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A comprehensive assessment on the durability of gas diffusion electrode materials in PEM fuel cell stack

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Abstract Polymer electrolyte membrane (PEM) fuel cell is the most promising among the various types of fuel cells. Though it has found its applications in numerous fields, the cost and durability are key barriers impeding the commercialization of PEM fuel cell stack. The crucial and expensive component involved in it is the gas diffusion electrode (GDE) and its degradation, which limits the performance and life of the fuel cell stack. A critical analysis and comprehensive understanding of the structural and functional properties of various materials involved in the GDE can help us to address the related durability and cost issues. This paper reviews the key GDE components, and in specific, the root causes influencing the durability. It also envisages the role of novel materials and provides a critical recommendation to improve the GDE durability.

Keywords PEM fuel cell, gas diffusion electrode(GDE), gas diffusion layer(GDL), membrane electrode assembly, durability, fuel cell catalyst

1 Introduction

Energy has become the fundamental component of our day-to-day activities which impacts the society and the environment. As a consequence, energy and environment are two indispensable constituents in many respects, especially in relation to sustainability [1].

Conventional energy systems, though highly reliable, pose devastating consequences due to the toxic gas emission. To circumvent this effect, the use of the renewable systems has been significantly escalating over the last few decades. Regrettably, even the most accredited

renewables such as wind and solar power systems pose reliability concern due to their intermittent nature, causing a mismatch between the energy supply and demand.

Fuel cells can be a promising solution to addressing these issues, as they are both reliable [2] and renewable. In addition, fuel cells can be operated over a wide range of applications starting from mobile to automotive applications and thus significantly contributing to the global energy and environmental stabilization. Moreover, the fuel for fuel cells, namely hydrogen can be derived from both renewable and non-renewable sources by several possible processes [3,4]. The various fuel cell technologies are polymer electrolyte membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC) [5]. Among them, the most widely used fuel cell technology is PEMFC due to its versatile characteristics such as high power density (compatible for transportation), low operating temperature (60°C–90°C) and dynamic response [6].

2 PEM fuel cell principle and components

PEM fuel cell essentially consists of a pair of gas diffusion electrode (GDE), anode and cathode, and a PEM sandwiched between the electrodes. The GDE normally consists of a gas diffusion layer (GDL) and a catalyst layer (CL). Platinum or platinum alloys are principally used as an electro catalyst in most of the PEM fuel cell stack due to its activity, selectivity, and chemical stability [7].

The GDEs are usually bonded to the membrane and the whole unit is entitled “membrane electrode assembly (MEA).” In some cases, the catalyst is coated directly onto the membrane to form catalyst-coated membrane (CCM). Flow field plates are placed on both sides of MEA for supply of reactant gases to the GDEs. These flow field plates also function as a current collector. The operation of the fuel cell involves the hydrogen (fuel) gas being supplied to the anode and oxygen/air being fed to the cathode. At the anode catalyst region, the hydrogen is

Received Mar. 23, 2018; accepted Jul. 21, 2018; online Apr. 24, 2019

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oxidized to protons and electrons. The Nafion (proton exchange) membrane which is a proton conductor and electron insulator conducts the protons through the membrane to the cathode and impedes the electron flow. As a consequence, the electrons are forced to travel from the anode to the cathode through an external circuit which is shown in Fig. 1. At the cathode catalyst region, the oxidant is reduced and water is produced as the by-product of the reaction.

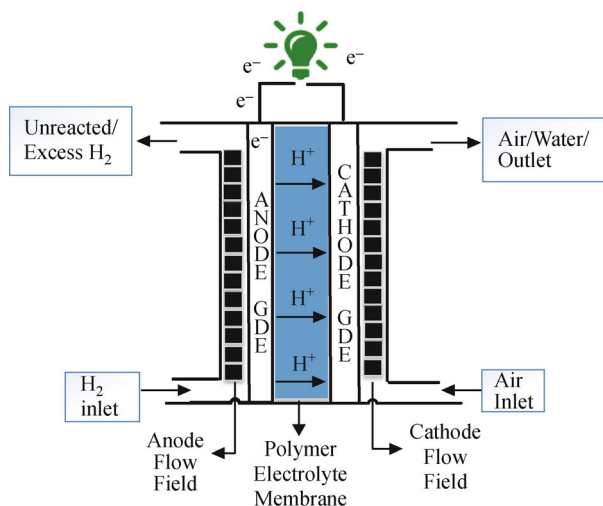
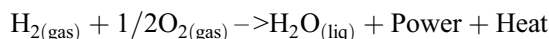


Fig. 1 A plan of PEM fuel cell (single cell) indicating electron and proton transfer

The overall electrochemical reactions occurring in a PEM fuel cell are



$$E^\circ = 1.229 \text{ V.}$$

A considerable amount of thermal power (heat) is produced in addition to the electric power. The crucial components involved in the PEM fuel cell stack are GDE, membrane, and flow field plate (bipolar plate).

Among the above components, GDE is the most vital and most expensive material, and the fuel cell stack performance and durability are extensively impacted by its characteristics. Though other material components such as flow field plate and membrane contribute to the PEM fuel cell performance and durability, there have been numerous literatures dealing with the PEM [8–12] and flow field plates [13–15]. The proposed paper gives emphasis on the durability mechanism of GDE.

3 GDEs and its functional characteristics

GDEs in a PEM fuel cell stack usually comprises of the CL and the GDL. The CL of PEM fuel cell encompasses

precious catalysts, usually supported by carbon materials, bonded/impregnated polymer electrolytes, with [16] or without additional binder such as PTFE [17]. Conventionally, platinum nano-particles are used as catalysts for PEM fuel cells [18] whose catalytic reactivity is dependent on the shape, size, and morphology of the particle [19]. Pt has the highest activity toward ORR compared to all elemental catalysts and thus stands at the peak of the so-called ‘volcano’ plot illustrated in Fig. 2 which are based on the Sabatier principle [20,21]

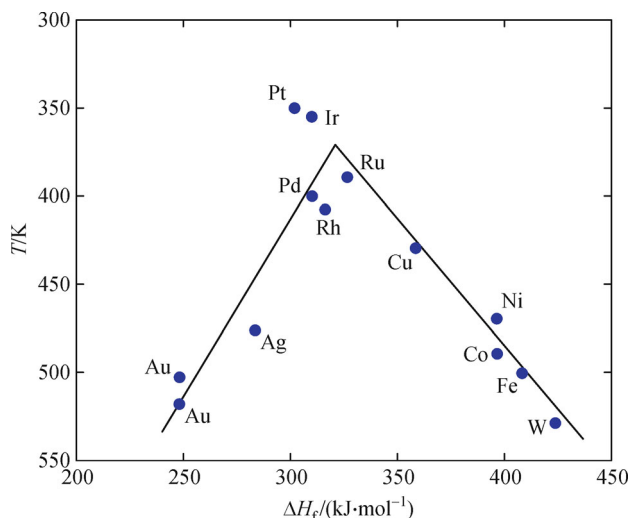


Fig. 2 Volcano plots showing the trends in oxygen reduction activity as a function of the oxygen binding energy

GDL consists of a macro porous backing layer, generally made up of highly porous and conductive carbon paper or carbon cloth, and a micro porous layer (MPL) [22]. Its features are: (a) good diffusion characteristics (aiding gases to come in contact with the catalyst site), (b) stability in the fuel cell environment, (c) good electrical conductivity, (d) high permeability for gases and liquids, and (e) elastic property under compression [23]. Figure 3(a) provides a functional plan of the key GDE component, namely, the catalyst and GDL. Figure 3(b) is a cross sectional view of GDE that provides a physical micro-porous support for the CL while allowing gas and water to transport to and from the CL [24].

It is inferred from Refs. [25–30] that the use of micro porous layer (MPL) typically results in a better performance, increased electrical conductivity and water management, and in turn the power density. As the name implies, MPL, consisting of porous, nano-sized carbon powders, provides the proper pore structure for the diffusion of reactant gases and liquids, minimizing electric contact resistance between the CL and bipolar plates, and managing the water balance during production, expulsion, supply and evaporation [22,31–34].

MPL improves performance by reducing mass-transport

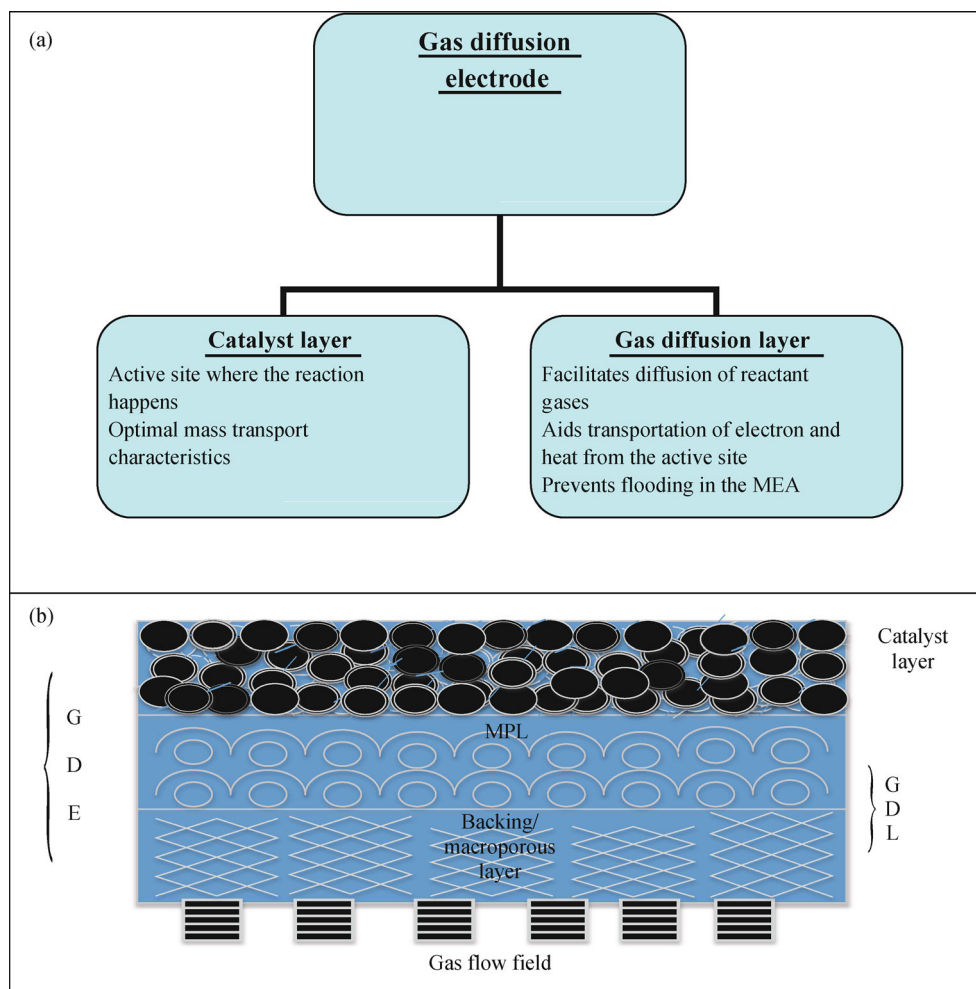


Fig. 3 Functional plan of key GDE component and cross sectional view of GDE
(a) Functional chart of GDE components; (b) cross-sectional view of a GDE

limitations, especially with the air feed and also by reducing ohmic losses especially with oxygen feed [35]. The binders such as teflon or PTFE are added which serve two functions: binding the high surface area carbon particles into a cohesive layer, and imparting hydrophobicity to the layer in order to facilitate the removal of water [36].

4 Durability of GDE

All power systems suffer degradation over time, from gas and wind turbines to solar PV [37] panels, and so do fuel cells. Though a lot of advances have been made in PEM fuel cells and many fuel cell systems have been successfully deployed for many applications, there are still a few challenges for its widespread commercialization, specifically the cost and durability. The phenomena involved in PEM fuel cell operations are complex, specifically, the multi-physics phenomena, including heat

transfer, species and charge transport, multi-phase flows, and electrochemical reactions which critically contribute to the durability [38].

Ironically, the study on the degradation causes in PEM fuel cell is still in its infancy. The significance of reviewing lifetime degradation and understanding the sources of PEM fuel cell degradation was proposed by Wilkinson and Steck [39]. The targets set by the US Department of Energy (US DOE) is 5000 h of operation for PEM fuel cell system/stack/MEA, for transportation application (with < 10% drop in rated power when tested under durability testing protocols) [40] and 10000 h for backup power systems [41]. It is difficult to quantify because of the testing complications involved in such a duration (i.e., up to several thousand hours or more) [42]. It is practically impossible to control the degradation mechanism without a proper measurement of the degradation rate and the DOE has developed Accelerated Durability Test (ADT) protocols to measure and analyze the durability. The classical testing protocols used to study the cathode catalyst

durability is fast potential cycling from a lower potential limit of 0.6 V to an upper potential limit of 0.9 V to simulate cathode potential variations during transient operation (idle-to-peak) or up to an upper potential limit of 1.2 V for start-up/shutdown cycles [43]. Alternatively, the offline potential cycling proposed by Borup et al. [44] can make a significant transformation to examine the durability of electrode materials in a simulated environment. A novel current distribution measurement proposed by Úbeda et al. [45] enables a deeper analysis than the conventional methods because it gives information about the current density profile at any instant. Thus, it is feasible to detect and diagnose failures and to eventually associate them with the phenomena occurring inside the fuel cell.

4.1 CL degradation

The electro CL facilitates hydrogen oxidation reaction (HOR) that takes place at the anode and the oxygen reduction reaction (ORR) on the cathode of the cell. The CL significantly influences the mass transport losses and its degradation is the primary cause for both recoverable and irreversible performance losses.

The Pt electro-catalysts, usually in the form of nanoparticles, are supported on carbon powder materials, in order to have a high Pt surface area per unit weight [46]. Vulcan XC-72, a commercially available carbon black, is normally used as the support material for the platinum catalyst, because of its low cost, good microstructure, good electrical conductivity, and easy availability. Degradation of CL, associated with the loss of electrochemically active surface area (ECSA), is considered as the substantial factor impacting the life of the cell.

The predominant CL degradation losses are classified as catalyst support corrosion, catalyst degradation, and catalyst support corrosion.

Carbon powder, which is used as a support for the Pt catalyst in the CL, is susceptible to corrosion. The corrosion of the carbon support takes place as per the equation:



$$E_0 = 0.207 \text{ V vs. SHE}$$

Though the above reaction is kinetically sluggish, Pt catalyst and the high cathode potentials ($> 1.5 \text{ V}$) experienced during start-stop modes accelerates the carbon corrosion. Carbon loss leads to a decrease in the conductivity of CL, a reduction of ECSA, and an aggregation/detachment of catalyst (Pt) particles from the support [47,48].

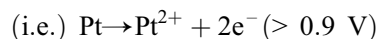
Carbon support corrosion can also lead to a decrease in the porosity and hydrophobicity of the CL [49], resulting in increased flooding and fuel cell performance decay.

Though carbon support corrosion is more common at cathode, it has also been reported at the anode, especially during fuel starvation leading to cell reversal [50].

Catalyst degradation/loss of catalyst activity takes place due to catalyst agglomeration, catalyst dissolution, loss of alloying elements from the alloy catalyst, and loss of catalyst due to carbon support corrosion. Pt agglomeration and Pt dissolution are predominantly the two sub phases involved in catalyst degradation and are elucidated as follows:

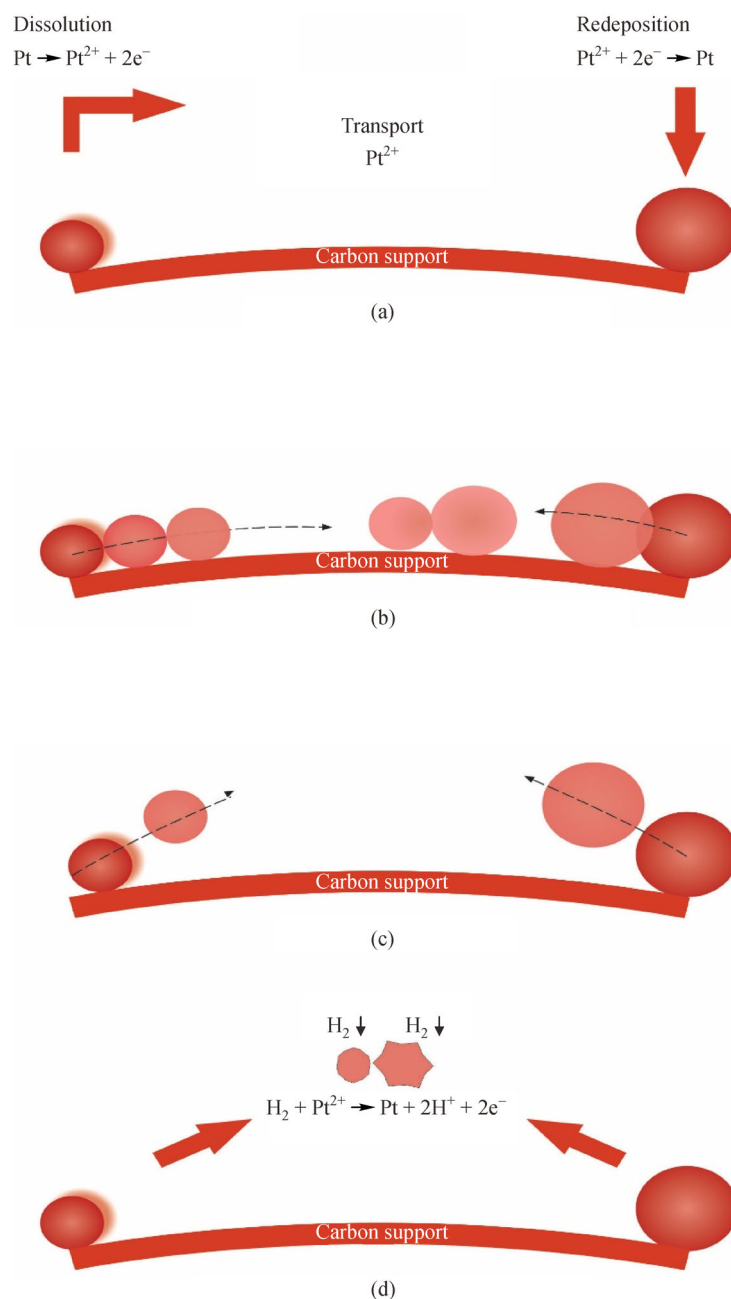
Pt agglomeration: The nano-size Pt catalyst particles are thermodynamically unstable and they tend to join with the other particles to form more stable, larger particles, and thus lead to a decrease in the catalyst surface area and activity. When Pt nanoparticles agglomerate to bigger ones, the electrochemical surface area of Pt catalysts decreases, and consequently the performance of PEM fuel cell degrades. In addition, this coarsening process can be accelerated under PEM fuel cell conditions [51]. The investigation of Qi and Buelte [52] was also inline sensing strong electrochemical degradation in terms of enhanced platinum catalyst agglomeration, triggered by an open circuit voltage operation for high temperature-PEM fuel cell operation. However, for a constant current density operation at 0.7 A/cm^2 , the agglomeration of platinum [53] is significantly induced at a lower rate.

Pt dissolution: Despite being a noble metal, Pt still dissolves in the aggressive environments on PEM fuel cells, such as low pH, high temperatures, and high potentials, leading to the formation of platinum ion.



The corresponding dissolution rate will be higher at higher potentials, especially above 0.9 V and exceptionally higher under potential cycling conditions. During the operation of fuel cells, the cathode potential oscillates between 0.9 and 0.6 V, and during idle-to-peak power operation, it can reach as high as 1.5 V during start-up/shutdown [54]. The dissolved Pt, such as Pt^{2+} , may migrate through the membrane and may be reduced to Pt inside the membrane, in case it meets the hydrogen diffused from the anode, and this platinum will no longer be accessible to the reacting gases, leading to a decrease in catalytic activity and a consequent loss of ECSA. The dissolved Pt may also precipitate onto numerous metal particles, leading to particle growth; or the particles may directly coalesce with each other due to movement on the carbon surface [55]. All these factors subsequently lead to a decrease in the catalyst surface area and ultimately the catalytic activity. The CL degradation mechanism is methodically represented in Fig. 4.

Ionomer-free ultra-thin CLs (UTCLs) emerge as a promising alternative to reduce the Pt loading by improving catalyst utilization and effectiveness [56].

**Fig. 4** Mechanisms of Pt degradation

(a) Ostwald ripening; (b) migration and coalescence; (c) detachment; (d) dissolution and precipitation

4.2 GDL degradation

GDL consists of carbon cloth or carbon paper (backing layer) coated with a porous layer of high surface area carbon with PTFE binder. The GDL performance loss has been caused by the corrosion of carbon in GDL, the mechanical factors/high clamping pressure, the loss of hydrophobicity due to carbon oxidation, the damage of porous structure, and the microstructure, etc. The tortuous structure of the carbon paper leads to severe mass transport limitation under high-humidity operations and conse-

quently, the carbon cloth is a better choice for humid operations. However, under the dry condition, the carbon paper is found to be superior because of its highly tortuous pore structure, which retains product water in the MEA and improves the membrane hydration hence its proton conductivity. However, both the two GDL materials degrade contributing to the PEM fuel cell performance [57]. The snapshot on the key degradation factors for GDL is revealed in Table 1.

Clamping pressure in the cell is indispensable to seal the cell from gas leakage and improves conformity to give

Table 1 Snapshot on GDL degradation factors

Electrochemical degradation	Mechanical degradation
Carbon oxidation	Clamping pressure
Low relative humidity and high temperature	Reactant flow (predominantly humidified)
High voltage accelerate carbon oxidation	High temperature

good electrical connection. However, it might contribute to the mechanical degradation due to the high GDL compression, resulting in changes in thickness due to the breakage of fibers at high pressures. At high compression, crushing of the GDL can lead to shearing of fibers at the land-channel interface, causing permanent damage to the GDL and much higher losses in porosity [58].

This kind of mechanical degradation actually accelerates at higher temperatures, causing more augmented damage. High temperatures can also possibly weaken the PTFE and microporous layer (MPL) from the GDL [59,60]. The *ex-situ* experiments by Lee and Merida also have concluded that the compressive strain of GDL increases with the applied pressure even more strongly with temperature, and is influenced by the PTFE stability [61]. Though PTFE content yields a more hydrophobic property, it reduces the GDL's porosity and possibly the mean pore size [62].

Wu et al. [63] have compared the physical characteristics of the GDLs before and after corrosion tests and validated that GDLs are susceptible to electrochemical oxidation. *Ex-situ* experiments by Chen et al. [64] are also inline for the durability characterization of the GDL. Chen et al. have also inferred that there is not only carbon loss but also performance loss, which is observed to be more significant with the increasing potential. Thus, the potential chemical causes for the GDL degradation may stem from carbon erosion, carbon corrosion, as well as changes in the characteristics such as porosity, hydrophobicity, micro-structure, etc., which principally leads to mass transport problems. The hydrophobicity of GDL accomplishes water management in a fuel cell and PTFE is currently used as a hydrophobic agent. The changes in hydrophobicity lead to excess water accumulation (flooding problems), which can block the gas pathways to the catalyst sites, and accelerate the degradation [65,66]. Bazylak et al. [67] have reported the deterioration of the hydrophobic coating after applying high clamping pressures on the GDL which alters the structure and affects the water pathway. Transport equations pertinent to GDL [68–73] elucidate the impact of operational parameters on the thermal properties of GDLs and provide insights into the thermal conductivity of the GDL materials and its correlation to durability.

GDL components of PEM fuel cells degrade in different protocols and the mechanisms involved in the degradation are not entirely implicit because there are different techniques employed to prepare functional components at various operating conditions that are not well stated by

researchers. The various mechanisms are interrelated, so one degradation mechanism may essentially trigger or exacerbate another. For instance, when the applied stress of GDL increases, it significantly influences not only the electrical conductivity but also the porosity. Another such example is that water build-up at the cathode CL arises not only due to the product water but also due to the electro-osmotic drag, which can also drastically decline the cell performance by hindering the gas diffusion [74].

5 Recent developments in GDE materials

Of all the catalysts exploited, Pt electro catalysts are still the best in terms of comprehensive evaluation [75].

5.1 Novel catalyst and support materials/Fabrication technique

The activity of a catalyst increases with the increase in surface area and consequently, one strategy is to reduce the diameter of catalyst particles to increase the active surface [76]. The factors leading to exploration of a novel CL are primarily due to its expensiveness, and loss of catalyst due to Pt dissolution, and detachment of Pt from carbon support. Pourbaix illustrations indicate that most metals such as Co, Cr, Fe, Ni, Mn, Cu, and V are soluble at a potential between 0.3 and 1 V vs. SHE and at a pH value of around 0 [77]. CO tolerant anode electrocatalyst, namely Pt–BeO, is proposed by Kwon et al. [78] recently for PEM fuel cell operation instead of conventional Pt–Ru alloy. Incorporation of carbon nano tube as a material for GDE can also significantly contribute to the performance and durability due to its exceptionally high transport rates as a result of the inherent smoothness of the nanotubes [79]. The better performance of the nanotube electrode is also attributed to its 3D characteristics [46].

Carbon is a common choice for supporting nanosized electro catalyst particles in low temperature fuel cells because of its large surface area, high electrical conductivity, and pore structures [80]. Single walled and multi-walled carbon nanotubes, graphene carbon nanofibers, ordered mesoporous carbons, carbon aerogels, carbon shells, boron-doped diamond structures, etc. have been tried as catalyst supports [81]. However, their synthesis costs are relatively high. Yu et al. [82] have used graphitized carbon as a catalyst support instead of a conventional support and yielded a lower degradation rate than that of a conventional carbon by a factor of 5 after 1000 start-up/shutdown cycles. Kou et al. [83] have proposed functionalized graphene sheets as Pt catalyst supports in PEM fuel cell environment and obtained a good activity and a better stability than the commercial catalyst.

Considerable research efforts have focused on alternative catalyst supports for PEM fuel cell. The required

properties of an alternative fuel cell catalyst support are high electrical conductivity to assure the electron transfer, high surface area to provide a high dispersion of platinum nanoparticles, and a good corrosion resistance under oxidizing conditions.

Sn, W, Si, and Ti based oxides, carbides or borides have attracted much attention in the last years to be used as electrocatalyst supports for fuel cell applications, realizing promising outcomes in terms of durability [84–91]. However, the limitations of these non-carbon materials are the low conductivity and deprived platinum dispersion. TiN also acts as a promising alternative to carbon supports due to its higher electrical conductivity, comparable to that of carbon and outstanding oxidation and acid corrosion resistance [92,93].

Lobato et al. [91] have been able to successfully deposit Pt on new SiC based supports, which exhibit a high electrochemical stability. Their results are remarkable, illustrating that the Pt/SiCTiC have a higher stability for a high temperature PEM fuel cell operation. Table 2 provides the ECSA values and the degradation values achieved from the cyclic voltammetries of each MEA tested [91]. It can be observed that MEAs prepared with non-carbonaceous based catalyst on the cathode side exhibit a very low degradation (1.27% and 6.08%) as compared to the carbonaceous catalyst (21.70%).

Table 2 Evolution of ECSA obtained from H₂ desorption peak of cyclic voltammetry performed during the different protocol tests

Cathode catalyst	Net ECSA/(m ² ·g ⁻¹ Pt)	Total degradation/%
Pt/Vulcan XC72	13.36	21.7
Pt/SiC	13.20	1.27
Pt/SiCTiC	12.98	6.08

Sundar Pethaiah et al. have recommended the concept of platinum nano-catalyzed MEA by the non-equilibrium impregnation-reduction method to improve the performance and durability for the PEM fuel cell operation [94–96]. Nano-catalyzed membrane groundwork is a striking strategy since it is a single step for durable catalyst preparation and application. Moreover, it facilitates the self-humidification to enhance the cell performance.

The catalyst support has a substantial influence on the initial mean size of the catalyst particles as well as the performance [97]. Modification of anode structure [98] and new configurations, such as core-shell and novel catalyst supports, have also shown great promise toward improving the catalysts' durability [99].

Fabrication techniques can also significantly enhance the durability apart from reducing the catalyst loading. Adoption of advanced manufacturing practices/3D printing techniques for the fabrication of multi-functional GDL components [100,101] is endorsed for the improvement in the durability as well as reduction of fuel cell stacks cost

and complexity especially to be manufactured for a large scale. Mass production of GDL is a critical topic for its progress [102].

5.2 Novel GDL materials

Conventional GDLs are consistently imperilled to compression. Therefore, the desired attribute of an ideal GDL is to be mechanically stable to withstand the stress. In addition, they are also susceptible to electrochemical oxidation [63] which can be eliminated by using a non-carbon based material. Metallic GDLs are not only carbon free, but also exhibit better electrical and mechanical characteristics. In addition, the heat dissipation is effective with metallic GDLs, thus averting the hot spot of the membranes and electrodes. Wood and Borup [103] have discussed the physical properties to have an insight on GDL durability and subsequently long-term performance for next-generation GDL components.

Water management, thermal management, and degradation minimization are intricately correlated to each other, among which thermal management can be considered as the core-controlling factor, which directly affects the others [104].

However, the thermal conductivity values of GDL encountered in the literature are so disseminated [112], as illustrated in Table 3. Though GDL carbon fibers are highly conductive, the effective conductivity can be low when the porosity is high [62]. Thus, the porosity is interrelated to the thermal conductivity as well as the current density. Damage in the CL has been observed by Lee et al. [113] when MPL is employed and the degradation is accelerated beyond 40 cycles of operation. Similarly, MPL degradation in a simulated PEM fuel cell water flooding conditions is also in line with the observations of Lin et al. [42].

Hottinen et al. [114] have incorporated titanium sinter material as a gas diffusion backing for a low power density PEM fuel cell application. These titanium sinter materials can also operate as a direct gas diffusion path in a free-breathing fuel cell. Zhang et al. [115] have fabricated a porous GDL with 12.5 μm thick copper foil and inferred

Table 3 Effective thermal conductivities of the GDL-review

Parameter	Material/value	References
$k_{\text{eff}}/(W \cdot (mK)^{-1})$	Graphite matrix/150.6	[105]
	Carbon paper/1.6	[106,107]
	Carbon fiber paper/1.3	[108]
	Carbon paper/0.1 to 1.6	[109]
	Toray carbon paper 1.8 ± 0.27 at 26°C 1.24 ± 0.19 at 73°C	[110]
	Diffusion and CL 0.2 ± 0.1	[111]

improved thermal and electrical conductivity. In addition to high thermal and electrical conductivity, the material also exhibits controllable permeability. Recently Trefilov et al. [116] have fabricated carbonic materials (Xero gel based) with tailored structural, morphological, and electrical properties, to address the key GDL parameters: stability, electrical conductivity, hydrophobicity, thickness, and porosity.

The performance of PEM fuel cells are greatly influenced by the MPL and its design, apart from the GDL properties. Although GDL is treated as a homogenous material, in reality, the GDL substrate and MPL are distinct layers [117]. Lobato et al. [118] have fabricated a durable MPL based on SiC, which does not have mass transport problems, unlike carbonaceous-based MPL. Though the electrical conductivity decreases with the SiC content, it has much better thermal and electrochemical stability. Ito et al. [119] have developed a self-supporting MPL which is fabricated and applied to a GDL. Interestingly, they have inferred that the GDL composed of only the MPL have a better performance than the GDL which comprises of the integrated gas diffusion backing medium and MPL.

If GDL can be integrated along with the flow field as conversed by Hottinen et al. [114] it can be a cutting edge configuration with a robust design and a reduction in the cost as well.

6 Modeling strategies to address GDE degradation

Modeling studies can be an economical and promising solution to mitigate the degradation issues as it can optimize the process parameters which are complex phenomenon involving mechanical, thermal, and electrochemical operational environment taking place simultaneously. These process parameter while occurring concurrently (in fuel cell environment) accelerate the degradation of components [120]. Modeling studies can provide a better insight into these process parameters because it is difficult to evaluate the influence of one parameter discretely with other properties [33].

Wang and Chen [121] have proposed an advanced three-dimension (3-D) numerical model and their findings state that a liquid-free GDL zone can be created despite the channel stream being a two-phase flow. Such a liquid-free zone is adjacent to the two-phase region, can circumvent not only flooding but also the degradation issues due to dryness. Similarly, Janssen [122] have presented a steady-state, two-dimensional model to investigate the water transport in the electrode which can indirectly alleviate the degradation issues. This is due to the insight on the respective transport rates at which these processes take place, which is proportional to the driving force for the

water transport in both directions and the permeability of the components. It is plausible that if GDL permeability changes over time in an operating fuel cell, subsequent PEM fuel cell performance and durability could be affected [61].

Comprehensive understanding in the heat transfer phenomena occurring in porous media is also a crucial factor for durability consideration. For instance, at high temperatures of around 80°C, the heat pipe effect is significant for the hydrophilic GDL paper compared to its hydrophobic counterpart [62].

Moreover, carbon corrosion is accelerated not only with an increase in potential, but also due to a decrease in relative humidity [44]. Incorporating artificial intelligence techniques as proposed by Jayakumar et al. [123] is an alternative route where the operating parameters such as humidification and temperature are optimized to enhance the durability and reduce the sub-system cost.

7 Critical assessment and discussion

A major gap impeding the commercialization of PEM fuel cell technology in automotive and stationary applications is the cost and durability [102]. In specific, if the PEM fuel cell technology has to compete with the matured internal combustion engine, it must be robust and capable under diverse operating conditions. The GDE configuration of a PEM fuel cell is a significant factor of concern which structurally encompasses the catalyst and diffusion layer and functionally necessitates the characteristics such as, electrochemical activity, conductivity, porosity, hydrophobicity and specific weight.

To content the electrochemical activity, the durability and electrode performance of the GDEs materials must be significantly improved because these components are consistently exposed to strongly acidic/oxidizing environments, large potential gradients, high current density, extreme humidity conditions and temperature variations. Conductivity is an essential characteristic that facilitates the electron transfer. Porosity is an integral property of a GDE which can apparently assist in the removal of the product water.

The size/specific weight of Pt-based catalyst can also impact the durability of the GDE used in PEM fuel cell. On the nanometre scale, the catalyst sizing is usually in the range of 2–6 nm [51]. Nanoparticles inherently [124] indicate a strong tendency to agglomerate due to their high specific surface energy [125]. The results from an alternate research group is also inline, specifying that the Pt nanoclusters with sizes smaller than approximately 3 nm have electrochemical stabilities weaker than that of bulk Pt (1.01 V relative to a SHE) [126]. For nanoparticles, the smaller the size, the higher the specific surface area, and the easier to agglomerate/sinter [127]. Therefore, when Pt

nanoparticles agglomerate to bigger ones, the electrochemical surface area of Pt catalysts decreases, and consequently, the performance of PEM fuel cell degrades. In addition, this coarsening process can be augmented under PEM fuel cell conditions [51]. Advanced fabrication techniques such as electro spraying technique, can drastically reduce the Pt loading of about 1/10 of the DOE 2020 target [128,129] with reasonable durability. 3D printing are also considered as promising manufacturing techniques for improved durability and mass production of electrodes.

Understanding the functional behaviors of various materials involved in GDE layer fabrication in a holistic basis can be a sensible solution to many of the degradation issues. For instance, ionomers (such as Nafion) which are added into the CL to enhance Pt utilization can also lead to the degradation of ionomer in the CL and poisoning of the catalyst by the impurities, contributing to the decrease in catalyst activity and subsequent performance loss. A similar circumstance is sensed with regard to the operating parameters, where the operation of a PEM fuel cell stack at a low voltage can limit the degradation. However, it is not practically possible because the efficiency of the stack at low voltage can be very low due to the high current density and the related mass transport losses. In the same way, a humidified reactant operating condition can cause more complexity not only from the system perspective but also from the stack perspective as the water molecules can block the active sites of the GDL. Incorporating the artificial intelligence technique to control the operating parameters can be a promising strategy to improve the durability [123]. Investigating the basic relationships between polarization losses at diverse current density for the various composition in GDLs functional properties might provide an insight into those predominant parameter that contribute to degradation.

Selection of appropriate materials involves an iterative design process that eventually becomes specific to that particular product and application [130]. Development of the non-corrosive metallic component with a more strength to weight ratio should be given priority, as it will have additional advantage of high heat flux removal, thereby preventing hot spots, especially during high current density operations, and may improve the stack durability.

Predominant recoverable loss for PEM fuel cells includes catalyst poisoning by membrane degradation products [131] which requires removal from the catalyst surface and then from the electrode layer for the performance recovery [132]. Irreversible loss includes catalyst dissolution and ripening, loss of alloying agents from Pt-X catalysts, plus the effects of the various forms of carbon used in PEMFC components, which include changing hydrophobicity, carbon corrosion and loss of porosity of electrode layers, and GDLs. These increasing losses are primarily in the cathode CL and attribute not only to mass transport, but also to the kinetic losses. Non-

carbonaceous catalyst supports oxides, carbides and nitrides of Ti, W, Mo etc. and can significantly enhance the durability of the catalytic layer [81,84–87]. Optimal stack design strategies can also circumvent catalyst degradation issues. Knights et al. [98] have accomplished reduced catalyst degradation through modification of the anode structure to favor oxidation of water over carbon.

Asset et al. [133] have investigated the low Pt loading and durable GDEs for PEM fuel cell application. Pt-M/C electrocatalysts (coarsening of the nanoparticles, loss of their shape/texture, selective dissolution of the M element, corrosion of the carbon support, etc.) still function for the state-of-the art electro catalysts.

8 Conclusions

For the penetration of PEM fuel cells to the market, the role of GDE is very substantial. In this paper a comprehensive and critical analysis on the various factors leading to the GDE durability is assessed to have a better insight for the PEM fuel cell researchers. Altering the electrode configuration such as the integration of membranes, CL and GDL, enhancing the specific and mass activities of catalysts and improving catalyst tolerance to air, fuel and system-derived impurities are other critical factors influencing the durability.

Acknowledgements The authors would like to acknowledge the management of Chennai Institute of Technology for extending their support and Jo Stone for an effective proofreading.

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