydrophobic material, to decrease the mass transport losses and enhance oxygen diffusion. To minimize the Ohmic losses in GDL, the assembly pressure should be less than 1 MPa [53]. When the thickness of GDL is large enough, it will be suitable to ensure the protection of the CLs from corrosion and erosion, mechanical support for CL, facilitating the electron conductivity between BPs and CL, and controlling heat/water removal. The electrode compositions are varied in fuel cell systems. For example, Lim and Wang [66] carried out an experimental study to compare the performance of PEMFC with MEAs containing fluorinated ethylene propylene (FEP) at 10 to 40 wt.%. The results

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exhibited that 30 wt.% FEP-impregnated GDL coated with an MPL (40 wt.% PTFE + Vulcan carbon black) provided more diffusion resistance to oxygen movements, leading to a low current density. Polarization curves displayed a maximum current density of 800 mA/cm² at 0.6 V for a 10 wt.% FEP-impregnated cathode GDL, exceeding by 40% that of a 30 wt.% FEP-impregnated cathode GDL with MPL (330 and 440 mA/cm² at 0.6 V). Overall, the excessive wt.% of the FEP-impregnated cathode GDL affected the local effective mass diffusivity of fuel gas in the MPL [67]. In a similar study, 20 wt.% PTFE loadings-GDL showed the best fuel cell performance, while a 40 wt.% PTFE loading in the MPL had the highest gas permeability [68].

3.2. The Membrane

The membrane is the most significant part of the fuel cell and is usually sandwiched between the CLs of the anode and cathode [69]. The membrane is a thin layer, and whenever the membrane is thinner the performance of PEMFC can be enhanced, as thicker membranes can impose mass transfer limitations, due to an increase in the diffusion path [70]. Perfluorosulfonic acid is the polymer electrolyte membrane material used in PEMFCs, and it is categorized into two types: long side chain-like, such as Nafion, and short side chain, such as Aquiviun[®] membranes [69]. Nafion membranes consist of a copolymer fluoro-3,6-dioxo 4,6-octane sulfonic acid with polytetrafluoroethylene (PTFE), while the backbone structure of PTFE provides the hydrophobic feature to the membrane simultaneously, the sulfonic acid that is related to the membrane is responsible for the hydrophilic properties to the membrane should provide some advantages, such as a high rate of proton conductivity, high durability, being stability chemically and thermally, preventing the cross-over of the fuel between the anode and cathode, and preventing electron transport through it [72,73].

Usually, a perfluorosulfonic acid type of membrane guarantees all the advantages needed to obtain a more efficient fuel cell. However, at the same time, there are many disadvantages of perfluorosulfonic acid membranes. The disadvantages include the following: (1) the high rate of proton conductivity requires a higher water content, which in turn needs more humidifiers for reactant gases; (2) the formation of swellings and shrinking that occurs during the change of humidity rate; (3) the structure is weakened under fuel cell conditions, formation of radicals can occur, then it will be vulnerable to damage and reduce the rate of proton conductivity; (4) chemical degradation of the membrane happens, because there is the possibility of a reaction between the radicals and polymer backbone, (5) high-cost materials; and (6) being impractical at higher operating temperatures, due to the loss of conductivity and the low glass transition temperature [69].

Nafion is the most commonly used membrane in PEMFCs, whether the fuel is hydrogen or alcohols (methanol and ethanol). However, it suffers from drawbacks, especially fuel crossover. Hence, researchers developed modified types of membranes, such as modified perfluorinated composite membranes, inorganic nanocomposite membranes, hydrocarbon polymers membranes, fullerene-based membranes [34], polystyrene-sulfonic acid membranes, sulfonated polyimide-based membranes, and polybenzimidazole based membranes [69,74–77].

3.3. Bipolar Plates (BPs)

The BPs in a PEMFC represent about 70% of the weight and about 40% of the expenses [78]. In general, BPs are a significant contributor to controlling the water and heat content, collecting the generated current, providing a high mechanical strength for the cells, and organizing the movement of the gas particles at the anode and cathode [79]. Previously, graphite was the common material used in the manufacturing of BPs, due to its high rate of electrical conductivity and high corrosion resistance. Furthermore, the drawbacks of graphite are in the form of high cost, high permeability for gases, and brittle structure; thus, graphite is inoperable for a long period of operation [80]. Recently, several types of

research have moved toward a metallic material to compose the BPs, such as stainless steel, titanium, nickel, and aluminum. The advantages of metallic materials include the high rate of electrons and thermal conductivity, low cost, durable mechanical strength, and lower permeability for gases, leading to the predominance of metallic materials in the market in contrast with carbon-based materials [78]. However, bare metallic BPs suffer from a low rate of corrosion resistance, and to increase the rate of corrosion resistance, researchers have upgraded the coating for metallic BPs, such as with carbon, chromium, noble metals, and titanium nitrides [81]. Maharudrayya et al. [82] proposed bipolar gas distribution channels for PEMFCs as multiple U- and multiple Z-type flow configurations, as shown in Figure 8, followed by calculation of the flow distribution and pressure drop via three-dimensional computational fluid dynamics (CFD) simulations.



Figure 8. Bipolar geometry illustrations: (**a**) single serpentine design; (**b**) multiple serpentine design; (**c**) single/parallel Z- design; (**d**) single/parallel Z- design; (**e**) symmetrical design; (**f**) discontinuous design; (**g**) interdigitated channeling (Reprinted with permission from Ref. [82], license No. 5353101426858).

4. Fuels for PEMFCs

The selection of fuel is considered key to operating the fuel cell with suitable efficiency and generating more power. Below, the most commonly used fuels are discussed.

4.1. Hydrogen Fuel

Hydrogen fuel has several characteristics for consideration as a fuel in PEMFCs, such as a low heating value, zero-to-low emissions of greenhouse gases (depending on the purity), and a high energy density, from 120–142 MJ/kg [83,84]. Hydrogen is mainly produced by steam reforming [85]; however, it could be also produced via thermal cracking of coal, oil, or methane [86], and by electrolysis [87]. There are potentially several ways to produce hydrogen fuel from fossil fuels. These technologies consist of hydrocarbon reforming, hydrocarbon pyrolysis, and biomass pyrolysis. Steam reforming technology generates about 49% of global hydrogen [88]. Steam reforming technology is performed at high temperatures and low pressures and can be thermodynamically stable and significantly endothermic [89]. This process also generates carbon monoxide (CO) along with hydrogen; thus, the combination passes through several stages to eliminate the CO by a water gas shift reaction. The yield of the produced hydrogen is estimated at between 60–70% [90]. The electrolysis process depends on an external energy source, and the energy source can be a clean and renewable source, such as solar, wind, or biomass, to avoid the production of pollutants such as carbon dioxide [91]. The water splitting by the electrolyzer produces pure hydrogen and oxygen, while the purity of the hydrogen is approximately 99.99% [92]. Nowadays, the percentage of hydrogen generated by the electrolysis process is only about 4%, due to the high capital costs [92]. The integration of solar water-splitting technology with the utilization of efficient electrocatalysts (i.e., CoPi, CoFeO_x, NiCeO_x, NiCuO_x, etc.) has shown promising results for the oxygen evolution reaction (OER), as well as hydrogen production [93]. The cost and efficiency goals (18%) associated with solar watersplitting technology are under discussion for plausible long-term hydrogen production [94]. However, thermochemical water splitting cycles are considered an alternative, with costeffective hydrogen production system efficiencies of up to 50% and have shown a major application in nuclear power interfaces (high-temperature gas-cooled reactors) [95]. Usually, the high-pressure compressed hydrogen is stored in the cylindrical tank with 350–700 bar of pressure; this has the advantages of a short refueling time, which is about 3 min, and uninterrupted supplying of the fuel to the stack. However, hydrogen storage systems have a high weight. On the other hand, the high-pressure compressed hydrogen technique suffers from a high cost of the storage materials of the tank, the low storage capacity of hydrogen (by volume), and several safety concerns [96]. The liquid hydrogen storage technique possesses the characteristics of effective storage density, suitable for long-distance transportation, and suitability for large-scale storage applications [97], while, at the same time, it requests a high energy intensity, which is about 64% more than the energy needed for compressed hydrogen storage systems [98]. To liquefy the hydrogen, it has to be cooled to 20 K; hence, the temperature difference between the room temperature and storage temperature should be around 280 K [97]. Therefore, a proper thermal isolation system is also required, to increase the pressure and decrease the evaporation losses in the tank. Overall, a maximum efficiency has been found of 79.3 and 75.7% for hydrogen/oxygen and hydrogen/air fuel cells, respectively [99].

The solid form of hydrogen storage functions in the form of a metal hydride storage system. The metal hydride (MH) combination is a result of a reversible reaction between metal alloy and hydrogen at a certain pressure and temperature. The hydrogen in the MH mixture has absorption and desorption processes, which are considered exothermic and endothermic reactions, respectively. Thus, the storage system will require accessories to control the heating and cooling conditions, resulting in a high-cost system [98]. The positive sides of using the MT technique include the operation at low pressure, suitability for stationary applications, being thermodynamically stable, high volumetric density, high gravimetric capacity, and being safe, and reversibility [100]. Examples of metal hydride compounds are alkali metal borohydrides, such as lithium borohydride (LiBH₄), and sodium borohydride (NaBH₄). Alkali metal borohydrides possess a gravimetric capacity of 18.4 and 10.6 wt.%, respectively, for the preceding lithium and sodium borohydrides.

Sodium hydride (NaH), lithium hydride (LiH), and magnesium hydrides (MgH₂) could also be used [98].

4.2. Methanol Fuel

Methanol fuel could be generated from natural gas and coal, as conventional sources, or from green hydrogen, captured carbon, and biomass, as non-conventional sources [101]. Methanol has a high energy density of 3800 kcal/L, which is more than that of hydrogen (658 kcal/L) at 360 atm [102,103], a low boiling temperature, a high octane number of 113 [101], low production cost [104], is cheaper than hydrogen, and easier to store and transport [105], can be used under normal temperature and pressure, does not ignite rapidly, and is biodegradable [106]. Likewise, its toxicity and corrosiveness are the main disadvantages of methanol [107,108]. The overall efficiency of a direct methanol fuel cell (DMFC) is 35–60% [109]. About 90% of methanol in the world is extracted from natural gas as it undergoes the stream reforming process to produce syngas, which is a blend of hydrogen, CO, and CO_2 [110]. Syngas can be transformed into crude methanol, which in turn becomes pure after distillation. Bio-methanol fuel is formed by syngas that goes through the gasification process under a temperature range from 800 to 1000 °C in a reactor [110,111]. The catalytic hydrogenation of the CO_2 process depends on the reaction, which occurs between the carbon dioxide generated from industry or human activities and the hydrogen that is produced from water by electrolysis [112]. Usually, a methanol fuel tank is manufactured from mild steel, stainless steel, polyethylene, and vulcanized natural rubber. The structure of the storage tank is composed of a floatable roof with a passive gas pedal to decrease the vapor revival. The outside of the storage tank could be surrounded by an embankment, which in turn is covered by a fire extinguishing system with a foam type of carbon dioxide or a dry chemical, since methanol is a flammable fuel [113]. Wiberg [114] used a fuel tank for direct methanol fuel cell (DMFC) made of polyethylene, due to the low melting temperature of the material. The bottom side of the tank contains four holes, two for methanol injection and the other two for CO_2 capture, and the four holes are connected to the DMFC. Liu et al. [115] reported a novel electrospun nanofiber membrane based on sulfonated poly(ether ether ketone) (SPEEK) integrated with long chains of poly(vinylidene fluoride) (PVDF) for direct methanol fuel cells (DMFCs), which showed a maximum power density of 104 mW/cm^2 with 5 M methanol, higher than 2 M methanol with a value of 89.3 mW/cm². Furthermore, a methanol permeability values 23.5×10^{-7} cm²/s at 70 °C were exhibited by the novel membranes, comparable to pristine SPEEK (48.3 × 10^{-7} cm²/s).

4.3. Hydrocarbon Fuels

The components of hydrocarbon fuels are hydrogen and carbon atoms. Generally, hydrocarbon fuels are extracted from hydrocarbon compounds, in the form of gasoline, diesel, and/or jet fuel. Hydrocarbon fuels are distinguished by their availability, high calorific value [116], high power and energy density for liquid hydrocarbon fuels (e.g., diesel and gasoline) [117], high storage energy density, and being easy to store, which leads to a reduced cost of the system [118]. The efficiency of direct hydrocarbon fuel cells is 70–80% [119]. Hydrocarbons are found preserved inside porous rocks in the ground, planet, and trees. Hydrocarbons are produced in many ways, such as the conversion of coal to syngas by a Fischer–Tropsch reaction, pyrolysis-derived bio-oil treatment, and the conversion of sugars into biomass [117].

4.4. Ethanol Fuel

Ethanol fuel is an attractive fuel because it is non-toxic and available with a high energy density of 25 MJ/kg fuel [120]. Crossover is the unwanted passage of the fuel from the anode to the cathode. This leads to combustion rather than having an electrochemical reaction. The presence of CO_2 at the cathode site is an indication of ethanol crossover, which increases with the increase in ethanol concentration at the anode [121]. The

crossover of ethanol leads to low fuel cell performance [122]. Azam et al. [123] investigated the fuel cell performance with an ethanol fuel concentration 0.5–3.0 M and operating temperature at ambient temperature to 85 °C, which resulted in a maximum power density of 8.70 mW/cm² at 85 °C, ethanol flux of values 3.71×10^{-4} and 8.79×10^{-4} g/m²·s for 0.5 and 3.0 M ethanol concentrations, respectively. Conventional ethanol fuel is produced from the chemical path via hydration of ethylene (which is a by-product from the manufacturing of oil) [124]. Bioethanol can be usually obtained from bio-sources such as sugarcane, corn, date palm, paper mill sludge, and wheat [125–129]. Fermentation, distillation, and dehydration are the main methods to produce bioethanol fuel [130]. Generally, ethanol fuel can absorb humidity, so ethanol fuel is stored in a dry environment [131]. Stainless steel and carbon steel are the major materials in ethanol storage tank manufacturing [132]. Moreover, ethanol is a flammable fuel at room temperature. Overall, the efficiency of the fuel cell is 20–40% [109]. Table 1 summarizes the above discussion about the different types of fuels used in PEMFCs.

Table 1. A summary of fuels used in PEMFCs.

Fuel Type	Production Methods	Efficiency (%)	Advantages	Application
Hydrogen	 Steam reforming Thermal cracking of coal, oil, or methane Electrolysis 	75–79	High energy storage densityEasy store and transport	Backup/portable powerSmall distributed generationVehicle transportation
Methanol	 Steam reforming Gasification process Catalytic hydrogenation CO₂ 	35–60	 High energy density Low boiling temperature High octane number of 113 Low production cost Cheaper than hydrogen Ease of storage and transportation 	Backup/portable powerAutonomous power
Hydrocarbons	 Hydrocarbon compounds, in form of gasoline, diesel Fischer–Tropsch reaction Pyrolysis-derived bio-oil treatment Conversion of sugars in biomass 	70–80	 High calorific value High volumetric and gravimetric energy density Less cost of the system 	 Auxiliary power Large distributed generation
Ethanol	 Thermal cracking of coal, oil, and gas Fermentation Distillation Dehydration 	20-40	Non-toxicAvailable with a high energy density	• Transport and stationary applications

5. Sustainability Aspects of Fuels

A sustainable fuel is a fuel that is produced via sustainable methods, such as solar or wind-driven electrolysis, turbines, or hydroelectric systems. In the following sections, the sustainable paths for producing PEMFCs fuels are presented.

5.1. Sustainable Hydrogen Fuel

Sustainable hydrogen could be produced by the photon-driven solar to hydrogen method. Solid oxide electrolyzers have been considered for the production of hydrogen. Karayel et al. [133] found that the hydrogen production yield was 431.16 metric tons by using this system, with solar radiation varying from 1400–2000 kWh/m²/year.

Haider et al. [134] predicted hydrogen production using machine learning methods and found out that it would be 93.3×10^3 kg/km by applying the prophet method. The results were obtained with a mean absolute percentage error of 3.71% algorithm, while the production system consisted of a mono-facial PV panel that had a capacity of 25,283 W_P, an efficiency of 17%, and a photovoltaic (PV) electrolyzer.

Wind energy systems coupled with electrolyzers are considered important renewable energy sources for hydrogen production. Ayodele and Munda [135] studied the production of green hydrogen using wind energy sources with a water electrolysis process. The results showed that the amount of produced hydrogen was 226.82 metric tons by consuming a wind power of 13,609 GWh annually. Hong et al. [136] implemented an optimization control strategy to improve the efficiency of hydrogen production. They used an electrolyzer with a power of 9.6 MW and an efficiency of 30.9 %. The maximum amount of hydrogen produced was 23.48 tons with a wind power of 195 MWh and consuming electricity for hydrogen production of 60.71 kWh/kg. Irfan et al. [137] used a biomass gasification method to produce hydrogen fuel from agriculture residue. In their study, the amount of hydrogen produced was 2.62 million MT/year of hydrogen under the optimal conditions of a 1:1 steam to biomass ratio and 750 °C temperature. Marcantonio et al. [138] examined a biomass gasification method for hydrogen production with a fluidized bed reactor and palladium membrane unit to separate the hydrogen. Their findings demonstrated that at the conditions of a gasifier temperature of 785–870 °C and steam to biomass ratio of 0.4–0.5, the hydrogen produced was 4.83 kmol/h, which is suitable for small and medium applications. Blanquet et al. [139] performed experimental work on hydrogen production using the biomass pyrolysis method with non-thermal plasma catalysis. They examined cellulose, lignin, and biomass, and the results exhibited 4.07, 4.29, and 3.94 mmol/g of hydrogen, respectively, at a reactor temperature of 800 °C.

It appears that the use of hydrogen in fuel cells, in particular, can best achieve a sustainable applicability of this fuel. For example, a study by Dincer and Rosen [140] in hydrogen in a PEMFC, followed by life cycle assessments of PEMFC vehicles and gasoline vehicles, demonstrated its usage as a renewable energy with improved efficiency for greenhouse gas emissions. The study showed that a fuel cell operating at 323 K and 3 atm with a membrane thickness of 0.016 cm had current densities of 0.05–2.0 A/cm² and showed a maximum power density of 0.935 W/cm².

5.2. Sustainable Methanol Fuel

The production of methanol from sustainable paths has been also investigated. For example, Alsayegh et al. [141] experimented with producing a green methanol fuel. They used a hydrogen plant, which was composed of a hybrid system of ultra-high concentrated solar cells and a grid to power a direct electrolyzer, CO₂ capture plant, and a methanol plant. The annual yield of methanol production was 77,738 tons, with a purity of 99.4 wt.%. The methanol production plant with concentrated solar thermal technology that had a mirror area of 880,685 m², a tower height of 220 m, and maximum thermal power of 350 MW, could produce 27.81 million liter/year of methanol fuel, as Monnerie et al. [142] reported. Wind energy is an important renewable energy source for methanol production. Ishaq and Dincer [143] indicated that a wind turbine had an exergy destruction rate of 46.3 kW with an efficiency of 45%, while a PEM electrolyzer with an exergy destruction rate of 115.7 kW and temperature of 80 °C, generated a methanol yield of 52.25 g/s. A methanol fuel production rate of 1333–1910 kg/h was obtained with a range of thermal power of 18–25 MW, which was produced with a chemical looping combustion (CLC) system, in association with a water electrolyzer [144]. Lundgren et al. [145] reported that a range of methanol production of 102,000–287,000 tons/year was gained from the off-gases that were generated by a steel manufacturing process with 300 MW_{th} of biomass.

Overall, it appears that the sustainability of methanol is represented by the potential of this liquid fuel as a promising candidate for long-term replacement of fossil fuels. Nowadays, there is a coupling of technology between CO_2 capture and its conversion

to methanol. Furthermore, the applicability of methanol as a fuel has been explored in energy carriers for industry i.e., cement/steel manufacturing plants, energy storage, or maritime fuel systems, which are further utilized for large-scale power generation and transportation [146].

5.3. Sustainable Hydrocarbon Fuels

The production of renewable hydrocarbons such as biodiesel has received attention in the literature. For example, Malins et al. [147] were able to produce a green hydrocarbon fuel by refining vegetable oil, while using product/waste soap stock, which consisted of nickel-supported SiO₂-Al₂O₃ composites through a hydro-treatment method. However, the highest yield of produced hydrocarbon was 79.1%, with a calorific value of 47.22 MJ/kg and 5.6 of C/H ratio, under optimum conditions of a 5% catalyst amount, 6 MPa reaction pressure, 320 °C reaction temperature, and 30-min of reaction time. Chaudry et al. [148] conducted a study on Botryococcus braunii, which are microalgae that can produce hydrocarbon fuel as a renewable source. They used a milking technique, which is a non-destructive extraction of Botryococcus braunii. The results exhibited that the hydrocarbon production yield was 7.31 MML/year by using 544 hectares of algae with an electricity energy demand of 3.98×10^7 kWh/year. A canola oil methyl ester conversion process was conducted using of HZSM-5-based catalyst and the process produced a yield of aromatic hydrocarbon of 42.6% under an optimum reaction conditions of atmospheric pressure, 450 °C of reaction temperature, and $2 h^{-1}$ of space velocity, as Bayat and Sadrameli [149] reported. Overall, sustainable hydrocarbons have been utilized for large-scale chemical storage of renewable sources for the generation of electrical energy as transportation fuel [150].

5.4. Sustainable Ethanol Fuel

The refining of vegetable waste by applying a depolymerization and fermentation process, especially sweet potato waste, gave a high yield of ethanol. Sweet potato waste has a sugar yield of 0.57 g/g, which in turn was converted to 251.85 mg/g of ethanol, with a productivity of 85.86% at a temperature of 35 °C, and a pH of 5 [151]. Petersen et al. [152] commenced a study on industrial off-gases, to obtain ethanol fuel by implementing a fermentation process with an acetogenic bacteria. The process generated a specific ethanol yield of about 114 L/ton of the feed, and surplus electricity of 293 kW under self-sufficiency mode. Dhandayuthapani et al. [153] reported that the microalgae biomass, which was defatted and had undergone an ultrasonic pretreatment, generated about 52.10 g/L of ethanol under a fermentation conditions of 30 °C of temperature, 4.0 pH, and 200 rpm. The literature shows that sustainable ethanol has promising applications in direct oxidation fuel cells (DOFCs) for portable/mobile applications, with superior performance over hydrogen and methanol. Table 2 shows a summary of the various fuels produced from sustainable paths, along with the study conditions and the yield.

Fuel	Extraction Method	Operating Parameters	Fuel Yield	Limitations	Ref.
Hydrogen	Solid oxide electrolyzer and mono-facial PV panel	 Operating temperature (20-40 °C) 67.95% efficiency Net Production Rate of 750 Nm³ h⁻¹ Power capacity of 440 W_P Solar radiation (1400– 2000 kWh/m²·year) 	 431.16 metric-ton 5–100% 	 Need for constant solar radiation for over a year Sufficient unoccupied spaces 	[133]

Table 2. Summary of the sustainable fuel yield with extraction method and operating parameters.

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Fuel	Extraction Method	Operating Parameters	Fuel Yield	Limitations	Ref.
Hydrogen	Mono-facial PV panel and electrolyzer	 17% efficiency Power capacity of 25,283 W_P The photovoltaic panel of an area of 1.501 m² 	 Daily production of H₂ 93.3 × 10³ kg/km² 75% (~1 kg hydrogen for 53 kWh) 	 Handle time-series problems Machines learning methods 	[134]
Hydrogen	Wind turbine with a water electrolyzer	 140 m height of wind turbine Area of 12,873 m² The rated power output of 4500 kW. 	 226.82 metric ton 24.04 to 54.55% 	 Economic and environmental impact assessment Localized wind-hydrogen system 	[135]
Hydrogen	Wind turbine and electrolyzer	 9.6 MW power output 30.9% efficiency 195 MWh wind power 	• 23.48 ton	• Economics of the wind-hydrogen system for commercial applications	[136]
Hydrogen	Steam gasification process	 Top bed temperature (85 °C) Bottom bed temperature (700 °C) 	• 28.08 mmol/g (dry)	 Management of wet biomass Operating conditions of hydrothermal carbonization with steam gasification 	[154]
Hydrogen	Fermentation process	 Heat treatment temperature (65 °C) 4.5 pH Reaction time of 30 min 	• 26.3 mL/h	 Pretreatment temperatures for activated and anaerobically digested sludge 	[155]
Hydrogen	Electro- hydrolysis of food waste process	 Potential of 5 V with a water electrolyzer 75 h operation 	 7000 mL H₂ content of 99% Production rate (2240 mL/d) Yield (493 mL H₂/g TOC) 	• High cost of electrohydrolysis	[156]
Hydrogen	Biomass gasification method	 750 °C reactor operation temperature Steam to biomass ratio (1:1) 	 2.62 Million metric tons/year 59.51% 	• Localized crops residue districts	[137]
Hydrogen	Biomass gasification method	 Fluidized bed reactor with Pd-membrane Gasifier temperature (785–870 °C) 0.4–0.5 steam to biomass ratio 	 4.83 kmol/h 49% 	• Range and improvement of the bed materials	[138]
Hydrogen	Biomass pyrolysis method with non-thermal plasma catalyst	• Reactor temperature (800 °C) with lignin	 4.29 mmol/g 10.13% 	Support material and plasma development	[139]

Table 2. Cont.

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Table 2. Cont.

Fuel	Extraction Method	Operating Parameters	Fuel Yield	Limitations	Ref.
Methanol	H ₂ plant of the concentrated solar cell, water electrolyzer, CO ₂ capture plant, and methanol plant	 75% efficiency Rates of H₂ and CO₂ energy consumption (5.08 and 0.75 MWh/ton_{MeOH}) 99.4 wt.% purified H₂ 	 9.727 ton/h 99.4% purity 	 Current electricity price for direct electrolysis Carbon taxation 	[141]
Methanol	Concentrated solar thermal system and methanol plant	 Solar panels area of 880,685 m² Tower height of 220 m Maximum thermal power of 350 MW Methanol reactor pressure (50 bar) H₂/CO = 3.588 	 27.81 Million liter/year Heliostat field efficiency of 52.1% 	 Cost of concentrated solar thermal components Life cycle analysis 	[142]
Methanol	Wind turbine and PEM electrolyzer	 Exergy destruction rate of wind turbine and electrolyzer of 46.3 and 115.7 kW 45% wind turbine efficiency 80 °C temperature Methanol production at 260 °C and 6000 kPa 	• 52.25 g/s	• System modeling and comprehensive analysis of wind locations	[143]
Methanol	CLC system with a water electrolyzer	 Production of methanol at 80 bar and 220 °C Density (1950 kg/m³) Bed porosity (0.4) 	 1820 kg/h 75% 	• Chemical and physical properties of biomasses as fuels	[144]
Methanol	Gasification biomass method	• Off gases at 210 °C and 8 bar	• 102,000–287,000 ton/year	Localized performance evaluation with biomass	[145]
Methanol	CO ₂ hydrogenation method	 Methanol reactor (210–270 °C and 50–100 bar) Alkaline electrolyzer (60–80 °C and < 3000 kPa) 	 1136–1988 ton/year 94.5% 	• Techno-economic feasibility of other sustainable bio-methanol production	[157]
Methanol	CO ₂ hydrogenation method	 NaTaO₃ as a photocatalyst Coating of 2 wt.% CuO and immerged in 2 mol/L NaOH solution 6 h exposure to sunlight irradiation 	• 137.48 µmol/g.h	 Selective formation of methanol with photocatalytic reduction of CO₂ 	[158]
Hydrocarbon	Refining of vegetable oil with existed of SiO ₂ -Al ₂ O ₃ metal to support Ni catalyst	 320 °C and 6 MPa 5% catalyst concentration A reaction time of 30 min 	• 79.1%	• Need for fast and inexpensive catalyst synthesis/recycling techniques	[147]

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Fuel	Extraction Method	Operating Parameters	Fuel Yield	Limitations	Ref.
Hydrocarbor	Milking method over Botryococcus braunii microalgae	 544 hectares of algae landing Annually energy demand of 3.98 × 10⁷ kWh Extraction efficiency of 50% 	• 7.31 MML/y	• High costs of an effective non-destructive extraction system for algae fuels	[148]
Hydrocarbon	Conversion of canola oil methyl ester process	 450 °C and 1 atm Space velocity of 2 h⁻¹ 	• 42.6%	• Temperatures and space velocities	[149]
Ethanol	Depolymerization and fermentation processes	 35 °C reaction temperature 5.0 pH 1.0 % H₂SO₄ (v/v) 	 251.85 mg/g Productivity 85.86% 	 pH and temperature of Vegetable wastes as a renewable feedstock 	[151]
Ethanol	Fermentation process	 Feed flowrate of 36,131 Nm³ hr⁻¹ 8000 operating hour Reactor temperature 37 °C at 1.5 atm of blower operation pressure 	• 114 L/ton	Build-up of contaminantsRecycling	[152]
Ethanol	The fermentation process and ultrasonic pretreatment	 30 °C reaction temperature 4.0 pH 200 rpm 	• 52.10 g/L	 pH, rpm, and temperature Biomass of green microalga as a renewable feedstock 	[153]
Ethanol	Fermentation method	 10% (w/v) of a stalk and 8% (w/v) of dried tuber powder 30 °C fermenter temperature 120 rpm stirring for 30 h 	• 45.3 g/L	• Localized bioprocessing operating conditions	[159]
Ethanol	Fermentation method	 Cellulosic anaerobic fermentation for 4 dyes 35 °C fermentation temperature Enzyme concentration of 10 U/g 	• 157.6 mg/g	• High cost of cellulases	[160]

The literature also demonstrated some other practical aspects on hydrogen application in fuel cells [161]. For example, biogas was studied and evaluated. A total power of 1280 MWh of biogas was generated from the manure of 300 milked cows on a dairy farm in Sweden [162]. A PEMFC-compound heat and power (PEMFC-CHP) system under a gasification process was able to generate 360 MWh annually, to supply the dairy farm with electricity. The PEMFC efficiency was 40%, with a power of 45 kW, as reported by Guan et al. [162]. A PEMFC of 48 cells, under a temperature of 65 °C, was supplied with green hydrogen, which represented 60% of the total gas percentage, while the hydrogen was derived from biogas by an anaerobic digestion process. Finally, the PEMFC generated 1190 W at 41 A [163]. It should be noted in this context that, among the available power sources

Table 2. Cont.

(e.g., batteries, fuel cells), fuel cells, in particular, are characterized by a high theoretical efficiency [164].

6. Challenges of Operation

Despite the various advancements in fuel cell systems that have been addressed in this context, the durability of these systems is still an issue. The PEMFCs still suffer from many issues that harm their durability, such as leaching of membrane components, agglomeration of catalyst platinum (Pt) particles, catalyst degradation, and cathode electrode decay. The typical durability of a PEMFC is approximately 5000 h for automotive applications and 60,000 h for stationary applications. Durability depends on the catalysts used. Andersen and Skou [165] investigated catalyst performance and durability with liquid electrolyte (sulfuric acid) and solid polymer electrolyte (Nafion) in carbon-supported Pt catalysts with various electrode structures. The results showed a high utilization, excellent stability, improved proton–catalyst interface, and good dispersion in the presence of Nafion ionomers.

A study conducted on high temperature HT-PEMFC by Alegre et al. [166], reported an aluminum-based cell and a graphite-based cell; the Al-based cell had a better initial performance in comparison with the graphite-based cell. Both cells experienced degradation problems, due to the agglomeration of Pt particles, especially on the cathode electrode, as well as the leaching of phosphoric acid from the membrane, which in turn decreased the conductivity, induces corrosion, generated high membrane resistance, and eventually reduced the thickness of the MEA. Likewise, there are many solutions to overcome the preceding issues. For example, low Pt and non-Pt electrocatalysts; designing a membrane with better structural specifications; reducing the leaching, by optimizing the parameters of operation conditions; and using a coating surface with a good corrosion resistance [166,167]. Marinoiu et al. [168] used gold nanoparticles on graphene oxide (Au/rGO) as a co-catalyst combination, to enhance the durability of the PEMFC, which led to a reduction in the degradation of the cathode layer.

Overall, it appears that the market for PEMFCs is still growing worldwide, triggered by the potential for zero emissions, high efficiency, fast startup, quiet operation, and high power density. However, many obstacles in the design of PEMFCs are still present and are related to reliability, cost, durability, fuel sustainability, and water/heat management. The cost of PEMFCs is still high, because of the high price of the materials involved, such as the platinum and ruthenium catalysts. The temperature of the cell should be optimum, to avoid the evaporation of the membrane's water content and, hence, a reduction in the performance of the PEMFC [12]. The CL degradation is another important challenge. Catalyst poisoning due to the adsorption of CO affects the fuel cell performance. Water management in the cell and the agglomeration of Pt particles on the cathode electrode is another challenge. The membrane is susceptible to degradation, which could be accompanied by significant changes to the mechanical characteristics if the temperature is increased beyond the glass transition temperature [169]. The flooding of the membrane represents a real problem for the performance of a PEMFC, which takes a place when the relative humidity and temperature are not at their optimal levels [170]. The variation of the pressure gradient inside the PEMFC, the electro-osmatic phenomena, and the back diffusion of water from the cathode to the anode are additional problems that need to be addressed [27]. Furthermore, the effect of fuel composition of the fuel, regarding the temperature conditions in the energy device, the toxic emissions after combustion, carbonization, and efficient power output at low cost should be future research directions for the adaptation of sustainable fuels for long-term applications.

7. Conclusions

PEMFCs are promising electrochemical, clean, high power density devices, with a high theoretical efficiency and effectiveness in comparison with other power sources. LT-PEMFCs operate at temperatures ranging between 65 and 85 °C, whereas HT-PEMFCs

operate in the temperature range of 120–140 °C. High-temperature operation enhances electrodes' kinetics, improves water management, and utilizes cheaper catalysts and fuels. Furthermore, an optimum relative humidity can reduce the membrane resistance, which, in turn, enhances the proton conduction and increases the performance of the cell. The performance of PEMFCs has been significantly enhanced by the new advancements in optimal designs, especially MEAs with excellent degradation resistance at high-temperature conditions and low Pt loading, which leads to improved durability for long-term applications. Moreover, the advancement in GDLs and MPLs has addressed their microstructure and mixed wettability. Hydrogen, methanol, ethanol, and hydrocarbons are the most commonly utilized fuels in PEMFC. Among them, hydrogen fuel is still the main fuel to operate PEMFCs, due to the promise of zero emissions and a high energy density. The fuel production from renewable and sustainable energy sources has opened new pathways for power generation and transportation applications at minimum operating costs. However, the durability of PEMFCs is still a challenge and needs to be improved to enhance their performance and productivity, and to facilitate the further penetration of PEMFCs into the market. Additional challenges in PEMFCs still exist regarding material costs, and research should be conducted to provide solutions for the stability of the materials, power enhancement, and better water management.

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