

## CHAPTER 9

# Degradation and failure modes in proton exchange membrane fuel cells

Samuel Simon Araya, Na Li and Vincenzo Liso

AAU Energy, Aalborg University, Aalborg East, Denmark

### 9.1 Introduction

Due to the advantages of high efficiency, zero-emissions, high power density, and noiseless operation, proton exchange membrane (PEM) fuel cells are considered among the most promising power sources for the future of transportation, backup power systems, and stationary heat and power generations [1]. However, the capital cost and durability are still two major challenges delaying the widespread commercialization of this technology. The lifetime targets vary significantly in different fuel cell applications with 20,000 h for buses, 5000 h for passenger cars, and 40,000 h for stationary applications [2]. The United States Department of Energy (DOE) plans to achieve an interim target of durability of 5000 h and cost of  $\$40 \text{ kW}^{-1}$  by 2025 in the Fuel Cell R&D subprogram, and the alternative expectation is to reduce the cost to  $\$30 \text{ kW}^{-1}$  with durability target of 8000 h in order to obtain long-term competitiveness [3]. It is worth noting that the fuel cell lifetime as defined in the DOE projects represents the time when the rated power decreases to below 90% of its initial value, which could be caused by the gradual cell performance deterioration or sudden cell component failures [4]. The definitions of fuel cell lifetime vary in different literatures, and therefore a more commonly used definition of degradation, usually cell voltage degradation rate, is often employed to illustrate the durability of fuel cells [5]. The commonly acceptable degradation rate of fuel cells is  $2\text{--}10 \mu\text{V h}^{-1}$  with a system efficiency loss of less than 10% [6].

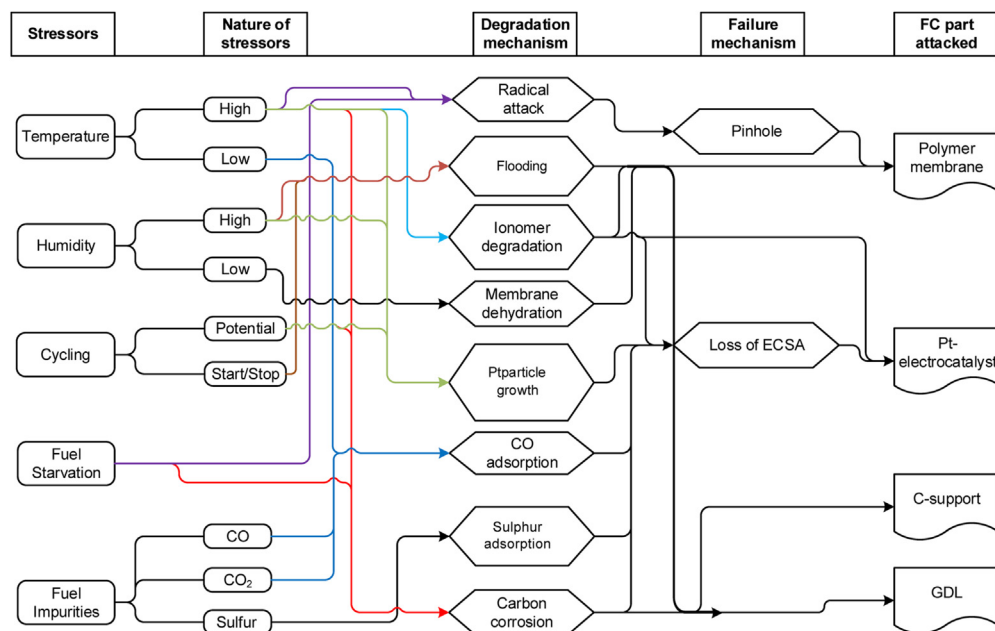
The durability of fuel cells can be affected by many factors, such as degradation of the cell components due to contamination by foreign impurities, nonideal operating conditions, and other factors related to the fuel cell design and assembly [2]. After decades of continuous research and development, improvements have been achieved on core materials, cell assembly, and overall system design. However, durability issues, especially the components degradation during operation, are still the main hurdles for the industrial commercialization of PEM fuel cells. Therefore, fully understanding the failure modes and the degradation mechanisms of the fuel cell system is an important step towards

improving fuel cell durability. In this chapter, the failure modes in PEM fuel cell are presented, and the corresponding degradation mechanisms are discussed.

## 9.2 Failure modes and degradation

The components of a PEM fuel cell play important roles during its operation, and therefore, their degradation or deterioration may lead to fuel cell performance decrease or even failure. Extensive research has been carried out to investigate the degradation of PEM fuel cell components, such as the catalyst degradation, membrane degradation, gas transport layers degradation, and so on [7–10]. These failures mainly occur as a result of nonideal operating conditions in the cell or due to impurities in the fuel or oxidant. Fig. 9.1 shows the relationship between these nonideal operating conditions and their degradation mechanisms and the fuel cell components involved.

The failure modes of PEM fuel cell components and the corresponding degradation mechanisms are summarized and discussed below.

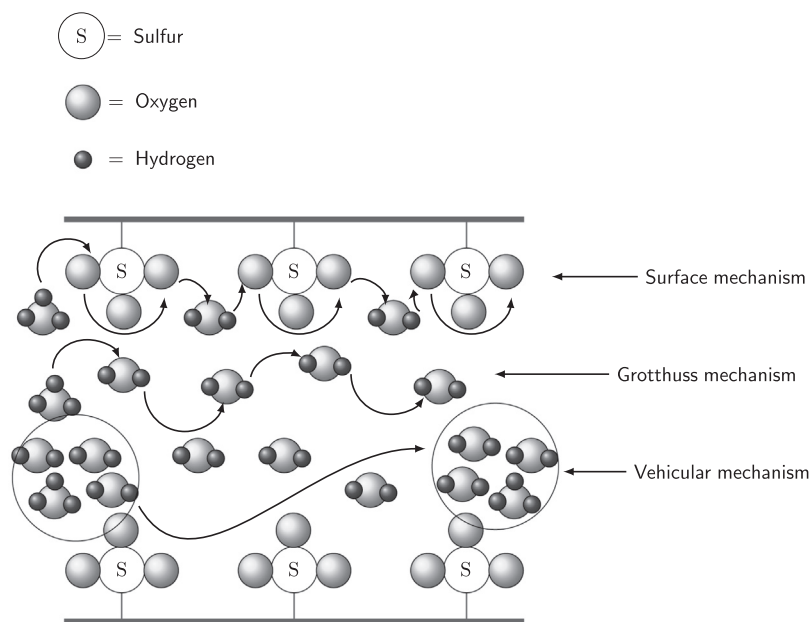


**Figure 9.1** Degradation flowchart of a proton exchange membrane fuel cell. Modified from S. Araya, F. Zhou, V. Liso, S. Sahlin, J. Vang, S. Thomas, et al., *A comprehensive review of PBI-based high temperature PEM fuel cells*. *Int. J. Hydrogen Energy* 41 (46) (2016) 21310–21344. <https://doi.org/10.1016/j.ijhydene.2016.09.024>.

### 9.2.1 Membrane degradation

PEM, also called polymer electrolyte membrane, is located at the center of the fuel cell and acts as the electrolyte. It has the function of conducting protons, blocking electrons, separating the electrodes, and hence the half-cell reactions on each electrode and supporting the catalyst layers on each side [2]. Therefore, the membrane used in a PEM fuel cell should possess characteristics, such as good proton conductivity, excellent chemical stability, strong mechanical strength, thermal stability, electron insulation, and gas impermeability. Currently, the most commonly used PEM materials are perfluorinated sulfonic acid (PFSA) membranes known as Nafion, developed by Dupont [11].

The properties and the structure of the polymer can significantly affect the proton conductivity of the membrane. Choi et al. [12] proposed mechanisms of surface diffusion, Grotthuss (proton hopping), and mass diffusion ( $\text{H}_3\text{O}^+$ ) for the proton conduction in Nafion membrane. They assume that protons are transferred along with the bulk water, predominantly via Grotthuss mechanism and to some extent via mass diffusion ( $\text{H}_3\text{O}^+$ ) in the middle region of the pores on the membrane when the water content of the membrane is high and a surface diffusion mechanism (protons are transferred between the surface water and  $\text{SO}_3^-$  groups) takes place close to the pore wall or under low water activity, as illustrated in Fig. 9.2. Therefore, water content in the membrane is an important factor for the proton transfer in the membrane.



**Figure 9.2** Schematic of proton transfer in Nafion membrane. Based on P. Choi, N.H. Jalani, R. Datta, *Thermodynamics and proton transport in Nafion*. *J. Electrochem. Soc.* 152 (3) (2005) E123. <https://doi.org/10.1149/1.1859814>.

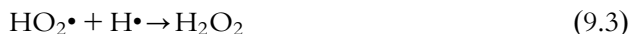
The membrane conductivity is also associated with the membrane thickness. A thicker membrane can have better mechanical and electrochemical strength and better electrical insulation but will lead to higher ionic resistance. Therefore, taking into account of the performance and durability, a membrane with proper thickness should be ensured for practical PEM fuel cell application.

Membrane degradation modes could be categorized into three types, namely, chemical/electrochemical degradation, mechanical degradation, and thermal degradation [2,5,7,13]. These are discussed below.

### 9.2.1.1 Chemical/electrochemical degradation of proton exchange membrane

Chemical/electrochemical degradation of the membrane is associated with the loss of ionic groups and functional groups. The chemical structure of the Nafion membrane is shown in Fig. 9.3, in which the C–C bonds are stable in the polymer backbone while the C–F, C=O, and S–O bonds are not stable enough in the presence of chemical radicals such as OH• and HO<sub>2</sub>• [11,14,15].

It has been reported that due to the incomplete oxygen reduction reaction (ORR), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) can be produced under normal PEM fuel cell operating conditions through a two-electron reduction reaction of O<sub>2</sub> (O<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>−</sup> → H<sub>2</sub>O<sub>2</sub>), without any gas crossover [15]. Moreover, gas crossover to either electrode can lead to H<sub>2</sub>O<sub>2</sub> production on the Pt catalyst surface and the intermediate chemical radicals generated during the formation of H<sub>2</sub>O<sub>2</sub> by the following reactions [16] can attack the membrane:



Open-circuit voltage (OCV) operation at low humidity can also accelerate the generation of chemical radicals [17]. This can lead to high membrane degradation rates due to radical formation during the H<sub>2</sub>O<sub>2</sub> generation caused by O<sub>2</sub> and H<sub>2</sub> crossover [18]. Inaba et al. [19] found that changes in the operating conditions, such as increase in cell

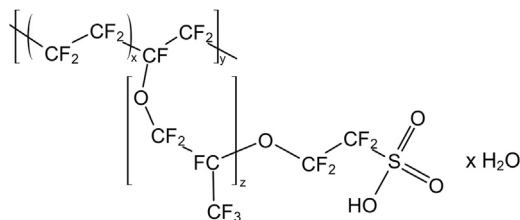
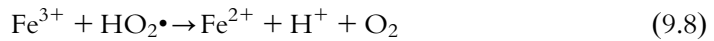
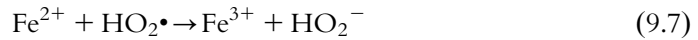
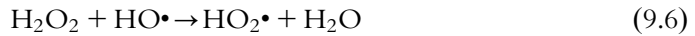
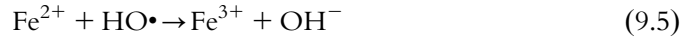
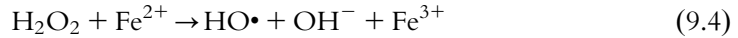


Figure 9.3 Chemical structure of Nafion membrane.

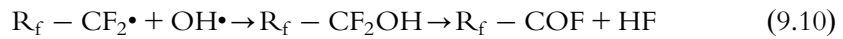
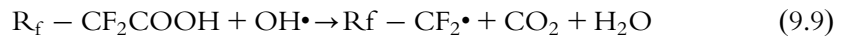
temperature, increase in hydrogen partial pressure, and increase in humidity can enhance the gas crossover phenomenon with degrading effects on the membrane.

In addition, the Pt on the cathode side can be oxidized to  $\text{Pt}^{2+}$  by excess  $\text{O}_2$  during the operation and the produced  $\text{Pt}^{2+}$  can migrate from cathode to the membrane [20]. Then when the migrated  $\text{Pt}^{2+}$  encounters hydrogen that crossed over from the anode side, the  $\text{Pt}^{2+}$  can be reduced and re-deposited as Pt crystal on the membrane, which will severely reduce the membrane conductivity and stability [20,21].

Foreign cations, which are typically originated from the MEA preparation, gas and coolant supplies, and corrosion of materials are other factors that can accelerate the chemical degradation of the membrane [22]. These cations have higher affinity to the  $\text{SO}_3^-$  group of the perfluorosulfonic acid membrane and can replace the protons during the proton conduction process, thereby lowering the ionic conductivity and the water content of the membrane, resulting in reduced oxygen reduction reaction (ORR) kinetics [23]. It has been reported that the durability of polymer electrolyte membrane is not stable in the presence of cations, especially  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ , which can lead to the decomposition of C–F bonds and sulfonic group due to the formation of hydroxyl radicals [14]. These cations can strongly accelerate the performance decay and membrane degradation of PEM fuel cells by catalyzing the chemical radicals formation through the following reactions [2,19]:



The radicals  $\text{OH}\bullet$  and  $\text{HO}_2\bullet$  produced during these processes can lead to chemical degradation of the membrane by attacking the end-group sites and can initiate decomposition of the polymer. An example of the attack process is shown in the following reactions [24]:



Several mechanisms can be proposed from these reactions [11,24]. Curtin et al. [24] proposed a sequential reaction mechanisms, where, first, hydrogen from the acid-end group forms the perfluorocarbon radical at the end of the chain and releases  $\text{CO}_2$  and water, causing loss of molecular weight and membrane thinning gradually, and then the formed perfluorocarbon radical reacts with the hydroxy radicals to generate vulnerable groups and hydrogen fluoride (HF), leading to further loss in molecular weight. The loss of molecular weight of the polymer will finally lead to the thinning of the membrane, which will increase gas crossover and thus further enhance the chemical degradation of the membrane, leading to further membrane thinning, formation of pinholes, and eventually fuel cell failure.

### 9.2.2 Mechanical degradation of proton exchange membrane

Mechanical degradation of PEM often occurs at the early stages of the PEM fuel cell lifetime due to the defects of cracks, tears, perforations, pinholes, etc., which could be formed due to improper manufacturing process of the membrane electrode assembly (MEA) [2]. Tang et al. [18] carried out a cyclic stress experiment on a PEM fuel cell to investigate the fatigue strength of Nafion membrane and found that no membrane dimension change occurred when the cyclic stress was less than 1.5 MPa, while significant membrane dimension change and microstructure breakdown were seen when the cyclic stress was higher than 3.0 MPa. With the cyclic stress of 4.0 MPa, the PEM was elongated and membrane thinning happened after 1000 cycles, and many cracks were observed when the cyclic stress reached to 6.5 MPa, which represented a rupture in the membrane microstructure.

Changes in the water uptake of the membrane and the operating temperature during the operation can also lead to the dimensional change of the PEM, which is associated with membrane swelling [18]. Other factors, such as nonuniform contact between the components, high differences of the initial gas pressure over the membrane, and the stress caused by cycling of temperature and humidity can also lead to punctures and fatigue of the membrane [7]. Furthermore, the catalyst degradation such as Pt migration and accumulation and the seal decomposition into the membrane during the operation could negatively affect the mechanical strength of the membrane [2].

Pinholes, cracks, and thinning of the membrane could result in gas crossover during the operation, which can lead to direct combustion of hydrogen and oxygen or severe deterioration of water and thermal management [2,5,25], leading to cell failure or even more severely, safety issues. The gas crossover caused by the mechanical defects could in turn lead to chemical degradation as discussed above, while membrane thinning caused by chemical degradation could lead to the formation of pinholes or hot spots. Therefore, the mechanical degradation of the membrane can not only be accelerated by chemical degradation but also in turn accelerate the chemical degradation itself.

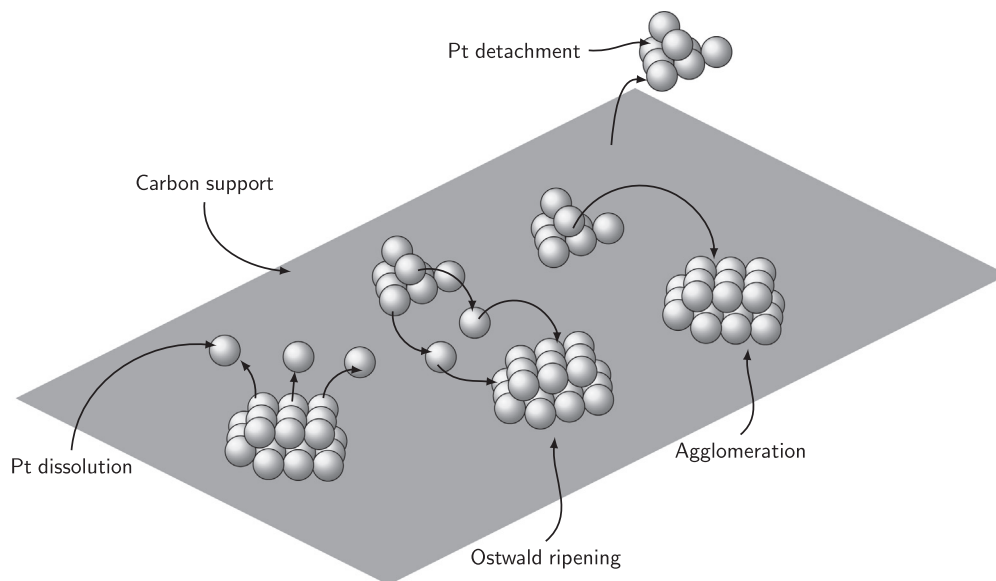
### 9.2.2.1 Thermal degradation of proton exchange membrane

Thermal degradation is usually associated with high temperature operation, temperature cycling, and subfreezing temperature, which can cause changes in the membrane properties due to thermal variations [11]. High temperature with insufficient humidification can cause critical membrane breakdown due to the temperature limits of PFSA polymers, which have a glass transition temperature ( $T_g$ ) of around  $80^\circ\text{C}$  [2,5]. It has also been reported that the sulfonated acid groups side of the PFSA-like molecular backbones could be decomposed at temperatures higher than  $280^\circ\text{C}$  [2,5]. Surowiec and Bogoczek [26] investigated the thermal stability of perfluorinated membrane by simultaneous TG-DTA and IR spectroscopy methods and found that the Nafion membrane was thermally stable below  $280^\circ\text{C}$ , but the sulfonic groups of the membrane were split off when the temperature was above  $280^\circ\text{C}$ . Similar loss of sulfonic groups of the membrane was also obtained by Chu et al. [27], where significant intensity decrease was found for S—O-related bonds at  $300^\circ\text{C}$ .

Moreover, freezing condition can lead to the contact resistance increase among the components of the fuel cell, which will lead to the formation of pinholes and cracks due to the dimensional changes of the membrane caused by contact pressure. It has also been found that due to the existence of water on the surface of the membrane, freeze/thaw (F/T) cycles can affect the thermal stability of the membrane. As reported by McDonald et al. [28], F/T cycles ( $+80^\circ\text{C}$  to  $-40^\circ\text{C}$ ) can affect the ionic conductivity, mechanical stress, and the gas permeability of the Nafion membrane. Therefore, thermal degradation can occur under both high- and low-temperature operation in certain PEM fuel cell applications and can lead to pinholes or hotspots formation.

### 9.2.3 Catalyst degradation

The catalyst layers are typically attached on the anode side and the cathode side of the membrane to form a sandwiched structure, MEA, which plays an important role in the PEM fuel cell operation. The catalyst layer provides the active reaction sites for the electrochemical reactions, flow path for the reactants and products, and transport of protons and electrons within the MEA [29–31]. Therefore, the catalyst layers should be porous, ionic, and electronic conductor and should have large active area. The commonly used catalysts are platinum (Pt) or Pt-based catalysts both for anode and cathode due to the high catalytic activity of Pt, and are often supported by carbon cloth/paper to enhance the mechanical strength of the catalyst layer [31]. However, the durability of Pt or Pt/C is still a challenge in the development of PEM fuel cells. The degradation modes of the catalyst layers consist of Pt degradation, including Pt dissolution, detachment, and sintering, and carbon corrosion and ionomer decomposition [5,32,33]. These degradation modes are illustrated in Fig. 9.4.

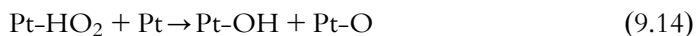


**Figure 9.4** Schematic of degradation mechanisms for platinum particles on a carbon support in fuel cells. Based on J.C. Meier, C. Galeano, I. Katsounaros, J. Witte, H.J. Bongard, A.A. Topalov, et al., *Design criteria for stable Pt/C fuel cell catalysts*. *Beilstein J. Nanotechnol.* 5 (1) (2014) 44–67. <https://doi.org/10.3762/bjnano.5.5>.

### 9.2.3.1 Pt degradation

The Pt-based catalysts in PEM fuel cells are usually nanoparticles with a size range of 2–6 nm [34]. Due to their high specific surface energy, these Pt nanoparticles are easy to agglomerate/sinter during the PEM fuel cell operation and the growth rate slows down gradually with the reduction of the surface energy [35]. The Pt nanoparticles usually agglomerate or detach from the carbon support [34], as shown in Fig. 9.4. Both of the agglomeration/sintering and the detachment can reduce the electrochemical surface area, leading to performance degradation of the PEM fuel cell electrode.

PEM fuel cells are operated at harsh environment, where the anode side is exposed to a strong reducing  $\text{H}_2$  atmosphere while the cathode is exposed to a strong oxidizing condition of high  $\text{O}_2$  concentration and high potential [34]. Since Pt has a small but finite solubility in the acidic ionomer of Nafion, the strong oxidizing environment and the high potential condition of the cathode can lead to Pt dissolution [36]. According to Xu et al. [37], the Pt exposed to the cathode oxidation condition can be oxidized through the following reactions:



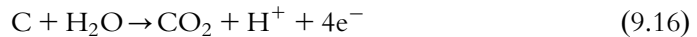


The dissolution of Pt will lead to reduced electrochemical surface area and thus results in irreversible cell performance deterioration [5,33]. The soluble Pt ions formed on the cathode can be transferred to the membrane through diffusion and migration [36]. The Pt ions dissolved into the ionomer of membrane can then redeposit on larger particles' surface, which leads to particle growth, known as Ostwald ripening phenomenon [34,38]. Moreover, the dissolved Pt ions can also be reduced by the hydrogen that crosses over from the anode and re-precipitate in the membrane, subsequently reducing the stability and conductivity of the membrane [35,39]. Recent studies on PEM fuel cell have found that both the potential and the humidity increase can enhance the Pt particle growth, and thus contribute to the dissolution and redeposition phenomenon [40,41].

It has been noticed that the degradation mechanisms of Pt-based catalysts are different under different operating conditions of potential, humidity, temperature, etc., which have significant effect on the catalyst degradation [34]. Borup et al. [41] found that potential cycling leads to the largest Pt particle size increase on the cathode side. They also found that catalyst coarsening rate increased linearly with temperature. The effect of humidity on the Pt catalyst degradation was also investigated, where the Pt surface oxidation degree increased with the increase in relative humidity [37,40].

### 9.2.3.2 Carbon corrosion

Due to the good electronic conductivity and low cost, carbon has been widely used as the catalyst support in PEM fuel cells. However, carbon corrosion can occur during the operation of a fuel cell, which is an important issue affecting the performance and the durability of the catalyst layers. Carbon corrosion is typically categorized into two modes of incomplete oxidation and complete oxidation according to the following reactions [34,35,42]:



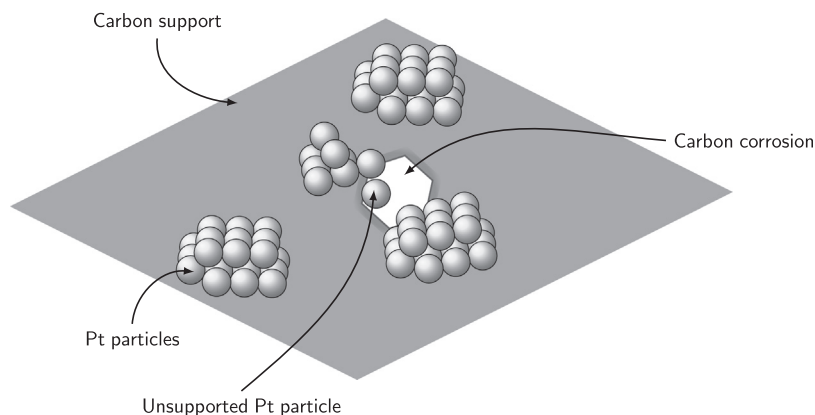
Carbon corrosion can be almost negligible under normal steady-state operation of a PEM fuel cell. However, in real operation, the frequent startup/shutdown and load response cycles often lead to non-uniform fuel distribution on the anode and oxygen crossover phenomenon, resulting in high cathode potential of around 1.5 V [35]. The thermodynamic potential for reaction (9.16) is 0.207 V at standard condition [43], therefore the carbon could be oxidized to  $\text{CO}_2$  according to reaction (9.16) when the potential is higher than 0.207 V. It has been reported that the dynamic processes such as startup/shutdown and load response cycles could accelerate the carbon oxidation

process due to the high cathode potential during the dynamic processes, especially in the presence of Pt as catalyst [42,44]. The thermodynamic potential for reaction (9.17) is 0.518 V, at which potential the carbon could be oxidized to CO according to reaction (9.17) [45]. Stevens et al. [46] found that the presence of water can also lead to the formation of CO through the heterogeneous water–gas reaction (9.17) and Pt can catalyze the carbon consumption, with higher Pt loading leading to faster carbon consumption rate. Carbon corrosion or oxidation can also enhance the detachment of the Pt nanoparticles from the carbon support surface, leading to Pt dissolution and agglomeration and thereby accelerating the catalyst layer degradation, which is more severe on cathode side than on anode side at normal steady-state operation [35]. A schematic of the effects of carbon corrosion on the catalyst layer is shown in Fig. 9.5.

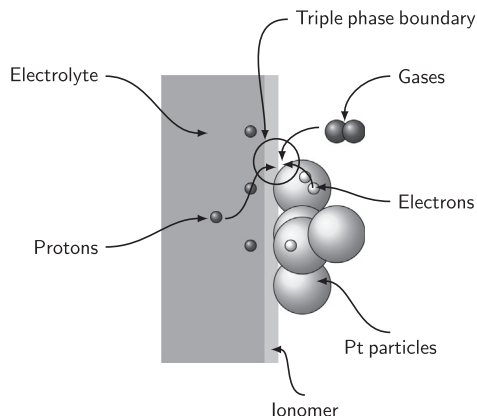
### 9.2.3.3 Ionomer decomposition

Another important degradation mode of the catalyst layer in PEM fuel cells is the ionomer decomposition. Besides the Pt and carbon support on the catalyst layers, the Nafion ionomer is also a significant component that can affect the performance and structure of the catalyst layer. The ionomer, together with the Pt and carbon, can form the three-phase interface as shown in Fig. 9.6 to enhance the transportation of protons, gases, and electrons, and its distribution and concentration in the catalyst layer can affect the ionic and electronic conductivity of the catalyst layer directly [35,47]. Saab et al. [48] reported that the ionic conductivity of the PEM fuel cell is primarily dominated by the recast ionomer on the catalyst layer; therefore, the degradation of the ionomer contributes significantly to the catalyst layer degradation.

Compared to the ionomer in the membrane, the ionomer in the catalyst layer is less stable in terms of structure, texture, and chemical resistance [49]. Therefore, similar to the chemical and thermal degradation of the membrane, the ionomer is prone to



**Figure 9.5** Schematic of the effect of carbon corrosion in fuel cells.



**Figure 9.6** A schematic of the triple phase boundary in fuel cells.

attack by the produced chemical radicals, such as  $\text{HO}\cdot$ ,  $\text{HOO}\cdot$ , and  $\text{PtO}$ , leading to the ionomer degradation/decomposition [5]. Zhang et al. [50] investigated the PEM fuel cell catalyst layer degradation quantitatively using X-ray photoelectron spectroscopy and scanning electron microscopy (SEM) measurements and they found that the concentration of  $\text{CF}_2$  and  $\text{CF}_3$  species in the ionomer of the catalyst layer decreased but the oxidized form of carbon such as  $\text{C}-\text{O}$  and  $\text{C}=\text{O}$  and also the nonfluorinated carbon forms of  $\text{CF}$  and graphitic, etc., increased after a 300-h operation, which represented the ionomer degradation/decomposition on the catalyst layer. In the study by Xie et al. [49], the degradation of Nafion ionomer network was also found and was mainly responsible for the MEA performance degradation after 500 h of high-humidity operation. Research works of both experimental and numerical nature were also carried out with variations of current density, temperature, and clamping stress, to investigate the ionomer degradation in the catalyst [51–53].

The ionomer degradation/decomposition can lead to the ionomer isolation and thus reduces protonic conductivity. Besides, the ionomer decomposition results in the loss of binding materials, which will accelerate the catalyst particles collision and agglomeration, thereby reducing the electrochemical surface area and leading to further catalyst layer degradation.

#### 9.2.4 Degradation of gas diffusion layers

The gas diffusion layer (GDL) is another important component in PEM fuel cells, which is used as a pathway for the reactants (hydrogen and oxygen), an effective capacity for the products removal, a structural support for the MEA, an electrical connector between the catalyst layers and the bipolar plates, and a thermal pathway

for the removal of the heat generated during the process [54]. The commercially used GDLs are typically dual-layer porous carbon materials, where a carbon fiber or carbon cloth usually acts as the substrate, which is covered by a thinner microporous layer, which consists of carbon particles and hydrophobic agent to enhance the removal of the produced water [2,5]. The carbon-based GDL is prone to degradation by the tough environment under which the fuel cell operates, such as high potentials, high temperature, and air and water flows that can cause the GDL to lose hydrophobicity and weight [55]. Studies have shown that the change in the GDL properties can significantly affect the performance of a PEM fuel cell during operation [56–58]. The degradation mechanism of GDLs is quite complex and can be categorized into two types, namely, chemical degradation and mechanical degradation.

#### **9.2.4.1 Chemical degradation of gas diffusion layers**

The chemical degradation of GDLs is mainly carbon corrosion as the typically used GDL materials are carbon-based. Similarly to the carbon corrosion in the catalyst layers, the carbon in the GDLs can also be oxidized into CO and CO<sub>2</sub> by reacting with water in acidic environment, leading to structural breakdown and weight loss of the GDLs [10,55]. Certain operating conditions such as startup/shutdown and local fuel starvation can lead to high electrode potential, which can promote carbon corrosion [56]. Moreover, the carbon-based GDLs can be attacked by the chemical radicals, causing the loss of conductivity and hydrophobicity of the GDL, which negatively affect the performance and durability of the fuel cell [2].

#### **9.2.4.2 Mechanical degradation of gas diffusion layers**

The mechanical degradation of GDLs denotes the physical damage caused by dissolution in water, erosion by gas flow, and mechanical breakdown by compression, and freezing/thawing, etc. [55,59,60]. The condensation of the humidified air and H<sub>2</sub> under saturated condition can lead to the formation of water, which along with the water produced from the electrochemical reactions of the fuel cell, can cause water accumulation in the GDL. This can provide a flooded and oxidative condition for the GDL, which can dissolve the carbon-based materials of GDL and produce hydroxides, oxides, and other species [61,62]. As the gases should flow through the GDL to the electrodes to react during the fuel cell operation, they can erode the GDL, which in turn can affect the transportation of gases between the GDL and flow channels in the bipolar plates, leading to an increase in both ohmic resistance and mass transfer resistance [10].

Furthermore, since a PEM fuel cell is a sandwiched structure with the MEA in the middle fixed between bipolar plates on each side, the compression used to fix the cell together to minimize the contact resistance and prevent the leakage of the reactants and products can cause damage to the cell. Studies have shown that compression

contributes significantly to the change in the morphology of the GDL and the water transport inside [63]. Inhomogeneous compression can also significantly influence the temperature distribution and the reaction rates below the channel parts of the electrodes, thereby causing degradation of the GDL and ultimately limiting the lifetime of the fuel cell [64].

Additionally, exposure to subzero temperature can cause the water produced during the PEM fuel cell operation to freeze, which can cause damage to the GDL [10,65]. It is worth noting that mechanical degradation of the GDL can also occur during the manufacturing and during the cell assembly process.

### 9.2.5 Degradation of bipolar plates

The functions of the bipolar plates in a PEM fuel cell consist of uniformly distributing the gases over the active area, heat removal, current conduction, and insulating reactants and coolant between different cell units [66]. The commonly used bipolar plates in PEM fuel cells are graphite, graphite polymer composite, and metal-based materials, and their degradation modes typically consist of corrosion and passivation [7,66].

For graphite and graphite polymer composite-based bipolar plate, the degradation is not significant under normal operating conditions. However, carbon corrosion can occur under extreme conditions, such as fuel starvation and startup/shutdown cycles, which can cause high electrode potentials that lead to carbon corrosion [2,7]. For metal-based bipolar plates, the degradation is related to the nature of the metal and surrounding conditions, such as the potential, relative humidity, and so on. When the metal-based bipolar plates are exposed to high potential or oxidative environment, oxidation and corrosion phenomena are likely to occur [67,68]. The oxidation layer formed on the surface of the bipolar plates can increase the contact resistance between the GDLs and the bipolar plates and the electrical resistance in the PEM fuel cells, leading to decreased cell performance and durability [2]. Metal ions in the PEM fuel cell system that originate from the corrosion of the metal-based bipolar plates can also accumulate on the membrane and catalyst layers, occupying the active catalytic sites and sulfonic acid sites by ion exchange and further enhancing the chemical degradation of the membrane and the catalyst. Therefore, the corrosion of the metal-based bipolar plates can generate metallic cations in the system, which can cause severe degradation on other components and even cause cell failure during the operation [69–71].

### 9.2.6 Degradation of other components

In addition to the above-discussed key components of a PEM fuel cell, the degradation of other components such as endplates, sealing gaskets, and accessory

devices, such as pipes in the system, pump, humidifier, and radiator, are also worth considering.

Endplates are usually used to maintain the compressed structure of fuel cell or stack from the outer ends and prevent the leakage of the reactants, which typically consist of two main material categories: nonmetallic endplates made of engineering plastics, polysulfons, etc. and metallic endplates such as titanium, steel, or aluminum. It has been reported that the nonmetallic endplates could be degraded at operational temperature due to insufficient material thermal stability [72]. Although the metallic endplates have better thermal and mechanical properties, Pozio et al. [73] reported that PEM fuel cell showed worse performance stability when using stainless steel as end plates, which could be due to metallic impurities that decrease the cell performance gradually during the operation.

Sealing gaskets are used to separate the reactant gases and avoid direct mixing of oxygen and hydrogen in PEM fuel cells. The sealing gaskets are usually made of silicone, fluorine caoutchouc, and EPDM (Ethylene Propylene Diene Monomer) [74]. Refs. [75,76] investigated the degradation of four commercial elastomeric gaskets and found that surface degradation occurred in the early stage of exposure to the acidic fuel cell environment and backbone de-cross-linking and chain scission occurred over time. Both the exposure time to the acid and temperature can affect the degradation of the sealing materials, where higher temperature can accelerate the sealing material degradation [77]. The degradation of the sealing gaskets can lead to the release of contaminants such as silicone residues, which can move to the electrodes, resulting in catalyst poisoning and since the sealing material is hydrophobic it can also alter the wetting behavior of the electrodes [74].

However, investigations regarding the degradation of these components are scarce in the literature and further studies of their degradation modes and the corresponding mitigation techniques should be considered to improve the durability of the whole system.

### 9.3 Stressors in proton exchange membrane fuel cells

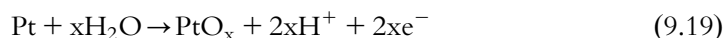
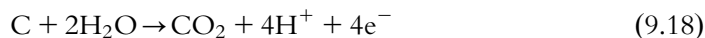
#### 9.3.1 Open-circuit voltage

Stressors in fuel cells are nonideal conditions (non-nominal operating conditions) that the fuel cell can run into from time to time and can cause temporary or permanent performance losses. The intensity and duration of these stressors usually determines the severity of their degrading effects. For instance, PEM fuel cell can be operated frequently at OCV conditions without current/voltage load or with rather low current density (idle condition), especially for automotive application. Degradation test of PEM fuel cell was carried out under open-circuit operation in a study by Teranishi et al. [78]. Results showed that a high degradation rate of up to  $5.8 \text{ mV h}^{-1}$  was observed for cells without humidification due to the formation of pinhole in the membrane leading to the  $\text{H}_2$  crossover through the membrane and consequently cathode degradation via radical attack. Similar enhanced membrane degradation phenomenon under OCV was also reported in a study by Tang et al. [18],

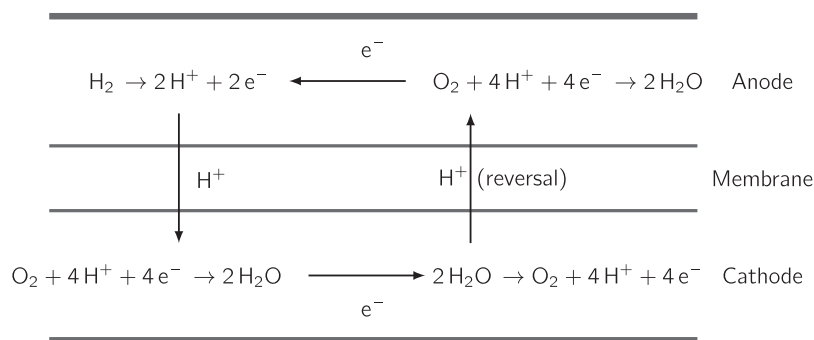
where the degradation was attributed to attack by  $\text{H}_2\text{O}_2$ , which was produced due to the gas crossover through the membrane. Degradation tests under OCV condition and mechanism analysis were also carried out by Zhang et al. [79], where membrane thinning and catalyst agglomeration were observed. The results also reported that while membrane degradation and catalyst layer agglomeration were unrecoverable, the kinetic loss of ORR caused by the water accumulation in the channels and electrodes during the OCV operation was recoverable. Therefore, extended OCV conditions should be avoided during the PEM fuel cell operation in order to achieve longer fuel cell lifetime.

### 9.3.2 Start/stop cycling

Start/stop (or on/off) cycling is another critical operating condition, especially for automotive application. Fuel cell shutdown/startup cycles can lead to high potential on the cathode and reverse current reactions as shown in Fig. 9.7. Moreover, the high potential can lead to Pt oxidation and carbon corrosion on the cathode according to the following reactions [80]:



Dyanty et al. [81] investigated the effect of on/off cycling on the lifetime of a PEM fuel cell used in aeronautic application. They found that the on/off cyclic operation can lead to the catalyst degradation, which is manifested as loss of electrochemical surface area (ECSA) due to the Pt particles redeposition caused by Pt agglomeration and oxidation. Seo et al. [82] carried out on/off cycling test under



**Figure 9.7** Mechanism of the reverse current reactions during the shutdown/startup process in fuel cells. Based on K. Eom, G. Kim, E. Cho, J.H. Jang, H.J. Kim, S.J. Yoo, et al., *Effects of Pt loading in the anode on the durability of a membrane-electrode assembly for polymer electrolyte membrane fuel cells during startup/shutdown cycling*. *Int. J. Hydrogen Energy* 37 (23) (2012) 18455–18462. <https://doi.org/10.1016/j.ijhydene.2012.09.077>.

different humidity conditions to investigate the MEA degradation of PEM fuel cell. Loss of ECSA as well as a decrease in electrode thickness both in the anode and the cathode side caused by carbon corrosion during the on/off cycling was reported in the study. Bona et al. [83] also found, using FE-SEM analysis, the thinning of cathode catalyst layer caused by carbon corrosion. Therefore, start/stop cycling can lead to the degradation of PEM fuel cell mainly through catalyst degradation, especially on the cathode side.

### 9.3.3 Thermal cycling and freeze/thaw cycling

PEM fuel cells must be able to operate in a wide range of temperatures as the surrounding temperature in which they are placed can vary significantly both in different seasons and different geographical locations. Especially, subzero operating temperatures, commonly seen in colder climates are particularly challenging. For instance, when a PEM fuel cell is operated at subfreezing temperatures,  $H_2O$  in the components can freeze and form ice after shutdown. Yan et al. [84] reported that significant MEA damage was observed after a PEM fuel cell was operated below  $-5^{\circ}C$ , where the catalyst layers were delaminated on both sides of the membrane and cracks and pinholes were observed on the membrane. They also reported damage to the back layer and the binder structure due to the ice formation. Through isothermal potentiostatic cold start measurements on single fuel cell, Oszcipok et al. [85] found that ice formed in the GDL, microporous layer, and porous structures of the cathode can lead to severe loss of the ECSA and structural change of the GDL and microporous layer on the cathode side, contributing to significant cell performance degradation. Mukundan et al. [86] also investigated the effect of freeze/thaw cycling on the electrical and mechanical properties of the components of PEM fuel cells with various subfreezing temperatures, but the results showed that no performance degradation was found when the cell was cycled down to  $-40^{\circ}C$ . The freeze/thaw cycling resulted in interfacial failure only when the cycling temperature was extremely low at  $-80^{\circ}C$ .

To investigate the effects of thermal cycling and/or relative humidity (RH) on the catalyst layer structure of a PEM fuel cell, Chang et al. [87] carried out three separate tests consisting of thermal cycling alone, RH cycling alone, and combined thermal and RH cycling. Results showed that the main catalyst layers' structural changes consist of crack growth, catalyst agglomerate detachment, and surface bulges. The thermal cycling alone had no severe effect on the catalyst layer structure, while RH cycling caused 13%–30% increase in the length of the cracks on the catalyst layer, and when thermal cycling and RH cycling were combined, the cracks length reached 2–6 times larger than the initial value. This shows that the combined effect of both thermal cycling and RH cycling can severely damage the fuel cell's performance and should be avoided.



### 9.3.4 Reactant starvation

Reactant starvation, which can be fuel starvation and oxidant starvation, can occur during the PEM fuel cell operation for various reasons. It can be caused by improper gas supply, sudden load increase, start-ups, and so on, and its main effects on PEM fuel cell are catalyst degradation and carbon corrosion [88]. According to Taniguchi et al. [89], reactant starvation can lead to cell reversal, resulting in irreversible damage to MEAs. The result of their single-cell experiments showed that both anode and cathode catalyst degradation were detected during fuel starvation. Liang et al. [90] also carried out experimental work to investigate the reversal process of PEM fuel cell under fuel starvation conditions. They found that fuel starvation can lead to uneven current distribution and severe fuel starvation can increase the current of water electrolysis process (cell reversal) and accelerate the carbon corrosion near the anode outlet. Similar results were also achieved by Liu et al. [91], who carried out fuel starvation test on a PEM fuel cell and detected carbon corrosion in the H<sub>2</sub>-starved area, where a decrease in the current density and structural damage were observed, confirming the reverse current decay mechanism.

### 9.3.5 Fuel impurities

Impurities such as CO, CO<sub>2</sub>, and SO<sub>x</sub> can be fed to PEM fuel cell along with hydrogen and air. Since their presence in the fuel cell can cause significant effect on the performance of the cell, it is worth addressing the mechanisms by which they attack the components of the fuel cell. Impurities in hydrogen are mainly from the byproducts produced during the H<sub>2</sub> generation process, for instance, when H<sub>2</sub> is produced through steam-reforming process of natural gas, methanol, and other organic fuels. The impurities in air are mainly from emission of industrial and automobile exhaust. Besides, metal ions such as Fe<sup>3+</sup> and Cu<sup>2+</sup>, originated from the corrosion of components in the system, can also cause significant performance decay of PEM fuel cells.

#### 9.3.5.1 CO<sub>x</sub> poisoning

The general CO poisoning mechanism lies in the preferential adsorption of CO on the Pt surface and its competition with H<sub>2</sub> for the active sites as shown in the equations below [92]:



where S represents the active sites on the catalyst surface.

It has been reported that the  $\text{CO}_2$  poisoning can lead to reverse water–gas shift reaction (RWGS:  $\text{CO}_2 + \text{H} \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ ), which can make the active catalytic sites inactive because of the hydrogen dissociation and adsorption of the produced CO on the catalyst surface [93]. Therefore,  $\text{CO}_x$  degrades the performance of a PEM fuel cell mainly through poisoning the effective catalytic sites on the Pt surface [92–94]. However, it is worth mentioning that the poisoning effects of CO are far more serious than those of  $\text{CO}_2$  as they directly adsorb on the catalyst occupying reaction sites, with only few tens of ppm of CO in the fuel causing serious performance losses while few percentage points by volume of  $\text{CO}_2$  are somewhat tolerable by the fuel cell [93].

### 9.3.5.2 Sulfur poisoning

$\text{SO}_2$  and  $\text{H}_2\text{S}$  are also commonly seen impurities in PEM fuel cell systems. Among many of the air impurities,  $\text{SO}_2$  is noteworthy due to its various emission sources and detrimental impact on a PEM fuel cell's performance. Studies have shown that exposing PEM fuel cells to  $\text{SO}_2$  can lead to the ECSA decrease due to growth of the Pt particle size, which leads to increased charge transfer resistance and performance decay [95,96].  $\text{H}_2\text{S}$ , on the other hand, is present in the anode feed of a fuel cell as a byproduct of the steam reforming of natural gas and can react with Pt through the reaction of  $\text{Pt} + \text{H}_2\text{S} \rightarrow \text{Pt}-\text{S}_{\text{ads}} + \text{H}_2$  to produce  $\text{Pt}-\text{S}_{\text{ads}}$  on the surface of the catalyst leading to irreversible cell performance decay [97].

### 9.3.5.3 Other impurities

Other impurities such as ammonia, and metal ions can also cause severe performance degradation of PEM fuel cells.  $\text{NH}_3$  was reported to lead to irreversible cell performance deterioration, and that the degradation extent increases with increasing exposure time and concentration of  $\text{NH}_3$  [98]. Chloride ions are also reported to adsorb onto the catalyst sites and lead to the dissolution of the electrocatalysts and reduction in the ECSA, resulting in slower electrochemical reactions [69]. Finally, metal ions such as  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , as mentioned above, can cause severe cell performance degradation by catalyzing the Fenton reaction to produce chemical radicals that can then attack the MEA [19,99].

## References

- [1] N. Guerrero Moreno, M. Cisneros Molina, D. Gervasio, J.F. Pérez Robles, Approaches to polymer electrolyte membrane fuel cells (PEMFCs) and their cost, *Renew. Sustain. Energy Rev.* 52 (2015) 897–906. Available from: <https://doi.org/10.1016/j.rser.2015.07.157>.
- [2] J. Wu, X.Z. Yuan, J.J. Martin, H. Wang, J. Zhang, J. Shen, et al., A review of PEM fuel cell durability: degradation mechanisms and mitigation strategies, *J. Power Sources* 184 (1) (2008) 104–119. Available from: <https://doi.org/10.1016/j.jpowsour.2008.06.006>.
- [3] DOE, The DOE hydrogen and fuel cells program, April 2019.

- [4] United States Department of Energy, Hydrogen storage, Department of Energy, October 1, 2012. <<http://energy.gov/eere/fuelcells/hydrogen-storage>>
- [5] 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) 112022. Available from: <https://doi.org/10.1016/j.enconman.2019.112022>.
- [6] S.D. Knights, K.M. Colbow, J. St-Pierre, D.P. Wilkinson, Aging mechanisms and lifetime of PEFC and DMFC, *J. Power Sources* 127 (1–2) (2004) 127–134. Available from: <https://doi.org/10.1016/j.jpowsour.2003.09.033>.
- [7] F.A. De Bruijn, V.A.T. Dam, G.J.M. Janssen, Review: durability and degradation issues of PEM fuel cell components, *Fuel Cell* 8 (1) (2008) 3–22. Available from: <https://doi.org/10.1002/fuce.200700053>.
- [8] W. Bi, T.F. Fuller, Modeling of PEM fuel cell Pt/C catalyst degradation, *J. Power Sources* 178 (1) (2008) 188–196. Available from: <https://doi.org/10.1016/j.jpowsour.2007.12.007>.
- [9] E. Padgett, V. Yarlagadda, M.E. Holtz, M. Ko, B.D.A. Levin, R.S. Kukreja, et al., Mitigation of PEM fuel cell catalyst degradation with porous carbon supports, *J. Electrochem. Soc.* 166 (4) (2019) F198–F207. Available from: <https://doi.org/10.1149/2.0371904jes>.
- [10] J. Park, H. Oh, T. Ha, Y.I. Lee, K. Min, A review of the gas diffusion layer in proton exchange membrane fuel cells: durability and degradation, *Appl. Energy* 155 (2015) 866–880. Available from: <https://doi.org/10.1016/j.apenergy.2015.06.068>.
- [11] A. El-Kharouf, A. Chandan, M. Hattenberger, B.G. Pollet, Proton exchange membrane fuel cell degradation and testing: review, *J. Energy Inst.* 85 (4) (2012) 188–200. Available from: <https://doi.org/10.1179/1743967112Z.00000000036>.
- [12] P. Choi, N.H. Jalani, R. Datta, Thermodynamics and proton transport in Nafion, *J. Electrochem. Soc.* 152 (3) (2005) E123. Available from: <https://doi.org/10.1149/1.1859814>.
- [13] A. Collier, H. Wang, X. Zi Yuan, J. Zhang, D.P. Wilkinson, Degradation of polymer electrolyte membranes, *Int. J. Hydrogen Energy* 31 (13) (2006) 1838–1854. Available from: <https://doi.org/10.1016/j.ijhydene.2006.05.006>.
- [14] Inaba, M., Degradation mechanism of polymer electrolyte fuel cells, in: 14th International Conference on the Properties of Water and Steam in Kyoto, 2004, pp. 395–402.
- [15] H. Liu, F.D. Coms, J. Zhang, H.A. Gasteiger, A.B. Laconti, Chemical degradation: correlations between electrolyzer and fuel cell findings, *Polym. Electrolyte Fuel Cell Durab.* (2009) 71–118. Available from: [https://doi.org/10.1007/978-0-387-85536-3\\_5](https://doi.org/10.1007/978-0-387-85536-3_5).
- [16] S. Obara, Load response characteristics of a fuel cell micro-grid with control of number of units, *Int. J. Hydrog. Energy* 31 (13) (2006) 1831–1837. Available from: <https://doi.org/10.1016/j.ijhydene.2006.02.029>.
- [17] E. Endoh, S. Terazono, H. Widjaja, Y. Takimoto, Degradation study of MEA for PEMFCs under low humidity conditions, *Electrochem. Solid-State Lett.* 7 (7) (2004) 209–212. Available from: <https://doi.org/10.1149/1.1739314>.
- [18] H. Tang, S. Peikang, S.P. Jiang, F. Wang, M. Pan, A degradation study of Nafion proton exchange membrane of PEM fuel cells, *J. Power Sources* 170 (1) (2007) 85–92. Available from: <https://doi.org/10.1016/J.JPOWSOUR.2007.03.061>.
- [19] M. Inaba, T. Kinumoto, M. Kiriake, R. Umabayashi, A. Tasaka, Z. Ogumi, Gas crossover and membrane degradation in polymer electrolyte fuel cells, *Electrochim. Acta* 51 (26) (2006) 5746–5753. Available from: <https://doi.org/10.1016/j.electacta.2006.03.008>.
- [20] T. Tian, J. Tang, W. Guo, M. Pan, Accelerated life-time test of MEA durability under vehicle operating conditions in PEM fuel cell, *Front. Energy* 11 (3) (2017) 326–333. Available from: <https://doi.org/10.1007/s11708-017-0489-z>.
- [21] W. Bi, Q. Sun, Y. Deng, T.F. Fuller, The effect of humidity and oxygen partial pressure on degradation of Pt/C catalyst in PEM fuel cell, *Electrochim. Acta* 54 (6) (2009) 1826–1833. Available from: <https://doi.org/10.1016/j.electacta.2008.10.008>.
- [22] J.G. Goodwin, Effect of cations (Na<sup>+</sup>, Ca<sup>2+</sup>, Fe<sup>3+</sup>) on the conductivity of a Nafion membrane, *J. Power Sources* 195 (21) (2010) 7213–7220. Available from: <https://doi.org/10.1016/j.jpowsour.2010.05.005>. 03787753.

- [23] C.J. Banas, Md.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 (13) (2018) 407–419. Available from: <https://doi.org/10.1149/08613.0407ecst>.
- [24] 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 (1–2) (2004) 41–48. Available from: <https://doi.org/10.1016/j.jpowsour.2004.01.023>.
- [25] A.Z. Weber, Gas-crossover and membrane-pinhole effects in polymer-electrolyte fuel cells, *J. Electrochem. Soc.* 155 (6) (2008) B521. Available from: <https://doi.org/10.1149/1.2898130>.
- [26] J. Surowiec, R. Bogoczek, Studies on the thermal stability of the perfluorinated cation-exchange membrane Nafion-417, *J. Therm. Anal.* 33 (4) (1988) 1097–1102. Available from: <https://doi.org/10.1007/BF01912735>.
- [27] D. Chu, D. Gervasio, M. Razaq, E.B. Yeager, Infrared reflectance absorption spectroscopy (IRRAS). Study of the thermal stability of perfluorinated sulphonic acid ionomers on Pt, *J. Appl. Electrochem.* 20 (1) (1990) 157–162. Available from: <https://doi.org/10.1007/BF01012486>.
- [28] R.C. McDonald, C.K. Mittelsteadt, E.L. Thompson, Effects of deep temperature cycling on Nafion® 112 membranes and membrane electrode assemblies, *Fuel Cell* 4 (3) (2004) 208–213. Available from: <https://doi.org/10.1002/fuce.200400015>.
- [29] W.R.W. Daud, A.B. Mohamad, A.A.H. Kadhun, R. Chebbi, S.E. Iyuke, Performance optimisation of PEM fuel cell during MEA fabrication, *Energy Convers. Manag.* 45 (20) (2004) 3239–3249. Available from: <https://doi.org/10.1016/j.enconman.2004.01.011>.
- [30] W.M. Yan, C.H. Yang, C.Y. Soong, F. Chen, S.C. Mei, Experimental studies on optimal operating conditions for different flow field designs of PEM fuel cells, *J. Power Sources* 160 (1) (2006) 284–292. Available from: <https://doi.org/10.1016/j.jpowsour.2006.01.031>.
- [31] J. Zhao, A. Ozden, S. Shahgaldi, I.E. Alaefour, X. Li, F. Hamdullahpur, Effect of Pt loading and catalyst type on the pore structure of porous electrodes in polymer electrolyte membrane (PEM) fuel cells, *Energy* 150 (2018) 69–76. Available from: <https://doi.org/10.1016/j.energy.2018.02.134>.
- [32] T.W. Hansen, A.T. Delariva, S.R. Challa, A.K. Datye, Sintering of catalytic nanoparticles: particle migration or ostwald ripening? *Acc. Chem. Res.* 46 (8) (2013) 1720–1730. Available from: <https://doi.org/10.1021/ar3002427>.
- [33] E. Pizzutilo, S. Geiger, J.-P. Grote, A. Mingers, K.J.J. Mayrhofer, M. Arenz, et al., On the need of improved accelerated degradation protocols (ADPs): examination of platinum dissolution and carbon corrosion in half-cell tests, *J. Electrochem. Soc.* 163 (14) (2016) F1510–F1514. Available from: <https://doi.org/10.1149/2.0731614jes>.
- [34] 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 (2) (2007) 558–566. Available from: <https://doi.org/10.1016/j.jpowsour.2007.07.004>.
- [35] S. Zhang, X.Z. Yuan, J.N.C. Hin, H. Wang, K.A. Friedrich, M. Schulze, A review of platinum-based catalyst layer degradation in proton exchange membrane fuel cells, *J. Power Sources* 194 (2) (2009) 588–600. Available from: <https://doi.org/10.1016/j.jpowsour.2009.06.073>.
- [36] W. Bi, G.E. Gray, T.F. Fuller, PEM fuel cell PtC dissolution and deposition in Nafion electrolyte, *Electrochem. Solid-State Lett.* 10 (5) (2007) 101–104. Available from: <https://doi.org/10.1149/1.2712796>.
- [37] H. Xu, R. Kunz, J.M. Fenton, Investigation of platinum oxidation in PEM fuel cells at various relative humidities, *Electrochem. Solid-State Lett.* 10 (1) (2007) 1–6. Available from: <https://doi.org/10.1149/1.2372230>.
- [38] M. Watanabe, K. Tsurumi, T. Mizukami, T. Nakamura, P. Stonehart, Activity and stability of ordered and disordered Co-Pt alloys for phosphoric acid fuel cells, *J. Electrochem. Soc.* 141 (10) (1994) 2659–2668. Available from: <https://doi.org/10.1149/1.2059162>.
- [39] Y. Li, K. Moriyama, W. Gu, S. Arisetty, C.Y. Wang, A one-dimensional Pt degradation model for polymer electrolyte fuel cells, *J. Electrochem. Soc.* 162 (8) (2015) F834–F842. Available from: <https://doi.org/10.1149/2.0101508jes>.
- [40] M.F. Mathias, R. Makharia, H.A. Gasteiger, J.J. Conley, T.J. Fuller, C.J. Gittleman, et al., Two fuel cell cars in every garage? *Electrochem. Soc. Interface* 14 (3) (2005) 24–35.

- [41] R.L. Borup, J.R. Davey, F.H. Garzon, D.L. Wood, M.A. Inbody, PEM fuel cell electrocatalyst durability measurements, *J. Power Sources* 163 (1 SPEC. ISS.) (2006) 76–81. Available from: <https://doi.org/10.1016/j.jpowsour.2006.03.009>.
- [42] Y. Yu, H. Li, H. Wang, X.Z. Yuan, G. Wang, M. Pan, A review on performance degradation of proton exchange membrane fuel cells during startup and shutdown processes: causes, consequences, and mitigation strategies, *J. Power Sources* 205 (2012) 10–23. Available from: <https://doi.org/10.1016/j.jpowsour.2012.01.059>.
- [43] B.J. Eastwood, P.A. Christensen, R.D. Armstrong, N.R. Bates, Electrochemical oxidation of a carbon black loaded polymer electrode in aqueous electrolytes, *J. Solid. State Electrochem.* 3 (4) (1999) 179–186. Available from: <https://doi.org/10.1007/s100080050145>.
- [44] J. Willsau, J. Heitbaum, The influence of Pt-activation on the corrosion of carbon in gas diffusion electrodes—a DEMS study, *J. Electroanalytical Chem.* 161 (1) (1984) 93–101. Available from: [https://doi.org/10.1016/S0022-0728\(84\)80252-1](https://doi.org/10.1016/S0022-0728(84)80252-1).
- [45] S. Maass, F. Finsterwalder, G. Frank, R. Hartmann, C. Merten, Carbon support oxidation in PEM fuel cell cathodes, *J. Power Sources* 176 (2) (2008) 444–451. Available from: <https://doi.org/10.1016/j.jpowsour.2007.08.053>.
- [46] D.A. Stevens, M.T. Hicks, G.M. Haugen, J.R. Dahn, Ex situ and in situ stability studies of PEMFC catalysts, *J. Electrochem. Soc.* 152 (12) (2005) A2309. Available from: <https://doi.org/10.1149/1.2097361>.
- [47] K. More, R. Borup, K. Reeves, Identifying contributing degradation phenomena in PEM fuel cell membrane electrode assemblies via electron microscopy, *ECS Trans.* 3 (1) (2006) 717–733. Available from: <https://doi.org/10.1149/1.2356192>.
- [48] A.P. Saab, F.H. Garzon, T.A. Zawodzinski, Determination of ionic and electronic resistivities in carbon/polyelectrolyte fuel-cell composite electrodes, *J. Electrochem. Soc.* 149 (12) (2002) A1541. Available from: <https://doi.org/10.1149/1.1516771>.
- [49] J. Xie, D.L. Wood, K.L. More, P. Atanassov, R.L. Borup, Microstructural changes of membrane electrode assemblies during PEFC durability testing at high humidity conditions, *J. Electrochem. Soc.* 152 (5) (2005) A1011. Available from: <https://doi.org/10.1149/1.1873492>.
- [50] F.Y. Zhang, S.G. Advani, A.K. Prasad, M.E. Boggs, S.P. Sullivan, T.P. Beebe, Quantitative characterization of catalyst layer degradation in PEM fuel cells by X-ray photoelectron spectroscopy, *Electrochim. Acta* 54 (16) (2009) 4025–4030. Available from: <https://doi.org/10.1016/j.electacta.2009.02.028>.
- [51] Y. Chang, J. Zhao, S. Shahgaldi, Y. Qin, Y. Yin, X. Li, Modelling of mechanical microstructure changes in the catalyst layer of a polymer electrolyte membrane fuel cell, *Int. J. Hydrogen Energy* 45 (54) (2020) 29904–29916. Available from: <https://doi.org/10.1016/j.ijhydene.2018.10.157>.
- [52] J. Hou, W. Song, H. Yu, Y. Fu, L. Hao, Z. Shao, et al., Ionic resistance of the catalyst layer after the PEM fuel cell suffered freeze, *J. Power Sources* 176 (1) (2008) 118–121. Available from: <https://doi.org/10.1016/j.jpowsour.2007.10.035>.
- [53] F. Rong, C. Huang, Z.S. Liu, D. Song, Q. Wang, Microstructure changes in the catalyst layers of PEM fuel cells induced by load cycling. Part I. Mechanical model, *J. Power Sources* 175 (2) (2008) 699–711. Available from: <https://doi.org/10.1016/j.jpowsour.2007.10.006>.
- [54] R. Omrani, B. Shabani, Review of gas diffusion layer for proton exchange membrane-based technologies with a focus on utilised regenerative fuel cells, *Int. J. Hydrog. Energy* 44 (7) (2019) 3834–3860. Available from: <https://doi.org/10.1016/j.ijhydene.2018.12.120>.
- [55] T. Ha, J. Cho, J. Park, K. Min, H.S. Kim, E. Lee, et al., Experimental study of the effect of dissolution on the gas diffusion layer in polymer electrolyte membrane fuel cells, *Int. J. Hydrog. Energy* 36 (19) (2011) 12427–12435. Available from: <https://doi.org/10.1016/j.ijhydene.2011.06.096>.
- [56] G. Chen, H. Zhang, H. Ma, H. Zhong, Electrochemical durability of gas diffusion layer under simulated proton exchange membrane fuel cell conditions, *Int. J. Hydrogen Energy* 34 (19) (2009) 8185–8192. Available from: <https://doi.org/10.1016/j.ijhydene.2009.07.085>.
- [57] J.T. Gostick, M.W. Fowler, M.D. Pritzker, M.A. Ioannidis, L.M. Behra, In-plane and through-plane gas permeability of carbon fiber electrode backing layers, *J. Power Sources* 162 (1) (2006) 228–238. Available from: <https://doi.org/10.1016/j.jpowsour.2006.06.096>.

- [58] M. Han, J.H. Xu, S.H. Chan, S.P. Jiang, Characterization of gas diffusion layers for PEMFC, *Electrochim. Acta* 53 (16) (2008) 5361–5367. Available from: <https://doi.org/10.1016/j.electacta.2008.02.057>.
- [59] T. Ha, J. Cho, J. Park, K. Min, H.S. Kim, E. Lee, et al., Experimental study on carbon corrosion of the gas diffusion layer in polymer electrolyte membrane fuel cells, *Int. J. Hydrogen Energy* 36 (19) (2011) 12436–12443. Available from: <https://doi.org/10.1016/j.ijhydene.2011.06.098>.
- [60] V. Radhakrishnan, P. Haridoss, Effect of cyclic compression on structure and properties of a gas diffusion layer used in PEM fuel cells, *Int. J. Hydrogen Energy* 35 (20) (2010) 11107–11118. Available from: <https://doi.org/10.1016/j.ijhydene.2010.07.009>.
- [61] J. Chlistunoff, J.R. Davey, K.C. Rau, R. Mukundan, R.L. Borup, PEMFC gas diffusion media degradation determined by acid-base titrations, *ECS Trans.* 50 (2) (2013) 521–529. Available from: <https://doi.org/10.1149/05002.0521ecst>.
- [62] Y. Hiramitsu, H. Sato, K. Kobayashi, M. Hori, Controlling gas diffusion layer oxidation by homogeneous hydrophobic coating for polymer electrolyte fuel cells, *J. Power Sources* 196 (13) (2011) 5453–5469. Available from: <https://doi.org/10.1016/j.jpowsour.2011.01.099>.
- [63] A. Bazylak, D. Sinton, Z.S. Liu, N. Djilali, Effect of compression on liquid water transport and microstructure of PEMFC gas diffusion layers, *J. Power Sources* 163 (2) (2007) 784–792. Available from: <https://doi.org/10.1016/j.jpowsour.2006.09.045>.
- [64] T. Hottinen, O. Himanen, PEMFC temperature distribution caused by inhomogeneous compression of GDL, *Electrochem. Commun.* 9 (5) (2007) 1047–1052. Available from: <https://doi.org/10.1016/j.elecom.2006.12.018>.
- [65] G. Gavello, E.P. Ambrosio, U.A. Icardi, S. Specchia, C. Francia, N. Penazzi, et al., Effect of freezing conditions on PEM-FC components, *ECS Trans.* 17 (1) (2019) 359–368. Available from: <https://doi.org/10.1149/1.3142765>.
- [66] E. Middelmann, W. Kout, B. Vogelaar, J. Lenssen, E. De Waal, Bipolar plates for PEM fuel cells, *J. Power Sources* 118 (1–2) (2003) 44–46. Available from: [https://doi.org/10.1016/S0378-7753\(03\)00070-3](https://doi.org/10.1016/S0378-7753(03)00070-3).
- [67] D.P. Davies, P.L. Adcock, M. Turpin, S.J. Rowen, Bipolar plate materials for solid polymer fuel cells, *J. Appl. Electrochem.* 30 (1) (2000) 101–105. Available from: <https://doi.org/10.1023/A:1003831406406>.
- [68] R.F. Silva, D. Franchi, A. Leone, L. Pilloni, A. Masci, A. Pozio, Surface conductivity and stability of metallic bipolar plate materials for polymer electrolyte fuel cells, *Electrochim. Acta* 51 (17) (2006) 3592–3598. Available from: <https://doi.org/10.1016/j.electacta.2005.10.015>.
- [69] S.M.M. Ehteshami, A. Taheri, S.H. Chan, A review on ions induced contamination of polymer electrolyte membrane fuel cells, poisoning mechanisms and mitigation approaches, *J. Ind. Eng. Chem.* 34 (2016) 1–8. Available from: <https://doi.org/10.1016/j.jiec.2015.10.034>.
- [70] A. Weiß, A. Siebel, M. Bernt, T.-H. Shen, V. Tileli, H.A. Gasteiger, Impact of intermittent operation on lifetime and performance of a PEM water electrolyzer, *J. Electrochem. Soc.* 166 (8) (2019) F487–F497. Available from: <https://doi.org/10.1149/2.0421908jes>.
- [71] J. Wind, R. Späh, W. Kaiser, G. Böhm, Metallic bipolar plates for PEM fuel cells, *J. Power Sources* 105 (2) (2002) 256–260. Available from: [https://doi.org/10.1016/S0378-7753\(01\)00950-8](https://doi.org/10.1016/S0378-7753(01)00950-8).
- [72] S. Asghari, M.H. Shahsmandi, M.R. Ashraf Khorasani, Design and manufacturing of end plates of a 5 kW PEM fuel cell, *Int. J. Hydrogen Energy* 35 (17) (2010) 9291–9297. Available from: <https://doi.org/10.1016/j.ijhydene.2010.02.135>.
- [73] A. Pozio, R.F. Silva, M. De Francesco, L. Giorgi, Nafion degradation in PEFCs from end plate iron contamination, *Electrochim. Acta* 48 (11) (2003) 1543–1549. Available from: [https://doi.org/10.1016/S0013-4686\(03\)00026-4](https://doi.org/10.1016/S0013-4686(03)00026-4).
- [74] M. Schulze, T. Knöri, A. Schneider, E. Gülzow, Degradation of sealings for PEFC test cells during fuel cell operation, *J. Power Sources* 127 (1–2) (2004) 222–229. Available from: <https://doi.org/10.1016/j.jpowsour.2003.09.017>.
- [75] J. Tan, Y.J. Chao, J.W. Van Zee, W.K. Lee, Degradation of elastomeric gasket materials in PEM fuel cells, *Mater. Sci. Eng. A* 445–446 (2007) 669–675. Available from: <https://doi.org/10.1016/j.msea.2006.09.098>.



- [76] J. Tan, Y.J. Chao, M. Yang, W.K. Lee, J.W. Van Zee, Chemical and mechanical stability of a Silicone gasket material exposed to PEM fuel cell environment, *Int. J. Hydrogen Energy* 36 (2) (2011) 1846–1852. Available from: <https://doi.org/10.1016/j.ijhydene.2009.12.048>.
- [77] J. Tan, Y.J. Chao, X. Li, J.W. Van Zee, Degradation of silicone rubber under compression in a simulated PEM fuel cell environment, *J. Power Sources* 172 (2) (2007) 782–789. Available from: <https://doi.org/10.1016/j.jpowsour.2007.05.026>.
- [78] K. Teranishi, K. Kawata, S. Tsushima, S. Hirai, Degradation Mechanism of PEMFC under open circuit operation, *Electrochem. Solid-State Lett.* 9 (10) (2006) A475. Available from: <https://doi.org/10.1149/1.2266163>.
- [79] S. Zhang, X.Z. Yuan, J.N.C. Hin, H. Wang, J. Wu, K.A. Friedrich, et al., Effects of open-circuit operation on membrane and catalyst layer degradation in proton exchange membrane fuel cells, *J. Power Sources* 195 (4) (2010) 1142–1148. Available from: <https://doi.org/10.1016/j.jpowsour.2009.08.070>.
- [80] K. Eom, G. Kim, E. Cho, J.H. Jang, H.J. Kim, S.J. Yoo, et al., Effects of Pt loading in the anode on the durability of a membrane-electrode assembly for polymer electrolyte membrane fuel cells during startup/shutdown cycling, *Int. J. Hydrogen Energy* 37 (23) (2012) 18455–18462. Available from: <https://doi.org/10.1016/j.ijhydene.2012.09.077>.
- [81] N. Dyantyi, A. Parsons, P. Bujlo, S. Pasupathi, Behavioural study of PEMFC during start-up/shutdown cycling for aeronautic applications, *Mater. Renew. Sustain. Energy* 8 (1) (2019) 1–8. Available from: <https://doi.org/10.1007/s40243-019-0141-4>.
- [82] D. Seo, J. Lee, S. Park, J. Rhee, S.W. Choi, Y.G. Shul, Investigation of MEA degradation in PEM fuel cell by on/off cyclic operation under different humid conditions, *Int. J. Hydrogen Energy* 36 (2) (2011) 1828–1836. Available from: <https://doi.org/10.1016/j.ijhydene.2010.02.053>.
- [83] D. Bona, D.E. Curtin, F. Pedrazzo, E.M. Tresso, Using a stack shunt to mitigate catalyst support carbon corrosion in polymer electrolyte membrane fuel cell stacks during start–stop cycling, *J. Fuel Cell Sci. Technol.* 11 (1) (2014) 1–15. Available from: <https://doi.org/10.1115/1.4025535>.
- [84] 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 (2 SPEC. ISS.) (2006) 1242–1250. Available from: <https://doi.org/10.1016/j.jpowsour.2006.02.075>.
- [85] M. Oszipok, D. Riemann, U. Kronenwett, M. Kreideweis, M. Zedda, Statistic analysis of operational influences on the cold start behaviour of PEM fuel cells, *J. Power Sources* 145 (2) (2005) 407–415. Available from: <https://doi.org/10.1016/j.jpowsour.2005.02.058>.
- [86] R. Mukundan, S.K. Yu, F. Garzon, B. Pivovar, Freeze/thaw effects in PEM fuel cells, *ECS Trans.* 1 (8) (2005) 403–413. Available from: <https://doi.org/10.1149/1.2214572>.
- [87] Y. Chang, J. Liu, R. Li, J. Zhao, Y. Qin, J. Zhang, et al., Effect of humidity and thermal cycling on the catalyst layer structural changes in polymer electrolyte membrane fuel cells, *Energy Convers. Manag.* 189 (2019) 24–32. Available from: <https://doi.org/10.1016/j.enconman.2019.03.066>.
- [88] N. Yousfi-Steiner, P. Moçotéguy, D. Candusso, D. Hissel, A review on polymer electrolyte membrane fuel cell catalyst degradation and starvation issues: Causes, consequences and diagnostic for mitigation, *J. Power Sources* 194 (1) (2009) 130–145. Available from: <https://doi.org/10.1016/j.jpowsour.2009.03.060>.
- [89] A. Taniguchi, T. Akita, K. Yasuda, Y. Miyazaki, Analysis of electrocatalyst degradation in PEMFC caused by cell reversal during fuel starvation, *J. Power Sources* 130 (1–2) (2004) 42–49. Available from: <https://doi.org/10.1016/j.jpowsour.2003.12.035>.
- [90] D. Liang, Q. Shen, M. Hou, Z. Shao, B. Yi, Study of the cell reversal process of large area proton exchange membrane fuel cells under fuel starvation, *J. Power Sources* 194 (2) (2009) 847–853. Available from: <https://doi.org/10.1016/j.jpowsour.2009.06.059>.
- [91] Z.Y. Liu, B.K. Brady, R.N. Carter, B. Litteer, M. Budinski, J.K. Hyun, et al., Characterization of carbon corrosion-induced structural damage of pem fuel cell cathode electrodes caused by local fuel starvation, *J. Electrochem. Soc.* 155 (10) (2008) B979. Available from: <https://doi.org/10.1149/1.2956198>.

- [92] C.G. Farrell, C.L. Gardner, M. Ternan, Experimental and modelling studies of CO poisoning in PEM fuel cells, *J. Power Sources* 171 (2) (2007) 282–293. Available from: <https://doi.org/10.1016/j.jpowsour.2007.07.006>.
- [93] W.M. Yan, H.S. Chu, M.X. Lu, F.B. Weng, G.B. Jung, C.Y. Lee, Degradation of proton exchange membrane fuel cells due to CO and CO<sub>2</sub> poisoning, *J. Power Sources* 188 (1) (2009) 141–147. Available from: <https://doi.org/10.1016/j.jpowsour.2008.11.107>.
- [94] G.A. Camara, E.A. Ticianelli, S. Mukerjee, S.J. Lee, J. McBreen, The CO poisoning mechanism of the hydrogen oxidation reaction in proton exchange membrane fuel cells, *J. Electrochem. Soc.* 149 (6) (2002) A748. Available from: <https://doi.org/10.1149/1.1473775>.
- [95] J. Fu, M. Hou, C. Du, Z. Shao, B. Yi, Potential dependence of sulfur dioxide poisoning and oxidation at the cathode of proton exchange membrane fuel cells, *J. Power Sources* 187 (1) (2009) 32–38. Available from: <https://doi.org/10.1016/j.jpowsour.2008.10.103>.
- [96] T. Reshetenko, V. Laue, U. Krewer, K. Artyushkova, Poisoning effects of sulfur dioxide in an air stream on spatial proton exchange membrane fuel cell performance, *J. Power Sources* 438 (2019) 226949. Available from: <https://doi.org/10.1016/j.jpowsour.2019.226949>.
- [97] X. Cheng, Z. Shi, N. Glass, L. Zhang, J. Zhang, D. Song, et al., A review of PEM hydrogen fuel cell contamination: impacts, mechanisms, and mitigation, *J. Power Sources* 165 (2) (2007) 739–756. Available from: <https://doi.org/10.1016/j.jpowsour.2006.12.012>.
- [98] 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 (3) (2002) A293. Available from: <https://doi.org/10.1149/1.1447221>.
- [99] J. Qi, X. Wang, U. Pasaogullari, L. Bonville, T. Molter, Effect of Al<sup>3+</sup> contaminant on polymer electrolyte fuel cell performance, *J. Electrochem. Soc.* 160 (9) (2013) F916–F922. Available from: <https://doi.org/10.1149/2.022309jes>.