Degradation mechanisms in PEM fuel cells: A brief review

Veeresh Patil [a], P.V. Reshmi [a], S. Prajna [a], Yashaswi [a], Yashaswini [a], D. Haleshappa [a,*], A. Jayarama [b,*],
Richard Pinto [c]

[a] Department of PG Studies and Research in Physics, Sri Dharmasthala Manjunatheshwara College (Autonomous), Ujire 574240, India
[b] Department of Physics, Alva's Institute of Engineering and Technology, Moodbidri 574225, India
[c] Department of Electronics and Communication Engineering, Alva's Institute of Engineering and Technology, Moodbidri 574225, India

ARTICLE INFO

ABSTRACT

One of the most important features of polymer electrolyte membrane (PEM) fuel cells is durability. Improving fuel cell life and membrane electrode assemblies (MEA) durability translates to significant cost savings for fuel cells. This review is about the study of the degradation mechanisms of PEM fuel cells. The Degradation mechanisms include chemical, mechanical, catalyst, and thermal degradation. The reason for degradation also may be due to the presence or formation of contaminants during dynamic conditions. From the review, it has been observed that Pt catalysts made of Pt or Pt-alloy catalyst value superior to those required for complete Pt oxide.

Copyright © 2023 Elsevier Ltd. All rights reserved.
Selection and peer-review under responsibility of the scientific committee of the 10th National Conference on Condensed Matter Physics and Applications.

1. Introduction

Energy sustainability is a critical challenge due to the depletion of fossil fuels and the release of large amounts of CO_2 into the air which causes global warming. So alternatively, fuel cells are among the most essential energy devices because they can directly transfer chemical energy from fuel (such as methanol, hydrogen, etc.) to electrical energy with great efficiency and zero carbon emission in the case of hydrogen fuel. Depending on the electrolytes and fuels employed, there are many distinct types of fuel cells such as polymer electrolyte membrane fuel cells (PEMFC), direct methanol fuel cells (DMFC), solid oxide fuel cells (SOFC), molten carbonate fuel cells (MCFC), phosphoric acid fuel cells (PAFC), alkaline fuel cells (AFC), and alkaline anion exchange membrane fuel cells (AEMF) [1–4]. Among all, PEMFCs are the most sustainable with a variety of applications [5] in particular, for automotive applications [6]. The main benefit of PEMFC is that it operates at low temperatures below 100 degrees Celsius.

The PEMFC's key component is the MEA. A PEM fuel module is composed of two catalyst layers and two gas diffusion layers (GDL): because of their superior proton conductivity, mechanical and chemical stability nafion membranes are the most used electrolytes.

One of the most serious obstacles to the commercial use of PEMFCs is the high cost of electro-catalyst platinum (Pt) and fabrication process. One technique to reduce the cost is to expand the surface area of the Pt catalyst and use it more efficiently without sacrificing cell performance. It will assist in reducing the fuel cell's size, and its high cost. The factors which reduce the PEM fuel cell performances are temperature control and water control capabilities, ohmic resistance, and rate of long-term performance deterioration of PEMFCs which are all determined by the membrane, catalyst degradation, and efficiency. The performance is impacted by a variety of input factors and output factors of a PEM fuel cell which encompass both design and construction of fuel cells, material deterioration, impurities or pollutants, and operating situations. The long-term endurance of PEM fuel cells is a major roadblock to their commercialization in stationery and transportation applications. Improved fuel cell component durability is required for commercial viability. Individual components must be thoroughly described to determine and quantify deterioration mechanisms to expand fuel cell durability. In this review, we summarise some of the progress made in identifying chemical, mechanical and thermal degradation mechanisms in PEM fuel cells over the years, as well as a solution to the degradation due to contaminants.

* Corresponding authors at: Department of Physics, Alva's Institute of engineering and Technology, Mijar, Moodbidri 574225, India (A. Jayarama).

E-mail addresses: halesh.phy@gmail.com (D. Haleshappa), jrmarasalike@gmail.com (A. Jayarama).

2. Degradation of PEM fuel cells

Membrane failure can result in prolonged performance leading to decline of structural, physicochemical, and deterioration by electrochemical processes, which can be caused by an increase in mass transport resistance as a result of improper cell operation [7]. Understanding these degradation processes is necessary for the development of long-lasting membranes. Chemical, mechanical, and thermal deterioration [8] are the three most prevalent failure modes of membranes.
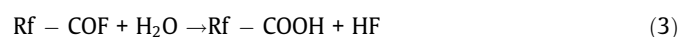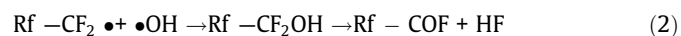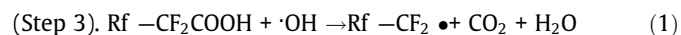
2.1. Chemical degradation in PEM fuel cell

The chemical degradation of membranes has been thoroughly described [9–11]. While the Nafion PFSA polymer has shown in fuel cell applications, to be highly effective and dependable, an indication of thinned membrane and fluoride ion identification in the product water has been discovered suggesting that the polymer is being attacked chemically. The main degradation mechanism is thought to be peroxide radicals action on polymer end groups [12] with remaining terminal connections involving H. In this degradation mechanism, oxygen molecules infiltrate from the cathode to the anode, where oxygen from the anode side can reduce the Pt catalyst to create HOO and HO radicals, causing membrane breakdown. Fluorocarbon is the backbone of PFSA; membranes are destroyed by radical assault, which has a direct impact on membrane mechanical strength and proton conductivity [10]. Any terminal bonds in the polymer that include H can be attacked by these radicals. The main degradation process is thought to be a peroxide radical attack on H-containing end groups. In the presence of peroxide radicals, this type of chemical attack is high at an active temperature above 90 °C and humidity levels are minimal. The hydrogen peroxide degradation targets the polymer at its end group sites and starts the degradation process. Furthermore, pollution of transition metal ions, hydrogen crossover, and changes in operating conditions can all have a direct impact on the chemical deterioration of the PFSA membrane [13].

The following sequence reactions are among the proposed mechanisms:

Step 1 extraction of a perfluorocarbon radical is formed by hydrogen from an acid end group, CO_2 and H_2O.

Step2: The hydroxy radical can react with the perfluorocarbon radical to generate a phase that reverts to fluoride acid and one hydrogen fluoride similar (step 2). The acid fluoride is hydrolyzed, yielding a second counterpart of HF and a new acid end group.

$$(\text{Step 3}).\ \text{Rf} -CF_2COOH + \cdot OH \rightarrow \text{Rf} -CF_2 \bullet + CO_2 + H_2O \quad (1)$$

$$\text{Rf} -CF_2 \bullet + \bullet OH \rightarrow \text{Rf} -CF_2OH \rightarrow \text{Rf} - COF + HF \quad (2)$$

$$\text{Rf} - COF + H_2O \rightarrow \text{Rf} - COOH + HF \quad (3)$$

2.2. Mechanical degradation in PEM fuel cell

Another important component that affects membrane lifetime is mechanical degradation, which is caused by mechanical stress created under different conditions inside the membranes (such as cracks, pinholes, tears, punctures, etc.) [14,15]. Khorasany et al. [13] discovered a strong connection between membrane fatigue and stress, temperature, and relative humidity are examples of operating factors. The membrane's sandwich construction allows it to withstand complicated stresses, and its resistance increases as compression pressure increases [16]. Furthermore, the membrane's dimensional change is extremely sensitive to humidity [17]. The membrane absorbs water and swells when fuel cells are first turned on, causing swelling pressure. Khorasany et al. [18] investigated the Membrane longevity when subjected to cyclic chemical and mechanical loads using modelling techniques. The model outcomes demonstrated that fluctuating humidity causes greater harm to membranes than fluctuating temperature and that a minor rise in amplitude of humidity can result in a large drop in membrane lifetime.

2.3. Catalyst degradation in operating MEAs

Long-term degradation of catalyst layers (CLs) comprises catalyst aging, catalyst particle movement, catalytic outflow, electrolyte dissolution (Nafion ionomer), and carbon coarsening. All these activities cause an apparent reduction of activity in the catalyst layer, might be caused by changes in the active surface which loses the electric/ionic connection, or microstructure of the catalyst. The reduction in the amount of electrochemically active surface area (ECSA) of nanoparticles as a result of particle development caused by a combination of dissolution/reprecipitation and coalescence processes is the main catalyst degradation mechanism seen during accelerated stress tests (ASTs) [19,20].
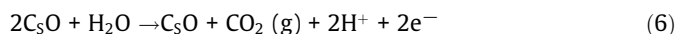
The electrochemical surface area (ECSA) of Pt is widely considered to be one of the most critical metrics for determining PEM fuel cells' apparent catalytic activity [21–24]. CO gas-phase chemisorption, cyclic voltammetry (CV), and CO stripping voltammetry are all common methods for determining ECSA. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are two regularly utilized techniques to analyse microstructural changes in catalyst layers after degradation. While RDE is the most widespread method for evaluating catalyst activity, electrochemical performance and lifespan in operational PEMFC, MEAs are more relevant parameters. Accelerated stress tests, which combine the rapid catalyst testing and support endurance, potential cycle with interrupted performance testing and diagnostics [25–27].

Physicochemical features of catalysts, such as BOL size of particles, form, structure, support characteristics and interactions, pore size and inter-particle distance dispensation, and particle placement on the assistance, as well as operational factors like potential sweep speed, temperature, humidity, and the upper/lower potential limits (UPL, LPL) of the sweep, all influence nanoparticle growth (RH) [26,28,29]. According to modelling of Pt solubility data obtained from ASTs of MEAs, during the cathodic scan, the amount of Pt that dissolves reductively as PtOx greatly outnumbers the quantity that melts oxidatively as Pt and PtOH. [30]. The volume of leached Co is likewise a positive function of UPL, and it is smaller when UPL is higher influenced by the LPL, according to measurements [29].

According to several studies, the breadth of the ECSA stability is determined by the particle-size distribution (PSD): Pt nanoparticles with high surface area carbon (HSC), starting particle sizes of 2, 3, and 4 nm and narrow PSD standard deviations were supported (10%) degraded over the entire AST duration, regardless of particle size and ECSA reductions were found to be roughly equal to changes in MA [30]. The most persistent Pt nanoparticles were found to be as small as 2 nm, with the highest MA [30]. Catalysts made of Pt-TM alloy nanoparticles demonstrate a high after ASTs and realistic vehicle drive cycles, the degree of TM draining, and ECSA loss is a significant degradation mechanism [27]. It was recently observed that restricting the lowest possible outcome encountered by a Pt or Pt-alloy catalyst to value superior to those required for complete Pt oxide decrease, could prevent dissolution-related deterioration [28,31]. Carbon corrosion can take place either chemically or electrochemically [32,33].

To be precise, carbon oxidation occurs via two pathways, which are thought to proceed through electron movement, hydrolysis, and CO_2 production as the following: 1) Partial oxidation results

V. Patil, P.V. Reshmi, S. Prajna et al.

in surface group formation (Eqs. (4) and (5)). and 2) Finished oxidation yields to gaseous CO_2(Eq. (6)) [34].

$$C_S \rightarrow C_S{}^+ + e^- \tag{4}$$

$$C_S{}^+ + H_2O \rightarrow C_SO + 2H^+ + e^- \tag{5}$$

$$2C_SO + H_2O \rightarrow C_SO + CO_2 \,(g) + 2H^+ + 2e^- \tag{6}$$

The subscript "s" denotes the surface species.

Under stable operating circumstances, when the potential is around 0.4 and 0.7 V, carbon corrosion isn't severe. As a result, the impact of carbon instability on PEMFC electro-catalyst durability is limited within this possible range. Under harsh conditions, particularly at anomalous potentials, the corrosion reaction is greatly accelerated. For example, Carbon support oxidation gets such when voltage reverse occurs throughout cell operation, so severe that it can harm fuel cells irreversibly [35–38]. Whenever the fuel cell is running out of fuel because of inadequate flow distribution, gas obstacles, or an abrupt current change to the heavy load in intermittent situations, as well as start-up and shut-down operations, this situation might be noticed. Due to reduced hydrogen coverage in the anodes, local cathode voltage can approach 1.5 V during uncontrolled and repeated start-up as well as extended shut-down of a fuel cell, which substantially accelerates carbon corrosion. [39,40] The two proposed ASTs given here are meant to explore the electro-catalysts and carbon supports durability individually and independently. If carbon degradation is prevented, it's feasible to anticipate the performance of a deteriorated sample merely by monitoring or modelling the ECSA during the MEA's tenure.

Latest operando X-ray computed tomography (XCT) analyses of an electrode layer during ASTs reveal that the CCL changes porosity drastically throughout cycling, with a greater porosity increase during the initial stages as well as a change to lower porosity during the later step [41]. After AST, FIB-SEM examination revealed that specimens have a pore-size concentration change toward larger pores, while the cathode's overall porosity stays unaltered. While finishing at improved cell temperature, ASTs lead in a smaller cathode, the CL porous size in the cells that were subjected to higher temperature cycling compared to those cycled at 80 °C is significantly different and showed no discernible variations [42]. In addition to performance, the changing climate within the CL drives other deterioration caused by potential-driven processes such as the development of catalyst particles, carbon corrosion, and loss of metal transition.

2.4. Thermal degradation in PEM fuel cell

High temperature can improve the membrane's capability of ion transport and speed up the electrochemical reaction rate. If the temperature rises to a high level, membrane collapse occurs. Several research and reviews [43–45] have been published to explain the thermal deterioration of PFSA membranes. The decomposition of the side sulfonate acid group initiates heat deterioration of Nafion, similar to chemical degradation, a decrease in both water content and material deterioration. Thermal deterioration of the membrane occurs not just during the hot start phase, but also during the cold start phase. The majority of the water in the membrane is trapped in polymer chains, which do not freeze till the membrane is soaked at the freezing. Water passes through the membrane and is more prone to freeze on its surface [46]. Freezing and thawing cycles produce a thermal deterioration of the membrane, which can create a variety of structural and functional problems [47]. For example, the increasing volume of ice that accumulates among the membranes as well as the catalyst

layer membrane surface damage (e.g., pinholes, fissures, etc.) and harm to the catalyst layers to delaminate [48].

3. Degradation due to contaminants

Among the most critical concerns in the fuel cell industry in functioning and their servicing are the influence of contaminants on fuel cells [49]. In recent years, there have been efforts to determine the potential consequences of contamination, recognize the mechanisms of contamination, and develop fuel cells and their uses in the vehicle market have received a lot of interest as part of mitigation strategies. When it comes to fundamental understanding, it has been discovered that the component of the fuel cell, MEA is the part of the system that is most affected by contamination.

3.1. Contaminants in gas diffusion layer (GDL)

The literature on the effects of contaminants on GDLs is limited. Following MEA lifetime testing, it was noted that GDLs appeared to be less hydrophobic, and indications of foreign substances were discovered on the GDL surface that had not been there before lifetime testing. The contamination effect might be partially responsible for this. Contaminants, such as transition metal ions may bind to or deposit on carbon fibers affecting surface characteristics like hydrophobicity and hydrophilicity, which may cause issues with water management or mass transfer.

When a PEM fuel cell is poisoned by ionic contamination, supplying highly pure hydrogen or neat air cannot recover deteriorated performance. A part of this behaviour can be attributed to effects like salt accumulation on GDL and flow channels and the physical deterioration of the fuel cell's compartments, such as the membrane and catalyst layer. The major cause of such degradations is salt precipitation, which blocks GDL pores and flow channels. They also investigated how PEM fuel cells performed when exposed to chloride-salt contamination, and they determined that lower relative humidity levels lead to higher salt deposition and worse degradation.

Yan et al. [50] also investigated the effect of sodium chloride and calcium chloride salts on the performance of a 600 W PEM fuel cell system and discovered that these salts have no significant effects on the PEM fuel cell's performance in short-term operations. However, due to 1.082 mV h^{-1} voltage decay rate for ~1M NaCl and 3.446 mV h^{-1} for 0.5 M CaCl2 under the current density of 1 A cm^{-2}, they still have the potential to damage PEM fuel cells over time, especially at higher current densities. It was also established that decreasing current density may result in less produced water, a drier cathode, and more precipitated cations, all of which could block GDL (and occasionally flow channels) and degrade the operation of the fuel cell's performance. The degradation mechanisms of various components are professed along with the causes in Table 1.

Pasaogullari et al. [51–54] also conducted several studies to figure out how calcium ion contamination affected PEM fuel cell performance. They stated that in addition to salt deposition on GDL and Microporous Layer (MPL), which raised mass transport resistances and negatively impacted reactant movement by up to 40% [55], Ca2+ can facilitate the catalytic layer on the cathode and enhance Pt particle agglomeration [56,57].

The study of Uddin et al. [58] scrutinized the impact of the hydrophobic properties of GDL on cation contamination and revealed that the hydrophobic properties of GDL and the MPL prevent the cationic solution from reaching CCM and, as a result, cations cannot exit from the cell. A similar structure can be utilized to filter cationic solutions and prevent the transfer of cations in the

Table 1
Shows Fuel cell major degradation mechanisms of PEM fuel cell.

Component	Role	Mechanisms of degradation	Causes
Membrane	Permit flow of protons from the anode to the cathode, Stop electrons from traveling.	Mechanical degradation (cracks and pinholes).	Non-uniform pressure.Thermal stress/cycling; drying.
		Chemical degradation: poisoning;	Sealing; Peroxide attacks; Air pollutants and fuel toxicity;
Bipolar plate	Individual cell isolation; conduct current through cells; Assistance in water and energy management; Sustain the MEA mechanically, with low contact resistance.	Conductivity loss. Deformation and fracture	Corrosion. Thermal stress/cycling and mechanical stress
Electrodes, GDL + CL	An electrical conductor transports electrons from the anode to the cathode through external circuit.	Loss of conductivity and activation. Decrease of reactant diffusion;	Corrosion; Delamination; Oxidation; Flooding; Fuel poisoning. Mechanical stress;
Gas diffusion layers (GDL)	Ascertain gas diffusion from flow fields to active locations. Drain the water;	Mechanical deterioration; loss of hydrophobicity	Mechanical and thermal stress; Corrosion
Catalyst layer (CL)	Assist hydrogen oxidation and oxygen reduction processes;	Loss of conductivity; catalyst loss;	Mechanical and thermal stress; Corrosion

liquid phase to the fuel cell because of the hydrophobic GDL and MPL act as a barrier for cations. Altogether, the adverse effects of ionic contamination on GDL can be summarised as follows:

- Contect resistances and mass movement over-potentials are increased by salt precipitation and obstruction of GDL and flow channels.
- The degradation of polymers (a poisoning phenomenon) is catalysed by the presence of the cations.
- A 4-electron path of the reaction mechanism becomes a 2-electron path.
- Even at higher current densities, they can still damage PEM fuel cells and poison them if exposed for an extended period.
- Lowering current density can cause more precipitated cations and less produced water, which obstruct GDL and reduce the performance of the fuel cell.

3.2. Contaminants of operating gases

3.2.1. Fuel (hydrogen) contamination sources

In the current technological climate, in fuel cell research, as fuel hydrogen is utilized as a direct fuel, most of the available commercial sources are used for development and presentation and Production on-board. The most common approach for the generation of hydrogen by transforming hydrocarbons and/or oxygenated hydrocarbons in natural gas methane [59] and methanol from biomass [60,61]. Electrolysis and partial oxidation (or auto-thermal reforming) of tiny organics are two other ways [62] as sodium borohydride hydrolysis [63]. However, contaminants carbon oxides, such as CO and CO2, and sulfur compounds, such as H_2S and sulfur organics, are unavoidable during the hydrogen production process steam reformation, partial oxidation, and auto-thermal reforming are the most common methods for producing "reformate," a hydrogen-rich gas that comprises 40% to 70% H_2, 15% to 25% CO_2, 1% to 2% CO, minor amounts Sulphur & inert gases (vapour and nitrogen) contaminants. In natural gas distribution networks, with use of ammonia as a tracker gas can result in NH3 contamination in the reformate gas (at a level of a few ppm). The fuel cell needs a purer hydrogen supply, essential for better performance and a long lifetime.

3.2.2. Influence of carbon monoxide

In PEM fuel cells using reformate H2-rich gas as fuel, both carbon monoxide and carbon dioxide have grown to be serious issues, especially at typical operating temperatures (about 80 °C). It is widely known that CO forms a strong bond with Pt sites, which reduces the number of surface-active sites that are accessible for the adsorption and oxidation of hydrogen. Regarding this, Baschuk and Li [64] examined the characteristics, mechanism, mitigation, and theoretical models of the CO poisoning of platinum electrocatalysts utilized in PEM fuel cells. It appeared that the anode catalyst types, CO concentration, exposure time, and cell operation temperature all had a significant impact on the CO poisoning effect.

3.2.3. Influence of carbon dioxide

Currently, natural gas (CH4) is used to steam, and reform natural gas, which yields a significant amount of carbon dioxide as a by-product (25% [65]), which accounts for nearly 95% of the hydrogen produced. Particularly at higher current densities, the performance loss caused by CO2 contamination in anode fuel can be seen [65]. CO2 can be catalytically transformed into CO on a Pt catalyst, poisoning the catalyst in the process. A water-CO2 gas shift reaction (WGSR) can create between 20 and 100 ppm CO in equilibrium, according to thermodynamic simulations [66] as follows:

$$2Pt + H2 \rightarrow 2Pt-H_{ads} \tag{1}$$

$$CO2 + 2Pt-H_{ads} \rightarrow Pt-CO_{ads} + H2O + Pt \tag{2}$$
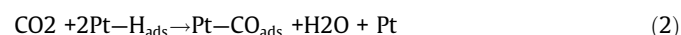
The CO concentration can be increased with decreased temperature and water content in the anode feed [66]. Even a low concentration of CO (30–50 ppm) in the presence of CO2 can significantly reduce cell performance, especially at higher current densities [67].

3.2.4. Influence of hydrogen sulphide

An even more harmful fuel pollutant than carbon monoxide (CO) is hydrogen sulfide (H2S), which has been thoroughly studied [68–72]. The performance of the cell was shown to be severely reduced by a trace amount of H2S when exposed to an anode or cathode, primarily due to the poisoning effect of the Pt catalysts [70]. A 0.1 ppm level of H2S in the fuel stream could cause a 250 mV cell voltage drop within 300 h at 0.5A cm^{-2} load [68]. When the fuel cell anode was exposed to the H2S-containing fuel for 3.8 h, significant performance losses were seen at H2S concentrations as low as 50 ppm at 70 °C. The load level and cell operation temperatures both had an impact on this poisoning effect [68]. Unlike the case of CO poisoning, the presence of Ru in the Pt catalyst was unable to offer enough resistance to H2S poisoning [69].

3.2.5. Influence of ammonia

The concentration amount and exposure duration affect how much ammonia-related performance degradation occurs. A 15-h exposure to 30 ppm NH3 in the anode fuel resulted in a sharp decline in cell performance and a considerable cell voltage loss [73]. The proton conductivities of the Nafion membrane and the

Table 2
Shows major pollutants discovered during PEM fuel cell operations.

Source of contamination	Typical pollutant
Air	NOx, N_2 (NO_2, NO), SO (SO_3, SO_2) O_3, NH_3
Reform of hydrogen	CO_2, CO, H_2S, CH_4, NH_3
Metal bipolar panels (plate ends)	Ni^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+},
Membranes (Nafion)	Ca^{2+}, Na^+,
Sealing cover	Si
Dilute water, coolants	Al, Si, Fe, K, V, Cl, S, Cu, Cr
Contaminants from battlegrounds	benzene, SO_2, NO_2, CO, propane
Blowers	Oil

anode catalyst ionomer layer were believed to be reduced by NH3 contamination [73,74]. However, the cathode of a fuel cell could also become contaminated by NH3 crossover from the anode to the cathode [74].

3.3. Other contamination sources

Aside from fuels and air pollutants already stated, fuel cell contamination can also be caused by metallic ions in trace levels corroding a system or a stack. Equipment such as bipolar flow field panels, valves, inlet/outlet manifolds, humid pools, and cooling circuits. From fuels are oxidants, membranes, and coolants. Other pollutants, such as silicon separated from the sealing gasket, [75] have been known to contaminate fuel cell performance. Table 2 shows the pollutants affecting during the functioning of the Fuel cells [76].

4. Conclusion

In PEM fuel cells, the membrane is among the most essential components (PEMFCs) and has a significant effect on performance and longevity. However, our present knowledge of the mechanisms that cause PEM fuel cell components to degrade is limited. More emphasis should be made on innovative diagnostic procedures and analytical devices to achieve this goal. Furthermore, there are strong links regarding the deterioration of various parts inside the fuel cell and their functionality. The deterioration of Pt and Pt-alloy catalyst nanoparticles, as well as the cathode electrode structure, is important challenges that are preventing PEMFCs from being commercialized for transportation applications due to particle depletion and leaching of transition metals affecting the stability of currently utilized PtCo catalysts. BOL catalyst with a low Co content (10%), mono-disperse nanoparticle dispersion, and bigger size of a nanoparticle (4-5 nm) have all been discovered as ways to address these difficulties.

Fuel impurities (CO, CO2, H2S, and NH3) are other sources of PEM fuel cell poisoning which can deteriorate cell performance by trace amounts. Literature demonstrated that, for instance, 100 ppm CO or 1 ppm H2S result in approximately 94% and 70% drops in the maximum current density that can be achieved by the fuel cell. Although ISO 14687-2 specification for hydrogen fuel strictly limits concentrations of fuel impurities, reaching this level imposes a considerable cost and equipment requirements. Hence, research should focus on electrode structure stabilization, catalyst nanoparticle sensitivity spanning PEMFC cathode-relevant potentials, to dissolve from oxide generation, and reductions, as well as support corrosion minimization.

CRediT authorship contribution statement

Veeresh Patil: Conceptualization, Methodology, Writing – original draft. **P.V. Reshmi:** Methodology, Writing – original draft. **S.**

Prajna: Methodology, Writing – original draft. **Yashaswi:** Methodology, Writing – original draft. **Yashaswini:** Methodology, Writing – original draft. **D. Haleshappa:** Conceptualization, Methodology, Writing – original draft. **A. Jayarama:** Conceptualization, Validation, Writing – review & editing. **Richard Pinto:** Conceptualization, Validation, Writing – review & editing.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

References

[1] P. Castelino, A. Shah, M. Gokhale, A. Jayarama, K.V. Suresh, P. Fernandes, S. Prabhu, S. Duttagupta, R. Pinto, Optimum hydrogen flowrates and membrane-electrode clamping pressure in hydrogen fuel cells with dual-serpentine flow channels, Mater. Today Proc. (2019), https://doi.org/10.1016/j.matpr.2020.02.791.

[2] S. Sundarrajan, S.I. Allakhverdiev, S. Ramakrishna, Progress and perspectives in micro direct methanol fuel cell, Int. J. Hydrogen Energy. 37 (2012), https://doi.org/10.1016/j.ijhydene.2011.12.017.

[3] A.S. Rao, D.V. Manjunatha, A. Jayarama, V.G. Achanta, S.P. Duttagupta, R. Pinto, Power enhancement of passive micro-direct methanol fuel cells with self-sulfonation of P(VDF-TrFE) copolymer during lamination on Nafion membrane, Int. J. Hydrogen Energy. 44 (2019), https://doi.org/10.1016/j.ijhydene.2019.09.184.

[4] A.S. Rao, K.R. Rashmi, D.V. Manjunatha, A. Jayarama, S. Prabhu, R. Pinto, Pore size tuning of Nafion membranes by UV irradiation for enhanced proton conductivity for fuel cell applications, Int. J. Hydrogen Energy. 44 (2019), https://doi.org/10.1016/j.ijhydene.2019.07.084.

[5] A.S. Rao, K.R. Rashmi, D.V. Manjunatha, A. Jayarama, R. Pinto, Enhancement of power output in passive micro-direct methanol fuel cells with optimized methanol concentration and trapezoidal flow channels, J. Micromech. Microeng. 29 (2019), https://doi.org/10.1088/1361-6439/ab1db7.

[6] Y. Chang, Y. Qin, Y. Yin, J. Zhang, X. Li, Humidification strategy for polymer electrolyte membrane fuel cells – A review, Appl. Energy. 230 (2018), https://doi.org/10.1016/j.apenergy.2018.08.125.

[7] P. Rama, R. Chen, J. Andrews, A review of performance degradation and failure modes for hydrogen-fuelled polymer electrolyte fuel cells, Proc. Inst. Mech. Eng. Part A J. Power Energy. 222 (2008), https://doi.org/10.1243/09576509JPE603.

[8] L. Placca, R. Kouta, Fault tree analysis for PEM fuel cell degradation process modelling, Int. J. Hydrogen Energy. 36 (2011), https://doi.org/10.1016/j.ijhydene.2011.06.093.

[9] N. Ramaswamy, N. Hakim, S. Mukerjee, Degradation mechanism study of perfluorinated proton exchange membrane under fuel cell operating conditions, Electrochim. Acta. 53 (2008), https://doi.org/10.1016/j.electacta.2007.11.010.

[10] D.E. Curtin, R.D. Lousenberg, T.J. Henry, P.C. Tangeman, M.E. Tisack, Advanced materials for improved PEMFC performance and life, J. Power Sources. 131 (2004), https://doi.org/10.1016/j.jpowsour.2004.01.023.

[11] S. Kim, M.M. Mench, Physical degradation of membrane electrode assemblies undergoing freeze/thaw cycling: Micro-structure effects, J. Power Sources. 174 (2007), https://doi.org/10.1016/j.jpowsour.2007.08.111.

[12] M. Pianca, E. Barchiesi, G. Esposto, S. Radice, End groups in fluoropolymers, J. Fluor. Chem. 95 (1999), https://doi.org/10.1016/S0022-1139(98)00304-2.

[13] R.M.H. Khorasany, A. Sadeghi Alavijeh, E. Kjeang, G.G. Wang, R.K.N.D. Rajapakse, Mechanical degradation of fuel cell membranes under fatigue fracture tests, J. Power Sources. 274 (2015), https://doi.org/10.1016/j.jpowsour.2014.10.135.

[14] D. Qiu, L. Peng, X. Lai, M. Ni, W. Lehnert, Mechanical failure and mitigation strategies for the membrane in a proton exchange membrane fuel cell, Renew. Sustain. Energy Rev. 113 (2019), https://doi.org/10.1016/j.rser.2019.109289.

[15] C. Zhang, S. Shi, Q. Lin, L. Wang, X. Chen, Interplay between temperature and biaxial loading on creep behavior of perfluorosulfonic-acid membranes, J. Power Sources. 444 (2019), https://doi.org/10.1016/j.jpowsour.2019.227309.

[16] M.B. Satterfield, P.W. Majsztrik, H. Ota, J.B. Benziger, A.B. Bocarsly, Mechanical properties of Nafion and titania/Nafion composite membranes for polymer electrolyte membrane fuel cells, J. Polym. Sci. Part B Polym. Phys. 44 (2006), https://doi.org/10.1002/polb.20857.

[17] Y. Singh, R.T. White, M. Najm, T. Haddow, V. Pan, F.P. Orfino, M. Dutta, E. Kjeang, Tracking the evolution of mechanical degradation in fuel cell membranes using 4D in situ visualization, J. Power Sources. 412 (2019), https://doi.org/10.1016/j.jpowsour.2018.11.049.

[18] R.M.H. Khorasany, E. Kjeang, G.G. Wang, R.K.N.D. Rajapakse, Simulation of ionomer membrane fatigue under mechanical and hygrothermal loading conditions, J. Power Sources. 279 (2015), https://doi.org/10.1016/j.jpowsour.2014.12.133.

[19] R. Borup, J. Meyers, B. Pivovar, Y.S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J.E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K.I. Kimijima, N. Iwashita, Scientific aspects of polymer electrolyte fuel cell durability and degradation, Chem. Rev. 107 (2007), https://doi.org/10.1021/cr050182l.

[20] E. Padgett, V. Yarlagadda, M.E. Holtz, M. Ko, B.D.A. Levin, R.S. Kukreja, J.M. Ziegelbauer, R.N. Andrews, J. Ilavsky, A. Kongkanand, D.A. Muller, Mitigation of PEM fuel cell catalyst degradation with porous carbon supports, J. Electrochem. Soc. 166 (2019), https://doi.org/10.1149/2.0371904jes.

[21] J. Xie, D.L. Wood, D.M. Wayne, T.A. Zawodzinski, P. Atanassov, R.L. Borup, Durability of PEFCs at high humidity conditions, J. Electrochem. Soc. 152 (2005), https://doi.org/10.1149/1.1830355.

[22] R. Borup, J. Davey, F. Garzon, D. Wood, P. Welch, K. More, PEM fuel cell durability with transportation transient operation, ECS Trans. 3 (2006), https://doi.org/10.1149/1.2356206.

[23] Y. Shao, G. Yin, Y. Gao, Understanding and approaches for the durability issues of Pt-based catalysts for PEM fuel cell, J. Power Sources. 171 (2007), https://doi.org/10.1016/j.jpowsour.2007.07.004.

[24] A.S. Arico, A. Stassi, E. Modica, R. Ornelas, I. Gatto, E. Passalacqua, V. Antonucci, Evaluation of high temperature degradation of Pt/C catalysts in PEM fuel cells, ECS Trans. 3 (2006), https://doi.org/10.1149/1.2356196.

[25] R. Mukundan, D.A. Langlois, R. Lujan, N. Macauley, S. Stariha, A.M. Baker, J.S. Spendelow, K.L. More, R.L. Borup, (Invited Plenary) Durability of Polymer Electrolyte Membrane Fuel Cells and the Development of Accelerated Stress Tests, ECS Meet. Abstr. MA2017-02 (2017). https://doi.org/10.1149/ma2017-02/38/1681.

[26] S. Stariha, N. Macauley, B.T. Sneed, D. Langlois, K.L. More, R. Mukundan, R.L. Borup, Recent advances in catalyst accelerated stress tests for polymer electrolyte membrane fuel cells, J. Electrochem. Soc. 165 (2018), https://doi.org/10.1149/2.0881807jes.

[27] B.T. Sneed, D.A. Cullen, R. Mukundan, R.L. Borup, K.L. More, PtCo cathode catalyst morphological and compositional changes after PEM fuel cell accelerated stress testing, J. Electrochem. Soc. 165 (2018), https://doi.org/10.1149/2.0091806jes.

[28] A. Martinez, (Invited) The Evolution of Membrane Electrode Assemblies for Automotive Applications, ECS Meet. Abstr. MA2019-02 (2019). https://doi.org/10.1149/ma2019-02/38/1764.

[29] S. Arisetty, S.M. Alia, J.W. Zack, A. Kongkanand, V. Yarlagadda, R.S. Kukreja, J.M. Ziegelbauer, K.C. Neyerlin, N. Kariuki, D.J. Myers, B. Lakshmanan, Catalyst Dissolution Rates during PEM Fuel Cell Operation, ECS Meet. Abstr. MA2017-02 (2017). https://doi.org/10.1149/ma2017-02/35/1528.

[30] R.K. Ahluwalia, X. Wang, J.-K. Peng, N.N. Kariuki, D.J. Myers, S. Rasouli, P.J. Ferreira, Z. Yang, A. Martinez-Bonastre, D. Fongalland, J. Sharman, Durability of de-alloyed platinum-nickel cathode catalyst in low platinum loading membrane-electrode assemblies subjected to accelerated stress tests, J. Electrochem. Soc. 165 (2018) F3316–F3327, https://doi.org/10.1149/2.0341806jes.

[31] C.A. Rice, P. Urchaga, A.O. Pistono, B.W. McFerrin, B.T. McComb, J. Hu, Platinum dissolution in fuel cell electrodes: enhanced degradation from surface area assessment in automotive accelerated stress tests, J. Electrochem. Soc. 162 (2015), https://doi.org/10.1149/2.0371510jes.

[32] F. Maillard, E. Guilminot, A. Corcella, F. Charlot, G. Berthomé, M. Chatenet, Detection of Ptz+ Ions and Pt Nanoparticles inside the Membrane of a used PEM Fuel Cell, ECS Meet. Abstr. MA2007-01 (2007). https://doi.org/10.1149/ma2007-01/7/406.

[33] B. Merzougui, S. Swathirajan, Rotating disk electrode investigations of fuel cell catalyst degradation due to potential cycling in acid electrolyte, J. Electrochem. Soc. 153 (2006), https://doi.org/10.1149/1.2353752.

[34] O.R. Brown, Carbon—electrochemical and physicochemical properties, Electrochim. Acta. 34 (1989), https://doi.org/10.1016/0013-4686(89)87066-5.

[35] T. Fuller, G. Gray, Carbon corrosion induced by partial hydrogen coverage, ECS Trans. 1 (2006), https://doi.org/10.1149/1.2214567.

[36] H. Tang, Z. Qi, M. Ramani, J.F. Elter, PEM fuel cell cathode carbon corrosion due to the formation of air/fuel boundary at the anode, J. Power Sources. 158 (2006), https://doi.org/10.1016/j.jpowsour.2005.10.059.

[37] P.T. Yu, W. Gu, R. Makharia, F.T. Wagner, H.A. Gasteiger, The impact of carbon stability on PEM fuel cell startup and shutdown voltage degradation, ECS Trans. 3 (2006), https://doi.org/10.1149/1.2356199.

[38] J.P. Meyers, R.M. Darling, Model of carbon corrosion in PEM fuel cells, J. Electrochem. Soc. 153 (2006), https://doi.org/10.1149/1.2203811.

[39] X. Wang, W. Li, Z. Chen, M. Waje, Y. Yan, Durability investigation of carbon nanotube as catalyst support for proton exchange membrane fuel cell, J. Power Sources. 158 (2006), https://doi.org/10.1016/j.jpowsour.2005.09.039.

[40] X. Yu, S. Ye, Recent advances in activity and durability enhancement of Pt/C catalytic cathode in PEMFC. Part II: Degradation mechanism and durability enhancement of carbon supported platinum catalyst, J. Power Sources. 172 (2007), https://doi.org/10.1016/j.jpowsour.2007.07.048.

[41] R.T. White, S.H. Eberhardt, Y. Singh, T. Haddow, M. Dutta, F.P. Orfino, E. Kjeang, Four-dimensional joint visualization of electrode degradation and liquid water distribution inside operating polymer electrolyte fuel cells, Sci. Rep. 9 (2019), https://doi.org/10.1038/s41598-018-38464-9.

[42] A. Kneer, J. Jankovic, D. Susac, A. Putz, N. Wagner, M. Sabharwal, M. Secanell, Correlation of changes in electrochemical and structural parameters due to voltage cycling induced degradation in PEM fuel cells, J. Electrochem. Soc. 165 (2018), https://doi.org/10.1149/2.0271806jes.

[43] J. Wu, X.Z. Yuan, J.J. Martin, H. Wang, J. Zhang, J. Shen, S. Wu, W. Merida, A review of PEM fuel cell durability: Degradation mechanisms and mitigation strategies, J. Power Sources. 184 (2008), https://doi.org/10.1016/j.jpowsour.2008.06.006.

[44] J. Zhao, X. Li, A review of polymer electrolyte membrane fuel cell durability for vehicular applications: Degradation modes and experimental techniques, Energy Convers. Manag. 199 (2019), https://doi.org/10.1016/j.enconman.2019.112022.

[45] M. Aoki, H. Uchida, M. Watanabe, Decomposition mechanism of perfluorosulfonic acid electrolyte in polymer electrolyte fuel cells, Electrochem. Commun. 8 (2006), https://doi.org/10.1016/j.elecom.2006.07.017.

[46] R. Alink, D. Gerteisen, M. Oszcipok, Degradation effects in polymer electrolyte membrane fuel cell stacks by sub-zero operation-An in situ and ex situ analysis, J. Power Sources. 182 (2008), https://doi.org/10.1016/j.jpowsour.2008.03.074.

[47] Y. Luo, K. Jiao, Cold start of proton exchange membrane fuel cell, Prog. Energy Combust. Sci. 64 (2018), https://doi.org/10.1016/j.pecs.2017.10.003.

[48] Q. Yan, H. Toghiani, Y.W. Lee, K. Liang, H. Causey, Effect of sub-freezing temperatures on a PEM fuel cell performance, startup and fuel cell components, J. Power Sources. 160 (2006), https://doi.org/10.1016/j.jpowsour.2006.02.075.

[49] J. Zhang, H. Wang, D.P. Wilkinson, D. Song, J. Shen, Z.S. Liu, Model for the contamination of fuel cell anode catalyst in the presence of fuel stream impurities, J. Power Sources. 147 (2005), https://doi.org/10.1016/j.jpowsour.2005.01.013.

[50] W.M. Yan, H. Sen Chu, Y.L. Liu, F. Chen, J.H. Jang, Effects of chlorides on the performance of proton exchange membrane fuel cells, Int. J. Hydrogen Energy. 36 (2011), https://doi.org/10.1016/j.ijhydene.2011.01.158.

[51] M.A. Uddin, X. Wang, J. Park, U. Pasaogullari, L. Bonville, Distributed effects of calcium ion contaminant on polymer electrolyte fuel cell performance, J. Power Sources. 296 (2015), https://doi.org/10.1016/j.jpowsour.2015.07.020.

[52] M.A. Uddin, J. Qi, X. Wang, M.O. Ozdemir, N. Khajeh Hosseini Dalasm, L.J. Bonville, U. Pasaogullari, T. Molter, Study of through plane cation contamination in polymer electrolyte fuel cell, ECS Trans. 61 (2014), https://doi.org/10.1149/06112.0037ecst.

[53] S. Ganesan, M.A. Uddin, J. Park, U. Pasaogullari, L.J. Bonville, T. Molter, Impact of cationic impurities on low-Pt loading PEFC cathodes, ECS Trans. 66 (2015), https://doi.org/10.1149/06624.0019ecst.

[54] M.A. Uddin, J. Qi, X. Wang, U. Pasaogullari, L. Bonville, Distributed cation contamination from cathode to anode direction in polymer electrolyte fuel cells, Int. J. Hydrogen Energy. 40 (2015), https://doi.org/10.1016/j.ijhydene.2015.07.134.

[55] C.J. Banas, L. Bonville, U. Pasaogullari, Linking Foreign cationic contamination of PEM fuel cells to the local water distribution, J. Electrochem. Soc. 164 (2017), https://doi.org/10.1149/2.0571712jes.

[56] C.J. Banas, M.T.A. Arman, M.A. Uddin, J. Park, L.J. Bonville, U. Pasaogullari, Polymer electrolyte fuel cell degradation through foreign cation contamination, proton depletion and carbon corrosion, ECS Trans. 86 (2018), https://doi.org/10.1149/08613.0407ecst.

[57] C.J. Banas, M.A. Uddin, J. Park, L.J. Bonville, U. Pasaogullari, Thinning of cathode catalyst layer in polymer electrolyte fuel cells due to foreign cation contamination, J. Electrochem. Soc. 165 (2018), https://doi.org/10.1149/2.0021806jes.

[58] M.A. Uddin, J. Park, L. Bonville, U. Pasaogullari, Effect of hydrophobicity of gas diffusion layer in calcium cation contamination in polymer electrolyte fuel cells, Int. J. Hydrogen Energy. 41 (2016), https://doi.org/10.1016/j.ijhydene.2016.06.188.

[59] A.L. Dicks, Hydrogen generation from natural gas for the fuel cell systems of tomorrow, J. Power Sources. 61 (1996), https://doi.org/10.1016/S0378-7753(96)02347-6.

[60] B. Höhlein, M. Boe, J. Bøgild-Hansen, P. Bröckerhoff, G. Colsman, B. Emonts, R. Menzer, E. Riedel, Hydrogen from methanol for fuel cells in mobile systems: Development of a compact reformer, J. Power Sources. 61 (1996), https://doi.org/10.1016/S0378-7753(96)02357-9.

[61] V.M. Schmidt, P. Bröckerhoff, B. Höhlein, R. Menzer, U. Stimming, Utilization of methanol for polymer electrolyte fuel cells in mobile systems, J. Power Sources. 49 (1994), https://doi.org/10.1016/0378-7753(93)01830-B.

[62] R. Parsons, T. VanderNoot, Sodium borohydride as the hydrogen supplier for proton exchange membrane fuel cell systems, J. Electroanal. Chem. 257 (1988), https://doi.org/10.1016/0022-0728(88)87028-1.

[63] J.H. Wee, K.Y. Lee, S.H. Kim, Sodium borohydride as the hydrogen supplier for proton exchange membrane fuel cell systems, Fuel Process. Technol. 87 (2006), https://doi.org/10.1016/j.fuproc.2006.05.001.

[64] J.J. Baschuk, X. Li, Carbon monoxide poisoning of proton exchange membrane fuel cells, Int. J. Energy Res. 25 (2001), https://doi.org/10.1002/er.713.

[65] N. Rajalakshmi, T.T. Jayanth, K.S. Dhathathreyan, Effect of carbon dioxide and ammonia on polymer electrolyte membrane fuel cell stack performance, Fuel Cells 3 (2003), https://doi.org/10.1002/fuce.200330107.

[66] F.A. De Bruijn, D.C. Papageorgopoulos, E.F. Sitters, G.J.M. Janssen, The influence of carbon dioxide on PEM fuel cell anodes, J. Power Sources. 110 (2002), https://doi.org/10.1016/S0378-7753(02)00227-6.

[67] Z. Qi, C. He, A. Kaufman, Effect of CO in the anode fuel on the performance of PEM fuel cell cathode, J. Power Sources. 111 (2002), https://doi.org/10.1016/S0378-7753(02)00300-2.

[68] D. Sieminski, The 2005 fuel cell seminar Palm Springs, California November 14-18, 2005, in: Adv. Fuel Cell Technol., 2006.

[69] M. Murthy, M. Esayian, W. Lee, J.W. Van Zee, The effect of temperature and pressure on the performance of a PEMFC exposed to transient CO concentrations, J. Electrochem. Soc. 150 (2003), https://doi.org/10.1149/1.1522383.

[70] R. Mohtadi, W.K. Lee, S. Cowan, J.W. Van Zee, M. Murthy, Effects of hydrogen sulfide on the performance of a PEMFc, Electrochem. Solid-State Lett. 6 (2003), https://doi.org/10.1149/1.1621831.

[71] A. Moreno, P. Lunghi, R. Bove, Proceedings of the 1st European Fuel Cell Technology and Applications Conference 2005, EFC2005 - Book of Abstracts: Preface, Proc. 1st Eur. Fuel Cell Technol. Appl. Conf. 2005 - B. Abstr. 2005 (2005).

[72] R. Mohtadi, W.K. Lee, J.W. Van Zee, The effect of temperature on the adsorption rate of hydrogen sulfide on Pt anodes in a PEMFC, Appl. Catal. B Environ. 56 (2005), https://doi.org/10.1016/j.apcatb.2004.08.012.

[73] F.A. Uribe, S. Gottesfeld, T.A. Zawodzinski, Effect of ammonia as potential fuel impurity on proton exchange membrane fuel cell performance, J. Electrochem. Soc. 149 (2002), https://doi.org/10.1149/1.1447221.

[74] R. Halseid, P.J.S. Vie, R. Tunold, Influence of ammonium on conductivity and water content of nafion 117 membranes, J. Electrochem. Soc. 151 (2004), https://doi.org/10.1149/1.1641035.

[75] S.Y. Ahn, S.J. Shin, H.Y. Ha, S.A. Hong, Y.C. Lee, T.W. Lim, I.H. Oh, Performance and lifetime analysis of the kW-class PEMFC stack, J. Power Sources (2002), https://doi.org/10.1016/S0378-7753(01)01032-1.

[76] N. Garland, T. Benjamin, J. Kopasz, DOE fuel cell program: durability technical targets and testing protocols, ECS Trans. 11 (2007), https://doi.org/10.1149/1.2781004.