

Review

Recent advances in activity and durability enhancement of Pt/C catalytic cathode in PEMFC Part II: Degradation mechanism and durability enhancement of carbon supported platinum catalyst

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Abstract

Polymer electrolyte membrane fuel cell (PEMFC) technology has advanced rapidly in recent years, with one of active area focused on improving the long-term performance of carbon supported catalysts, which has been recognized as one of the most important issues to be addressed for the commercialization of the PEMFCs. The cathode catalyst layer in PEMFCs typically contains platinum group metal/alloy nanoparticles supported on a high-surface-area carbon. Carbon support corrosion and Pt dissolution/aggregation are considered as the major contributors to the degradation of the Pt/C catalysts. If the platinum particles cannot maintain their structure over the lifetime of the fuel cell, change in the morphology of the catalyst layer from the initial state will result in a loss of electrochemical activity. This paper reviews the recent advances in the stability improvement of the Pt/C cathodic catalysts in PEMFC, especially focusing on the durability enhancement through the improved Pt–C interaction. Future promising strategies towards the extension of catalysts operation life are also prospected.

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Keywords: Pt/C cathodic catalyst; PEMFC; Interaction; Degradation; Durability

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1. Introduction

In fuel cell technologies, polymer electrolyte membrane fuel cells (PEMFCs), with the advantages of low operating temperature (60–100 °C) and the fast start-up, are promising candidates for application of portable power source, electric vehicle and transportation applications [1–6]. However, for successful large-scale commercialization, the effort is now focusing on increasing the durability and reliability of components and the system as a whole, in conjunction with lowering the costs. The use of precious metal catalysts (Pt and its alloys) is a major cost factor that must be addressed. Carbon-supported platinum or platinum alloys are commonly used as the cathode catalysts in order to lower the component cost. Because catalysis is a surface effect, the catalyst needs to have the highest possible surface area. So, the active phase is dispersed on a conductive support as carbon. From 1960s to present, great progress has been made on the low Pt-loading carbon supported catalysts [7–10]. At the current level of the state-of-the-art technology, platinum loading is reduced from 4 mg cm⁻² (as used in the Gemini space flights) to 0.4 mg cm⁻² or less at the cathode, and 0.05 mg cm⁻² at the anode [7]. According to the US Department of Energy (DOE) cost reduction targets, the total Pt catalyst loading in a membrane electrode assembly (MEA) must be reduced to <0.03 mg cm⁻² [11]. However, it is very difficult to maintain or improve catalyst layer performance when the Pt catalyst loading is reduced. Furthermore, a series of aspects, such as effective Pt catalyst layer utilization, the durability and reliability of such a supported catalyst component, are still problematic [12,13]. The durability of PEMFCs has been recently recognized as one of the most important issues to be addressed before the commercialization of the PEMFCs [14–18]. According to the DOE Technical Target for Fuel Cell Stack System, the durability of a PEMFC stack must be over 5000 h by 2010 [11]. It is believed that excessive degradation of stack voltage is the major failure mode for fuel cell systems. Among the reasons for the voltage degradation, activity loss of the catalysts is considered one of the major contributors [15].

If the PEM fuel cells are able to continue working efficiently for long periods of time (thousands of hours), then all materials need to survive under the cell operating conditions. For the PEMFC anode catalyst, when operating on pure hydrogen, is relatively stable, except being poisoned by sulfur and CO that originate from the fuel. The lower the operating temperature, the more severe is the poisoning effect. Much work has consequently been reported on improving the CO tolerance of PEMFC anodes, for example by alloying the Pt with Ru or Mo, and by incorporating other promoters [19]. However, for the cathode catalyst layer, this means that the materials need to be stable at elevated temperature (80 °C and higher, preferably greater than

100 °C), with oxygen present at 21–100%, under high potential (0.6 V versus the standard hydrogen electrode (SHE) and higher), at low pH, and with significant levels of water in both the vapor and liquid phase [20]. In addition, it is possible for a cathode to see high potentials (e.g., >1.2 V) for short periods of time. In such an operation condition, carbon supported platinum (Pt/C) cathode catalyst is not as stable as the anode [21].

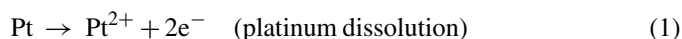
Catalyst support degradation was recognized as a potential area of concern for low-temperature fuel cells during the development of phosphoric acid fuel cell (PAFC) technology. In the 1970s and 1980s the stability of carbon-supported catalysts was studied under conditions relevant to PAFCs, notably high temperature (165 °C) with phosphoric acid [22–26]. Studies on the degradation of PEMFC cathodes have not, until recently, been considered as a big concern. The aim of this review paper is to provide a better insight into this stability studies on carbon-supported catalysts in PEMFC and to present some of the latest work in this area. Recently, the Pt–carbon support interaction has been paid more and more attention in the catalyst studies. This interaction has been considered to have the potential benefits to the improvement of catalytic properties and stability of the electrocatalyst [27–33]. This paper will also concern the studies on the stability enhancement of the catalyst through improving the interaction of platinum with carbon support.

2. Degradation mechanism of Pt/C and Pt(M)/C cathodic catalysts in PEMFC

2.1. Catalyst particle agglomeration and catalyst dissolution

One of the more significant problems hindering the large-scale implementation of PEM fuel cell technology is the cathode catalyst performance loss during extended operation. Mechanisms that contribute to cathode catalyst degradation have been proposed, including: catalyst particle sintering [34], catalyst dissolution [35], and cathode support corrosion. Wilson et al. proposed that the surface area loss of carbon-supported platinum in aged PEMFC is due to the platinum particle growth (Fig. 1) caused by crystallite migration in the gas-phase sintering [34].

Meyers and Darling [35] showed that Pt dissolution in PEM fuel cells is negligible at low and high potentials, but is remarkable at intermediate potentials. In their kinetic model of Pt dissolution in PEMFCs, they explained the effect of potential in the following way. They considered three reactions:



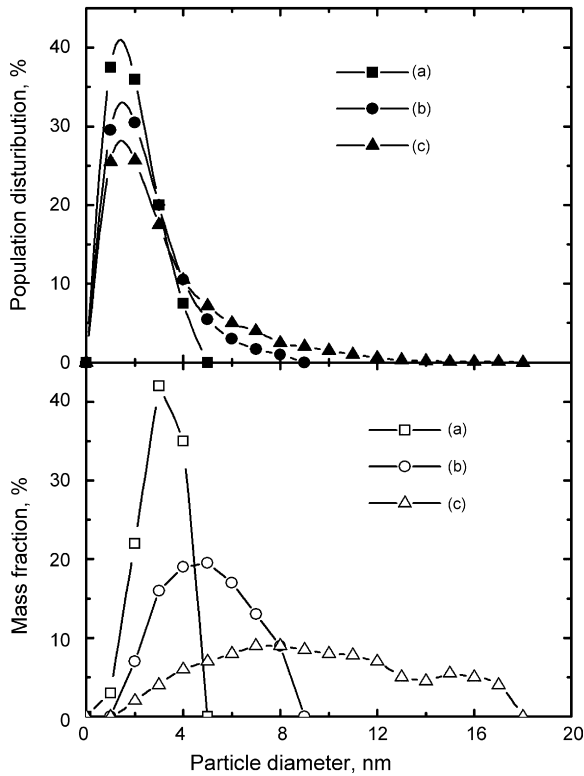
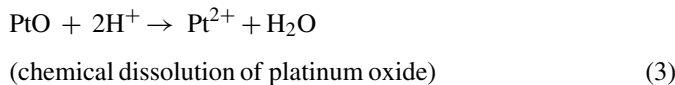
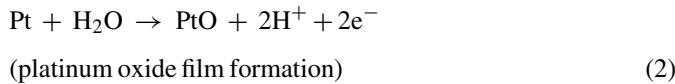


Fig. 1. *Top*: Particle-size population distributions of Pt in PEMFC cathodic catalysts. *Bottom*: Mass distributions of Pt in catalysts. (a) Fresh catalyst; (b) catalyst after 1320 h of operation; (c) catalyst after 2200 h of operation [34].



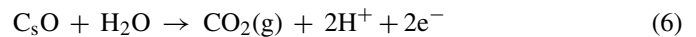
The reaction (3) is assumed to be slow, but is necessary for the model to relax to equilibrium at high potentials when Pt^{2+} and PtO are in equilibrium. The model and experimental data indicated that at lower potentials (i.e., under the conditions of normal H_2/air fuel cell operation), the solubility of platinum in acid is quite low. At higher potentials on exposure to air to form PtO , the oxide layer effectively insulates the platinum particles from dissolution. At intermediate potentials, however, the uncovered surface is prone to high rates of platinum dissolution [35].

2.2. Carbon support corrosion

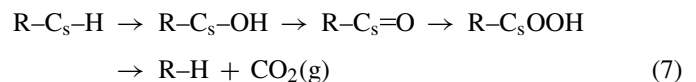
Carbon support corrosion of cathode catalysts in PEMFCs is a major contributor to the catalyst degradation. In the state of the art PEMFC, carbon black is normally used as catalyst support material for PEMFCs. Despite its widespread use, high-surface-area carbon support in PEMFC electrodes is susceptible to corrosive conditions, which include high water content, low pH (<1), high temperature (50–90 °C), high oxidative potential (0.6–1.2 V), and high oxygen concentration. Oxygen atoms are being generated by the catalyst particles, and at elevated

temperature, carbon atoms are able to react with oxygen atoms and/or water to generate gaseous products such as CO and CO_2 which leave the cell. Furthermore, during the start-up and shut-down of a fuel cell, local cathode potential can reach as high as 1.5 V, which significantly speeds up the carbon corrosion. In addition, Pt catalysts have been suspected to accelerate the rate of carbon corrosion [36]. This loss mechanism removes carbon from the cell, leading to a reduction of the carbon content in the catalyst layer with time. As carbon is corroded away, noble metal nanoparticles will be lost from the electrode or aggregated to larger particles, which may cause a loss of catalyst activity, and, in the extreme, a structural collapse of the electrode. Oxidation of carbon support can also lead to changes in surface hydrophobicity that can cause gas transport difficulties.

Early investigations of carbon corrosion in fuel cell environment were motivated by phosphoric acid fuel cell (PAFC) which runs at higher temperature than PEMFC [37]. Several studies of electrochemical formation of surface oxides on carbon black in acidic electrolytes at elevated temperatures have appeared in the literatures [38–42]. The kinetics of carbon oxidation to surface oxides, adsorption of these oxides on the platinum surface, and ease of subsequent carbon oxidation to CO_2 have been investigated. Surface oxide generation in acidic electrolytes involves the general steps of oxidation of carbon in the lattice structure (Reaction (4)) followed by hydrolysis (Reaction (5)) and finally gasification of oxidized carbon to CO_2 (Reaction (6)), wherein the subscript s denotes surface species [26,41,43].



Significant oxidation of carbon to CO_2 can be expected to decrease the performance of a PEM fuel cell [44]. Electrochemical oxidation of carbon at room temperature to CO_2 and, to a lesser extent, CO, has been reported to occur at potentials above 0.9 V (RHE) [45]. There is presently no detailed, widely accepted mechanism in the literature that explains carbon surface oxide generation and conversion into CO_2 . One proposed generic stepwise mechanism of surface oxide formation and CO_2 evolution is shown schematically in Reaction (7), [46–50]. Water is understood to be the source of oxygen in Reaction (7).



Stevens and Dahn [17] studied effect of Pt on the carbon oxidation in the air at high temperature. They measured the weight loss on heating catalyst samples in air. The samples comprised Pt (5–80 wt%) on BP 2000 carbon of high surface area. For the base carbon heated in air at 195 °C, no weight loss was detected even after 3000 h. With Pt/C samples, however, significant weight loss occurs arising presumably from the catalyzed combustion of carbon with oxygen. This weight loss increased as the temperature was raised from 125 to 195 °C and also as the Pt loading was increased. TEM images indicated that the weight loss was

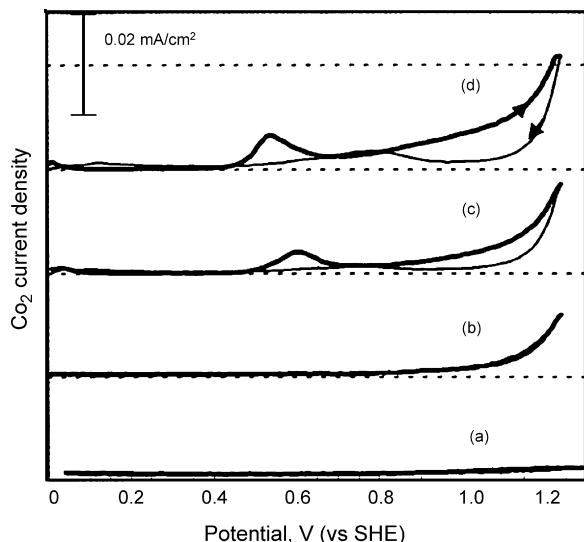


Fig. 2. Comparison of CO₂ mass spectra profiles for MEAs with (a) Vulcan-coated gas-diffusion layer pressed against the Nafion 117 membrane; (b) 0% Pt (Vulcan only) on Nafion 112; (c) 10% Pt/C on Nafion 112; (d) 39% Pt/C on Nafion 112. The electrochemical cycles were performed at 2 mV s⁻¹, 50 °C, with He on the cathode (50 cm³ min⁻¹), and dilute H₂ (4% H₂/N₂) on the anode (500 cm³ min⁻¹). The mass spectra were converted by a known 1% CO₂ calibration gas, and converted into Faradaic current of CO₂ [51].

primarily from the carbon and that the Pt particles did not sinter or agglomerate during exposure to air at high temperatures [17].

Jarvi and co-workers [51] investigated the influence of platinum on the corrosion of carbon catalyst supports with varying Pt mass fraction, catalyst type, and temperature under PEMFC condition. From their investigation, carbon-only electrodes in a PEM MEA showed low CO₂ emissions at high potentials. When Pt was present in the electrode layer as Pt/C catalysts, the rate of CO₂ emission was higher than in the carbon-only electrode at temperatures lower than ~50 °C. Furthermore, the CO₂ generation rates increased with higher Pt mass fraction (0, 10, and 39% balanced by carbon support) in the electrode (as shown in Fig. 2). In addition, a peak occurring at low potential of 0.4–0.6 V_{RHE} depended on the catalyst type. When a PtRu/C electrode was tested, CO₂ emission occurred ~0.1 V more negative than the Pt/C electrode, suggesting that the CO₂ is emitted from the electro-oxidation of CO adsorbed on the catalyst surface. The temperature dependence of CO₂ emission indicated that the platinum catalyzed support was more easily oxidized to CO₂ than a support without platinum (at low temperatures). All of these observations suggested that the corrosion rate of carbon catalyst support is accelerated in the presence of Pt-containing catalysts [51].

The same group (Jarvi and co-workers) [52] also investigated electrochemical surface oxidation of Vulcan XC-72 at different potential and temperature ranges under PEMFC condition. Potential holds at 1.0 V at room temperature only resulted in slight oxidation of Vulcan XC-72. But the experiments at 65 °C showed clear signs of surface oxidation after only 16 h at potentials >0.8 V, verifying that surface oxides can be generated under simulated PEM fuel cell conditions [52].

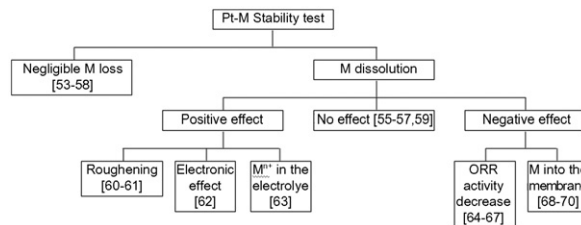


Fig. 3. Reference based scheme of the stability of Pt–M alloy catalysts in PAFC and PEMFC fuel cell environment [53–70].

2.3. Leaching of base-metal from a Pt-alloy/C catalysts

Carbon supported platinum metal alloy catalysts (Pt–M/C) are widely used in low temperature fuel cells. Pt alloyed with first-row transition elements is used as improved cathode material for low temperature fuel cells. A major challenge for the application of Pt–transition metal alloys in polymer electrolyte membrane (PEMFC) fuel cells is to improve the stability of these binary catalysts. Dissolution of the non-precious metal in the acid environment can give rise to a decrease of the activity of the catalysts and to a worsening of cell performance. Base-metal loss mechanism of Pt(M)/C catalysts was analyzed by Gasteiger et al. [53], there are at least three possible causes for the leaching of base-metal from a Pt-alloy/C catalyst in PEMFCs: (i) excess base-metal deposited onto the carbon support during preparation, (ii) incomplete alloying of the base element to Pt due to a low alloying temperature applied during formation of the alloy, (iii) even a well-alloyed base-metal may leach out of the surface under PEMFC operating conditions and leave a Pt-enriched surface or skin since thermodynamically base-metals are unstable under PEMFC potentials in acidic electrolytes (even Pt-alloys do not have high enough heats of mixing to confer stability). The effect of the base-metal loss on the catalysts performance has been widely studied. The results of the different tests on the stability of Pt–M alloy catalysts in PAFC and PEMFC conditions and the consequences on the electrocatalytic activity and cell performance are summarized in Fig. 3.

3. Stability investigation methodologies

Catalysts durability study in PEMFC has remained a difficult topic because of the lengthy duration of the test time required (i.e., several thousand hours or more), the complexity of failure analysis, the overlapping of causes of failure, and the difficulty of in situ, nondestructive examination of the structure of electrocatalysts and membrane electrode assemblies (MEAs). Any catalyst degradation contribution would therefore be very difficult to deconvolute from the large intended fuel cell reaction signal.

In industry, three methodologies are always used for the PEMFC durability studies. One major methodology involved in long-term durability studies in PEMFCs has been the so-called post-mortem examination of individually boiled components. Another common approach within the industry is to operate a cell or stack for a given period of time, and

then disassemble the components for post-mortem examination. Also as an integrated PEMFC system, durability data is often accumulated in bulk to determine the expected power loss over time and sources of catastrophic failure for prototypes or nearly commercial ready sets of components.

As discussed in Section 2, Pt/C cathode catalyst degradation has been studied and three mechanisms that contribute to the degradation have been proposed. Wilson et al. [34] studied the Pt particle growth with XRD and TEM using carbon supported Pt catalyst in thin film catalyst layers after running for up to 4000 h at maximum power. Particle ripening is readily evident in the electrodes that the initial platinum specific surface areas of $100\text{ m}^2\text{ g}^{-1}$ Pt eventually stabilize to about $40\text{--}50\text{ m}^2\text{ g}^{-1}$ in the cathode and $60\text{--}70\text{ m}^2\text{ g}^{-1}$ in the anode. They suggested this particle growth (sintering) is attributed to the crystallite migration mechanism. Darling and Meyers [71] presents a mathematical model for the oxidation and dissolution of supported platinum catalysts in PEMFCs, and developed a kinetic expression for the oxidation and dissolution reactions of Pt/C catalyst and compared to available experimental data. Electrochemical surface oxidation of carbon support has been studied by Kangasniemi et al. [52], following potentiostatic treatments up to 120 h at potentials from 0.6 to 1.2 V at room temperature and 65°C . Surface oxidation study was then followed using cyclic voltammetry (CV), thermal gravimetric analysis coupled to on-line mass spectrometry (TGA-MS), X-ray photoelectron spectroscopy (XPS), and contact angle measurements [52]. They also investigated the influence of platinum on the corrosion of carbon catalyst by on-line mass spectrometry during cyclic voltammetry, with varying Pt mass fraction, catalyst type, and temperature [51]. Stevens and Dahn explored ex situ and in situ fuel cell catalyst degradation test methods and the impact of catalyst degradation on fuel cell performance [72]. For ex situ method, samples of platinum-loaded carbons were held isothermally at elevated temperature under either dry or humidified air conditions for extended periods of time. At regular intervals, the samples were sealed from the atmosphere, removed from the oven, cooled, and then weighed, giving weight change profiles as a function of time. The in situ method was carried out using a 1.2-V fuel cell accelerated test [72]. Colon-Mercado and Popov [73] evaluated the catalytic, corrosion and sintering properties of commercial Pt/C and Pt₃Ni/C catalysts using an accelerated durability test (ADT). The ADT cell consists of a three-electrode system, which includes a reference electrode, a platinum mesh counter electrode and the catalyst-coated gas diffusion layer (GDL) as a working electrode. For the ADT, the electrodes were immersed in a 0.3 M H₂SO₄ solution, which mimics the environment of the electrode–membrane interface on the cathode side. Unlike the case of an electrode–membrane assembly (MEA) interface, in which only the catalyst in contact with the membrane is active, in the case of the ADT the entire active surface area of the catalyst is exposed to protons, since the electrode is completely immersed in the electrolyte. Under this specific condition, the deterioration of the catalysts is accelerated [73].

4. Stability enhancement of Pt/C and Pt(M)/C catalysts through using more stable carbon support and alloying proper metals with Pt

4.1. Using carbon nanotube as catalyst support

One strategy to reduce Pt/C catalyst performance degradation due to carbon corrosion is to use alternative more stable carbon support. For example, it has been proposed that carbon material with more graphite component can be more stable [28]. Recently, carbon nanotube has been proposed as promising support material for fuel cell catalyst due to its unique characteristics, including high aspect ratio, high electron conductivity, and enhanced mass transport capability [74,75]. Wang et al. compared the electrochemical surface oxidation of carbon black Vulcan XC-72 and multiwalled carbon nanotube (MWNT) following potentiostatic treatments up to 168 h under condition simulating PEMFC cathode environment (60°C , N₂ purged 0.5 M H₂SO₄, and a constant potential of 0.9 V). The subsequent electrochemical characterization at different treatment time intervals suggests that MWNT is electrochemically more stable than Vulcan XC-72 with less surface oxide formation and 30% lower corrosion current under the investigated condition. As a result of high corrosion resistance, MWNT shows lower loss of Pt surface area and oxygen reduction reaction activity when used as fuel cell catalyst support [76]. Their result of Pt surface area loss with experimental time is as shown in Fig. 4. It can be seen that almost 80% of Pt surface area was lost for Vulcan XC-72 after 168 h oxidation treatment, while only 37% loss is observed for MWNT. Furthermore, most of the surface area loss for the case of MWNT occurs within 72 h, and after 72 h the rate for the Pt area loss is very small, indicating that MWNT could potentially provide much higher durability than Vulcan XC-72 [76].

4.2. Alloying proper metals with Pt

Both high and low stability of platinum based binary catalysts in PEMFC condition have been reported in the literatures. Some authors reported high stability of the catalysts after more than 1000 h of duration tests in PEM fuel cells. On the other hand, a poor stability of the materials was found following short

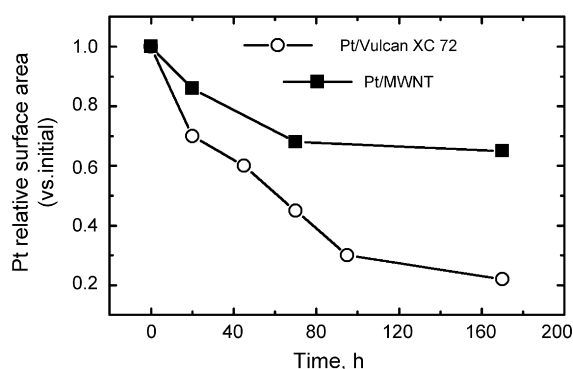


Fig. 4. Comparison of Pt active surface area loss for the case of Vulcan XC-72 and MWNT at different time intervals during oxidation treatment [76].

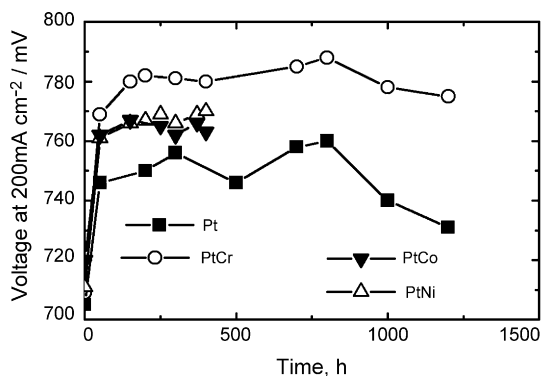


Fig. 5. Lifetime evaluation of carbon supported Pt and Pt-alloy electrocatalysts for oxygen reduction in PEMFCs. Current density: 200 mA cm^{-2} ; cell temperature: 50°C ; ambient pressure [54].

duration (few hours) measurements in half cells [65,77]. Tests in half cells are important to evaluate the electrochemical characteristics of a catalyst, but it has to point out that, from the practical point of view, the test in fuel cell is the ultimate evaluation criterion for novel materials. The working conditions such as temperature, pressure and fuel flows are crucial to determine the real performance of a system. In this regard, duration tests in PEMFCs indicated a positive effect of the presence of the non-precious metal on the stability of the catalyst.

Mukerjee and Srinivasan [54] investigated durability and stability of carbon supported Pt_3Cr , Pt_3Co and Pt_3Ni alloy catalysts in PEMFCs. The lifetime studies on these catalysts under PEMFC operational conditions showed only negligible losses in performance over periods of 400–1200 h, as can be seen in Fig. 5. In this time range a high stability of the ratio between the amount of the alloying component and the amount of Pt in the catalyst was observed.

Colon-Mercado et al. [66] evaluated the catalytic, corrosion and sintering properties of commercial Pt/C and $\text{Pt}_3\text{Ni}/\text{C}$ catalysts. The carbon supported Pt_3Ni alloy showed better resistance to sintering than a pure platinum catalyst. According to the authors, the mobility of platinum on a carbon surface is hindered when Ni is present; thus, the sintering effect of platinum atoms is suppressed. Yu et al. [78] evaluated the durability of a Pt–Co cathode catalyst in the Pt:Co atomic ratio 2.5:1 in a dynamic fuel cell environment with continuous water fluxing on the cathode. The overall performance loss over 2400 cycles of the PtCo/C membrane electrode assemblies (MEAs) was less than that of the Pt/C MEA. The performance losses of the Pt/C MEA over 1200 cycles mainly resulted from the cathode electrochemical area (ECA) loss due to platinum recrystallization, while the performance losses of the PtCo/C MEA resulted from the activity loss due to cobalt dissolution as well as the ECA loss. Gasteiger et al. [53] proposed a pre-leaching of the alloy to minimize the contamination of the MEA during operation owing to Co dissolution. They investigated the durability of the baseline on Pt/C and multiply leached Pt–Co/C MEAs tested in a short stack. They observed that the enhancement or performance offset of 15–25 mV between the Pt/C and the $\text{Pt}_x\text{Co}_{1-x}/\text{C}$ is maintained throughout the 1000 h of stack operation within limits of error. The surface area loss for the PtCo/C catalyst was lower than that

for Pt/C measured over the 1000 h of operation. These results indicated that the Pt-alloy catalyst starts life with a larger particle size and does not sinter as rapidly as Pt/C. Protsailo and Haug [55] investigated the performance and, most importantly, durability improvement of PEMFCs, that can be achieved using Pt–Co/C and PtIrCo/C, synthesized by the carbothermal technique. The alloys showed not only better activity compared to pure Pt, but also remarkable durability in the conditions at which Pt alone is prone to dissolution. The losses of the real surface area of Pt/C, PtCo/C and PtIrCo/C following 1800 cycles at 120°C were about 45% for Pt/C, 18% for PtCo/C and 8% for PtIrCo/C, respectively.

5. Stability enhancement of Pt/C catalysts through improved Pt–C interaction

5.1. Electronic interaction of Pt–C

Fundamentals of the electronic interaction between Pt and C in a carbon supported platinum catalyst were presented in the first part of this review paper. This interaction is attributed to the different Fermi-level of electrons in both Pt and C. Electron-spin resonance (ESR) and X-ray photoelectron spectroscopy (XPS) studies have demonstrated electron donation by platinum to the carbon support in the Pt/C catalyst [79,80]. The Pt–carbon support interaction is considered to be beneficial to the enhancement of catalytic properties and to improved stability of the electrocatalyst [81–83]. Interaction enhancement strategy for the Pt/C catalyst can be based on developing strong anchoring sites at the interface of Pt/C, through carbon surface modification to form the proper surface functional groups on the surface of carbon support.

5.2. Effect of the surface oxidation groups formed on carbon support

In a Pt/C catalyst, interaction of Pt with C and the stability of the catalyst are related to the chemical and nature of their interface [84]. It is important to recognize the role of the chemical nature of the carbon surface in the catalysts stabilization and the interaction between Pt and carbon support. Oxygen surface groups are of greatest interest in the preparation of carbon-supported catalysts, and can be obtained through surface treatment of carbon by chemical methods with different oxidants: HNO_3 , H_2SO_4 , H_3PO_4 , H_2O_2 , O_2 or O_3 , K_2ClO_3 , KMnO_4 , etc. Prado-Burguete et al. [85,86] examined and clarified the effect of oxygen surface groups on the dispersion and sintering of Pt/C catalysts. In this study, the oxygen surface groups on carbon black are formed by H_2O_2 treatment. These authors concluded that the acidic oxygen groups introduced by treatment with H_2O_2 decreased the hydrophobicity of the carbon, and platinum particles dispersion increases with increasing amount of oxygen surface groups. Furthermore, the less acidic oxygen groups introduced increased the interaction of the metal precursor or the metal particle with the support and thus minimized the sintering propensity of the Pt/C catalysts. The more stable oxygen surface groups are more effective for

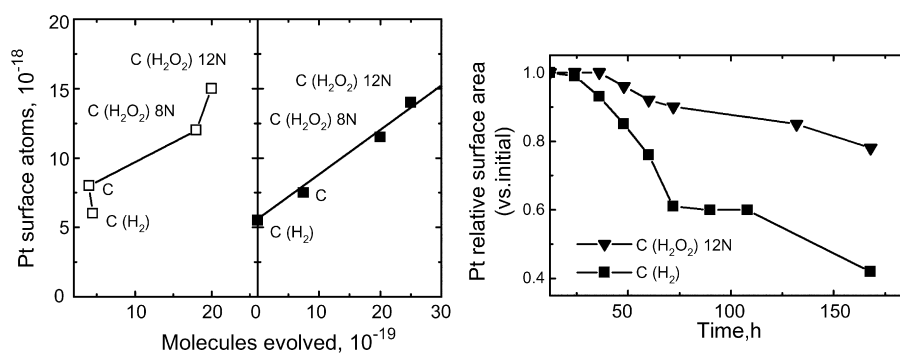


Fig. 6. *Left*: Relationship between the Pt surface atoms and the number of molecules evolved upon TPD (temperature programmed desorption) of the carbon support. *Right*: Effect of surface oxidation treatment of carbon support on the stability of Pt/C catalysts [85].

the anchorage of platinum particles (reduction under hydrogen was carried out at 350 °C temperature at which the less stable oxygen groups have decomposed), thus enhancing the thermal stability of the platinum particles supported (Fig. 6) [85]. In most literatures [85–89], the dispersion of Pt particles increases with increasing the number of oxygen surface groups in the support. Rodriguez-Reinoso summarized the interactions taking place between the sites on the carbon surface and the Pt, and indicated that maximum catalyst dispersion and resistance to sintering can be obtained by either: (i) oxidation of the carbon typically renders the carbon surface more acidic and thus negatively charged over a wide range of pH; (ii) increasing the basic C π sites on the basal plane surface of oxygen-free carbon; and (iii) C=O groups acting as anchoring centers hinder agglomeration and surface diffusion of catalyst particles across the graphene layers [28].

On the other hand, an important point to be taken into account is that some oxygen surface groups may not be stable under the reduction conditions to which the catalysts are subjected to obtain the active phase, and their decomposition would favor the sintering of the Pt. Coloma et al. studied this effect [90], and the results indicate that the dispersion of Pt particle is favored by the presence of oxygen surface groups. However, after reduction procedure at a high temperature, the main part of the less stable oxygen surface groups are decomposed, and those remaining affect the electron delocalization in the π sites, weakening their capability to act as anchoring centers, diminishes the metal–support interaction [90,91].

5.3. Effect of thermal treatment of carbon support

Thermal treatment can increase the basicity of the carbon surface, which cannot be explained by basic groups. The basicity of the carbon surface has been explained in terms of the π sites of the carbon basal plane [92]. Furthermore, there is an increase in the resistance to sintering of the platinum crystallites with increasing degree of pregraphitization of the supports (Table 1) [92], because the interaction of the platinum particles with the support increases. This increasing metal–support interaction is related to the increasing strength of the π sites on the support upon pregraphitization, which act as anchoring centers for platinum [93]. Thus, proper heat treatment of carbon support can increase the stability of Pt/C catalyst.

5.4. Prospective strategies for durability enhancement of Pt/C catalysts

Effects of surface treatment of carbon supports on the Pt particle dispersion and the electrochemical activity of P/C catalysts in PEM fuel cells have been widely studied [94–106]. But the effects of carbon modification on the durability of Pt/C catalyst in a real PEMFC condition have not yet been systemically investigated. However, this effect would be an interesting area for the durability enhancement of Pt/C catalysts towards the extension of PEM fuel cells operation life. According to the degradation mechanism of Pt/C cathode catalysts in PEMFC, strategies towards the improvement of the catalysts stability are proposed here: (a) building proper surface functional groups (including surface oxygen functional groups), or increasing the basic sites on carbon supports to enhance the Pt–C interaction; (b) increasing surface stability of carbon support. Since carbon corrosion in a PEM fuel cell condition is an electrochemical process, the increasing of the hydrophobicity through proper surface treatment of the carbon surface would be beneficial to the suppression of carbon degradation; (c) preparing catalysts with high platinum uniformity and low platinum load. As discussed in previous sections, the presence of Pt deposition has been proposed to have the negative effects on the carbon corrosion [51], lower Pt load on the carbon support would provide an assistance to stabilize the Pt/C catalyst in a PEMFC condition. However, in order to maintain the high catalytic activity, the Pt particle must be highly dispersed on the carbon support

Table 1
Effect of sintering treatments on platinum dispersion [92]

Sintering treatment		[D/D ₀] ^a			
Temperature (K)	Time (h)	C16	C18	C20	C22
623	12	1.00	1.00	1.00	1.00
673	12	0.92	0.95	0.96	–
723	12	0.81	0.88	0.90	0.91
773	12	0.59	0.78	0.89	0.86
773	36	0.33	0.66	0.79	0.79

^a Determined by H₂ chemisorption at 298K. D₀ is the Pt dispersion after the first H₂ treatment at 623 K for 12 h. C16, C18, C20 and C22: Carbon black support (CC-40-220) was heat-treated for 1 h at 1673, 1873, 2073, and 2273 K, respectively.

under the low Pt load. Pt dispersion improvement by proper surface treatment of carbon supports has been commonly accepted. However, more efforts need to be fulfilled for the detailed correlation between the Pt dispersion and the stability of Pt/C catalyst in PEM fuel cells.

6. Summaries

The durability of polymer electrolyte membrane fuel cells (PEMFCs) has been recently recognized as one of the most important issues to be addressed before the large scale commercialization of PEMFCs. It is believed that carbon supported platinum (or platinum alloys) cathode catalysts degradation is the major failure mode for fuel cell systems. A number of mechanisms that contribute to the cathode catalyst degradation have been proposed, including platinum particle sintering, platinum dissolution, and carbon support corrosion. Platinum sintering (particle growth) was proved to be caused by the crystallite migration. Pt dissolution in PEM fuel cells was negligible at low and high potentials, but was remarkable at intermediate potentials. Cathode carbon support corrosion in PEMFC can occur because: (i) the cathode is held at relatively oxidative potentials and oxygen atoms are being generated by the catalyst particles; (ii) furthermore, the cells are at elevated temperature and carbon atoms are able to react with oxygen atoms and/or water to generate gaseous products such as CO and CO₂ which leave the cell. This loss mechanism removes carbon from the cell, leading to a reduction of the carbon content in the catalyst layer with time. Base-metal loss mechanism for Pt(M)/C catalysts in PEMFCs was mainly attributed to (i) excess base-metal deposited onto the carbon support, (ii) incomplete alloying of the base element to Pt, and (iii) thermodynamically instability of base-metals under PEMFC potentials in electrolytes.

Catalysts durability study in PEMFC is a difficult topic because of the lengthy duration of the test time required and the complexity of failure analysis. In industry, post-mortem examinations are always used for the PEMFC durability studies, including post-mortem examination of individually boiled components, disassembling the components for post-mortem examination after operating a cell or stack for a given period of time. Accelerated durability test (ADT) methodology has also been used for a Pt/C or Pt(M)/C catalyst durability study.

One strategy to reduce Pt/C catalyst performance degradation due to carbon corrosion is to use alternative more stable carbon support. Using carbon nanotube as a Pt support has been attempted to increase the durability of the catalyst. The multi-walled carbon nanotube (MWNT) showed lower loss of Pt surface area and oxygen reduction reaction activity when used as fuel cell catalyst support than that for Vulcan XC-72. Another approach for increasing P/C catalyst durability is alloying other transition metals with Pt. Both high and low stability of platinum based binary catalysts in PEMFC condition have been reported in the literatures. However, in the real working conditions, duration tests in PEMFCs indicated a positive effect of the presence of the non-precious metal (in Pt/C catalyst) on the stability of the catalyst.

Interaction between the carbon support and the Pt plays an important role in the properties of the Pt/C catalyst. It has been demonstrated that this interaction is attribute to the electron transferring from platinum to carbon support. Electronic structure change of platinum catalytic layer by the presence interaction leads to the change of the catalyst properties. Generally, this electronic interaction has the positive effects towards the enhancement of catalytic properties, and the improvement of the catalysts' stability in PEMFC operation.

Oxygen surface groups are of greatest interest in the preparation of carbon-supported catalysts, and can be obtained through surface treatment of carbon by chemical methods with different oxidants. It is important to recognize the role of the chemical nature of the carbon surface in the catalysts stabilization. In most literature, the stable oxygen surface groups are more effective for the anchorage of platinum particles, thus enhancing the thermal stability of the platinum particles supported. However, some oxygen surface groups may not be stable under the reduction conditions during catalyst formation, and their decomposition would cause a negative effect on catalysts. Thermal treatment can increase the basicity of the carbon surface, which is explained in terms of the π sites of the carbon basal plane. The increasing metal–support interaction is related to these π sites which act as anchoring centers for platinum particles. Thus, proper heat treatment of carbon support can increase the stability of Pt/C catalyst.

Interaction enhancement of Pt with carbon through surface treatment of carbon support would be a very interesting area to improve the stability of Pt/C catalysts in PEMFC. The promising strategies for the durability improvement of Pt/C catalysts are proposed: (a) building proper surface functional groups (including surface oxygen functional groups), or increasing the basic sites on carbon supports to enhance the Pt–C interaction; (b) increasing surface stability of carbon support, e.g., increasing the hydrophobicity of carbon support through proper surface treatment; (c) preparing catalysts with high platinum uniformity and low platinum load.

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