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Review

Proton Exchange Membrane Fuel Cell Catalyst Layer Degradation Mechanisms: A Succinct Review

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Abstract: Increasing demand for clean energy power generation is a direct result of the rapid depletion of fossil fuel reserves, the volatility of fossil commodity prices, and the environmental damage caused by burning fossil fuels. Fuel cell vehicles, portable power supplies, stationary power stations, and submarines are just some of the applications where proton exchange membrane (PEM) fuel cells are a prominent technology for power generation. PEM fuel cells have several advantages over conventional power sources, including a higher power density, lower emissions, a lower operating temperature, higher efficiency, noiseless operation, ease of design, and operation. The catalyst layer of the membrane electrode assembly is discussed in this paper as a vital part of the proton exchange membrane fuel cell. Along with that, the platinum (Pt)-based catalyst, carbon support, and nafion ionomer found in the catalyst layer often degrade. Catalyst growth, agglomeration, Pt loss, migration, active site contamination, and other microscopic processes are all considered in the degradation process. Employing experimental and numerical research with a focus on enhancing the material properties was suggested as a possible solution to understanding the problem of catalyst layer degradation. Ultimately, this review aims to prevent catalyst layer degradation and lower the high costs associated with replacing catalysts in proton exchange membrane fuel cells through the recommendations provided in this study.

Keywords: platinum; degradation; proton; membrane; catalyst layer; fuel cell

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1. Introduction

There have been global needs for a greener environment and renewable energy power generation [1]. Due to the versatility in design, operation, and application, proton exchange membrane fuel cells (PEMFCs) have emerged as one of the viable options for reducing greenhouse gas emissions [2,3]. In recent years, renewable energy technology has developed significantly with a focus on several applications [4–6]. Nevertheless, the PEMFC technology has been faced with several challenges: primarily, the cost of system component materials and material durability. Studies have shown that the lifespan of fuel cell components can be increased through careful consideration of the materials used in manufacturing them [7,8]. It was shown that the enhanced property of the material used in fabricating a catalyst increased the proton conductivity and chemical stability with the fuel cell [9,10]. However, the high price of materials used in manufacturing catalysts and relatively high operating temperatures have been demonstrated to affect the use of catalysts in different applications [11]. For the fuel cell to function at its best, materials that can withstand the prevailing operating conditions in the PEMFC environment are required.

During typical fuel cell operation, membrane and catalyst degradation have been experienced and investigated in several impressive studies [12,13]. It has been hypothesized that radical species generated during the PEMFC operation could attack the carboxylic end group of the nafion ionomer [14]. The Pt catalysts and carbon support degradation have also been associated with activity reduction at the catalytic surface and contamination of the PEMFC membrane [15]. Okonkwo et al. [16] showed that as the degradation rate increased, the relative moistness of the membrane decreased [16,17]. In another related study, degradation was shown to occur and continue in the presence of a catalyst, hydrogen, and oxygen, as reported by Ghassemzadeh et al. [18]. Although several interesting studies have been performed to understand the degradation mechanism of the catalyst layers used in the PEMFC, the consensus in the mechanism has not been reached since the mechanisms are influenced by the working environment of the fuel cells [12]. To understand the degradation of catalyst layers, it is necessary to understand the mechanisms that Pt, nafion, and carbon support display in various operational conditions. Carbon (C) corrosion causes catalysts to degrade through an adsorbed contamination process that alter catalyst properties [19,20]. Researchers have focused on developing carbon-support metal composites to improve the performance of catalysts [21]. Another approach is alloying the catalyst with different materials thereby enhancing catalytic durability, reactivity, and sustainability [22].

Recently, catalyst layer degradation and its sustainability have been hot topics in the scientific community [23,24]. However, detailed understanding of the catalyst's material behavior and degradation in the PEMFC are lacking in the literature and can be achieved through a systematic review of the literature, which is the objective of this study. Moreover, understanding the impact of system component degradation on the PEMFC performance appears to be lacking and seeks to be addressed in this study. Furthermore, through this study, enhancing the catalyst's material is suggested as a possible solution to the problem of catalyst layer degradation.

2. PEMFC Design

The PEMFCs are composed of several components that together form a membrane electrode assembly (MEA). A cross-section of commercial MEA is visible in Figure 1.

Attached directly to both sides of the membrane are the catalyst layers (CLs) as shown in Figure 1. The catalyst, which is often composed of Pt/C, is dispersed with Pt and carbon nanoparticles, serving as a mechanical binder, and providing proton conductivity to catalyst sites [25]. The anode and cathode are normally fabricated by spraying inks of the ionomer and catalyst directly onto the PEM to produce a catalyst-coated membrane (CCM). The high levels of porosity required of the membrane allows for better mass transport of gases into and out of the film [26]. The microporous layers (MPL) enhance electrical contact between the gas diffusion layer (GDL) and CL and reduces flooding in the fuel cell. Nguyen et al. [27] reported that the MPL also provides a contiguous, intermediate interface with properties between the nanoscale features of the CL and the layers above it containing micron-scale features. The MPL also helps in distributing gases homogeneously in the fuel cell and reducing mechanical strain on the CCM. The gas diffusion layer (GDL) shown in Figure 1 consists of carbon fiber paper made with hydrophobic polytetrafluoroethylene (PTFE) coating. The large carbon fibers in the GDL provide a high level of mechanical rigidity and electrical conductivity relative to the carbon [28]. The properties of the GDL ensure minimum resistive losses and mechanical distortion while maintaining sufficient porosity to allow for gas diffusion and humidification of the device. Around the edges of the GDL, a gasket liner is provided as a tight seal against gas leakage in the fuel cell. In the design of PEMFC, the MEA is held between flow field plates and the plates, normally graphite. The flow channels direct the flow of reactant gases from the gas inlet toward the outlet of the MEA.

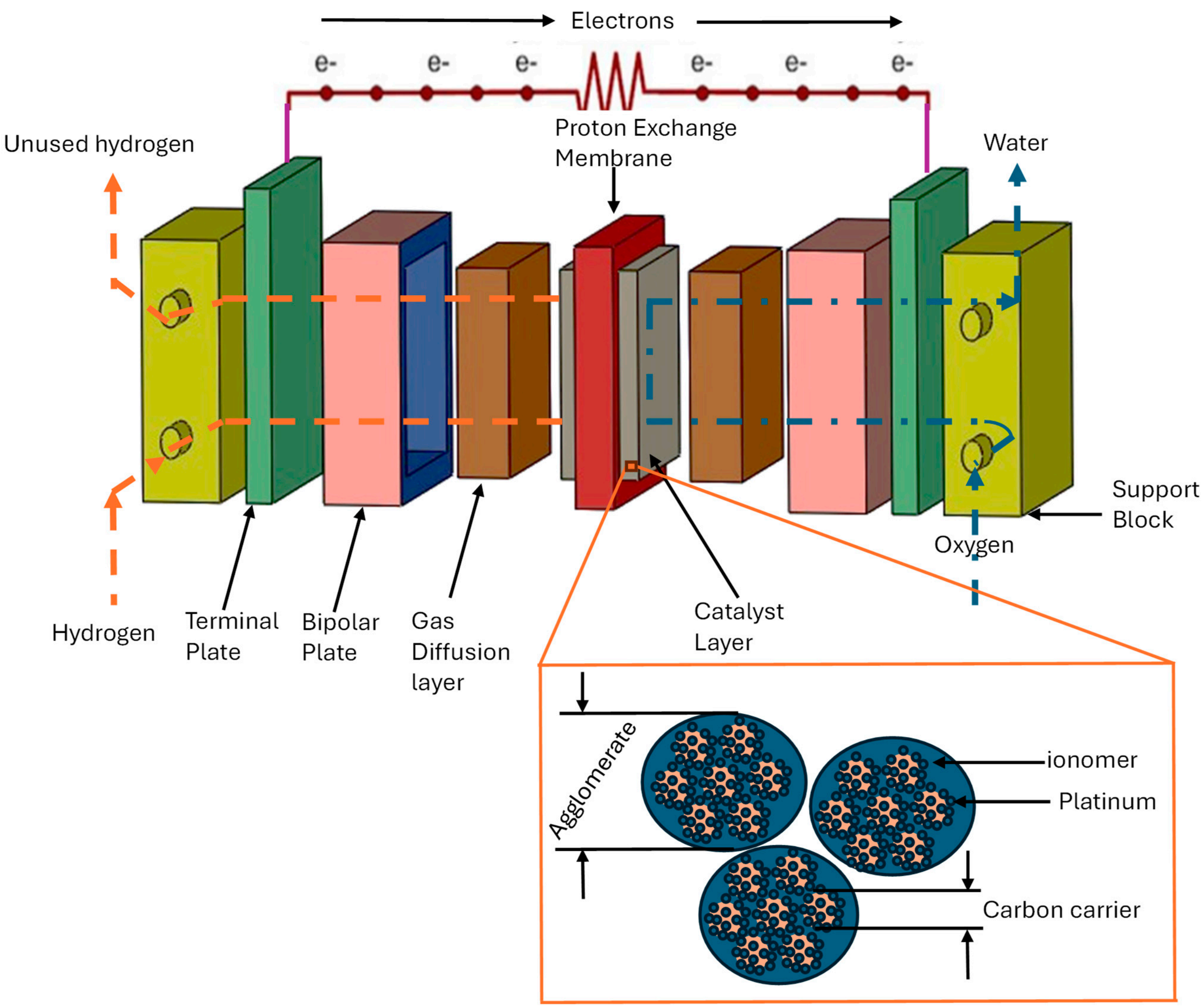


Figure 1. Schematic diagram of a typical PEMFC structural design.

2.1. Basic Components of the PEMFC

In the operation of the fuel cell, electricity moves into the anode and flows out from the cathode. The anode is located at the positive side of the fuel cell while the cathode is sited at the negative side. The anode and cathode play a critical role in allowing the passage of ions and gases between them [29].

2.1.1. Bipolar Plates

Bipolar plates (BPPs) act as a shield for the fuel cell, providing it with the necessary foundation and mechanical backing. The BPP must have good mechanical and chemical properties so that it can serve its purpose [30]. There are only a few metals typically used in BPP production [30]. However, protecting the BPP with coatings has proven to be an effective method of preventing corrosion.

2.1.2. Gas Diffusion Layer

The gas diffusion layer (GDL) is one of the components included in the technology of PEMFC. In the design, the GDL is often wet-sealed with a PTFE coating to block liquid water from obstructing the pores [31]. To achieve the above function, the selection of appropriate materials and layout is required.

2.1.3. Membrane

While the membranes can be fabricated with the PFSA, the permeability of gases through the system and hydration of the PFSA are critical aspects of its performance. The condition places several limits on PEM operation that the temperature must not exceed 100 °C, and the gas streams must be continuously humidified [32]. If bulk liquid water condenses on or inside either electrode, the mass transport of gases is locally disrupted [33]. The need for membrane hydration is driven by the unique nanomorphology of the PFSA [34]. Luo et al. [35] revealed that the membrane must remain fully hydrated to conduct protons. Fuel or oxygen starvation has been shown to greatly affect the degradation of the fuel cell, performance, and lifetime. Therefore, operating a fuel cell requires it to be dynamically balanced to keep the membrane hydrated while preventing "flooding". The PTFE fraction of the polymer is hydrophobic and the acidic side chains are hydrophilic [36]. The difference in the design leads to microscopic phase segregation of the two fractions [37]. Proton transport takes place in the polar hydrophilic domains as the collapsible PTFE backbone is responsible for the mechanical stability of the membrane [38]. During the electrochemical process, the most widely accepted models of the non-polar PTFE backbones of the polymer collapse together with the polar sulfonic acid groups [39]. This leads to pronounced phase separation, as the water is concentrated around the polar sulfur groups to form a large percolating water domain at high-water activities [40].

2.1.4. Catalyst Layer

The catalyst layer is the key element of the fuel cell, where the electrochemical reactions take place that generate the voltage and current [41]. The catalyst layer is another critical component of the PEMFC, where electrochemical reaction occurs in the fuel cell. In the process, the voltage and current are generated [42]. The catalyst layer is made up of the high conductive hydrophobic carbon-based materials [43]. While the catalyst layer is often made up of carbon, platinum, and nafion, a significant amount of Pt/C powder is often combined as an essential component in the fuel cell. Wang et al. [44] revealed that as the catalyst in a PEMFC must be both corrosion resistant and chemically active to activate oxygen, the oxygen reduction reaction (ORR) process at the cathode serves as a crucial test for the performance of the PEMFC technology. It has been reported that the difficulties of the ORR process necessitate a higher Pt loading at the cathode side of the PEMFCS than at the anode side [45].

Carbon Support

Carbon support is one of the vital components of PEMFC technology. The carbon supports are made up of smaller internal pores that enhance the passage of Pt particles [46]. Although there are several types of carbon supports used in the PEMFC design, the Vulcan (Vu) and high-surface area (HSC) are commonly employed in the design of carbon support used in the PEMFC [46].

The Ionomer

An understanding of ionomer chemistry is necessary to explain how PEMFCs are designed and operated. Virtually all ionomers used in commercial hydrogen fuel cells are composed of a perfluorosulfonic acid (PFSA) copolymer. The polymer consists of a polytetrafluoroethylene (PTFE) backbone, periodically branched by side chains terminating in a sulfonic acid [47]. The perfluorination of the polymer prevents radical damage by reactive oxygen species (ROS) and degradation of the polymer under highly acidic conditions. The negatively charged sulfonic acid functional group contains the ionomer and PTFE backbone. The negative ions are allowed to be transferred between the sulfonic acid group while the protons are not allowed [48]. The PEMFC contains two types of ionomers. The first type of ionomers called PEM performs the function of electrically insulating the anodic catalyst layer (ACL) from the cathode catalyst layer (CCL), thereby preventing electrical shorting. The second type of ionomers made of thin film covers and binds the exposed carbon/catalyst matrix of the CCL. The thin films help proton transport within the ACL and CCL to extend the hydrogen oxidation reaction (HOR) and ORR reactions. Though the interior structure of the ionomer is of great complexity, universal consensus has not been achieved regarding its operation and degradation mechanism [49].

Pt-Based Catalyst

Pt-based catalysts are widely used in PEMFCs due to their excellent ability to facilitate the electrochemical reactions at both the anode (hydrogen oxidation) and cathode (oxygen reduction). The Pt is highly effective in reducing activation energy, which improves the overall efficiency of the fuel cell. However, Pt is expensive and prone to deactivation over time due to factors like carbon monoxide poisoning or catalyst sintering. Researchers are focused on enhancing Pt-based catalysts by improving their durability and reducing the amount of platinum required, often by alloying it with other metals or using nanostructured materials.

3. Operation of the PEMFC Process

The electrochemical process of the PEMFC involves the combination of hydrogen (H_2) and oxygen (O_2) to produce water, heat, and electricity, as shown in Figure 2.

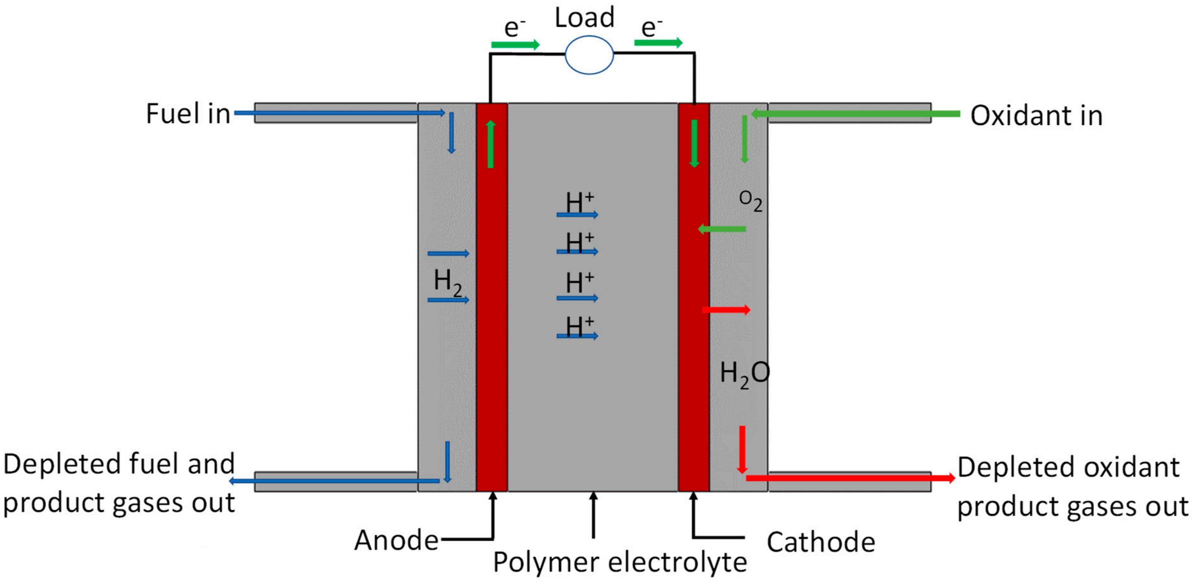


Figure 2. Schematic diagram of PEMFC processes.

During the electrochemical process, the ion-conducting polymer allows the conduction of the protons to the electrocatalyst surface to react with O_2 to form water through the ORR process. Equations (1)–(3) display the reaction process [50].

$$H_2 \rightarrow 2H + 2e - (\text{Anode HOR}) \tag{1}$$

$$2e - +2H + 12O_2 \rightarrow H_2O\ (\text{Cathode ORR}) \tag{2}$$

$$H_2 + 12O_2 \rightarrow H_2O + \text{heat} + \text{electricity}\ (\text{Full}) \tag{3}$$

The basic functions of the PEMFC system components are shown in Table 1.

Table 1. Functions of the catalysts used in the PEMFC.

Catalytic Layer Component	**Function**	**Ref.**
Platinum	Resistance to the stresses imposed by PEMFC operation	[51]
	Protect the PEMFC from contamination and contamination-induced poisoning	[52]
	Large gas–electrode contact area	[53]
	Removal of byproducts and oxygen, as well as an efficient mechanism for transporting protons	[54]
	Provides superior electronic and mechanical characteristics	[55]
	Resistance to the stresses imposed by PEMFC operation	[56]
Carbon support	Provides structural stability to the catalyst	[57]
	Creates a partway for electrons to access the catalyst particles	[58]
	Used as catalyst support material due to its high surface area	[59]
	Employed as support for the active metal in the catalyst layer	[58]
	Used in bipolar plate fabrication	[60]
	Employed in the gas diffusion layer design	[61]
	Enhances the ORR process	[62]
Nafion	Acts as a barrier to the self-diffusion of water	[63]
	In terms of temperature and mechanical stress, PEMFC-compatible designs must be robust enough for use in actual applications	[64]
	Carries out the fuel cell's water management and electrical conductivity	[65]
	Carries out the role of binder within the catalyst layer	[66]
	Helps the electrolyte's proton transport properties	[67]
	Offers resistance at the interface to oxygen diffusion and helps regulate cellular humidity	[68]

4. Catalyst Layer Degradation Mechanisms

The microstructure of a nafion membrane, platinum particles, and the agglomerate structure of a PEMFC catalyst layer are both depicted schematically and are shown in Figure 3. The degradation mechanisms of each catalyst are discussed in the subsequent section.

4.1. Platinum Degradation in the PEMFC

An important challenge for fuel cell functionality and efficiency is the durability and dependability of catalysts. Applying high potentials to the anode–electrode can accelerate Pt disintegration, leading to corrosion of the cathode [69]. However, for some time now, the reliability and consistency of catalysts have been recognized as a major challenge in the operation of fuel cells [56]. In a working PEMFC, the gas at the catalyst of the fuel side electrode is oxidized through the HOR and ORR processes, turning it into electrical power [64]. Subsequently, the degradation of membrane electrode assemblies occurs with Vulcan (Vn) carbon-supported Pt catalysts as the voltage increases [70].

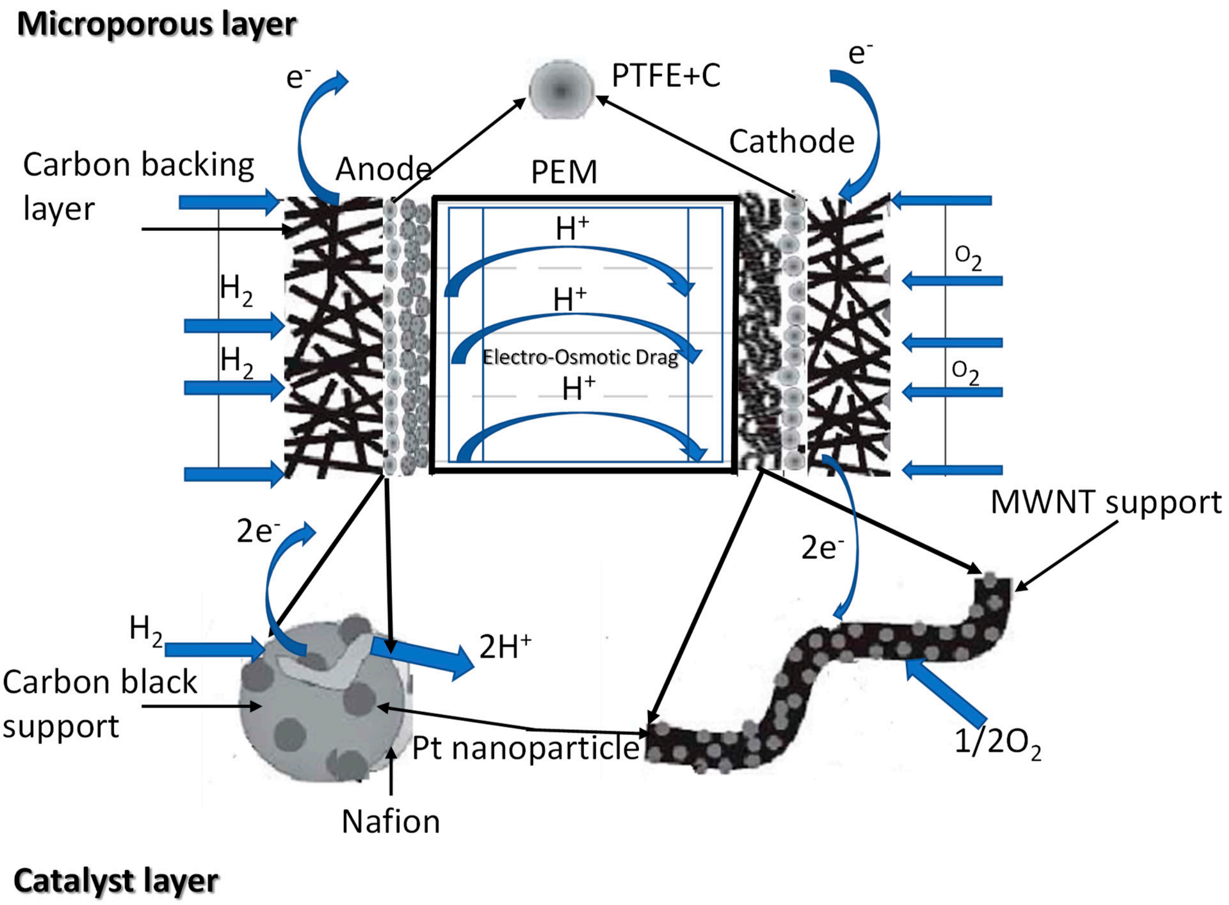


Figure 3. The microstructure of platinum particles, carbon support, nafion membrane, and the agglomerate structure of a PEMFC catalyst layer.

Pt-based catalyst degradation upon voltage cycling has been extensively demonstrated in numerous studies, leading to the well-known electrochemically active surface area (ECSA) loss [71]. This behavior is attributed to the instability of Pt and transition metals under the electric potential and acidic conditions of a PEMFC [71]. The noble metal disintegration by researchers has been attributed to both anodic and cathodic processes [72]. At high potentials and in an acid medium, Pt is stripped by the surface of the particles and ionized, thus giving its form as Pt2+ [73]. The Pt2+ cations are absorbed, and then diffuse/migrate through the water/ionomer network. Under cell conditions, the Pt2+ cations can either be reduced back to zero-valent Pt via crossover of H_2 from the ACL (forming a Pt band) or they may be deposited onto another Pt particle, a process referred to as particle coarsening [74]. All the above electrochemical processes cause an ECSA loss or degradation and, as a result, a significant reduction of PEMFC power in an irreversible manner occurs. On the other hand, Fuchs et al. [75] demonstrated that the Pt dissolution is one of several processes that can lead to Pt loss in a PEMFC during operation, which is a major contributor to CL degradation. Other researchers [46] have shown that processes like Pt particle migration to the carbon support surface play a significant role in the catalyst degradation process. Because some of the Pt particles are lost during migration, this phenomenon can be used as proof of Pt losses in the PEM. Guilminot et al. [76] determined that Pt particles were propelled from the cathode through the layer and onto the anode due to electro-osmotic drag and substance distribution processes.

During fuel cell activity, the catalyst layer is gradually degraded, increasing the particle size of the Pt catalyst, and drastically decreasing the accessible electrochemical surface area [77]. Chowdury et al. [78] showed that the Pt disintegration has the most notable degradation mechanism, along with carbon corrosion and the subsequent separation of Pt from carbon supports. When the fuel cells are actively producing energy, Pt disintegration occurs, as evidenced by the presence of fragmented Pt in the effluent water stream [69]. In the process, the Pt particles are redeposited on the surface of the PEMFC as the gas that saturates the ionomer decreases [79]. Smaller Pt particles, which have a higher surface energy and are predicted to break up at lower potentials than the bulk Pt, are thought to experience a more severe disintegration because of the Gibbs–Thomson effect [80]. Through the Ostwald ripening mechanism, disintegrated Pt particles are redeposited on larger Pt particles, as shown in Figure 4.

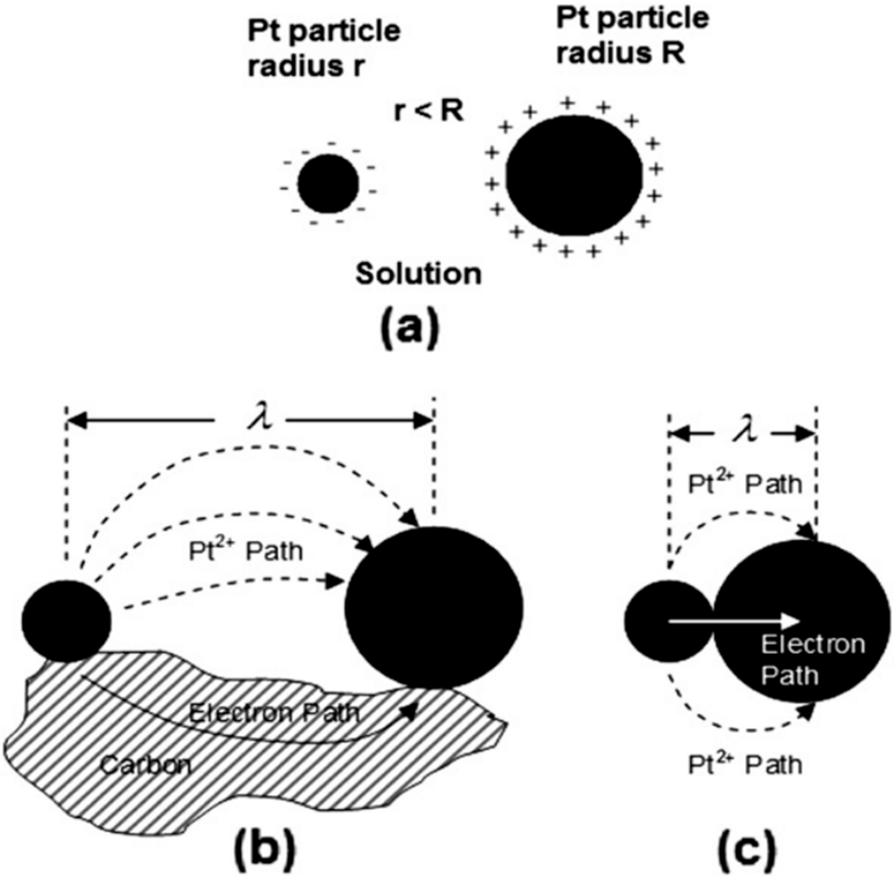


Figure 4. Particle agglomeration via electrochemical Ostwald ripening when (**a**) two opposite charged particles of the Pt particles are dispersed in solution due to the lack of an electron path between them, (**b**) two particles are isolated while sitting on a carbon support, and (**c**) two particles are in direct contact with each other, and ions are transported through the ionomer or aqueous medium and electrons are transported through the carbon support via electrochemical Ostwald ripening [81].

In the design of the PEMFC system, alloying elements are incorporated into the catalyst surfaces with a few Pt particles embedded around the core of the catalyst to increase its electrochemical process. Consequently, during the process, the alloying elements are dissolved and absorbed by the system membrane where the leached cations remain in the ionomer film as contaminants [69]. In general, there are three primary mechanisms by which the Pt-based catalyst degrades: (1) Pt particle agglomeration and growth; (2) Pt loss and migration; and (3) contamination of active sites due to impurities [12]. Due to these factors, the catalytic layer's activity is significantly dampened over time of continuous operation by decreasing the active area of the catalyst or increasing the contact resistance with the catalyst support [82].

Degradation of Bimetallic Nanoparticles in PtM (M = Co, Ni, Cu) Catalysts and Comparison with Pt/C Catalysts

Bimetallic nanoparticles (NPs) have received a lot of interest as catalysts because of their ability to integrate the unique features of each metal component, resulting in improved catalytic performance in a variety of reactions such as hydrogenation, oxygen reduction, and fuel cell applications [83]. Platinum (Pt) is commonly utilized as a catalyst because of its superior catalytic characteristics. However, Pt-based catalysts, particularly Pt/C, have drawbacks such as high cost, limited availability, and degradation over time due to sintering, leaching, and alloying effects during the reaction [84]. To address these drawbacks, Pt is frequently alloyed with other metals such as cobalt (Co), nickel (Ni), and copper (Cu) to generate PtM (M = Co, Ni, Cu) bimetallic catalysts, which can provide greater stability, reactivity, and resistance to degradation than pure Pt catalysts. However, the degradation of PtM can occur following different mechanisms [85]. In the sintering process, the coalescence and growth of nanoparticles occur, leading to the decrease in active surface area. Zou et al. [86] reported that in the case of PtM catalysts, sintering occurs through thermal effects or due to interactions with reactants under catalytic conditions.

During the degradation that occurs in the Pt-Co bimetallic catalysts, poor thermal stability is exhibited, considering that Co has a relatively lower melting point, and its interaction with platinum is generally weaker than that of nickel or copper [87]. The process is enhanced by the potential of the Co atoms to generally be prone to migrate from the surface to the subsurface or even bulk upon heating, with a detrimental effect on the overall surface area of the catalyst. Additionally, Pt-Co alloys may exhibit phase segregation upon heating, leading to a deterioration of catalytic activity due to the exposure of less active Pt sites. In the Pt-Ni catalyst degradation process, there are stronger interactions between Pt and Ni compared to the case of Pt and Co. Cheng et al. [88] reported that the Pt-Ni catalysts showed a relatively better thermal stability than Pt-Co. In addition, Ni can help in stabilizing Pt nanoparticles by reducing sintering, especially when Ni is in core–shell form. In some cases, however, Ni can leach out from the nanoparticles, exposing the Pt core and thus reducing stability and performance of the catalyst. On the other hand, in the case of Pt-Cu catalysts, copper has a more considerable effect on the structure and stability of the catalyst. In the degradation process, Cu can segregate to the surface of the Pt nanoparticle, and its interaction with Pt is often weaker compared with Ni. However, Cu can enhance stability by forming a protective oxide layer during reaction conditions that may suppress sintering and improve resistance to degradation of the catalyst at high temperatures [89]. In sharp contrast, Pt/C catalysts exhibit a high sintering tendency under reactive conditions and can be ascribed to the significant loss of active surface area that occurs due to the Pt atoms having the tendency to migrate and coalesce into bigger particles. Nevertheless, the sintering of Pt/C catalysts can be stabilized by supports such as carbon; though, the sintering issue still prevails [90].

Leaching is another process that involves the dissolution of metal atoms in the reaction medium, which naturally results in some loss of metal from the catalyst. The degradation process has been reported to be more significant in nature for bimetallic systems, where one constituent metal is leached more than another [91]. In the Pt-Co catalyst degradation, Co has been thought to have a high leaching potential, particularly in acidic settings [92]. Under such strong electrochemical or acidic conditions, the Co component of the Pt-Co alloy may be preferentially leached during reaction cycles, reducing catalytic activity. Furthermore, Co leaching might weaken the structural integrity of the catalysts, leading to Pt exposure during subsequent sintering. Nickel in Pt-Ni bimetallic catalysts can leach under certain reaction conditions. However, Ni leaching is typically less severe than Co leaching. In general, the inclusion of Ni improves the overall stability of the catalyst, and Ni loss is usually less harmful to catalyst performance than Co leaching. Despite the degradation process of the mechanism, alloying between Pt and the second metal can modify the electronic and geometric properties of the catalyst, thus affecting catalytic activity and stability.

In comparison, the interaction of alloying, leaching, sintering, and phase segregation has been demonstrated to cause the degrading behavior of PtM (M = Co, Ni, Cu) catalysts and the processes are found to be generally more complex than that of Pt/C [93,94]. Because Pt sinters and leaches from the surface, for Pt/C catalysts, which are made entirely of Pt supported on carbon, the process shows a simpler deterioration path. On the other hand, PtM catalysts may degrade more severely as a result of sintering, phase segregation, and the migration or leaching of the second metal (Co, Ni, or Cu). Additionally, the second metal can have a substantial impact on the stability of PtM catalysts as the Pt-Ni frequently shows better resistance to deterioration than Pt-Co or Pt-Cu. Moreso, PtM catalysts frequently exhibit better catalytic activity than Pt/C catalysts because of the synergy between the two metals, which can lead to lower activation energies.

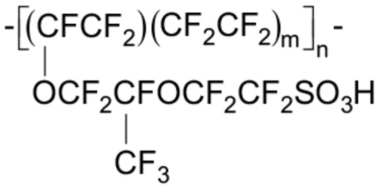
4.2. Carbon Support Degradation

In the design of PEMFC, nanoparticles of Pt or Pt compounds are dispersed across carbon supports to create an optimal active site for the electrocatalyst, which improves the reaction rate between the anode and cathode. While carbon carriers are susceptible to degradation in the presence of elevated temperatures, high water content, and high potential, carbon corrosion is a primary degradation mechanism that can reduce PEMFC performance. The process occurs by decreasing the hydrophobicity of the catalyst, increasing the particle size of the catalyst, and breaking down the connectivity of the catalyst to the pore structure of the electrode.

Furthermore, the start/end conditions that occur in the PEMFC working environment can be particularly damaging to the electrocatalyst [69]. The process enables inciting drastic shifts in the cathode potential, leading to rapid catalyst depletion. To understand what causes the carbon-supported Pt catalyst (Pt/C) to degrade, Zhang et al. [95] used a combination of three different techniques to investigate the carbon-support degradation mechanism. The findings suggested that the degradation process could be broken down into recoverable and permanent losses. The loss of recovery activity was blamed on the decrease in Pt oxide or, more commonly, on the evacuation of carbon monoxide (CO) produced during carbon corrosion, while the loss of un-recovery activity was attributed to Pt detachment, agglomeration, dissolution/redeposition, and corrosion [15]. During the PEMFC operation, the Pt atoms diffuse alongside the carbon support as the material is degraded and one possible explanation for the emergence of Pt particles in the catalyst layer is the combined phenomena processes [95]. However, as illustrated in Figure 4, aggregation of the Pt particles or corrosion of the carbon could decrease the contact between the Pt particles and the supported carbon. The breakdown of Pt can be added to the list of primary degradation phenomena with Ostwald ripening, Pt deposition in the ionomer, and other processes already covered in this review. In conclusion, carbon corrosion is a primary degradation mechanism that can decrease the efficiency of a PEMFC by destroying the electrode's pore structure, decreasing the catalyst's hydrophobicity, increasing the particle size of the catalyst, and diminishing the catalyst's connectivity. Three common conditions lead to carbon corrosion: normal operating potential, inadequate hydrogen delivery to the anode, and incomplete hydrogen coverage of the anode [96].

4.3. Nafion Degradation Mechanism

The distribution and content of nafion ionomer's PFSA molecules in the catalytic layer directly affect the ion/electron transfer in the catalytic layer [96]. Nafion's inherent properties make it a popular choice for PEMFC [97]. The nafion's molecular structure is depicted in Figure 5.



$$-[(\mathrm{CFCF_2})(\mathrm{CF_2CF_2})_m]_n- \quad \begin{array}{l} | \\ \mathrm{OCF_2CFOCF_2CF_2SO_3H} \\ \quad\quad | \\ \quad\quad \mathrm{CF_3} \end{array}$$

Figure 5. Nafion's molecular structure [98].

As a result of the electrochemical process that occurs in the PEMFC environment, the membrane electrode assembly loses its ability to conduct ions and electrons. Chemical, thermal, and mechanical degradations all have an impact on membrane integrity, despite the variety of degradation phenomena reported by different researchers [99,100].

When considering catalyst degradation, the low-temperature fuel cell is the primary focus of this review, specifically, the chemical degradation of the nafion membrane [101,102]. According to Frühwirt et al. [103], there are two primary degradation mechanisms of nafion in chemical degradation which are chain unzipping and side chain degradation. First, carbon fluoride (CF) is quickly eliminated by the fluoro alcohols to generate an acyl fluoride, which hydrolyzes to generate a second CF equivalent and a carboxylic acid [103]. The breakdown of acidic hydrogen by another hydroxyl radical, as observed by Chen et al. [98], likewise propagates the unzipping process, resulting in the same initial phase and the same succeeding steps.

Nafion, a PFSA-based membrane material, has been shown to degrade in the presence of unsteady or hydrogen-bearing end groups, as discovered by Xie et al. [104]. Under normal conditions, the rate-determining step is the hydrogen abstraction from the fluoro carboxylic acid by hydro-oxide ion (OH^-), which is a rather sluggish interaction. The strong O-H agreement with the perfluoro carboxylic acid was proposed as the likely cause of the low rate reaction consistent with this abstraction [16]. According to the researchers [16], due to the lack of a fundamental chain reaction that would increase the number of end groups with time, this degradation mechanism cannot account for the observed trend. Since the reaction inside chain scission degradation is moderate and only detectable after extended use, it is more difficult to understand and implement. Increased concentrations of free radicals may attack C-O-C groups in a fuel cell's low-humidity environment, leading to relatively stable radicals [105], as shown in Figure 5. Lee et al. [106] showed that the carbon–sulfur (C-S) bond cleavage results in a fluoro-terminal radical formation in PFSA materials like nafion [106]. Once formed, the terminal perfluoro radical will continue along the degradation pathway, converting to an oxy radical at the PFSA backbone's connection site [107]. Nafion ionomers can be completely dissolved due to the formation of a backbone during membrane fabrication, as reported by Xie et al. [104]. However, the formed carboxyl end group can travel through the fuel cell independently of the backbone. As can be seen in Figure 5, the oxyradical can break down into an acyl fluoride and another fluorocarbon radical. It is important to note that only a small amount of these side-chain radicals is required to create additional chain breaks that lead to an increased degradation rate observed during the chemical degradation process of PFSA materials such as nafion [108]. The unzipping process allows the degradation to spread during moderately wet conditions, but it allows for a clear beginning to the side chain degradation during extremely dry conditions [103].

In the nafion degradation, the main unzipping process that occurs encompasses the fluoroalcohols promptly disposing of CF to produce an acyl fluoride that hydrolyzes to produce another carboxylic acid group together with a supplementary equivalent of CF [109]. Figure 6 shows the main degradation mechanism of nafion.

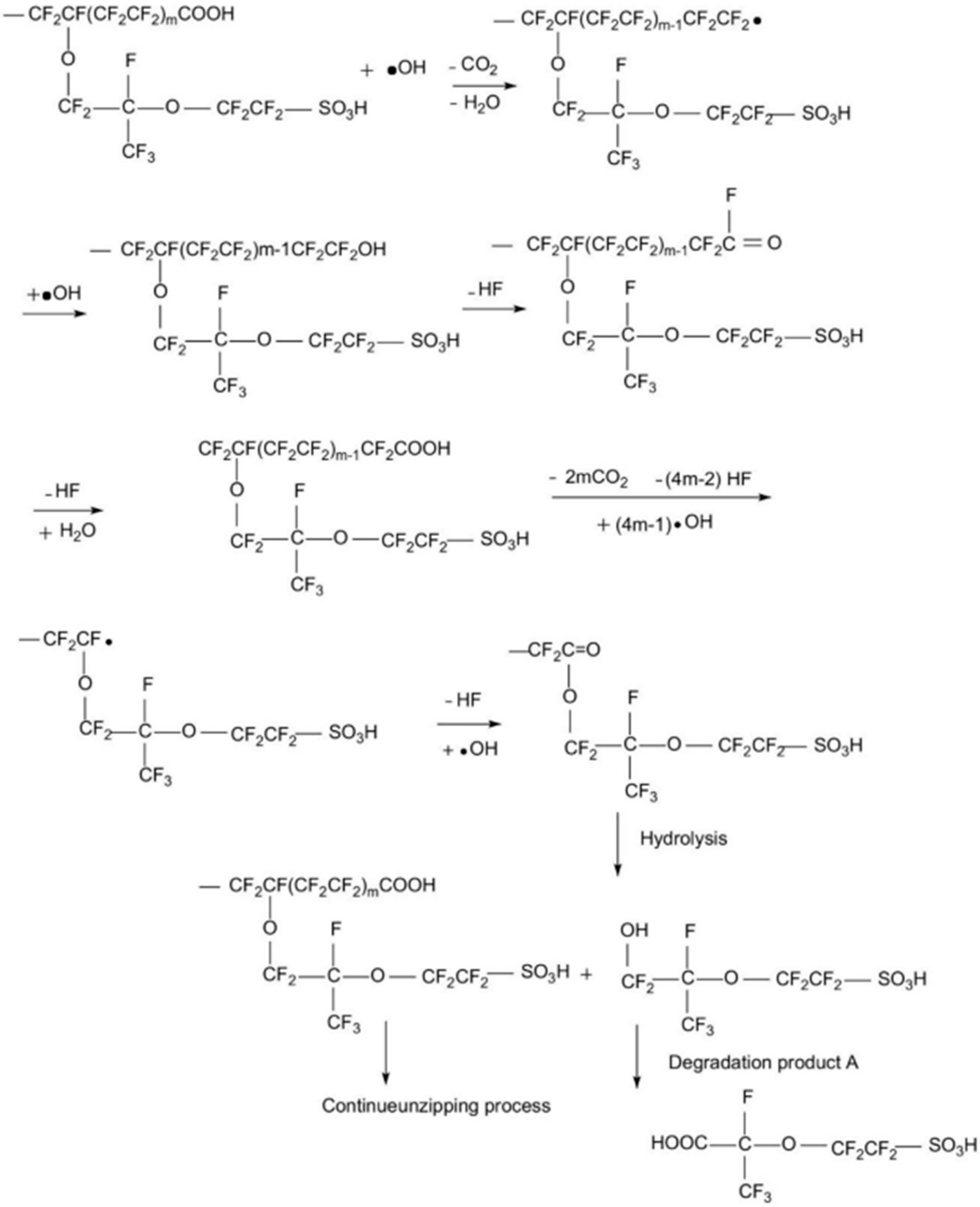


Figure 6. The main-chain unzipping process [98].

In the process, the unzipping process is furthermore generated by degradation of the acidic hydrogen by an additional hydroxyl radical causing an identical steps initiation and propagation as reported by Chen et al. [98]. A group of researchers [110] revealed that nafion being a PFSA-based membrane material requires the existence of unstable or hydrogen-bearing end groups to start the degradation process.

Degradation of the nafion in PEMFC has been investigated further and the results are presented by researchers [111,112]. Benziger et al. [113] modeled PEMFCs as two stirred tank reactors (STRs) and sought to understand the dynamic system output response to changes in the operating parameters of the PEMFC. After changing the resistive load on the fuel cell from 20 Ω to 7 Ω, an unusual multistep system response was observed. There was an expected jump in current initially following the decrease in load and also a completely unexpected second jump in current that occurred 1500 s after the load change. With a decrease in load and the resulting increase in current, the fuel cell would produce more water, thus causing an increase in water activity level [113]. The authors conjectured that while the initial response of the fuel cell was due to a jump in current at a constant water activity level, the later secondary response was due to changes in membrane properties stemming from the increase in water activity level. Alison Lehr [114] proposed that the increase in water production associated with the initial jump in current caused the nafion membrane to swell and deform into the porous catalyst layers present at the electrodes. The increase in the contact area between the membrane and the catalyst particles results is attributed to the increase in the rates of the reactions taking place at the anode and cathode which are attributed to the second increase in current observed by Benziger et al. [113]. Majsztrik et al. [115] investigated the creep rates of nafion at different temperatures and water activity levels. The creep observed was ascribed to deformation of a material caused by exposure to stress for an extended period and can affect the deformation of nafion into a catalyst layer if pressed for a prolonged period [115]. The result revealed that at room temperature, an increase in water activity level was associated with higher rates of creep, while at 90 °C, the reverse relationship was observed. In another study, Lehr [114] was not able to investigate the relationship between water activity level and deformation and revealed that the nature of the deformation of nafion about temperature and water activity level is complicated.

5. The Sources and Effects of Contamination in PEMFC

The PEMFC has been seen as promising technology for clean energy applications in different fields, particularly in transport and stationary power production [116]. Nevertheless, contamination from various sources can considerably affect the performance, effectiveness, and lifetime of PEMFCs [117]. The following outlines the impacts of contamination on PEMFCs, incorporates the supplies, mechanisms, and the effects on fuel cell performance.

a. Types of Contaminants in PEMFCs

Contamination in PEMFCs can originate from both the fuel and the air supplied to the system, as well as from the materials and components within the fuel cell stack. Common contaminants include the following:

i. Carbon monoxide: A primary contaminant in hydrogen fuel, CO can come from impurities in hydrogen during production or storage.
ii. Sulfur compounds such as hydrogen sulfide: Sulfur is a well-known poison for platinum-based catalysts in PEMFCs. It may be present in low concentrations in hydrogen or in trace amounts in fuel sources.
iii. Nitrogen compounds: Nitrogen oxides from ambient air can infiltrate the fuel cell system and poison the catalyst.
iv. Ammonia: Ammonia is another potential contaminant in hydrogen fuel, typically arising from industrial processes.

   - v. Water contaminants: Impurities in water used in the fuel cell, like chlorine or chlorides, can lead to catalyst degradation.
   - vi. Catalyst poisoning: Many contaminants, especially CO and sulfur compounds, can directly poison the Pt catalyst.

- b. Membrane Degradation: The MEA of the PEMFC can be affected by contaminants such as ammonia and chlorine. In the process, chloride has been particularly reported to chemically degrade the fuel cell membrane, resulting in cracks and a reduction in mechanical strength of the membrane. This process generally affects the performance of the PEMFC.

5.1. Effect of Contamination on PEMFC Performance

Contamination can affect PEMFC in different ways. The following outlines some of the impacts contaminants can have on PEMFC:

- a. They reduce the power output of the PEMFC.
- b. They increase the internal resistance, thereby reducing the voltage and efficiency of the fuel cell.
- c. They increase fuel consumption by blocking the active sites on the catalyst, which necessitates the fuel to require more hydrogen to generate the required same amount of power.
- d. They increase fuel consumption: When contaminants block active sites on the catalyst, the fuel cell requires more hydrogen to generate the same amount of power, thereby increasing fuel consumption and reducing overall efficiency.
- e. They cause accelerated catalyst degradation which decreases the fuel cell lifetime.

5.2. Strategies for Mitigating Contamination

Researchers [118] have explored and developed several methods to address and alleviate the impact of contamination on PEMFC performance. Some of these methods include improving hydrogen purification, development of new catalysts, purification of air systems, and improvement in the membrane materials [119]. Haque et al. [120] revealed that employing these techniques and approaches will enhance the effectiveness, durability, and efficiency of PEMFC in different applications.

6. The Operational Parameters and Circumstances That Affect the Degrading Mechanisms in PEMFC

The Pt agglomeration and migration are key degradation mechanisms that can significantly affect the performance and longevity of Pt-based catalysts, especially in applications like automotive exhaust treatment, fuel cells, and industrial catalytic processes [69]. These mechanisms lead to a reduction in catalytic activity as Pt particles coalesce into larger clusters, reducing the surface area available for catalytic reactions and causing loss of active sites. There are several operational parameters and circumstances that exacerbate Pt agglomeration and migration. Some of the operational parameters and circumstances are detailed below.

6.1. High Operating Temperatures

- i. Increased atomic mobility: Platinum is a noble metal, and while it has high thermal stability, its atoms become more mobile at elevated temperatures. When the temperature exceeds a certain threshold, Pt atoms move more freely, which can lead to migration and agglomeration into larger clusters. These larger clusters have fewer available catalytic sites, which diminishes the catalyst's overall activity.

ii. Thermal sintering: At temperatures above 600 °C, Pt tends to undergo sintering, a process where smaller Pt particles combine to form larger ones. This process reduces the number of active sites and thus the efficiency of the catalyst, as larger particles are less effective in catalyzing reactions compared to small ones with a high surface area.

6.2. Reduction–Oxidation Cycles

i. Reduction conditions: In catalytic applications, such as in automotive exhaust systems, redox cycling occurs—where the catalyst is exposed to alternating reducing and oxidizing conditions. Under reducing conditions (e.g., exposure to hydrogen), Pt can lose its oxygen atoms and become more mobile, leading to the migration of Pt atoms across the surface or even between the catalyst's support and platinum particles.
ii. Oxidation conditions: On the other hand, oxidizing conditions (e.g., exposure to oxygen or high temperatures) can cause platinum to form platinum oxides. The instability of these oxides at high temperatures can drive Pt migration and agglomeration, especially if the oxidation–reduction cycles are frequent or severe.

6.3. High Pressure Conditions

i. Pressure-induced migration: Under elevated pressure, platinum atoms may shift positions to minimize their energy state, leading to migration and potentially agglomeration if the Pt atoms encounter favorable conditions for coalescing.
ii. Phase transition effects: In high-pressure environments, Pt can undergo structural changes, such as shifting from a smaller nanoparticle form to larger agglomerated clusters, particularly at elevated temperatures. This can further diminish the catalyst's surface area and its effectiveness in driving catalytic reactions.

6.4. The Pt Particle Size and Distribution

i. Smaller Pt particles: Initially, platinum is often deposited as nanoparticles to maximize surface area. However, smaller platinum particles are more susceptible to agglomeration and migration under extreme conditions (high temperature, redox cycling). As small Pt particles migrate, they are more likely to combine, forming larger particles that are less active.

The development of new materials to mitigate catalyst layer degradation is an exciting and active area of research, with many promising advancements [121]. Pt alloys, core–shell nanostructures, advanced supports, and self-healing catalysts have shown to offer substantial potential to improve the durability and efficiency of catalytic systems [122].

7. PEMFC Catalyst and Ionomer Degradation Tests

The reliability of a fuel cell depends on its performance under regular use and the rate of degradation. Therefore, it is essential to learn about the components of the system and the degradation processes that occur in the fuel cell [123]. This can be achieved by understanding different experimental tests that simulate the operation of the fuel cell by employing high-performance and reliable tests. Several methods and publications have been offered by researchers to understand the depletion of PEMFC catalyst layers and ionomers [12,16,124]. Steady-state durability and acceleration tests are at the heart of cutting-edge experimental strategies for investigating the degradation mechanisms as reported in the literature [125,126]. One of the most popular methods is the acceleration test, which, in addition to estimating the material's degradation rate over time, shortens the time it takes for the natural degradation process to reach a result [107]. Since the fuel cell system is typically used in a stationary setting, it is best to test the behaviors of the catalysts, ionomers, and membranes under steady-state conditions during durability testing [107,124]. Unfortunately, it is impossible to conduct this test continuously due to the inevitable interruptions that arise due to maintenance and refresh procedures in the PEMFC. Although the steady-state durability test is straightforward, it is impractical for widespread use and even for scientific investigations because of its high cost, enormous effort, and limited throughput [124].

In most cases, Fenton's test [107] has been used for different PEMFC degradation tests. Healy et al. [127] used Fenton's solution and peroxide concentrations ranging from 29% to 100% to study the chemical degradation behavior of the ionomer used in the PEMFC. Fenton's reagent was found to be responsible for the degradation of membranes and the release of compounds similar to those found in fuel cell testing, as determined by careful comparison and analysis. Further results were said to corroborate with those of other studies that discovered the same phenomena with longer membrane immersion in a similar environment [127]. The results also revealed that the Fluoride ion loss from nafion was shown to scale logarithmically with peroxide concentration in Fenton's solution, as shown by Vielstich and colleagues [128]. However, the results revealed that there is no best degradation strategy and technique that most accurately reflects in in situ degradation of the catalyst layers and particles. On the other hand, ex situ acceleration techniques have been used to study the degradation of Pt, and it was found that testing under acceleration was crucial for understanding the materials' degradation mechanisms. To determine what causes carbon-supported Pt/C catalysts to degrade, Zhang et al. [15] employed a multi-pronged approach involving three distinct accelerated stress tests (ASTs). By comparing the electrochemically active surface area (ECSA) and ORR activity loss across different AST methods, it was found that the activity loss in AST can be broken down into recoverable activity loss and unrecoverable activity loss. The PEMFC's irreversible loss of activity is caused by several factors, including Pt dissolution/redeposition, agglomeration, detachment, and carbon corrosion.

7.1. Microscopic Investigation

The PEMFC's perfluoro sulfonic acid ionomer membranes undergo gradual chemical and mechanical degradation at the same time during operation which affects the performance of the PEMFC. Understanding the structural degradation of a membrane is important because of the need to enhance its longevity and performance. Different methods can be used to study PEMFC material degradation, and this has been performed by several researchers [100]. To learn how the chemical and mechanical degradation of fuel cell perfluoro sulfonic acid membranes affects their longevity, Shi et al. [129] used scanning electron microscopy (SEM) to identify the degradation behavior of nafion membrane when subjected to the PEMFC environment, as shown in Figure 7.

The morphologies of membranes at varying degrees of Pt degradation are compared in Figure 7. In Figure 7a, membranes that have been degraded for 24 h showed rough crack surfaces, as evidenced by severely deformed, irregular edges along the crack. Near the main fracture, there are a number of smaller cracks that run perpendicular to the loading direction, further demonstrating plastic deformation and a ductile failure mode. The 24 weakened membrane shows no signs of bubbles or pores as displayed in Figure 7b. Plastic deformation features are less pronounced for membranes degraded for longer than 24 h, specifically for membranes degraded for 48 and 72 h. In particular, the cross-section of the crack is flat for 72 h degraded membranes (Figure 7d), indicative of brittle failure, and almost no plastic deformation is observed. Therefore, brittle failure is the result of prolonged chemical degradation and the ionic interaction between sulfonic acid groups influences the failure mode, and the decomposition of the sidechain may account for the change in failure mode following chemical degradation [129]. Taniguchi et al. [130] used transmission electron microscopy (TEM) to investigate the degradation of the PEMFC catalyst layer due to cell reversal during air starvation that occurs in the PEMFC environment. Characterization was performed on samples obtained from MEAs that had degraded. An in situ cyclic voltammetry test detected the reduction in the electrochemical surface area of the cathode platinum, and TEM analysis identified the formation of sintering in the Pt. In a similar study, other researchers have investigated the degradation of the Pt using the TEM technique and the results provided [12,69]. The outcomes of the studies have revealed that the microscopic analysis of fuel cells can be an effective method for elucidating the mechanisms of Pt disintegration down to the nanoscale. Figure 8 shows that TEM analysis was able to distinguish Pt sintering from electrochemical surface area loss.

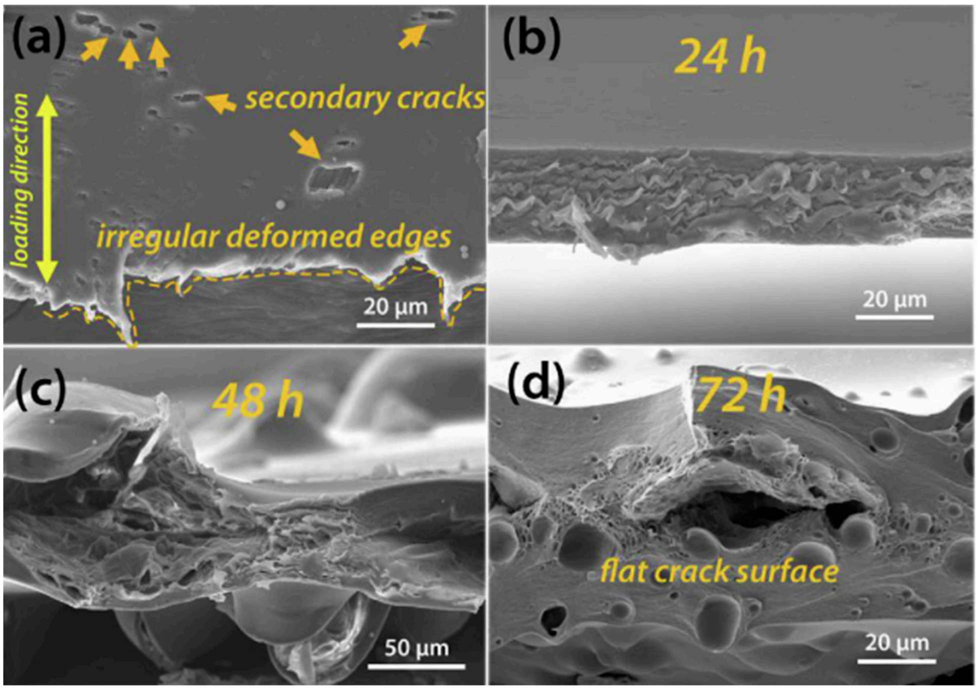


Figure 7. (**a**,**b**) Surface and cross-sectional microstructure of membranes degraded for 24 h; (**c**,**d**) cross-sectional microstructure of membranes degraded for 48 h and 72 h [129].

Researchers found that fuel cell performance and catalyst degradation both dropped dramatically due to cell reversal for 120 min as a result of the Pt degradation. Recent research has also shown that the disintegration process is highly dependent on the particle geometry at the surface [131,132]. Other researchers have found that the disintegration/redeposition mechanism of Pt at the atomic scale is still poorly understood, and a detailed understanding can be attained through the use of microscopic techniques [133,134]. Tang et al. [135] sought to better understand the conditions at which nafion would deform furthest in the PEMFC environment. The author modeled the catalyst layer as a series of trenches in silicon. The author then pressed nafion into the trenches at various temperatures and viewed the resulting nafion–silicon interface with an SEM. It was found that as the temperature increased, the deformation of the nafion into the silicon substrate also increased. The author also found that below 140 °C, nafion deformed into the trenches in a single peak manner. In a related study, identical location transmission electron microscopy (IL-TEM) was used to examine the decomposition and deterioration of carbon-supported Pt nanoparticles under ORR conditions [136]. After the fuel cell's startup and shutdown operation, some Pt particles vanished while others sintered.

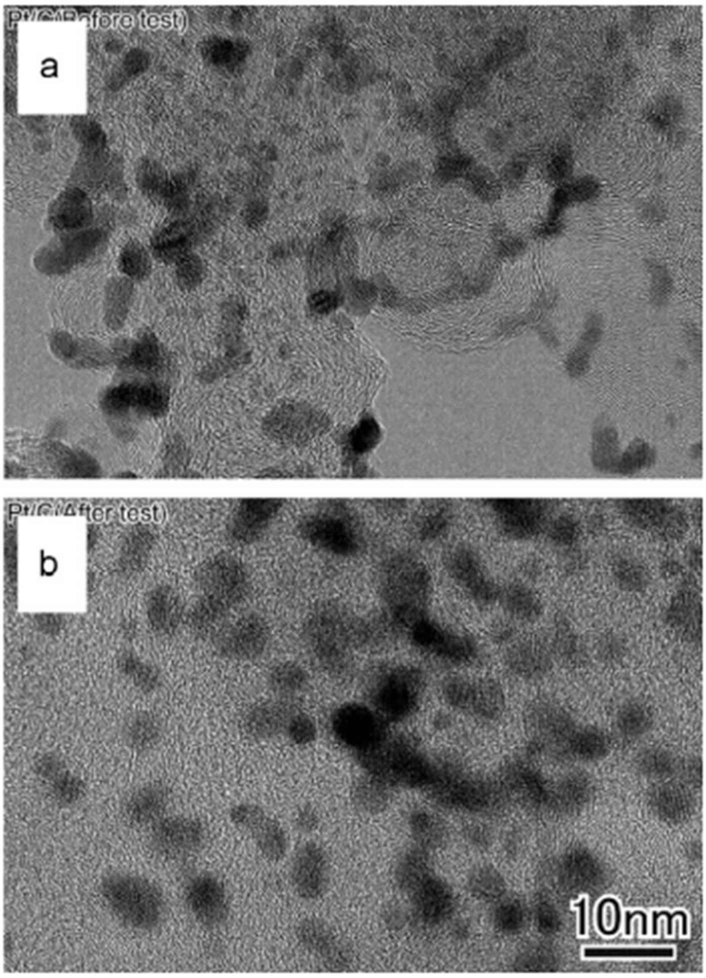


Figure 8. TEM images of the cathode catalyst: (**a**) before and (**b**) after the cell-reversal experiment for 120 min [12].

Despite the significance of membrane performance and durability, knowledge of its structural deterioration is required. Several researchers have looked into the degradation of the membrane and the interaction of the material degradation in the fuel cell using various techniques [137,138]. The outcomes demonstrated that Pt agglomeration and dissolution enhanced carbon corrosion, which in turn affected Pt sulfide composite formation. The energy dispersive X-ray (EDX) analysis revealed that PTFE and nafion's carbon and fluorine contents were dominant, with only a trace amount of Pt [16]. Researchers claim that while the Pt disintegration is the atomic scale process, the disintegration/redeposition is still unknown, and microscopic techniques can help in understanding the material degradation mechanism significantly [139]. In another study, the degradation and disintegration of carbon-supported Pt nanoparticles were examined under ORR conditions [140]. After simulating the startup and shutdown of a fuel cell, some Pt particles disappeared while others began to sinter. The outcome also showed nanoparticles with smaller particle sizes as a result of material degradation. Carbon corrosion destroys membrane electrode assemblies, as seen in Figure 9, from research by Jae-Hyun Park et al. [141], who utilized TEM to examine microstructural changes in the cathode catalyst layers and polarization losses in proton exchange membrane fuel cells.

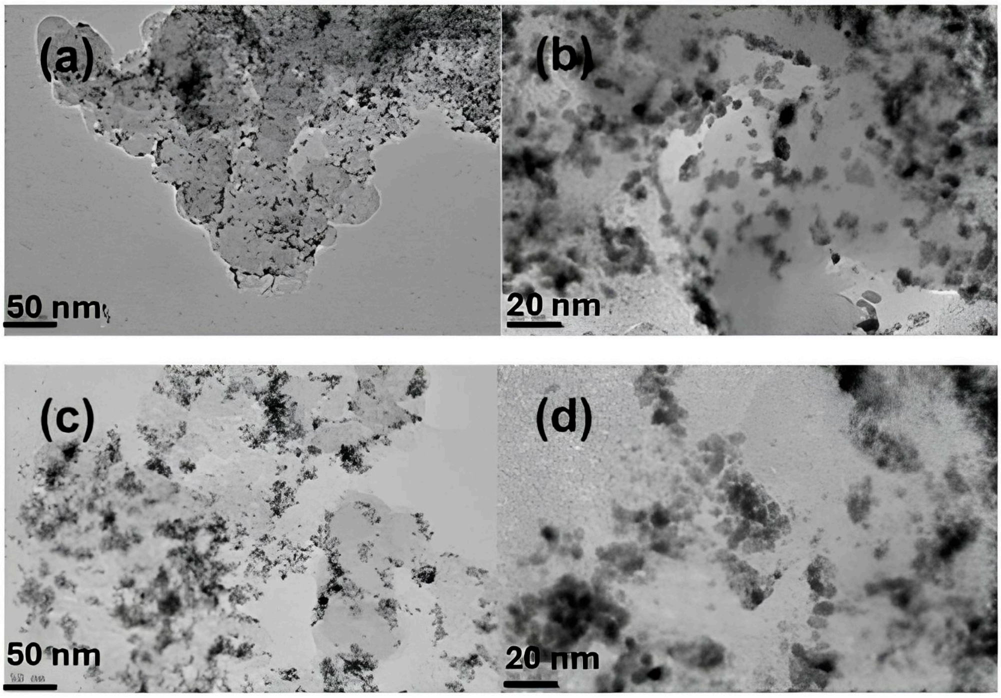


Figure 9. TEM images of CCLs for (**a**,**b**) fresh and (**c**,**d**) after 50 h of carbon corrosion AST [141].

Changes in the morphology of Pt/C nanoparticles were observed by TEM after 50 h of carbon corrosion AST (Figure 9). The result showed that carbon primary particles became more contrasted following AST, suggesting that the carbon particles were shrunk and were possibly hollowed out in the middle by corrosion [141]. The result further revealed that carbon corrosion disrupted the regular distribution of Pt particles on the carbon support, displaying clusters of Pt nanoparticles on the corroded carbon. The result also showed that after carbon corrosion, the size distribution of over 200 particles of Pt nanoparticles displayed a modest increase in particle size, from 3.7 to 4.3 nm [141]. The result revealed that a considerable number of Pt nanoparticles were either dislodged from the carbon surface and washed away or relocated to a location where they would not contribute to electrochemical activity.

7.2. Microstructure of PtM (M = Co, Ni, Cu) Catalysts Before and After Testing

Platinum-based catalysts, particularly those alloyed with transition metals such as cobalt (Co), nickel (Ni), and copper (Cu), have been extensively studied for their superior catalytic properties in a variety of electrochemical applications, including hydrogen oxidation and oxygen reduction reactions in proton exchange membrane fuel cells (PEMFCs) [142]. The addition of a second metal to Pt alters the electrical structure and surface properties of the catalyst, frequently resulting in better performance such as higher activity, durability, and resistance to poisoning. However, the degradation mechanisms and changes in the microstructure of PtM (M = Co, Ni, Cu) alloys before and after testing is critical for catalyst optimization and long-term stability. PtM alloys are commonly produced via co-precipitation, chemical reduction, or vapor deposition. The resulting alloy has a well-dispersed distribution of Pt and M on a conductive support material (e.g., carbon black). The microstructure of these alloys is influenced by a number of parameters, including the atomic distribution of Pt and the second metal (Co, Ni, Cu), as well as particle size and shape.

7.2.1. Microstructural Changes Before and After Testing

Electrochemical testing, which may involve exposure to reactive species, high current density operation, or potential cycling, significantly alters the microstructure of PtM catalysts. Studies [86] have shown that degradation processes such alloying effects, leaching, and sintering are the main causes of these alterations. Before testing, the PtM alloys typically contain tiny, well-dispersed nanoparticles that provide a large electrochemical surface area. Jayasayee et al. [143] showed that Pt alloying with Co, Ni, or Cu stabilizes the nanoparticles and reduces the tendency for sintering as compared to pure Pt catalysts. During electrochemical cycling, particularly at high voltages, PtM nanoparticles may sinter, resulting in particle growth. This process diminishes the available surface area, resulting in decreased catalytic activity. For example, Pt-Co and Pt-Ni alloys may experience particle coalescence, which causes the nanoparticle size distribution to shift towards larger particles, resulting in a loss of active sites [144]. The Cu is especially vulnerable to oxidation and leaching in PtCu alloys, which can weaken the structure of the catalyst.

Generally, when electrochemical testing is performed on PtM (M = Co, Ni, Cu) catalysts, the microstructure changes significantly [93]. Sintering, leaching, and phase separation are the main modifications that might result in a reduction in catalytic activity and long-term stability. The instability of the second metal (Co, Ni, Cu), which dissolves or oxidizes at extreme operating conditions, is the main cause of PtM catalyst degradation. Designing more stable and effective PtM-based catalysts for use in PEMFCs and other electrochemical applications requires an understanding of these degradation mechanisms. Characterization methods that shed light on these structural alterations include TEM, XRD, XPS, and CV and are often employed in understanding the microstructural changes that occur [145].

7.2.2. Structural Size and Composition Before and After Testing

In proton exchange membrane fuel cells (PEMFCs), the structural parameters of Pt-based catalysts, including the size of nanoparticles and the composition of PtM (M = Co, Ni, Cu) catalysts, can change significantly before and after testing. These changes can impact the catalyst's performance and durability.

Size of Nanoparticles

The Pt-based catalysts often have finely dispersed nanoparticles before testing, which maximize surface area and catalytic activity. After testing, the nanoparticles can agglomerate or sinter, especially under high operating temperatures or voltages. This leads to a decrease in the active surface area and, consequently, a reduction in catalytic performance [141]. The particle size may increase, reducing the number of active sites available for reactions.

Composition of PtM (M = Co, Ni, Cu) Catalysts

Frequently before testing, in alloyed catalysts like PtM, the Pt is often mixed with metals such as cobalt (Co), nickel (Ni), or copper (Cu) to improve the catalytic properties, such as enhancing the oxygen reduction reaction (ORR) at the cathode or improving the hydrogen oxidation reaction (HOR) at the anode. These alloys can also help reduce the amount of Pt needed, lowering material costs. After testing, the composition of the PtM catalyst can change due to leaching or migration of the non-platinum metals (Co, Ni, Cu) under harsh operating conditions. For instance, the less noble metals may dissolve or diffuse into the Pt structure, altering the surface composition and potentially degrading catalytic activity. This degradation can reduce the catalyst's overall stability and longevity. These changes in the structural parameters of PtM catalysts, especially the size and composition of nanoparticles, are key factors influencing the long-term performance and efficiency of PEMFCs.

7.3. PEMFC Catalyst and Ionomer Degradation Stress Tests for Catalyst, Membrane, and Carbon Support

The catalyst in a PEMFC, typically Pt or Pt alloys (e.g., Pt-Ni, Pt-Co), is required to facilitate electrochemical reactions at the anode and cathode. Despite its strong catalytic capabilities, Pt is particularly vulnerable to a variety of degradation mechanisms, which can impair fuel cell efficiency and lifetime. Various kinds of stress tests are carried out in order to characterize the mechanisms of catalyst degradation under realistic operational conditions [15]. Although potential cycling is often used to test the degradation behavior of the catalyst layer, the accelerated stress test (AST) in which the catalysts are subjected to high current densities at elevated temperatures for extended periods is often employed in the catalyst degradation test [146]. This method is utilized to simulate accelerated degradation conditions and to quantify the loss of ECSA. AST enables an evaluation of the stability of pure Pt and Pt alloy catalysts in hostile conditions at the cathode. For the degradation of ionomer, simulating operation stresses prevailing in the PEMFCs is employed, causing accelerated oxidation of the acid sulfonic group that induces fast degradation. Schmittinger et al. [147] revealed that long-term exposure to high temperature and humidity increases the rates of oxidation and mechanical degradation and that testing under these conditions may provide information about the ionomer material interaction and mechanical strength over a certain period. The test provides an understanding of how the ionomer behaves in real-life service situations and gives an idea of its possible lifetime. Carbon support materials, typically high-surface-area carbon blacks, serve as structural support for Pt catalysts in PEMFCs. They promote electron conduction between catalyst particles and the external circuit. However, carbon supports are susceptible to deterioration, which can affect catalyst stability and overall fuel cell performance. To evaluate the stability of carbon supports, many stress tests are widely used [148]. While carbon supports are subjected to repetitive potential cycling between high and low voltages to imitate the cathode's oxidative conditions, the test accelerates carbon corrosion and assesses the support's integrity [149]. When employing the high-temperature test to access the degradation behavior of carbon support, the carbon support is subjected to high temperatures, which accelerate corrosion and determine the support's resilience in extreme situations.

7.3.1. AST Condition for Catalysts, Ionomers, Membranes, and Carbon Supports Tests

Accelerated stress testing (AST) conditions are commonly employed in the literature to simulate the harsh operating conditions of PEMFCs and evaluate the durability of catalysts, ionomers, membranes, and carbon supports. These tests are designed to accelerate degradation processes, enabling researchers to assess the long-term stability of fuel cell components. Below are the typical AST conditions reported for the degradation of catalysts, ionomers, and other components in PEMFCs:

Potential Range

For catalyst degradation and durability testing, the potential range typically spans from 0.6 to 1.2 V vs. the reversible hydrogen electrode (RHE) during cycling. This range is chosen to encompass the operating voltages of PEMFCs, with the lower end representing the hydrogen oxidation reaction (HOR) region and the higher end representing the oxygen reduction reaction (ORR) region. For the membrane test, the membrane may be subjected to a potential range from 0.0 to 1.5 V in some tests, especially in conditions where oxidative degradation is expected (like in the cathode environment).

Time

AST testing for catalyst and ionomer degradation typically runs for several hours to a few hundred hours, with the time depending on the specific test and testing protocol.

Typical tests for catalyst stability in PEMFCs last around 100–500 h, while ionomer stability tests may vary between 50 and 200 h. Carbon supports, on the other hand, undergo corrosion in oxidative environments, and testing usually lasts for 100–300 h to observe significant degradation.

Number of Cycles

In typical AST protocols for the catalyst degradation of Pt-based and PtM alloys, catalyst degradation is evaluated by cycling the potential between 0.6 V and 1.2 V (or similar ranges) for a specified number of cycles. It is common to subject the catalyst from to 10,000 to 50,000 cycles to simulate a long-term fuel cell operation, as catalysts in PEMFCs experience frequent potential cycling during real-world operation. Ionomer degradation is often assessed by exposure to voltage cycling between 1.0 V and 1.5 V for around 10,000 cycles. The number of cycles can vary depending on the specific materials and conditions used in the test.

Environmental Conditions

The ASTs are typically carried out at temperatures of 60–80 °C, which are typical operating conditions for PEMFCs. Humidity is also controlled during ASTs, as it influences membrane hydration and overall fuel cell performance. Conditions often range from 30% to 100% relative humidity.

7.4. Catalyst and Ionomer Enhancement in the PEMFC

In the corrosive acidic fuel cell medium, the electrode catalyst layer degrades over time which has been a major barrier to the widespread commercialization of low-temperature PEMFCs. Nanoparticle disintegration has been reported as a major mechanism in carbon corrosion [96,150]. Nanoparticle electrocatalysts can be improved, in particular, when composed of de-alloyed core–shell type particles [151]. A type of Pt monolayer electrocatalysts evaluated by the researchers showed enhanced catalytic activity and remarkable stability throughout a long durability test [151].

In recent years, enhancements and modifications of the materials used in PEMFCs have been proposed to lessen the losses of the active surface area and the degradation of the catalyst in various conditions [152]. Researchers [153] have shown that corrosion resistance is very high in carbon-free materials when used in fuel cells. Alloying the catalyst with transition metals has been shown to enhance the catalyst's performance and the most desirable Pt alloy components come from the family of transition metals [154]. Platinum composites with various transition metals, including chromium (Cr), cobalt (Co), nickel (Ni), iron (Fe), and palladium (Pd), have been combined using various arrangement strategies to improve the performance of the PEMFCs [155]. Additionally, the performance of the catalyst is enhanced by the formation of stable bonds between the metal and its support, which also reduces the amount of catalyst that is lost and regulates charge transfer [156]. It has been shown that the size, distribution, and scattering of Pt nanoparticles on the surface of the carbon support are considerably influenced by parameters such as the Pt-deposition process, even when using the same type of carbon support. Compared to unalloyed Pt, catalysts made from Pt-cobalt alloys have been demonstrated to withstand possible cycling with far greater durability [157]. On the cathode side of a PEMFC, however, a group of researchers [158] have devised a revolutionary process for depositing highly dispersed Pt on carbon black, which displays much better electro-catalysis.

Although Pt's intermediate adsorptive quality is reduced by the carbon support, the synergistic effect between the two influences the formation of more dynamic sites for oxygen adsorption, which in turn helps to speed up the ORR. For many fuel cell research projects, the most pressing issue is trying to investigate what causes particles to clump together and then fall apart. Research and development are needed to learn more about the Pt, nafion, and carbon degradation mechanisms and ultimately enhance the performance of PEMFCs. It has been reported that the membrane can be made better by using new nano-composite material, extending the membrane's lifespan and boosting the ionomer's performance. Coating the membrane is another option for improving its performance and utility in the PEMFC. This review also recommends implementing the developed enhancement strategies to boost PEMFCs' performance. Incorporating these methods into research and development efforts will allow for the creation of catalysts that boost PEMFC performance and open up new avenues of use.

8. Prospect and Concluding Remarks

Many issues about the principal degradation mechanism remain unsolved, despite the critical data given on parameters that alter the catalyst's effectiveness, such as alloying Pt with transition metals or modifying the particle size [159]. If the fuel cell is to be durable and environmentally friendly, the Pt must not degrade during an operation to maintain its activity over the course of its entire lifetime. To be effective, a fuel cell catalyst must be stable over its entire operation and resistant to degradation, manifested in the form of electrochemically dynamic surface region losses. A fuel cell's useful life is limited by the rate at which its active surface area degrades, which in turn determines the fuel cell's efficiency and performance over time. Several factors, including the fuel cell's operating state and the electrocatalyst's synthesis and structure, contribute to a decline in performance [43]. Activity methods that involve start/stop states were found to be particularly damaging to the electro-catalyst because of high potential variations at the cathode, resulting in a rapid decline in the catalysts' performances [160]. Although significant effort has been put into gaining an understanding of Pt, nafion, and carbon degradation and developing novel structures and catalysts, more effort is needed to make an efficient and long-lasting catalyst layer that can be used without difficulty in commercializing the fuel cell. Sustainability, efficiency, and a lengthened PEMFC lifespan can all be achieved by striking the right balance between Pt, nafion, and carbon loading in the catalyst and the loss during operation.

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Abbreviations

Pt	Platinum
PEMFC	Proton exchange membrane fuel cells
C	Carbon
MEA	Membrane electrode assembly
CLs	Catalyst layers
CCM	Catalyst-coated membrane
MPL	Microporous layers
GDL	Gas diffusion layer
PTFE	Polytetrafluoroethylene
BPP	Bipolar plates
Vu	Vulcan
HSC	High-surface area
ROS	Reactive oxygen species
ORR	Oxygen reduction reaction
PFSA	Perfluorosulfonic acid

ACL	Anodic catalyst layer
CCL	Cathode catalyst layer
HOR	Hydrogen oxidation reaction
H_2	Hydrogen
O_2	Oxygen (O_2)
CO	Carbon monoxide
CF	Carbon fluoride
OH^-	Hydro-oxide ion
AST	Accelerated stress tests
ECSA	Electrochemically active surface area
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
IL-TEM	Identical location-transmission electron microscopy
EDX	Energy dispersive X-ray
Cr	Chromium
Co	Cobalt
Ni	Nickel
Fe	Iron
Pd	Palladium

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