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Review

A review of accelerated stress tests of MEA durability in PEM fuel cells

Shengsheng Zhang[a,b], Xiaozi Yuan[a], Haijiang Wang[a,], Walter Mérida[a,b], Hong Zhu[c], Jun Shen[a], Shaohong Wu[a], Jiujun Zhang[a]*

[a]*Institute for Fuel Cell Innovation, National Research Council of Canada, 4250 Wesbrook Mall, Vancouver, B. C. V6T 1W5, Canada*
[b]*Department of Mechanical Engineering, University of British Columbia, Vancouver, B. C. V6T 1Z4, Canada*
[c]*College of Science, Beijing University of Chemical Technology, Beijing 100029, China*

ABSTRACT

This paper is a review of recent work done on accelerated stress tests in the study of PEM fuel cell durability, with a primary focus on the main components of the membrane electrode assembly (MEA). The accelerated stressors for each component under different conditions are outlined, in an attempt to gain a detailed understanding of cell degradation with respect to microstructural change and performance attenuation in the perfluorosulfonic acid membrane, catalyst, and gas diffusion layers. Various techniques for evaluating the components' performance are presented, along with representative mitigation strategies. In addition, different degradation mechanisms proposed in recent publications are briefly reviewed.

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1. Introduction

Increasing the durability of proton exchange membrane fuel cells (PEMFCs) is a major challenge and a growing focus of research attention. So far there remains a wide gap between the ideal and the reality of state-of-the-art PEMFC technology. For example, the durability of PEMFCs for transportation applications is far from the 5000-h target for the full range of external environmental conditions ($-40\,°C$ to $+40\,°C$), which is the minimum requirement for vehicles in practical use. To improve the durability and lifetime of PEMFCs, a better understanding of failure modes and corresponding mitigation strategies is urgently required.

To assess the durability of a fuel cell, a steady-state lifetime test can be employed. However, this method is impractical for large-scale application because it is time-consuming and costly. Therefore, most researchers prefer accelerated stress tests (ASTs). The AST has been proven to be a valuable tool for significantly reducing the extent of experiments in lifetime evaluation and degradation mode analysis [1–4]. In an AST, different accelerated stressors are applied to the fuel cell either in-situ or ex-situ, to determine the durability of the whole cell or a particular component. These accelerated stressors include most of the factors that significantly affect cell performance. The performance degradation rate and component damage level under specific working conditions

are always examined during or after ASTs, in order to better predict the fuel cell's lifetime or explain the probable degradation mechanism.

Currently, three major points have been addressed in the research on PEMFC durability: 1) experimental investigation and validation, 2) mathematical modeling, and 3) degradation mitigation strategies. Extensive reviews of fuel cell durability from several points of view have recently been published. Borup et al. [5] presented a very detailed paper on the fundamental aspects of PEMFC durability and degradation. Another review by Wang [6] summarized the fundamental models for fuel cell engineering, and emphasized the increasing demand to develop fuel cell technologies with high performance and excellent durability. In a more recent review, Wu et al. [7] presented a comprehensive overview of degradation mechanisms, mitigation strategies, and theoretical modeling with respect to PEMFC durability. Shao et al. [8] introduced the material challenges to developing high-temperature PEMFCs, specifically the durability of cell component materials, including electrocatalysts, carbon supports, polymers, and bipolar plates. Other reviews have focused on specific PEMFC components, such as membranes [9] and electrocatalysts [10]. These syntheses will undoubtedly help researchers understand what has been done and still remains to be done in this field. However, to the authors' knowledge, existing summaries of accelerated stress tests on PEM fuel cells have not concentrated sufficiently on durability issues, considering their high importance.

In this paper, the authors review recent work on durability and accelerated stress test strategies for PEMFCs. The relationships, identified in the literature, between accelerated conditions, physicochemical properties, and performance are summarized from the viewpoint of the MEA, the key component of a PEMFC. Discussion of the major durability-related factors for in-situ and ex-situ accelerated degradation tests on the MEA are organized by component: membrane, Pt catalyst, carbon support, and gas diffusion layer. Methods developed to diagnose component damage and performance decay are introduced from both chemical and mechanical perspectives. Finally, existing strategies for improving the lifetime of the components are also discussed.

2. Membrane accelerated stress test

2.1. Membrane degradation mechanism

A proton exchange membrane (PEM) functions as an electrolyte for transferring protons from the anode to the cathode, as well as a barrier to prevent gas permeation between the anode and the cathode. Currently, the most commonly used PEMs are perfluorosulfonic acid (PFSA) membranes such as Nafion®,
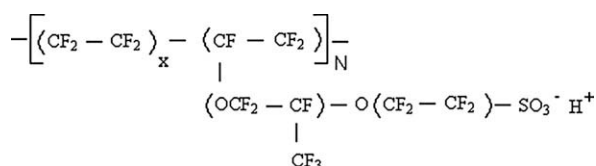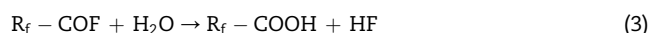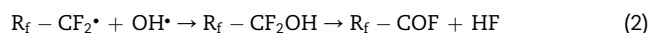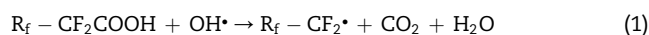

Fig. 1 – Chemical structure of Nafion®, $x \approx 6.5$.

which have high hydrolytic and oxidative stability and excellent proton conductivity. Fig. 1 shows the chemical structure of Nafion®. In this section, all the membranes refer to PFSA membranes in particular, unless otherwise stated.

Typical membrane degradation in a fuel cell results from mechanical, thermal, and chemical mechanisms occurring over time or under harsh conditions. Mechanical damage includes membrane cracks, tears, punctures, and pinholes as a result of uneven stress or other mechanical factors, and is often the main cause of early failures, especially for very thin membranes. High temperatures present several advantages for PEMFCs, e.g., increased electrochemical kinetics and decreased susceptibility to contamination. Unfortunately, degradation of the polymer membrane (along with other parts of the cell) increases with temperature. It has been proposed that chemical degradation leading to ionomer damage and loss in PEM functionality and integrity results from a chemical attack initiated by active oxygen species. Such species as HO• and HO₂• originate from the hydrogen peroxide that is generated through incomplete reduction in the oxygen reduction reaction (ORR) [11,12]. Membrane failure could also result from a combination of chemical attack, thermal attack, and mechanical stresses when the fuel cell is subjected to specific extreme conditions.

Recently, considerable research has been conducted on polymer electrolyte chemical degradation during fuel cell ASTs. The degradation mechanism is thought to be breakage of the per-fluorocarbon backbone and side-chain groups in the Nafion® membrane, and subsequent loss of mechanical strength and proton conductivity, leading to an increase in total cell resistance and loss of power output capability.

The proposed reaction is as follows [13]:

$$R_f - CF_2COOH + OH^\bullet \rightarrow R_f - CF_2^\bullet + CO_2 + H_2O \tag{1}$$

$$R_f - CF_2^\bullet + OH^\bullet \rightarrow R_f - CF_2OH \rightarrow R_f - COF + HF \tag{2}$$

$$R_f - COF + H_2O \rightarrow R_f - COOH + HF \tag{3}$$

Therefore, in a durability test, membrane degradation is often monitored by changes in gas crossover rate, fluoride-ion emission rate (FER), and ion exchange capacity (IEC). Table 1 presents a comparison of these methods for membrane degradation analysis, and lists positive and negative traits. Inaba et al. [14] pointed out that gas crossover and catalytic combustion at the electrodes was one of the key factors in membrane degradation, due to hydrogen peroxide formation. Sethuraman et al. [15] also found that lower oxygen crossover rates to the anode resulted in lower anode peroxide formation rates, and lower hydrogen crossover to the cathode resulted in less Pt deposition inside the membrane.

According to numerous experimental results, membrane degradation is strongly dependent on operating conditions such as temperature, humidity, freeze-thaw cycling, transient operation, and start-up/shut-down. All these working conditions can be employed as accelerated stressors in membrane ASTs.

2.2. Accelerated stressors for membrane degradation

2.2.1. Undesirable temperature and relative humidity

Temperature is an important operating condition for PEMFCs. Currently, the operating temperature of a PEM fuel cell is under

Table 1 – Comparison of several metrics for membrane degradation analysis.

Testing items	Technologies	Characteristic		References
		Positive	Negative	
Gas crossover rate	Electrochemical method (linear sweep voltammogram)	Non-destructive analysis	Need to stop the operation of the fuel cell for measurement	[14,15,26]
Fluoride-ion emission rate	Ion (fluoride) selective electrode	Can be conducted either in-situ or ex-situ	Cannot provide detailed information for the degradation site of the membrane	[11,13–15,26]
Morphology change	Scanning electron microscopy (SEM)	Visual representation	Postmortem analysis	[15,36,44]
Ion exchange capacity change	Standard chemical method	Gives information on the degradation ratio of backbone to side-chain groups	Postmortem analysis	[19,34,44]

90 °C (usually from 60 to 80 °C), despite the advantages of high electrochemical kinetics, a simplified water management system, and enhanced contamination resistance at higher temperatures [16]. Experimental results show that material durability is one of the key challenges to overcome in order to operate PEM fuel cells at high temperatures. Mechanical and chemical degradation of the polymer ionomer that comprises the PEM both increase with temperature. Thermal degradation of PFSA membrane has been investigated by several researchers using accelerated testing [17,18]. Ramaswamy and co-workers analyzed membrane durability from the perspective of peroxide radical initiated chemical attack [19]. They used a segmented fuel cell to separate the membrane evaluation process into cathode and anode aspects, and concluded that from room temperature to 80 °C, membrane degradation rates increased linearly with higher ORR activity and consequent higher peroxide generation at the interface. Their experiment also showed that the main effects of temperature on membrane degradation during a 24-h cathode side test were conductivity loss and IEC change.

As noted by Beuscher et al. [20], progress is needed to withstand the aggressive operating conditions of higher temperatures and/or lower humidities, as well as the longer operating lifetimes demanded of PEMFC applications. Since temperature and relative humidity (RH) are not completely independent in fuel cell systems, these two interrelated factors will be discussed together.

RH may have complex effects on component durability since both flooding and dehydration are well-known factors in PEMFC performance loss [21]. First, inadequate humidification is detrimental to the membrane, as lack of water makes the membrane brittle and fragile. At the same time, higher chemical degradation of the ionomer membrane will occur under conditions of prolonged low humidity [15,22]. For instance, Yu et al. [23] discovered a dramatic degradation of the membrane under non-saturated humidification, which resulted in accelerated collapse of the fuel cell during a 2700-h lifetime test. Moreover, degradation can be significantly increased when the membrane is subjected to a higher temperature and lower humidity simultaneously under some conditions [24]. On the other hand, excessive humidification can also cause many problems during fuel cell operation, such as flooding and corresponding reactant diffusion blockages. According to a report from Gore Fuel Cell

Technologies [21], under-saturated as compared with over-saturated outlet conditions can result in much longer life and lower fluoride-ion release rates from the membrane. Other factors, such as contamination level, which is correlated to water content, as well as material properties and processing conditions, might also play a critical role in determining the rate of membrane degradation during such experiments.

Change in RH is another serious condition that may result in mechanical degradation of the membrane during practical operation. Researchers in General Motors Corporation developed a series of ASTs on RH cycling to investigate mechanical degradation of the membrane. One of their representative reports was a RH cycling test between 150% and 0% at 80 °C under air/air to study mechanical failure of membranes in the absence of chemical degradation [25]. Results showed that the stresses imposed solely by cycling between wet and dry operating conditions could create membrane failures, owing to repeated swelling and shrinking. Tang et al. [26] also measured the stress and strain on the membrane due to shrinkage caused by changes in RH, from complete soaking in water to 25% RH at 90 °C. The maximum stress on a Nafion® 111 membrane during RH cycling was as high as 3.1 MPa.

2.2.2. Open circuit voltage
It has been observed that open circuit voltage (OCV) without electric loading enhances MEA degradation, especially for membrane materials with reactant gases [27–32]. Peroxide radicals (from hydrogen peroxide), which can lead to chemical decomposition of the membrane, are considered the main cause of this kind of degradation. Hydrogen peroxide can be generated either through the incomplete reduction of oxygen at the cathode under normal operating conditions, or the reaction of hydrogen and oxygen when significant gas crossover occurs at the anode catalyst/membrane interface under OCV [33,34]. Once generated, hydrogen peroxide can be readily homolysed into peroxide radicals, which are capable of breaking polymer constituent bonds [35]. Teranishi et al. [36] found that the decreased rates of OCV after a 24-h test were 1.3 and 5.8 mV/h for cells with full and no humidification in the gas supply, respectively.

To explain the membrane degradation under OCV conditions, Liu and Crum [27] reported that the membrane suffered homogenous degradation at OCV potential, resulting in massive ionomer loss and uniform thinning of the membrane

throughout the active area. Inaba et al. [14] demonstrated that the average OCV degradation rate was ∼83 μV/h during 60 days of aging. They also suggested that the hydrogen peroxide formed by oxygen gas crossover and the resulting catalytic combustion at the anode side was the primary reason for membrane degradation and subsequently cell performance loss. Similarly, significant hydrogen crossover increase, attributed to membrane damage, was also observed by Endoh and co-workers [37] after accelerated OCV testing. Inadequate water content and high temperature can also accelerate membrane thinning or pinhole formation, and lead to severe performance degradation under OCV due to more serious reactant gas crossover [15,38]. In an accelerated RH cycling test, where the inlet gases alternated between dry and 100% RH every 10 min at 90 °C, the OCV of the fuel cell assembled with Nafion® 111 membrane decreased at a reduction rate of 13.2 mV/h during a 60,000-s AST [26]. The corresponding mechanism of free radical formation has also been suggested on the basis of experiments in regular fuel cell setups under OCV [39].

2.2.3. Load cycling

Load cycling, which is somewhat related to the humidity effect, is another stressor addressed during accelerated stress testing. The frequent wet-up and dry-out cycles create mechanical stresses on the membrane due to the drastic current change, and the FER was also found to be affected by the load value [40].

Kusoglu et al. [41] investigated the mechanical response of fuel cell membranes subjected to a hygro-thermal cycling test simulating a simplified single fuel cell duty cycle. Hygro-thermal cycling was applied by linearly increasing the relative humidity of the membrane up to 100% and defining an esti-mated temperature profile to give reasonable values for fuel cell operation at 80 °C. The authors concluded that compared with the minor contribution of the through-plane and shear stresses, the in-plane stress in the membrane contributed most to the overall stress, which may explain the occurrence of membrane cracks and pinholes during cyclic loading operation.

To simulate real road driving conditions for automotives, Liu and Case [42] aged PEM fuel cells using cyclic current loading conditions. They demonstrated that hydrogen cross-over increased dramatically after 500 h of current cycling due to pinhole formation in the membrane. In contrast, the MEA hydrogen crossover rate remained approximately the same under constant current operation. Moreover, the fluoride-ion concentrations from the MEA under cyclic current aging conditions were found to be about 30-fold higher than those under constant current operation.

2.2.4. Fenton's test

Fenton's test is commonly employed as an ex-situ accelerated chemical degradation stressor for fuel cell membranes, using either the solution method or the exchange method [43–45]. Accelerated stress testing of Nafion® membrane in Fenton's reagent has been widely carried out in both membrane degradation mechanism research and evaluations of novel membrane durability. Fig. 2 shows SEM images of Nafion® membrane subjected to Fenton's test by the solution method
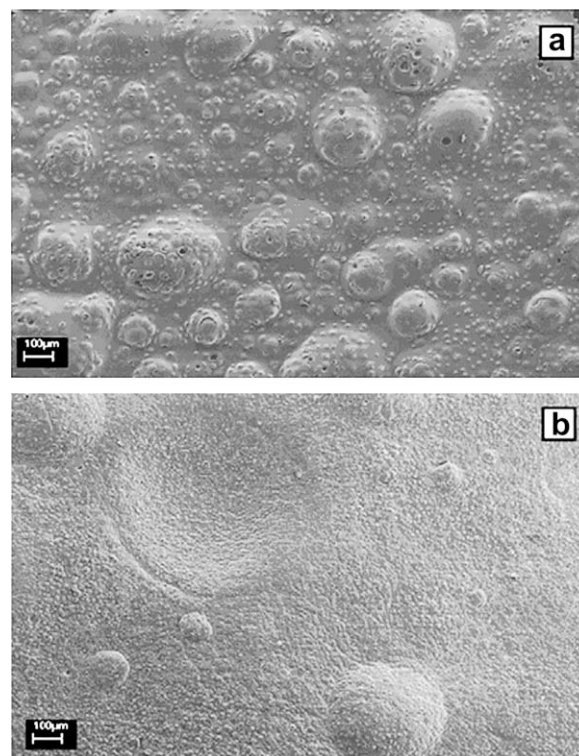

Fig. 2 – Comparison of the surface morphologies of Nafion® membrane degraded by a Fenton's reagent AST, (a) solution method 100× magnification, (b) exchange method 100× magnification (from [44] with permission).

and the exchange method [44]. Degradation products from Nafion® membranes in Fenton's medium have been found to resemble those detected in PEMFC product water, using F^{19} nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry; this can be viewed as convincing support for the use of this method in membrane research [46].

Generally, Fenton's reagents are made by combining hydrogen peroxide with Fe^{2+} ions in order to produce radicals:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^\bullet + OH^- \tag{4}$$
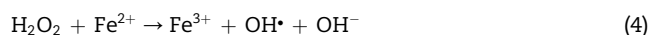
The radicals then attack the membrane and produce further radicals, such as $R\text{-}CF_2$, in the presence of excessive peroxide. In practice, trace Fe^{2+} or other contaminants such as Cr^{2+} or Ni^{2+} come from the end plates or coolants [47,48].

Peroxide solution without iron cations has also been shown capable of degrading Nafion® membrane. Qiao et al. [49] reported that the conductivity and water uptake charac-teristics of Nafion® samples decreased with H_2O_2 processing after exposure to 30% H_2O_2 solution for 30 days. LaConti et al. [38] proposed that the effect of accelerants decreased in the following order: temp. $> Fe^{+2} > H_2O_2$. They also found that the rate of chemical degradation by certain contaminant species decreased as follows: $Fe^{+2} >> Cu^{+2} >> TiO^{+2} > Co^{+2} > Pt^{+2} > Ni^{+2} > Al^{+3}$.

2.2.5. Freeze/thaw cycling and subzero start-up

A freezing environment is another severe stressor for PEM fuel cell automobile applications. It is essential for vehicle fuel cells to retain rapid start-up and good self-maintenance capabilities

from low temperatures to normal operating temperatures when they are used outdoors in cold environments. To understand membrane durability under thermal cycling conditions at subzero temperatures, McDonald and co-workers [50] examined the impact of ex-situ freeze/thaw cycles on Nafion® 112 membranes. They reported that ionic conductivity and mechanical properties changed minimally after 385 freeze/thaw cycles between −80 and 40 °C. However, the anisotropy of tensile strength, the oxygen permeability, and the water swelling behavior of the membrane decreased after the dry freeze/thaw cycles, which suggested some degree of rearrangement in the ionomer at the molecular level.

Cho et al. [51] conducted in-situ experiments and determined that performance degradation occurred after 4 thermal cycles when the temperature had been lowered to −10 °C and kept there for 1 h. The current density measured at 0.6 V was 880 mA/cm^2 before exposure to subzero temperature, then decreased to 860 mA/cm^2 and 780 mA/cm^2 after the first and fourth freeze/thaw cycles, respectively, due to phase transformation and volume change of water during thermal cycling. They also used AC impedance measurement to measure the difference in resistance between the frozen and non-frozen electrode, and this showed that the increase in ohmic resistance during the thermal cycles was due to an increase in the contact resistances but not in the proton conductivity of the PEM. The effect of water removal on PEMFC performance degradation was also examined in their subsequent research [52]. The fuel cell degradation rate decreased from 2.3% to 0.06% when the gas purging water removal method was applied to the PEMFC before the temperature dropped below zero.

Basically, the impact of super-low temperature on water within the MEA has been the subject of intense discussion in terms of the freeze/thaws and subzero start-ups of PEMFCs. The state of the water in a Nafion® membrane at subzero temperatures has been classified into non-freezing and freezing water at temperatures far below zero, since the freezing point of water in Nafion® decreases drastically compared with water under normal conditions [53]. Therefore, identifying the exact place where ice formation occurs is vital for ascertaining different temperature conditions. By using a scanning electron microscopy (SEM), Yan et al. [54] investigated the cracks, pinhole formations, and surface roughness of the membrane in frozen conditions. They concluded that membrane damage could be due to water freezing on the membrane surface, but not to water inside the membrane when it is exposed to subzero start temperatures and operation from −20 °C. Similarly, Oszcipok et al. [55] also confirmed that product water increased the membrane humidity even at −10 °C, and the membrane/contact resistance increased with the number of subzero start-up experiments, which may be good evidence to prove that water within the membrane is not frozen.

2.3. Summary

The failure modes of the PEM, primarily mechanical, chemical/electrochemical, and thermal degradation can be identified by AST methods. Other than the experiments mentioned above, other AST strategies exist, such as stress cycling under tension, high-pressure testing, and high-temperature exposure. For instance, air bleeding was carried out by Inaba et al. [56] to investigate its effects on membrane degradation in PEM fuel cells. From the viewpoint of simulating practical fuel cell operation, different stressors must be combined to estimate the durability of membrane materials. Also, different fuel cell applications and particular operating conditions are important issues to be considered when designing ASTs and exploring failure models.

Based on the degradation mechanisms addressed, several alternative membranes are being developed, including reinforced or modified PFSA membranes [57–59], alternative ionomer polymers and their composite membranes, such as SPSF (sulfonated poly-sulfone) [60], SPEEK (sulfonated poly-ether ether ketone) [61], modified PBI (poly-benzimidazole) [62], and modified PVDF (poly-vinylidene fluoride) [63]. The microstructural differences between these non-fluorinated or partially-fluorinated membranes and PFSA membranes result in different degradation mechanisms during long-term operations. For example, Sethuraman et al. [15] found that the durability of the hydrocarbon membrane under OCV operation was better than that of the PFSA membrane, while its stability in the Fenton's test was poorer. Therefore, different AST designs should be employed during durability evaluations of these membranes as compared to PFSA membranes. Overall, at the present stage questions remain about the abilities of these novel proton exchange membranes to meet the requirements outlined previously and replace the PFSA membrane for stationary and automotive applications.

3. Pt catalyst accelerated stress test

Traditionally, nanoscaled Pt (or Pt-alloy) particles (typically 2–6 nm in diameter) are supported on high surface area carbon to form a PEM fuel cell electrocatalyst. Pt/C (or Pt-alloy), together with a recast Nafion® ionomer network, forms a complex composite catalyst layer with multiple interfaces, which is critical for the transport of reactant gas, protons, electrons, and water. In this review, we concentrate on work that involves platinum metals.

3.1. Catalyst degradation mechanism

According to experimental results, degradation of catalyst layers (CLs) during long-term operation includes cracking or delamination of the layer, catalyst ripening, catalyst particle migration, catalyst washout, electrolyte dissolution (Nafion® ionomer), and carbon coarsening. All of these effects, which result either from change in the catalyst microstructure or loss of electronic or ionic contact with the active surface, can result in apparent activity loss in the catalyst layer. It is generally believed that the electrochemical surface area (ECSA) of Pt is one of the most important parameters for characterizing the apparent catalytic activity of PEM fuel cells [64–67]. Widely used methods to determine ECSA include cyclic voltammetry (CV), CO stripping voltammetry, and CO gas-phase chemisorption. Microstructural changes in catalyst layers are usually examined postmortem through transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

3.1.1. Pt agglomeration

Due to their high specific surface energy, nanoparticles have the inherent tendency to agglomerate into bigger particles. As particles grow, their surface energy is minimized and the process simultaneously slows down. Pt nanoparticle agglomeration is accelerated under harsh operating conditions, which may result in a drop in the number of active sites and hence a decreased ECSA, and this will in turn lead to performance deterioration in PEM fuel cells.

Ferreira et al. [68] analyzed degraded MEAs using TEM and hypothesized that changes in Pt particle structure occurred, according to the two processes illustrated in Fig. 3: (1) small Pt particles dissolve in the ionomer phase and redeposit on larger Pt particles that are separated from each other by a few nanometers, forming a well-dispersed catalyst; this is called "Ostwald ripening"; (2) dissolved Pt species diffuse in the ionomer phase and subsequently precipitate in the ionomer phase of the electrode or in the membrane; this occurs via reduction of the Pt ions by hydrogen that has crossed over from the anode, and is called the micrometer-scale diffusion process.

3.1.2. Pt migration

Besides increased Pt nanoparticle size, migration of Pt catalytic metals either inside the membrane or at the electrode/membrane interface also results in decreased ECSA and consequent PEMFC performance degradation.

Several studies have reported a very high concentration of Pt particles directly at the CL/PEM interface, even forming a Pt band several micrometers into the membrane after an aging test [68–72]. Rong et al. [73] found that frequent start-up/shutdown of a fuel cell, which means shorter RH periods and thermal cycles, led to an earlier onset of delamination between the Nafion® and the Pt/C agglomerate, which can undoubtedly limit the catalyst activity because of inferior proton transport at the interface.

3.2. Accelerated stressors for Pt catalyst degradation

3.2.1. Undesirable temperature and relative humidity

The effect of temperature on catalyst durability was subjected to detailed experimental study by Borup et al. [74]. They

Fig. 3 – Schematic of platinum surface area loss on the nanometer scale and the micrometer scale in the PEMFC (from [68] with permission).

concluded that the rate of Pt particle growth increased with increasing temperature. By using a conventional electrochemical cell in combination with a quartz crystal microbalance, Dam and de Bruijn [75] reported on the influence of temperature and potentials on Pt thin film dissolution in 1 M HClO$_4$ solution. It was found that the amount of dissolution was too small to measure at temperatures as low as 40 °C. When temperature was increased from 60 to 80 °C, the Pt dissolution rate increased from 0.87 ng/h cm^2 to 1.58 μg/h cm^2 when exposed to a potential of 1.15 V. They concluded that dissolution rate was accelerated by increasing the temperature and the dissolution potential, according to the Nernst equation. Cai et al. [76] investigated the thermal and electrochemical degradation of fuel cell catalysts and compared the results of these two accelerated stressors. They introduced a convenient ex-situ heat treatment of the catalyst at 250 °C in an environment containing about 0.7% oxygen and 8% water and helium (balance) to simulate long periods of electrochemical potential cycling and potential hold, and thereby to observe platinum surface area loss and carbon corrosion. The results showed that the Pt surface area loss during 10 h of thermal degradation under this condition was comparable to the loss from electrochemical degradation after 500 cycles between 0 and 1.2 V vs. the reference hydrogen electrode (RHE) for the Pt/C catalyst.

For high-temperature PEM fuel cells using commercially available H$_3$PO$_4$-doped poly-benzimidazole (PBI)-based MEAs (PEMEAS Fuel Cell Technologies), the degradation rate was also found to increase with increasing temperature [16]. When the operating temperature of the PEMFC went from 240 to 300 °C, both the membrane and the kinetic charge-transfer resistances increased dramatically, mostly due to membrane and catalyst layer degradation. Schmidt [77] recently reported the durability modes of a Celtec®-P Series 1000 MEA. Based on the in-situ high-temperature operation experimental results, the author proposed that 55% of the cathode degradation was due to increased mass transport overpotentials, 30% to reduced oxygen reduction kinetics, and 15% to increased ohmic cell resistance at the operation point of 0.2 A/cm^2 at 160 °C.

Xie et al. [78] used TEM to show morphological changes in and migrations of Pt in the anode and cathode CLs during high-humidity PEFC durability tests. During 1000-h testing, they found that cathode catalyst agglomeration occurred mainly in the first 500 h of operation. There were also significant morphological changes in the agglomeration, and migration of Pt particles occurred at the anode catalyst layer–Nafion® membrane interface. Similar experiments showed that Pt particle size growth is dependent partly on relative humidity. Borup et al. [65,74] found that Pt particle size increased with rising RH when other operating conditions were kept constant during load-cycling test. In their research on Pt surface oxidation in the PEMFC cathode at different RHs, Xu et al. [79] found that the degree of Pt oxidation increased significantly with an increase in RH from 20% to 72%, but further increase was not apparent when the RH went above 72%.

3.2.2. Potential control

A survey of the literature shows that one of the most frequently employed AST stressors for exploring MEA durability in the PEM fuel cell is potential control. Ordinary
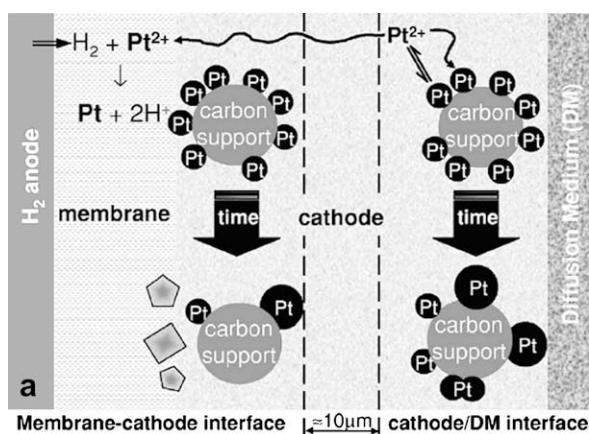
potential control protocols used to study cathode carbon corrosion and Pt dissolution/agglomeration are square (or triangular)-wave potential control and steady-state potential control at specified voltage values [7,80–82]. Generally, if the potential is lower than 0.9 V, the influence is limited to Pt catalyst degradation; otherwise, the possibility of carbon support corrosion increases. Issues related to carbon corrosion will be discussed in detail in Section 4.

A notable phenomenon is the dissolution and migration of the Pt electrocatalyst under AST potential control. Potential value plays an important role during ASTs, since higher potentials can accelerate Pt dissolvability. Dam and de Bruijn's [75] ex-situ experimental results showed that the Pt dissolution rate increased about 54-fold as the potential increased from 0.85 to 1.15 V at 80 °C in 1 M HClO$_4$ solution; the dissolution rate became saturated at 80 °C with potentials higher than 1.15 V, which they considered to be due to the formation of protected surface platinum oxide at high potentials. Wang et al. [83] also suggested that the concentration of dissolved Pt increased monotonically from 0.65 V to 1.1 V, then decreased at potentials larger than 1.1 V due to the formation of a protective oxide film.

The most serious migration of Pt is reported to occur at the cathode side of the MEA after potential cycling to OCV or higher voltages. Through an in-situ experiment, Ferreira et al. [68] found a Pt band near the cathode/membrane interface after 2000 h of open circuit operation under H$_2$/air supply conditions. Other reports of Pt migration into the PEM under OCV have also been made [70,71]. When conducting a square-wave potential between 0.87 V and 1.2 V vs. RHE, Bi and co-workers [84,85] found a Pt band in the PEM near the cathode for MEAs at different operating temperatures. Fig. 4 uses SEM–EDS to show the effect of temperature on the location of the Pt band in the PEM. Since the brighter Pt bands in the picture indicated higher Pt atom density and more Pt loss from the cathodes, the authors drew the conclusion that higher degradation temperatures resulted in greater Pt loss through dissolution. Pronounced growth and redistribution of nanoparticles as well as platinum enrichment at the anode membrane interface were also observed by Guilminot et al. [86] at potentials above 0.6 V vs. RHE, and by Xie et al. [78] for high RH conditions. According to Akita et al. [87], the Pt aggregates formed in the PEM have a well-ordered crystalline

structure after the application of a potential AST, which indicates that Pt particles seem to form nuclei and grow atomically by the deposition of dissolved Pt ionic species.

Generally, the Pt migration profile across the catalyst/membrane interface and the Pt band position in the polymer membrane are thought to be dependent on potential control during cycling [71,72], number of cycles accumulated [72], cell operating temperature [72], relative partial pressure of H$_2$ and O$_2$ [70,88], and relative humidity [72,78]. The migrated platinum particles during potential control are considered to be generated by the reduction of diffused platinum ionic species by hydrogen that has permeated through the polymer electrolyte membrane from the anode compartment:

$$H_2 + Pt^{2+} \rightarrow 2H^+ + Pt \qquad (5)$$

An interesting phenomenon is that platinum dissolution and deposition out of the catalyst layer are greatly reduced when a Pt black electrode is substituted for the Pt/C [89]. The authors attributed this phenomenon to the different Pt ion species recapturing capabilities of Pt black and Pt/C catalyst. Darling and Meyers [90,91] developed a mathematical model for potential-dependent oxidation and dissolution of metallic Pt and chemical dissolution of Pt oxide under a range of PEMFC operating conditions. They thought that Pt dissolution was activated by potential ($E > 0.8$ V vs. RHE), and that Pt^{2+} during potential cycling can be recaptured by the electrode or can diffuse to other regions of the MEA, which is somewhat helpful for understanding Pt migration from the cathode to the PEM. Guilminot et al. [92] believed that the redistribution of Pt nanoparticles and Pt^{2+} species, facilitated by the presence of F$^-$ or SO$_x^-$ that contained counter ions, was actually a very complex process related to many factors, including environmental conditions and each of the MEA components.

3.2.3. Load cycling

To better understand the durability of PEM fuel cell electrocatalysts for transportation applications, researchers have used load-cycling tests to investigate performance changes during operation under various conditions [65,93]. As an AST strategy, the load-cycling profile of a fuel cell has been found to have a significant effect on its lifetime [9,94]. Fig. 5 shows some load-cycling profiles (a, b, c) employed in catalyst ASTs
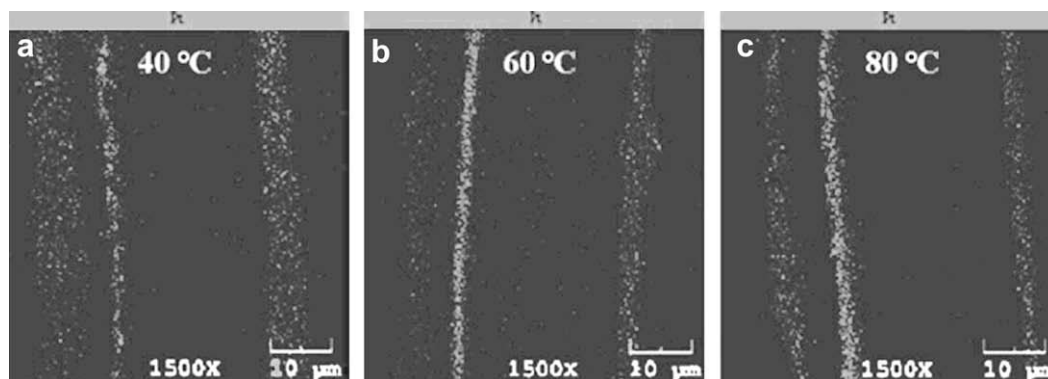

Fig. 4 – Pt distribution in degraded MEA cross-sections at different temperatures (the right side is the anode, the white band within the membrane is the Pt band) (from [84] with permission).
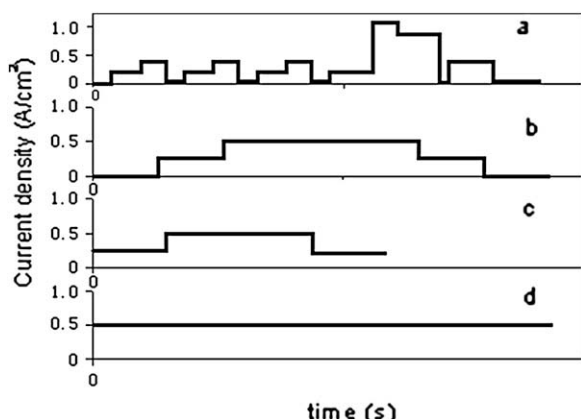
Fig. 5 – Some load-cycling profiles used in catalyst ASTs.

compared with the constant current condition (d). It is worth noting that the aging effects on profiles with and without start-up during cycling are different.

Numerous experiments have indicated that the cathode catalyst layer shows a more extensive agglomeration trend than the anode side when undergoing the same load-cycling test, which implies that the catalyst particle size increases with increasing potential. Borup et al. [65] concluded that Pt particle size distribution could exhibit bi-modal particle size distributions after extended tests simulating automotive drive cycles. In addition, the active surface area of a fuel cell electrocatalyst was found to decrease more rapidly when accompanied by increased hydrogen crossover during a load-cycling AST [42]. With respect to the investigation of load cycling in PEMFCs, it is worth noting the suggestion of Wahdame et al. [95] and Harel et al. [96] that the average value of the current over the cycle has a significant impact on the aging result. Table 2 compares constant current aging and dynamic load-cycling aging effects on PEM fuel cells. According to the experimental results, if the performance criterion is linked to aging time, the degradation rate for the fuel cell with constant current load is higher than that of the one with dynamic current load cycling. Conversely, when the same electrical charge quantities are released, the degradation is greater in the fuel cell with dynamic load cycling. Also, the degradation rate is not constant during different stages of the operation period. Since the amount of electrical charge delivered by the fuel cell is an important parameter during the evaluation process, the average value of the cell current over a dynamic cycle has a significant impact on the evaluation result.

Therefore, the criteria for comparing different profiles of load cycling should be carefully considered in order to obtain accurate conclusions during different aging processes.

Under conditions of dramatic load changes, corrosion of the carbon support due to fuel starvation can also lead to the aggregation of Pt catalyst particles, which will ultimately result in fuel cell durability losses.

3.2.4. Contamination

Among PEMFC operating conditions, one of the most likely causes of severe degradation or failure is contamination of the electrocatalyst or membrane. In general, contamination can be categorized into two groups based on the source: fuel contaminants and air contaminants. On the fuel side, most contaminants probably arise from the H_2 production process, including hydrocarbons (CH_4), carbon oxides (CO and CO_2), sulfur compounds (H_2S and sulfur organics), and ammonia (NH_3). On the air side, possible contaminants include nitrogen oxides (NO and NO_2), sulfur oxides (SO_2 and SO_3), carbon oxides (CO and CO_2), ozone, and other organic chemical species. There are also some other system-derived contaminants, including trace amounts of metallic ions (Fe^{3+}, Ni^{2+}, Cu^{2+}, Cr^{3+}, Na^+, Ca^{2+}) or silicon from system components (bipolar metal plates, membranes, sealing gaskets, storage system, etc.) [97]. In the literature, the most extensively investigated contaminant is CO. Currently, the most effective and popular method of mitigating the CO effect in PEMFCs is to use a Pt–Ru/C electrocatalyst.

For both anode and cathode catalyst layers, the most influential theory about the effect of impurities is catalyst site poisoning and decreased catalyst activity. Even trace amounts of impurities in the reactant gas are likely to reduce fuel cell performance due to kinetic losses, especially in long-term operation. Garzon et al. [98] observed that performance losses were evident after just 4 h of exposure to 1 ppm of H_2S in hydrogen. The cell was almost completely deteriorated after 21 h of operation at a constant voltage of 0.5 V and the same H_2S concentration. When the test was continued, now operating on ultra-pure H_2 for many hours, no significant recovery occurred, indicating the irreversibility of the H_2S poisoning process. Cyclic voltammetry results demonstrated the presence of sulfur species chemisorbed onto the Pt surface. The authors also found negative effects on PEMFC performance even with levels of H_2S as low as 10 ppb. Some other sulfur-containing species such as SO_2 are also contaminants that can create irreversible effects in the MEA and have a strong negative impact on cell performance. According to Mohtadi et al. [99], the rate of SO_2 poisoning at the cathode was found

Table 2 – Comparison of the degradation rate of a 3-cell stack under constant current aging and dynamic load-cycling conditions.					
100 cm² 3-cell PEMFC stack operating conditions		Degradation rate in different stages (mV/h)			
		Constant current, 0.5 A/cm²		Dynamic load cycling, average current 0.125 A/cm²	
Fuel/oxidant	Dry H_2/humidified air	0–350 h	Constant	0–500 h	0.1
Air dewpoint	25 °C	350–400 h	3	500–700 h	A little improvement
Cell temperature	55 °C	400–600 h	0.22	–	–

to be strongly dependent on the bulk concentration of SO_2. For instance, the poisoning effect of 5 ppm SO_2 was more severe than that of 2.5 ppm. Similarly, Wang et al. [100] demonstrated that the poisoning ability of SO_2 depended not only on the dosage, but also on its concentration in the air. SO_2 could cause severe degradation in cell performance when its air concentration was as low as 0.1 ppm.

However, for some kinds of contaminants in the feeding gas, such as NO_2, the negative influence on the fuel cell is reversible when the contaminating gas is switched to pure reactant gas after poisoning. Experimental results show that fuel cell performance can be recovered after applying neat air (Fig. 6) [99]. CV spectra for the clean and poisoned MEA indicate that the poisoning mechanism of NO_2 is not catalyst surface poisoning. This could be because of an ionomer and/or catalyst–ionomer interface effect due to the formation of NH_4 from NO_2.

Some impurities, such as NH_3, degrade the fuel cell to different degrees depending on the impurity level and the time of cell exposure. Uribe et al. [101] proved that high trace levels (e.g., 30 ppm) and long exposure (e.g., 15 h) to NH_3-contaminated fuel resulted in severe and irreversible disability of the PEMFC even after several days of operation on pure hydrogen. The conductivity of the membrane was also found to be affected after longer exposure to NH_3. In contrast, degradation after short periods of exposure (1–3 h) could be fully recovered. The primary reason for cell degradation was the replacement of protons by NH_3 ions within the catalyst layer and a drop in membrane conductivity after long-term exposure.

Currently, combining a stressor with impurity mixtures has drawn considerable attention. Using a hydrogen mixture of H_2S (10 ppb), CO (0.1 ppm), CO_2 (5 ppm), and NH_3 (1 ppm), which simulated the preliminary maximum allowable fuel impurity specifications, Garzon et al. [98] operated a 50 cm^2 fuel cell at 0.8 A/cm^2 for 1000 h at 80 °C. The authors attributed the total performance loss of 100 mV to NH_3 and H_2S impurities in the fuel supply, as apparently very little was attributable to CO and CO_2. The CV spectrum showed that about 40% of the Pt surface was covered with adsorbed H_2S during 1000 h of exposure; they explained the lack of CO adsorption from the multi-component test as due to competitive adsorption effects.
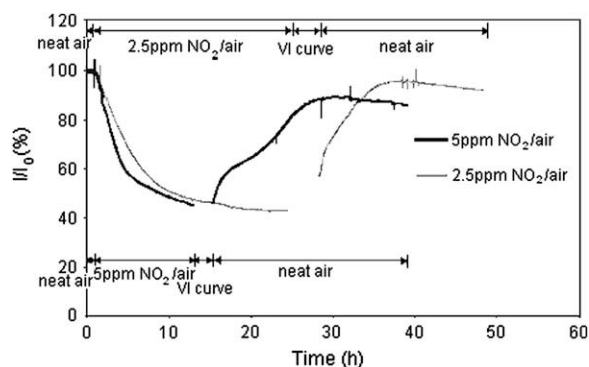

Fig. 6 – Transient response of cell performance exposed to 2.5 and 5 ppm NO_2/air (with the same dosage of NO_2) and the recovery process (from [99] with permission).

3.3. Summary

Electrocatalyst degradation mechanisms depend on factors such as potential, temperature, humidity, contaminants, and carbon support stability. AST stressors can be any combination of these factors when testing is conducted in a complex environment. Table 3 classifies the general reasons for catalytic activity loss in Pt-based catalysts and their characterization techniques. It can be seen from the table that more analysis methods, such as techniques to measure the amount of Pt loading and the effective catalytic sites, are needed to characterize changes in the catalyst state during degradation testing. Also, more work is needed to understand in depth the connection between the in-situ degradation model and the post-mortem analysis. For example, a fundamental understanding of the relationship between microstructural change in the catalyst and decreased cell performance after aging should be developed through both experimental design and mathematic modeling. This will help in the search for more effective methods to improve the durability of PEMFC catalysts in the near future.

According to the currently understood decay mechanisms, a high-durability PEM fuel cell in practice requires the development of a catalyst with proper resilience to sintering and corrosion under universal working conditions. Therefore, current work on improving the durability of PEMFC electrocatalyst is focused mainly on using Pt-alloy catalysts, lowering Pt loading, improving dispersion of Pt particles on the carbon support, improving the stability of the carbon support, and optimizing the fuel cell operating conditions. Some reports have demonstrated that Pt-alloy catalyst containing cobalt shows significantly improved stability in potential cycling compared with unalloyed platinum. This is explained by the Pt–Pt bond distance and surface electronic properties [102–105]. Non-precious metal catalysts are also under development to increase the durability and lower the cost of PEM fuel cells.

4. Carbon corrosion accelerated stress test

Carbon is an excellent material for supporting electrocatalysts, allowing facile mass transport of reactants and fuel cell reaction products, and providing good electrical conductivity and stability under normal conditions [106]. However, under prolonged conditions of high temperature, high water content, low pH, high oxygen concentration, and/or high potential [107], oxidation of carbon (carbon corrosion) is prone to acceleration. Carbon oxidation or corrosion weakens the attachment of Pt particles to the carbon surface, and eventually leads to structural collapse and the detachment of Pt particles from the carbon support, which results in severe Pt agglomeration and performance degradation during long-term operation. In addition, when carbon oxidizes to form surface groups, it changes the hydrophilicity of the electrode, causing the development of wettability and probably slackening mass transport during long-term operation of the PEM fuel cell [108,109].
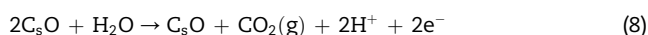
4.1. Carbon corrosion mechanism

Carbon corrosion may occur via a chemical or an electrochemical route [86,106]. More specifically, carbon oxidation

Table 3 – General reasons for catalytic activity loss in Pt-based catalysts.

Classification of catalytic activity losses	Failure mechanisms	Characterization techniques	AST examples
Catalyst agglomeration	Ostwald ripening; thermal sintering	SEM; TEM; CV; XRD	[42,65,74,76,77,95]
Catalyst migration	Metal dissolution and re-deposition	SEM-EDS; TEM	[68,70,71,78,84–86,88]
Catalytic sites poison	Contamination from the gas supply or system	CV; EIS	[98–101]
Others	Layer delaminations; Pt trapped in the ionomer, etc.	SEM; TEM; EIS	[51,73,141]

takes place along two pathways that are believed to proceed by electron transfer, followed by hydrolysis and CO_2 production, as follows: 1) incomplete oxidation leading to the formation of surface groups (Eqs. (6) and (7)); 2) complete oxidation leading to gaseous carbon dioxide (Eq. (8)) [110].
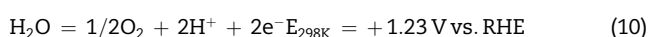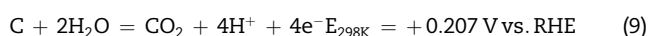
$$C_s \rightarrow C_s^+ + e^- \tag{6}$$

$$C_s^+ + H_2O \rightarrow C_sO + 2H^+ + e^- \tag{7}$$

$$2C_sO + H_2O \rightarrow C_sO + CO_2(g) + 2H^+ + 2e^- \tag{8}$$

The subscript "s" denotes the surface species.

In actual fact, carbon corrosion will not be severe under normal operating conditions when the potential is between 0.4 and 0.7 V. Therefore, within this potential range the impact of carbon instability is limited for PEMFC electrocatalyst durability. However, the corrosion reaction is markedly accelerated under extreme conditions, especially at abnormal potentials. For instance, when voltage reversal occurs during cell operation, carbon support oxidation becomes so serious that it can cause irreversible damage to fuel cells [111–114]. This situation can be observed when the fuel cell experiences fuel starvation resulting from bad flow distribution, gas blockages, or sudden current change to heavy load in transient conditions, as well start-up and shut-down processes. According to the literature, during unprotected and frequent start-up as well as prolonged shut-down of a fuel cell, local cathode potential can reach 1.5 V due to partial hydrogen coverage in the anodes, which significantly accelerates carbon corrosion [115,116].

4.2. Accelerated stressors for carbon support degradation

4.2.1. Fuel starvation

The carbon corrosion reaction that takes place at the electrode as a result of gross fuel starvation should be the direct cause of the electrocatalyst's degradation. When the fuel is insufficient to provide the expected current for the PEM fuel cell, the potential value of the anode continues to increase. With fuel starvation, the cell potential will decrease to a value substantially below normal and even drive the cell into reverse operation, with the anode potential higher than the cathode potential. This state entails water electrolysis and carbon oxidation at the fuel cell anode in order to provide the required protons and electrons for the oxygen reduction reaction happening at the cathode. The reactions are as follows [117]:

$$C + 2H_2O = CO_2 + 4H^+ + 4e^- \quad E_{298K} = +0.207\,V\,vs.\,RHE \tag{9}$$

$$H_2O = 1/2O_2 + 2H^+ + 2e^- \quad E_{298K} = +1.23\,V\,vs.\,RHE \tag{10}$$

Using TEM, EDX, and electrochemical methods, Taniguchi et al. [118] characterized electrocatalyst degradation caused by fuel starvation and found severe surface area loss of the electrocatalyst, as well as a drop in cell performance due to carbon support corrosion after cell reversal. The potential change of the anode and cathode during a cell reversal experiment is shown in Fig. 7. Mayer and Darling [114] developed a model to explain the reverse-current mechanism and suggested that the carbon corrosion rate induced by fuel starvation can be mitigated by careful system control and design.

4.2.2. Start-up/shut-down cycling

Another mode of carbon corrosion arises from non-uniform distribution of fuel to the anode and the crossover of reactant gas through the membrane. A fuel cell used in an automotive system is expected to experience 30,000 start-up/shut-down cycles during its life [119]. Both start-up and prolonged shut-down can result in this kind of carbon corrosion [120]. It was demonstrated that the air/fuel boundary [112], which may also be described as partial hydrogen coverage [111], developed under these conditions caused extremely rapid corrosion of the carbon support in the cathode, resulting in dramatic declines in catalyst active surface area and fuel cell performance.

Reiser et al. [121] ascribed this decay to the anode electrode being partially filled with hydrogen, and modeled this phenomenon using simplified mathematical approaches, thereby obtaining an electrolyte potential profile. Fig. 8 shows a schematic illustration of the reactions when an air/fuel
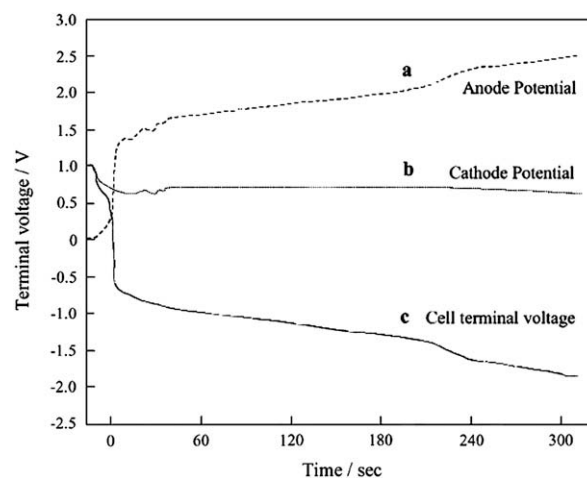

Fig. 7 – Time-dependent changes in anode and cathode potential during a cell reversal experiment (from [118] with permission).
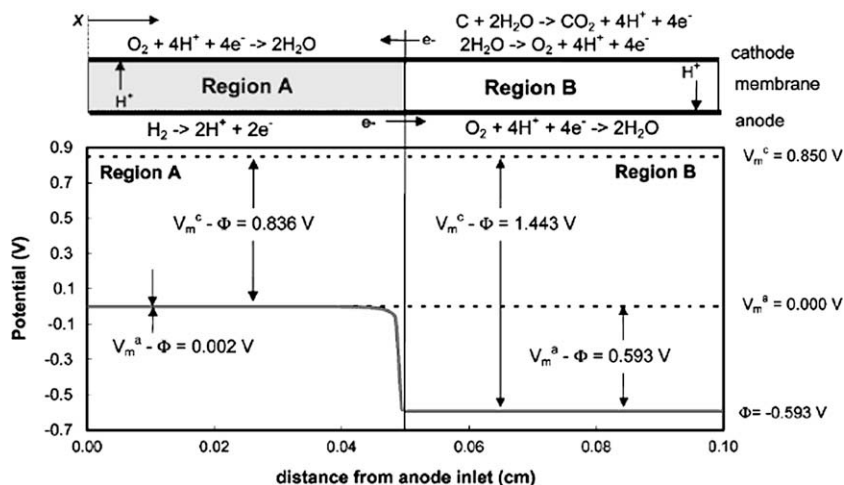
Fig. 8 – A schematic illustration of potential distribution along the anode flow path under reverse-current conditions; region A denotes the section of the cell where hydrogen is available; region B denotes the section exposed to oxygen (from [121] with permission).

boundary is formed at the anode. The authors concluded that the oxygen crossover from the cathode side was sufficient to cause a reverse-current condition.

Similarly, Tang et al. [112] explained this phenomenon with the air/hydrogen boundary theory, using both single-cell and dual-cell configurations. According to the experimental results, the most evident damage was found within the first 30 cycles of the corrosion process, when air and fuel were fed to the anode alternatively. The cathode ECSA loss was as high as 70% after 80 such cycles.

Carbon corrosion following this mechanism can also explain why the cathode layer, after start-up and shut-down aging, is normally thinner than the anode layer [112,121]. The sharp voltage change might also cause some damage to Nafion®, and the combination of these effects could entirely explain MEA degradation during ASTs involving start-up/ shut-down cycles [112,114].

4.2.3. Cold start-up at subzero temperatures

Cold start-up at subzero temperatures is another factor related to PEMFC degradation induced by carbon corrosion. Future experimental and simulation research is expected to dramatically advance our understanding of catalyst and carbon corrosion.

During cold start-up in subzero environments, water produced in the electrodes may freeze instantaneously in the catalyst layers, covering the electrochemical active sites and hence reducing reaction capability, as well as plugging the pores through which the reactant would normally pass. Therefore, carbon corrosion is more prone to happen under this condition due to local reactant starvation. It has been suggested that reduction in the catalyst ECSA, membrane damage, and layer delamination might be the major mechanisms leading to cell degradation under cold start-up conditions [53,122].

Since ice formation is the main reason for local starvation and subsequent carbon corrosion in cold start-up, much attention has been paid to determining the lowest

temperature at which fuel cells can start and successfully survive. Hishinuma and co-workers [123] studied the cold start-up performance of a single cell under a variety of operating conditions (−25 to −3 °C) and compared the results with simulations. Modeling analysis estimated that the heat generated by the fuel cell might be enough to warm it up from cold start at −5 °C, but external heat would be necessary for start-up below this temperature. However, Oszcipok et al. [124] reported that start-up of a portable fuel cell stack was possible at −10 °C. They suggest that at lower temperatures, although the initial droplets of water formed on the cathode catalyst surface will not freeze due to the super-cooling effect, the small water droplets will coalesce into large ones and refreeze if the cell is not rapidly brought above 0 °C.

4.2.4. Potential control

The rate of the carbon corrosion reaction is highly dependent on potential. During normal fuel cell operation, the highest potential the cathode encounters will be the OCV, which is 1.0 V or slightly lower. Makharia and co-workers [119] estimated a carbon weight loss of approximately 2–5% at idle (0.9 V vs. RHE) and OCV in a 2000-h test at 80 °C, respectively. Carbon corrosion was observed to increase with increasing potential when subjected to potential cycles from 0.1 V to 0.96 V, 1.0 V, 1.2 V, and 1.5 V [74]. Roen et al. [125] characterized the influence of platinum on carbon corrosion in a Pt/C catalyst by on-line mass spectroscopy during cyclic voltammetry at temperatures lower than ~50 °C. The results showed that carbon corrosion could only happen at potentials of ~1.1 V (vs. RHE) and higher when Pt was not present in the carbon electrode layer. By comparison, when 10% Pt was present, the CO_2 peak occurred at 0.55–0.6 V (vs. RHE). Similarly, according to the experimental results of Maass et al. [126], hydrogen peroxide formed on a carbon support and platinum catalyst led to increased corrosion at low potentials. Exposure time and high potentials indirectly influenced carbon oxidation because they led to the formation of platinum oxide layers. Carbon surface oxides such as phenols,

quinones, lactones, and carboxylic acids have also been detected by physical methods, including infrared spectroscopy [126], X-ray photoelectron spectroscopy [127], thermal desorption of surface oxides [108], and electrochemical methods [86].

4.3. Summary

Carbon corrosion has been identified as a crucial degradation mechanism, especially in automotive applications. Factors such as temperature [128], potential cycling [106], and humidity [126] can affect carbon corrosion. Potential control AST is the most widely used technique for the exploration of carbon support degradation, since carbon durability is more sensitive to high potential than to other conditions. Also, many stressors for carbon durability stem from the effects of potential on carbon.

The preferred strategy to reduce the negative influence of carbon oxidation on fuel cell performance is to use alternative, more stable materials as catalyst supports. It has been proposed that new types of carbon, such as carbon nanotubes (CNTs) and other novel carbon structures with higher graphite components, show greater stability than normal carbon black as support materials for PEMFCs [115,129–131]. Other species of materials, such as indium tin oxide (ITO) [132] and titanium oxide (Ti_4O_7) [133], have also demonstrated potential as novel catalyst supports in PEMFCs. However, little work has been published on the long-term stability of carbon substitutes used in PEM fuel cells. Some system strategies are also expected to successfully mitigate carbon corrosion in practical applications [134].

5. Gas diffusion layer accelerated stress test

The gas diffusion layer (GDL) is a typical carbon-based porous dual-layer substrate between the flow field and the catalyst layer. To increase the contact angle with water and prevent flooding, hydrophilic carbon materials are impregnated with a hydrophobic agent such as poly-tetrafluoroethylene (PTFE). To decrease the contact resistance and add a further control layer for water transport, there is always a thinner microporous layer (MPL), comprised of carbon powder and PTFE, between the CL and the GDLs [135]. In addition, there were new findings showed that the presence of MPL can improve the durability of the fuel cell to some extent [136]. Major degradation of the GDL and MPL is related to deterioration in mass transport function due to material loss.

5.1. Gas diffusion layer degradation mechanism

GDL function includes reactant transport, water transport, electronic conduction, thermal conduction, and mechanical support [137]. With respect to maintaining a mass transport balance, especially the proper equilibrium between water production and removal, the GDL has a significant role in terms of durability. The hydrophilic pores are for the transport of water and the hydrophobic pores for the transport of gases. The numbers of these two pore types should remain relatively stable overall to maintain normal mass transport

in the fuel cell. Ineffective water management will lead to liquid-phase water blockage (flooding) and mass-transport-limited performance, or to decreased proton conductivity as a result of ionomer dehumidification. Moreover, when water droplets in the GDLs block the transport of reactant gases to the CLs, local fuel starvation will occur and then induce carbon corrosion of the MPL, since its primary constituent is carbon.

5.2. Accelerated stressors for the gas diffusion layer

To date, only a limited number of studies have focused on durability and degradation issues for the GDL, even though more and more evidence has demonstrated that further investigation is needed. Thus, the effect of water management on GDL degradation is the least understood of the different degradation factors.

5.2.1. In-situ stressors
AST results show that loss of hydrophobicity is dependent upon operating conditions. For example, Borup et al. observed that loss of GDL hydrophobicity increased with operating temperature [65]. They also found that the performance loss of a GDL aged in nitrogen was less aggressive than for one aged in air, and ascribed this result primarily to MPL degradation.

Experimental findings have proven that PTFE concentration, which is related to the hydrophobic character of the MEA, changes during fuel cell operation. Wood et al. [138] used SEM to identify noticeable changes in the microstructure of the GDL's PTFE particles after extended operation. Schulze et al. [139] reported PTFE decomposition associated with a decrease in electrode hydrophobicity after 1600 h of operation with non-humidified reactant gases. The same authors also reported that PTFE decomposition, which results in critical water imbalance and partial loss of electrochemical performance, can be determined by X-ray photoelectron spectroscopy (XPS) [140].

As to the influence of freeze/thaw cycles on GDL stability, Kim et al. [141] reported interfacial delamination between the CL and GDL after 100 freeze/thaw cycles from −40 °C to 70 °C, which resulted from ice formation and in turn significantly increased GDL deformation. In order to test probable performance degradation Mukundan et al. [142] conducted freeze/thaw cycles down to −80 °C using dry ice. Their experimental results proved that multiple cycles could lead to interfacial delamination and GDL failure of the fuel cell, and that the preparation procedure for the MEA and the type of GDL could have a significant impact on freeze/thaw durability.

In addition, prolonged or repeated pulses of H_2 starvation and high potential control should cause further damage to the anode MPL and the GDL by way of microstructural and characteristic changes, since both of these components are carbon-based. For example, reduced GDL surface hydrophobicity in cold-start conditions has been observed by Oszcipok and co-workers [55]. From the perspective of the mass loss effect, high flow rate and hot pressing can also become GDL AST stressors to obtain useful information about GDL degradation during fuel cell operation. Unfortunately, research publications in these areas have not been identified.

5.2.2. *Ex-situ stressors*

To avoid potential confounding effects from other adjoining components in durability tests, many research studies have examined GDL degradation using ex-situ methods, which make possible individual GDL aging without the operation of an entire cell or stack.

Frisk and co-workers [143] submerged the GDL in hydrogen peroxide solution to simulate a complex environment during fuel cell operation, and detected weight loss and MPL contact angle increase in the GDL. Wood et al. [144] performed ASTs on GDLs by immersing the samples in liquid water at different oxygen concentrations and temperatures. Results showed that hydrophobicity decreased with exposure time and increased with water temperature, especially at higher oxygen concentrations. Lee and Mérida [145] investigated GDL compressive strain under steady-state and freezing conditions through a series of experiments. A maximum strain of 0.98% was measured over 1500 h of aging. The effects of freezing conditions on GDL properties – i.e., electrical resistivity, bending stiffness, air permeability, surface contact angle, porosity, and water vapor diffusion – were also studied in detail. The authors believed that freezing conditions weakened the MPL structurally and exacerbated material loss from air flow through the GDL. Also, air permeability increases of 18% and 80% were observed for in-plane and through-plane flow, respectively; this effect was attributed to material loss during the permeability test.

5.3. *Summary*

The durability research on GDL degradation, as well as effective characterization techniques, is relatively limited, although much attention has been paid to it more recently. Current understanding suggests that changes in the microstructure and surface characteristics of the GDL, which are mainly due to material loss and pore size distribution shifts, can cause changes in the water content level and transport properties of the MEA. Further AST methods and characterization protocols are expected to be developed to improve our understanding of GDL degradation and aging, which will aid progress in mitigating GDL degradation.

6.   Concluding remarks

To advance our fundamental understanding of PEM fuel cells, studying the degradation of MEA components during long-term operation and by accelerated stress tests are equally important methods. The AST is a shortcut to explore correlations between MEA microstructure and PEM fuel cell performance, with the goal of commercialization. Through experimental approaches, significant progress has been made in identifying different stressors and understanding their effects on PEMFC performance degradation. In terms of PEMFC material degradation research, the current primary focuses of R&D are membrane degradation, carbon corrosion, and platinum degradation. At the same time, more and more attention is being paid to degradation of the GDL and its properties with respect to water management. It is worth noting that establishing standardized accelerated test protocols and formal standards to evaluate the durability of various fuel cell components has been suggested by the U.S. Department of Energy [146,147], the U.S. Fuel Cell Council [148], and other research institutions.

As a fuel cell is a complex system with complicated interfaces between each of the conjoined parts, working conditions play important roles with respect to cell integrity, which is reflected in performance decay. However, our current understanding of the degradation mechanisms in cell components, especially regarding co-effects and interaction effects, is still not deep enough to provide sufficient direction for improving PEMFC durability. How to quantify degradation for each component is another problem. A great deal of effort has been put into studying the structural changes in individual components after long-term operation under various stressor conditions, while relatively little attention has been paid to predicting the lifetime of the whole fuel cell based on known information, whether from the viewpoint of pre-operation designs or of post-operation analysis. To date, efforts to predict fuel cell lifetimes based on experimental AST data are very limited. The only two detailed reports found were distributions of MEA lifetime predictions done by Pierpont et al. [3] and Marrony et al. [149]. Additional work is needed to correlate AST results with real-world lifetimes of PEM fuel cells. In addition, as progress is made on developing ASTs for PEM fuel cell degradation, in-situ monitoring and diagnostic techniques are expected to differentiate the individual contributions of each failure component under specific operating conditions.

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