

Review

# Understanding and approaches for the durability issues of Pt-based catalysts for PEM fuel cell

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## Abstract

The state-of-art understanding of durability issues (the degradation reasons and mechanisms, the influence of working conditions, etc.) of Pt-based catalysts for proton exchange membrane fuel cell (PEMFC) and the approaches for improving and studying catalyst durability are reviewed. Both carbon support and catalytic metals degrade under PEMFC conditions, respectively, through the oxidation of carbon and the agglomerate and the detachment from support materials of catalytic metals, especially under unnormal working conditions; furthermore, the degradation of carbon support and catalytic metals interact with and exacerbate one another. The working temperature, humidity, cell voltage (the electrode potential and the mode applied on the electrode), etc. can influence the catalyst durability. Carbons with high graphitization degree as support materials and alloying Pt with some other metals are proved to be effective ways to improve the catalyst durability. Time-effective and reliable methods for studying catalyst durability are indispensable for developing PEMFC catalysts.

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**Keywords:** Proton exchange membrane fuel cell (PEMFC); Electrocatalysts; Durability; Degradation; Accelerated degradation test (ADT)

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## 1. Introduction

Proton exchange membrane fuel cell (PEMFC) is considered as an ideal power source for mobile and stationary application. However, presently several factors (e.g., lifetime, reliability and

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cost) are hindering the commercialization of PEMFC. Lifetime of PEM fuel cell is the most important one and may change other factors [1], the requirement of which ranges from 5000 operating hours for car applications, up to 20,000 operating hours for bus applications and up to 40,000 operating hours for stationary applications [2]. Therefore, there is a rapidly growing interest in the investigation of performance degradation of PEM fuel cells and the degradation of the component materials [1,3]. The degradation of carbon-supported Pt (Pt/C) and its alloy (PtM/C) catalysts is one of the most important factors that decrease the operation life of PEMFC [4–7]. The durability of catalysts is of significance not only for lengthening PEMFC operation life, but also enhancing the reliability and reducing the total lifetime cost (gauged in US\$ kW<sup>-1</sup> h<sup>-1</sup>) [5].

The electrochemically active Pt sites in the membrane electrode assembly (MEA) are the only effective ones for fuel cell electrode reactions. So the more the sites of electrochemically active Pt (e.g., electrochemical surface area, ESA), the higher the performance of fuel cell electrodes. Most reports reveal that during PEMFC operation, Pt nanoparticles usually agglomerate or fall off from carbon support, as shown in Fig. 1, which results in the decrease in the ESA and consequently deteriorates the performance of PEMFC [2,8]. The carbon support can be

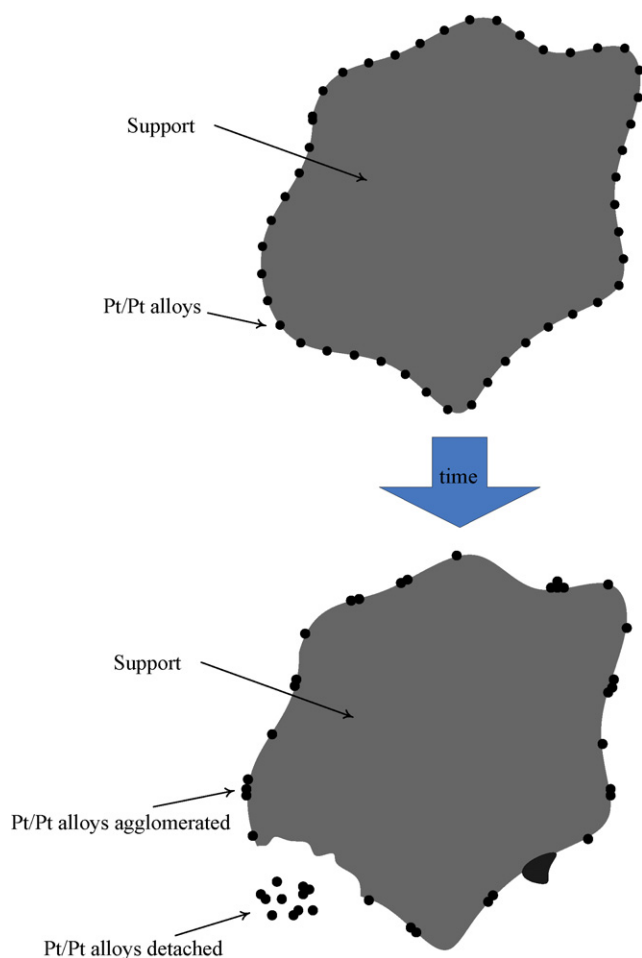


Fig. 1. Schematic representing Pt agglomeration on and Pt detachment from support material surface.

oxidized under PEMFC conditions which also degrades the performance of PEMFC [9–12]. The degradation mechanism is still being investigated and the approaches for improving the catalyst durability are also under extensive exploration. Great progresses have been achieved in this field in the past years. However, there are still discrepancies on catalyst durability [13–16], especially on the degradation mechanism of Pt/C (PtM/C) under PEM fuel cell conditions [17,18].

The state-of-art understanding of the durability issues of Pt-based catalysts under real or simulated PEMFC conditions is reviewed based on the selected reports from peer-reviewed journal publications. The approaches to improve catalyst durability and the methods for studying catalyst durability issues are also discussed. An insight into the future research and development of durable catalysts for PEMFC is provided.

## 2. Degradation model/mechanisms

### 2.1. Why catalysts degrade

The size of Pt-based catalyst used in PEMFC is in nanometer scale, usually in the range of 2–6 nm. Nanoparticles inherently [7,19] show a strong tendency to agglomerate due to their high specific surface energy [20]. For nanoparticles, the smaller the size, the higher the specific surface area, and the easier to agglomerate/sinter [7]. So when Pt nanoparticles agglomerate to bigger ones, the electrochemical surface area of Pt catalysts decreases, and consequently the performance of PEMFC degrades. In addition, as can be seen from the following, this coarsening process can be accelerated under PEMFC conditions.

PEMFC is operated under an extremely harsh condition [7,9,10,21]. The anode catalysts are exposed to a strong reducing H<sub>2</sub> atmosphere; for the cathode, the catalysts are under strongly oxidizing conditions: high oxygen concentration, high potential [ $>0.6$  V versus the standard hydrogen electrode (SHE)], and sometimes to see too high potentials (e.g.,  $>1.2$  V) for short periods of time [12]. In order to get higher efficiency, increasing cell voltage is the only way [22], which results in an increase of electrode potential in cathode, under which surface oxides of Pt are formed [18,23–26], which not only decreases the Pt activity toward oxygen-reduction reaction (ORR), but also accelerates the degradation of Pt catalysts. In addition, both the anode and cathode of PEMFC are operated under the condition of low pH ( $<1$ ), high temperature (80 °C or above), and with significant levels of water in both vapor and liquid phase. So the corrosion of Pt/C (PtM/C) catalysts, both catalytic metals and the support materials, is a common problem for PEMFC.

The degradation of catalysts can be exacerbated under unnormal operating conditions. The corrosion of catalysts in PEMFC under open-circuit situation is higher than when the current flows [27]. In the case of fuel starvation, i.e., hydrogen is no longer available to be oxidized [2], the anode potential will rise to that enough to oxidize water (if water is available) which can produce oxidative species, or the carbon support at the anode is oxidized instead (if water is not available). In the case of start–stop procedures, there might be local hydrogen starvation [11], that means that the anode is partially exposed to hydrogen and par-

tially exposed to air [28], which can raise the cathode interfacial potential difference to about 1.44 V [11], sometimes cathode potential as high as two times of open-circuit voltage (OCV) [28], at which the carbon in the catalyst layer can be corroded completely within a few hours. This is called the “reverse current” phenomena [11]. Oxygen crossover from the cathode to the anode can also cause the “reverse current” phenomena [11]. The oxidation of carbon can be further catalyzed by the presence of platinum [27,29–31]. When carbon support is oxidized, Pt or Pt alloy falls off carbon and the electrochemical surface area is decreased. Cell reversal during PEMFC operation with fuel starvation leads to severe ruthenium loss in PtRu catalyst [32].

## 2.2. Degradation mechanisms

The degradation of catalysts includes the two aspects of catalytic metals (Pt or Pt alloys) and carbon support, which influence each other. The catalytic metal, especially Pt catalyzes the oxidation of carbon [33,34], and the oxidation of carbon accelerates Pt sintering [9].

### 2.2.1. Carbon corrosion

As to the degradation of carbon support, there are almost no discrepancies on the oxidation of carbon. Carbon oxidation is often observed in an electrochemical system, according to  $C + H_2O \rightarrow CO_2 + 4H^+ + 4e^-$ , the thermodynamic potential at standard conditions for which reaction is only 0.207 V [35], which means that the electrochemical oxidation of the carbon is thermodynamically possible above 0.2 V [29]. Differential electrochemical mass spectroscopy (DEMS) investigation on the electrochemical oxidation of carbon reveals that in the presence of Pt,  $CO_{surf}$  is formed on the carbon at  $E > 0.3$  V (RHE), which is oxidized to  $CO_2$  at potentials between 0.6 and 0.8 V (RHE) [31].

In the presence of water, carbon can also be consumed through the heterogeneous water–gas reaction:  $C + H_2O \rightarrow H_2 + CO$  [12], especially in the presence of Pt, even though the rate of this reaction might be lower than that of the electrochemical oxidation at the cathode in PEMFC conditions [36,37]. The reaction product CO might poison the catalyst Pt. The reaction rate of carbon combustion increases as the platinum loading increases [38] because the higher the Pt loading, the more the interfacial area between Pt and carbon and the larger fraction of the carbon is in the “reactive zone”, implying that platinum catalyzes carbon combustion [12,39]. It is possible that the more efficient a catalyst is for the oxygen-reduction reaction, the more likely it is that the carbon support can degrade chemically through a water–gas type of reaction [12]. As expected, the degradation rate of carbon support increases with the temperature [21,38]. The properties of carbon can also influence its degradation rate [12]: carbon support with a higher degree of graphitization and/or a lower specific surface area exhibits an alleviated degradation. Either  $CO_2$  or CO formed during carbon oxidation decreases the amount of carbon available for Pt loading, which forces Pt nanoparticles fall off the carbon support and decreases the electrochemical surface area. On one other side, oxygen-

containing groups (e.g., carboxyl, carbonyl, hydroxyl, phenol, etc.) can also be formed on carbon surface under oxidative conditions [9,10,37,40]. The presence of oxygen-containing groups can both decrease the conductivity of catalysts and weaken the interaction between the support and the catalytic metal nanoparticles which results in an accelerated sintering of catalytic metal nanoparticles [9,10,41]. The electrochemical corrosion of the carbon surface leads to changes in the surface chemistry of the carbon and an increase in hydrophilicity for the catalyst layer and gas diffusion layer, which result in a decrease in the gas permeability [29] and might affect the water transport mechanisms which leads to ‘flooding’ of pores [16]. Carbon corrosion will increase the electrode resistance by decreasing the thickness of the catalyst layer [19] and thus decreasing the electric contact with the current collector [42,43].

### 2.2.2. Catalytic metals

It is generally believed that the electrochemical surface area of Pt is one of the important parameters for characterizing a fuel cell electrode [7,9,17]. A larger ESA implies a better electrode, as more catalyst sites are available for electrode reactions. It is reported that the performance degradation of PEMFC is largely due to the ESA loss of the electrodes [8,44]. The decrease in ESA mainly results from the increase of Pt or Pt alloy nanoparticle size, the dissolution of Pt and/or other alloyed catalytic metals into the electrolyte, and the detachment of Pt and/or Pt alloy nanoparticles from the carbon support. But so far, there is still no agreement on the respective contribution of the above factors to the total decrease in the ESA [17].

As to the increase in catalytic nanoparticle size, i.e., the sintering/agglomeration of Pt or Pt alloys, there are several fundamentally different pathways [4,17,19,45]: (i) Pt dissolution and redeposition [46,47], which is also called “Ostwald ripening”, (ii) the coalescence of Pt nanoparticles via Pt nanocrystallite migration on the carbon support [48–51], (iii) the transport of Pt atoms on the carbon support, so-called “2D Ostwald ripening” as compared with the case of (i), which is also called “3D Ostwald ripening”. There is still no agreement on which pathway mentioned above dominates the observed ESA loss [17]. Several approaches have been tried for this issue. Due to the potential-dependent solubility of platinum species in the electrolyte, there should be potential-dependent ESA loss for Pt dissolution/redeposition mechanism, which is observed in the case of concentrated phosphoric acid [46,52,53] or  $H_2SO_4$  aqueous solution [13]. The presence of Pt species in the polymer membrane [19,54,55] after extended life testing is another evidence for dissolution/redeposition mechanism [52,53]. Soluble platinum species have been found in the water collected from the reactant gases exiting the cell [15]. The evidence for the crystallite migration and coalescence mechanism is that in the case without electrolyte [49,56], Pt sintering in Pt/C catalysts is observed in gas-phase heating but is insignificant at low temperatures in the gas phase [13]. In the temperature of 125–195 °C, no noticeable platinum particle sintering occurred during long-term (3000 h) exposure to dry air conditions [38]. In liquid phase, the increase in Pt nanoparticle size is greatly accelerated, even though no external electrochemical force is

employed [13]. It was suggested that water molecules were able to penetrate between the metal islands and the substrate to lower the metal/substrate bonding energy and to facilitate migration of the metal crystals [49]. Other approaches are based on comparing experimental data with theoretically predicted particle size distributions of aged catalysts [17], i.e., [57] for the crystallite migration and coalescence process the distribution is negligible below a certain finite size, has a maximum on the small-particle side and a tail toward the large-particle side [58]; for the Ostwald ripening process the distribution is negligible above a certain finite size, is characterized by a tail toward the small-particle side and has a maximum on the large-particle side [59]. This is because that the two processes are quite different: in the first case the growth is caused by cluster–cluster collisions and it is a random process accompanied by liquid like coalescence of the particles, while in the second one the growth takes place by interparticle transport of single atoms, the driving force of this process being the minimization of the clusters Gibbs free energy [59]. But the problem is the limitation of the approaches for size characterization [17,38] and other disturbing factors [17].

It has been noticed that the proposed degradation mechanism of Pt/C (PtM/C) differs for different researchers' results and the different conditions under which the investigation is carried out. It is expected that the degradation mechanism for Pt/C (PtM/C) catalysts, especially for the nanoparticle size increase, should be different under various working conditions [13], for example, the dissolution/precipitation mechanism might be more prevalent when load cycling occurs [42].

### 2.3. Working condition influence on catalyst durability

It is observed that the loss in the ESA of PEMFC cathodes is much larger than that of anodes [14,60] and that voltage cycling of Pt/C (PtM/C) catalysts in aqueous acids leads to accelerated platinum dissolution compared to extended holds at constant potentials [17,61–64]. This implies that working conditions have a great influence on the degradation of catalysts, which include the electrode potential, the temperature, the humidity, etc. [63,64].

The electrode potential and the mode applied on the electrode both influence the degradation of catalysts. It is observed that in acidic solution (e.g.,  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  [13,17],  $0.57 \text{ mol L}^{-1} \text{ HClO}_4$  [65]) the dissolving rate of platinum wire electrode increases with increasing potentials from 0.65 to 1.1 V (versus SHE) under potentiostatic conditions and is logarithmically dependent on potentials in the 0.85–1.1 V region [65]. And above 1.1 V, the dissolving rate decreases, which is attributed to the formation of a protective platinum oxide film [13,65]. For Pt/C, the dissolving rate of platinum at 0.9 V is comparable with that of Pt wire electrode [65]; the dissolving rate of platinum increases monotonously with increasing potential (0.6–1.2 V) [13]. Cycling the potential between the oxide formation and reduction regions leads to higher dissolution rates than potential holding in the oxide formation region, with the later being three to four orders of magnitude lower than the former [65]. This is because once the oxides are reduced by negative potential sweep,  $\text{Pt}^{2+}$  ions are formed and dissolved in electrolyte [66,67], and an

accelerated corrosion takes place [68]. It is suggested that two types of Pt oxide,  $\alpha$ -Pt oxide and  $\beta$ -Pt oxide, with  $\alpha$ -Pt oxide being a thin monolayer and the  $\beta$ -Pt oxide being a thick, highly hydrated, porous, polymer-like or aggregate with a rather open structure material, are formed during Pt electrooxidation [67]. Both  $\alpha$ -Pt and  $\beta$ -Pt oxides include components of PtO, PtO<sub>2</sub>, Pt(OH)<sub>2</sub>, and Pt(OH)<sub>4</sub>. The  $\alpha$ -Pt oxide forms under a moderate oxidation condition and is reduced in the potential range from 0.7 to 0.8 V versus RHE. The  $\beta$ -Pt oxide forms under a severe oxidation condition and is reduced under a more negative potential than  $\alpha$ -Pt oxide [67]. However, when the lower voltage is set above the Pt oxide reduction potential [69], or the upper potential limit is set below the Pt oxide reduction potential, i.e., 0.8 V [45], the degradation of Pt catalysts is greatly alleviated. It is also observed that the number of cycles is the dominant effect in the loss of platinum surface area; time at high potential has a secondary effect [63,64].

The humidity is another important parameter that affects the degradation of catalysts, for example, Pt surface area loss is largely mitigated by operating the cell at 25% relative humidity (RH) as compared to 100% RH [70]. The degree of platinum oxidation on PEMFC cathode increased significantly with an increase in RH from 20 to 72% [71]. It has also been shown that the growth of platinum particles is accelerated in the presence of a liquid environment [13,49,72–74], which is attributed to the lowered activation energy of particle growth [49,72,74]. As described above, water molecules are suggested to be able to penetrate between the metal islands and the substrate to lower the metal/substrate bonding energy and to facilitate migration of the metal crystal [13,60]. Methanol might be more aggressive toward electrocatalysts than water, so for a DMFC, the ripening of catalysts is more significant [8]. In terms of carbon corrosion, there is some contradistinction: the rate of carbon combustion is higher when the samples were held at temperature under humidified air than when they were held at temperature under dry air [12], however, carbon corrosion of the electrode catalyst layer was found to increase with decreasing humidity [63,64].

The degradation of catalysts is also a function of temperature. Catalyst coarsening rates exhibited a linear increase with temperature [63,64]. In the experiment of Pt dissolution at a certain potential, it is estimated that the  $\text{Pt}^{2+}$  equilibrium concentration in acidic solution at 0.9 V increases by two orders of magnitude from 25 to 80 °C and an additional order of magnitude from 80 to 120 °C [5]. The corrosion of carbon support is exacerbated with increasing temperature [12,38].

Contaminants in fuel or from air can also influence the catalyst stability [75–77], some lead to reversible and temporary depression in cell performance [78], and some lead to permanent loss of performance [75,79]. Recent evidence has shown that the contaminant CO<sub>2</sub> in fuel can also have a degrading effect on cell performance by producing adsorbed CO that can poison the electrode catalyst [80–82] through in situ reaction with H<sub>2</sub> ( $\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$ ) in PEMFC or the electroreduction of CO<sub>2</sub> ( $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$ ) [83].

The crossover of reactant gas can facilitate the sintering of Pt catalyst, which is due to the highly exothermic chemical reaction of H<sub>2</sub> and O<sub>2</sub> on the surface of Pt catalyst which consequently

generates a local hotpoint, thus leads to an accelerated sintering of the catalyst with a resulting loss of ESA [1,84].

### 3. Approaches for the catalyst durability issues

The approaches for the catalyst durability issues include two aspects: one is that how to improve catalyst durability, the other is that how to test catalyst durability and screen catalysts with desirable durability and catalytic activity.

#### 3.1. Strategies to improve the durability

The durability of catalysts is inherently determined by the properties of both the catalytic metals and the support materials and the specific interaction between them. It is reasonably expected that the higher the durability of catalytic metals and support materials, and the stronger the specific interaction between them, the higher the durability of the resultant catalysts. So the strategies to improve the durability of catalysts can be in general categorized into two aspects: support materials and catalytic metals.

##### 3.1.1. Catalyst support

The support materials for catalysts currently used in most PEM fuel cells are porous carbon. There are several basic requirements for an improved carbon support [12]: high surface area, leading to the deposition of small platinum particles (maximizing catalytic surface area); low combustive reactivity under both dry and humid air conditions at low temperatures (150 °C or less); improved electrochemical stability under fuel cell operating conditions, and high conductivity. In addition, it should be easy to recover Pt in the used catalyst. The Vulcan XC-72 carbon black is the most popular one. But its durability under chemically and electrochemically oxidizing conditions needs further improvement [10].

It is found that the extent of graphitization of the carbon plays an important role on carbon support stability, with more graphitic carbons being more thermally and electrochemically stable [12,13,35,41], which is due to the decreased defect sites on carbon structure where carbon oxidation initiates [10,13]. Increasing the degree of graphitization leads to the increasing strength of  $\pi$  sites ( $sp^2$ -hybridized carbon) on the support, which acts as anchoring centers for Pt [85], thus strengthen the metal–support interaction and the resistance of Pt to sintering [41]. The graphitization can be achieved by heating carbon materials in protective gas to a high temperature (1600 °C or more), the higher the graphitizing temperature, the higher the graphitization degree in the resultant carbon materials [41,86]. Graphitization really produces a material which is highly resistant to oxidation and carbon corrosion, decreasing the number of active surface sites; however, the problem is, with fewer active sites, metal deposition on graphitized carbon support is more difficult [42].

With the development of novel carbon nanostructure materials [87], e.g., carbon nanotubes (CNT) [88,89], carbon nanofibers [90], etc. more and more attention is paid on their application as catalyst support [91–93]. The catalysts with these

novel carbon nanostructure materials as support show enhanced catalytic activity toward fuel cell reactions [93–96]. It has been reported by several research groups that CNTs are more resistant to electrochemical oxidation than carbon black in both cases of with and without Pt on them [9,10,34,97]. This is due to the higher durability of the support and the specific interaction between Pt nanoparticles and the novel support. CNTs are usually considered as the rolled graphene sheets with a coaxial and with less dangling bonds and defects than carbon black [10,98]. It is difficult for oxidative atoms/groups to attack CNTs' closed structure, and consequently it is stable in strongly oxidizing conditions. It is also proposed that the delocalized  $\pi$  bond of CNTs is much stronger due to their higher degree of graphitization than that in carbon black. Pt is believed to bond with carbon support through the interaction between Pt and  $\pi$  electrons of the graphene sheets in carbon support, the stronger the  $\pi$  bond ( $sp^2$ -hybridized carbon), the stronger the interaction [9,41]. The stronger interaction between Pt and CNTs is suggested to contribute to the high stability of resultant catalysts (Pt/CNTs) [9,13].

Doping of carbon support with a second element is expected to modify the properties of resultant catalysts. It has been shown that nitrogen-doped carbon nanotube/nanofiber (CNT/CNF) with catalytic metals or without catalytic metals on them show enhanced catalytic activity toward oxygen-reduction reaction [99–101]. Nitrogen-doped carbon as the catalyst support is also expected to improve the durability of the resultant catalysts, because of the enhanced  $\pi$ -bonding [41,102] and the basic property [103], which are due to the strong electron donor behavior of nitrogen [104–106]. It is known that the stability of the metal particles and the mechanism of platinum particle growth depend on the surface acid–base properties of the carbon support [4]. The acidic/basic environment present on carbon surface affects in the way the movement of Pt particle on the carbon surface. Increasing of Lewis basicity of carbon surface results in strong anchoring of Pt to carbon [85]. Both N atoms and  $\pi$ -bonding contribute to the basicity of carbon [85].

A new kind of support material nanostructured thin film (NSTF) developed by 3M shows promising performance in improving catalyst durability [43,107]. The NSTF support layer consists of a monolayer of oriented crystalline whiskers of an organic pigment material (CAS #PR149). The support layer is deposited first onto a microstructured catalyst transfer substrate via a vacuum roll-good process. Then catalysts are sputter-coated on top of the whiskers so as to encapsulate them with a polycrystalline thin film [107]. The organic whiskers are highly inert thermally, chemically, and electrochemically [107]. It has been shown that the NSTF catalyst is able to withstand 1.5 V under  $H_2/N_2$  (PEMFC conditions) without corrosion of the support or loss of surface area or loss of catalyst activity, for either pure NSTF Pt or NSTF ternary catalysts, which is a significant differentiating feature over carbon or graphitic carbon-supported catalysts [107]. Significantly reduced fluoride ion release rates (75 times lower) is also observed in the water effluent from NSTF ternary catalyst-based MEAs operating at 120 °C than in the case of conventional Pt/C electrodes [43,107]. However, one disadvantage with NSTF catalyst is its large Pt particle size

(10–15 nm) and low electrochemical surface area ( $10 \text{ m}^2 \text{ g}^{-1} \text{ Pt}$ ) [43,107].

### 3.1.2. Pt alloy

In addition to a higher activity toward fuel cell electrode reactions [108], the duration tests in PEMFC also indicate that Pt alloyed with non-precious metal catalysts present a higher stability against dissolution than the state-of-the-art pure platinum catalysts [109,110]. So alloying Pt with a second and/or third metal is an important strategy to improve the service life of catalysts [27]. Many efforts have been devoted in this field and obvious advances have been achieved in the past years.

Popov and co-workers [111] reported the investigation on the durability of  $\text{Pt}_3\text{Ni}_1/\text{C}$  with a so-called accelerated durability test (ADT). It is observed that platinum particles migrate on the carbon surface and aggregate to form larger particle sizes in Pt/C, however, no agglomerates of metal particles are observed for  $\text{Pt}_3\text{Ni}_1/\text{C}$  and this is not affected by the applied potential. The authors attributed these phenomena to the anchor effects of Ni to platinum on carbon substrates: the mobility of platinum on a carbon surface is hindered when Ni is present; thus, the sintering effect of platinum atoms is suppressed [111]. Similar results have been observed by Wei et al. for Pt/Fe alloy on a carbon substrate [112]. It is well known that Fe has a strong tendency to alloy with carbon. Therefore, Pt atoms are bonded more strongly to carbon through bridges of Fe [112]. The anchor effect was also observed on  $\text{Pt}_4\text{ZrO}_2/\text{C}$  [113,114], which is for potential application in high-temperature PEMFC. The existence of oxide or hydroxide can inhibit the agglomeration of catalyst crystallite to some extent, and hence prolong the life of the catalyst [115]. When  $\text{ZrO}_2$  is present on carbon, the highly dispersed Pt atoms are obstructed by the adjacent  $\text{ZrO}_2$  and the agglomeration of Pt particles could be inhibited [113].

The enhanced durability is also observed on ternary catalysts [116,117]. The improvement in durability of  $\text{PtRuNi}/\text{C}$  (40 wt% metal, Pt:Ru:Ni = 1:1:1) in acid solution is attributed to a Ni hydroxide passivated surface and/or the enhanced stability of Ni in the Pt lattice (anchoring of metallic nickel in the platinum lattice) [116]. It is observed [117] that the Pt alloy catalyst ( $\text{Pt}_6\text{Co}_1\text{Cr}_1/\text{C}$ ) still shows higher catalytic activity to ORR after life test (500 h) than Pt/C due to the lower oxidation-state of Pt in the alloy as compared to pure platinum as seen from curve-fitted Pt 4f XPS spectra, which means the alloyed metals might increase the resistance of Pt to oxidation.

But a common problem exists for all Pt/non-precious metals alloy catalysts [118–120]: non-precious metals in the alloys suffer from dissolution in acid solution, such as in the case of  $\text{Pt}_3\text{Ni}_1$  [111], Pt–Cu–Fe [121], Pt–Co [122,123], Pt–Ni [123], Pt–Fe [123], with Pt–Ni alloy showing the lowest metal dissolution followed by Fe [123]. The dissolution of non-precious metals results in the decrease in oxygen-reduction activity of the catalysts [123]. The dissolution of the alloying elements followed by diffusion into the membrane will lead to additional deterioration on cell performance [122]: (i) decreasing ionomer/membrane conductivity; (ii) reducing water content and dehydrating membranes [124]; (iii) suppressing oxygen-reduction kinetics by a decrease of oxygen concentration or oxygen diffusion

coefficient in ionomer film [125]. In order to lessen the detrimental effect of dissolved non-precious metals without losing durability and catalytic activity, pre-leaching of the alloy is proposed [126]. It is observed that the potential cycles lead to increased dissolution of Fe and the rearrangement of Pt at the surface and formation of a Pt skin layer, protecting the underlying Pt–Fe alloy from corrosion [118]. Other studies in wet cells have shown that after the catalysts have been briefly immersed in an acid electrolyte, a skin consisting of a monolayer of pure Pt forms on the surface of the Pt-alloys [118–120].

Alloying Pt with a non-dissolvable metal shows more promising results in terms of improving catalyst durability. Adzic and co-workers [110] modified Pt nanoparticles with gold (Au) clusters and the resultant oxygen-reduction fuel-cell electrocatalysts is stabilized against dissolution under potential cycling regimes without decreasing the oxygen-reduction kinetics. In their work [110], the Au clusters were deposited on a Pt catalyst (carbon-supported Pt nanoparticles) through galvanic displacement by Au of a Cu monolayer on Pt [127–129], on which a monolayer of Cu was in advance underpotentially deposited [130–132]. It was observed that the oxidation of Au/Pt/C electrocatalyst commences at considerably higher potentials than that for the Pt/C catalyst; thus, the oxidation of Pt nanoparticles modified by Au clusters requires much higher potentials than are necessary for unmodified Pt nanoparticles. The high Pt oxidation potential of the Au/Pt/C electrocatalyst (that is, the lower extent of Pt oxidation) is considered as the major mechanism for the stabilization effect of Au clusters [110]. It has been shown that potential cycling between the oxide formation and reduction regions of Pt leads to increased dissolution rates of Pt [61,64,65,67]. The increase in the oxidation potential of Pt expands the stable potential region for Pt catalysts, especially increase the up potential limit, which is of significance for improving fuel cell efficiency [22]. Other reports [119,120,133–135] have also shown that at high voltages ( $>0.8 \text{ V}$ ), there is an inherent Pt activity loss for oxygen-reduction reaction due to adsorption of oxygenated species ( $\text{OH}^-$ ) from water which is recognized as a poison to oxygen cathodes that contributes to the high  $\text{O}_2$  reduction overpotential [136] and contributes to the oxidation of Pt.  $\text{OH}^-$  adsorbs at more positive voltages on Pt alloys than on Pt surfaces. Thus, the Pt surfaces of these alloys are more active for the ORR because of slower  $\text{OH}^-$  species adsorption at high cell voltages [133], which is also confirmed with theoretical investigation [136] and experimental measurements [137].

### 3.2. Methods for studying catalyst durability

The investigation on the durability of materials for application in PEMFC is a time-consuming and complex task [15]. To test the durability of catalysts in a real normally working PEMFC is inefficient, if not impossible, because the life requirement for PEMFC, thus its materials, is, for example,  $>5000 \text{ h}$  for transportation and  $>40,000 \text{ h}$  for stationary application [2,126]. Therefore, the so-called accelerated degradation test (ADT) is developed [12,17,40,111]. These ADT methods include: (i) thermal degradation under hot air conditions [12,38,39], (ii) aging in hot aqueous acid solution [13,126], (iii) open-circuit cell

operation [138]; (iv) electrochemically forced aging under simulated cell conditions [9,10,111,123].

Cai et al. [40] developed an accelerated thermal sintering protocol, in which carbon corrosion and platinum surface area loss that are observed for electrocatalysts over long periods of electrochemical potential cycling and potential hold can be conveniently simulated by high temperature experiments at 250 °C in an environment containing about 0.7% oxygen, 8% water and helium (balance gas).

Dahn and co-workers [139–141] develops an acid treatment of Pt alloy to study the durability of catalysts, showing that the acid treatment could simulate the corrosion that occurs in the typical working environment of the PEMFC.

The open-circuit voltage tests have the advantage of an accelerated life evaluation over normal operating methods. The reaction at anode is the H<sub>2</sub> and the crossover O<sub>2</sub> and at cathode is the O<sub>2</sub> and the crossover H<sub>2</sub> [84], so H<sub>2</sub>O<sub>2</sub> and other oxidative species are expected to be formed [142–145], which is considered as a poison to both membranes and catalysts [146]. Base on the assumption that Pt degradation at the cathode is caused by H<sub>2</sub>O<sub>2</sub>, Teranishi et al. [147] developed a model to describe the degradation of Pt catalysts under OCV conditions in which the rate of Pt degradation is equivalent to that of H<sub>2</sub>O<sub>2</sub> generation and the generation rate of H<sub>2</sub>O<sub>2</sub> at the cathode would then be dependent on the amount of H<sub>2</sub> gas cross leak from the anode and on the rate of O<sub>2</sub> gas supply.

Electrochemically forced aging under simulated cell conditions is often carried out in a three-electrode half-cell system, in which aqueous acid solution is used to mimic Nafion [9,17,111]. Usually, a constant potential in the range of cathode potential in a working PEMFC [9,10,111] or a potential cycling in the potential region of between the oxidation and reduction of Pt [61,67,110] is applied on the catalyst electrode. During the life test, the electrochemical surface area is tested using cyclic voltammetry (CV) [9]; the concentration in the aqueous acid solution of dissolved metals (Pt and non-precious metals) is monitored [17,111]; and sometimes the catalytic activity toward ORR is also measured [111]. Usually, the catalyst sizes before and after degradation test is characterized using XRD and TEM.

Among all the above mentioned methods, Gasteiger and co-workers [70,148] proposed the following two test methods as reliable and efficient screening tools for fuel cell catalyst development: (i) catalyst voltage cycling test; (ii) support corrosion test at 1.2 V. And because the electrochemical surface area of the fuel cell electrocatalyst decreases faster during potential cycling, which is also more closely related to drive cycle operation of PEMFC on vehicles [148], than during constant potential or constant current testing, Borup et al. [63,64] suggested potential cycling as a possible accelerated testing method for electrocatalysts.

In most of the ADT methods, aqueous acid solution (0.5 M HClO<sub>4</sub> [144], 0.57 M HClO<sub>4</sub> [65], 0.6 M HClO<sub>4</sub> [149], 0.5 M H<sub>2</sub>SO<sub>4</sub> [9,10,17]) is employed to mimic the Nafion electrolyte in PEMFC conditions. It is believed that HClO<sub>4</sub> aqueous solution is preferred as the electrolyte in mimic the Nafion (but the concentration is still not identical), more closely than H<sub>2</sub>SO<sub>4</sub>

aqueous solution due to a significant anion adsorption effect in the later one [65,144].

Most of the ADT methods are ex situ ones, so how and to what extent the ex situ methods can mimic the real working condition of PEMFC is still in question. Time-effective and reliable methods for material durability investigation are indispensable. Much work is still needed in this topic.

#### 4. Conclusions and future directions

The significance of catalyst durability to PEMFC can never be overvalued. The reasons and mechanisms for the catalyst degradation, the influencing factors and approaches for improving catalyst durability and for studying the durability issues are reviewed. The degradation of Pt-based PEMFC catalysts can be categorized into two aspects: the corrosion of carbon support and the degradation of catalytic metals. To use carbon with higher graphitization degree as support materials and to alloy Pt with other metals can improve the catalyst durability. A time-effective and reliable method for studying catalyst durability is indispensable. More work is still needed in these topics.

The research and development of new catalysts for PEMFC is still largely based on traditional trial-and-error method and is still more an art than a science [148]. Recently, it has been shown that less costly and significantly improved electrocatalysts can be designed by developing a fundamental understanding of their atomic-scale phenomena, using a combination of state-of-the-art experimental techniques and modern quantum chemistry methods [150–152], which is more efficient and stronger than the traditional method [148,153,154]. Density functional theory (DFT) calculation has been employed in the investigation of catalysts durability [155,156]. The advances in modern quantum chemistry and computer science and technology should be well employed and are expected to play more and more significant role on studying durable catalysts, at the same time, with high catalytic activity and low cost.

Most of present investigations on PEMFC catalysts are carried out under low temperatures (<80 °C), only a few are on improved temperatures (120–150 °C) [51,60,138], under which condition PEMFC shows more promising advantages and has been devoted more and more efforts [21,157]. It has been shown that the degradation of catalysts is accelerated at improved temperatures [5]. So the durability issues of catalysts for potential application in high-temperature PEMFC is a still harder nut to crack, and should be put emphasis on.

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