PEM Fuel Cell Failure Mode Analysis

Haijiang Wang, Hui Li, Xiao-Zi Yuan

Catalyst Support Degradation

Publication details
Zhongwei Chen, Ryan Hsu
Published online on: 25 Aug 2011

Accessed on: 20 May 2020

PLEASE SCROLL DOWN FOR DOCUMENT

Full terms and conditions of use: https://www.routledgehandbooks.com/legal-notices/terms

This Document PDF may be used for research, teaching and private study purposes. Any substantial or systematic reproductions, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The publisher shall not be liable for an loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.
3

Catalyst Support Degradation

3.1 Introduction

Cost and durability are major challenges for the commercialization of polymer electrolyte membrane fuel cells (PEMFCs) (Antolini et al., 2006; Borup et al., 2006; Lee et al., 2008). Great strides in PEMFC research have achieved long-term operation under near-ideal operating conditions, but the durability still needs to be improved under more realistic conditions for a wide range of operating conditions (Debe et al., 2006). For instance, the U.S. Department of Energy (DOE) has set a minimum lifetime target of 5000 h under external environmental conditions (−40°C to +40°C) for PEMFCs for automotive applications. This target is increased to 20,000 h for buses and 40,000 h for stationary applications. Therefore, detailed understanding of the failure modes and degradation mechanisms of fuel cell components and developing design improvements to mitigate or eliminate degradation are required to meet these stringent requirements.

The membrane electrode assembly (MEA) is the heart of a fuel cell stack and most likely to ultimately dictate stack life. Recent studies have shown that a considerable part of the cell performance loss is due to the degradation of the catalyst layer, in addition to membrane degradation. The catalyst layer in PEMFCs typically contains platinum/platinum alloy nanoparticles distributed on a catalyst support to enhance the reaction rate, to reach a maximum utilization ratio and to decrease the cost of fuel cells. The carbon-supported Pt nanoparticle (Pt/C) catalysts are the most popular for PEMFCs. Catalyst support corrosion and Pt dissolution/aggregation are considered as the major contributions to the degradation...
of the Pt/C catalysts (Bi et al., 2007; Asano et al., 2008). The effect of catalyst support and the interaction between catalyst support and Pt are investigated for the improvement of catalytic activity and stability of the electrocatalysts. In the typical Pt/C catalyst, the carbon support is prone to carbon oxidation that occurs during operation and can become detrimental to the structure of the catalyst over long periods of operation (Shao et al., 2007). Carbon corrosion has been known to weaken the interaction of Pt nanoparticles with carbon support, and eventually aggravate platinum agglomeration and the detachment of Pt nanoparticles from carbon support, resulting in decreases in the electrochemically active surface area (ECSA) of Pt thereby lowering the fuel cell performance (Schmittinger and Vahidi, 2008).

Recently, several mitigation strategies have been studied to enhance the lifetime and increase the stability of the catalyst support. These strategies may include alternative synthesis techniques, additional treatment steps, or new materials that are capable of withstanding the harsh conditions of an operating fuel cell for long durations. For example, the graphitization of carbon (in the form of graphene, carbon nanotubes (CNT), or carbon nanofibers (CNF) is a common treatment step that has successfully retarded the corrosion problems seen in carbon blacks (Shao et al., 2006). From a thermodynamic perspective, however, corrosion still occurs and catalysts made with graphitized carbon as the catalyst support still experience a reduction of ECSA after prolonged testing. Support materials other than carbon have also been tested as catalyst supports including indium tin oxides, tungsten oxides, tungsten carbides, doped titanium oxides, and zirconium oxides (Iorio et al., 2005; Chhina et al., 2006, 2007a,b, 2008; Suzuki et al., 2007; Whitelocke et al., 2008; Antolini and Gonzalez, 2009). These mitigation strategies and novel materials are discussed in detail in this chapter to shed light on the direction of catalyst support research.

In this chapter, the following sections related to catalyst support degradation will be discussed in detail. Section 3.2 deals with the mechanisms, kinetics, and thermodynamics of support degradation; Section 3.3 discusses the effect of operating conditions on the support stability; Section 3.4 explains the degradation testing protocols, and Section 3.5 focuses on the mitigation strategies. The scope of this chapter will focus on traditional carbon black support degradation with further discussion on the reliability and stability of alternative catalyst supports. Failure modes dealing with the membrane, catalyst metals, or ancillary components of the fuel cell are beyond the scope of this chapter and thus will only be briefly mentioned. This chapter will be geared toward understanding the fundamental principles of catalyst support degradation and selectively reviewing peer-review journal articles which focus and discuss on the material stability and practical applications in PEMFCs.

### 3.2 Mechanisms, Thermodynamics, and Kinetics of Support Degradation

The durability has recently been recognized as one of the most important issues to be addressed before the large-scale commercialization of PEMFCs. Carbon-supported platinum (or platinum alloys) cathode catalysts degradation is considered as the major failure mode for fuel cell systems. Considerable effort has been made into detailing the mechanisms and thermodynamics of fuel cell degradation, including but not limited to, platinum contamination, platinum agglomeration/dissolution, and corrosion of the carbon support (Wu et al., 2008). The kinetics of the degradation over long-term operation has been modeled both theoretically and experimentally in numerous studies (Meng, 2008; Takeshita et al., 2008; Takeuchi and Fuller, 2008). Carbon support corrosion of cathode catalysts in PEMFCs is a major contributor to the overall catalyst degradation. The following sections provide background on the use of carbon blacks as a support for PEMFC catalysts and illustrate the commonly accepted mechanisms and kinetic models of the catalyst support degradation proposed by several research groups.

#### 3.2.1 Carbon Catalyst Support

Currently, platinum is the only element having sufficient catalytic activity and stability for PEMFC applications. It is well known however, that platinum is scarce and expensive. To lower material costs for
PEMFCs, it is advantageous to disperse platinum as nanoparticles onto the supports to increase the active surface area (Antolini, 2009). In this manner, a good electronic network is formed providing one of the three critical pathways to the active metal sites. The second pathway, being the polymer electrolyte must be present at the active site to provide the pathway of protons. And finally, the third required pathway, the flow channel, is required for the mass transport of reactant gases (H₂/O₂). These three pathways are necessary for the formation of an active site and are termed as the triple phase boundary (TPB).

The support being the electronic pathway for the TPB must have good electronic conductivity to provide a pathway for electrons to reach the platinum nanoparticles. It is also beneficial for the support to be cheap, environmentally friendly, have high surface area, and be able to withstand the operating conditions of a fuel cell. The support surface properties are also of great importance when considering the interaction and dispersion between the support and the metal catalyst (Antolini, 2009).

Carbon black is favorable as a support material not only because of its high surface area and electronic properties, but it is also abundant, chemically inert, and environmentally friendly (Bleda-Martinez et al., 2007). Carbon blacks are typically used as supports which are manufactured by the pyrolysis of hydrocarbons or oil fractions using oil furnaces or acetylene processes. Some of the most common carbon blacks used for platinum deposition in PEMFC catalysts are synthesized using the furnace method where the input materials are burned with limited air at about 1400°C (Dowlapalli et al., 2006). Vulcan XC-72 and Black Pearl 2000 represent these types of carbon blacks. These carbon blacks are easily made and abundant making them popular choices for carbon black supports for Pt/C catalysts (Cameron et al., 1990).

In the state-of-the-art PEMFCs, carbon black is normally used as a catalyst support material. Although carbon black has been widely utilized as a fuel cell catalyst support material, it is susceptible to corrosion in PEMFC operating conditions: high temperatures (50–90°C), low pH (<1), high operating voltages (0.6–1.2 V), and high water and oxygen concentrations. Especially during prolonged use, oxygen has the ability to react with the carbon support to produce CO or CO₂ which leaves the cell as a byproduct (Maillard et al., 2009). This oxidation of the carbon support reduces the electroconductive network of the electrocatalyst and may liberate platinum that has bonded onto the carbon support. This loss of ECSA is the reason why the carbon support corrosion of the cathode catalysts in PEMFCs is a major contributor to the catalyst degradation. Carbon support corrosion in the cathode of PEMFCs can occur because: (1) the cathode is held at relatively oxidative potentials and oxygen atoms are being generated by the catalyst particles; (2) furthermore, the cells are at elevated temperatures and carbon atoms are able to react with oxygen atoms and/or water to generate gaseous products such as CO and CO₂ that leave the cell (Guilminot et al., 2007). In the following section, the thermodynamics, mechanisms, and kinetics of carbon support corrosion will be discussed.

### 3.2.2 Mechanisms and Thermodynamics of Carbon Support Degradation

In a typical Pt/C catalyst, there are several modes of degradation that can occur through the oxidation of the carbon support. Figure 3.1 illustrates many of the mechanisms of performance loss in a PEMFC which are mainly due to the loss of TPB active sites. The first method (Figure 3.1a) in which TPB sites become inactive is from the loss of contact between the catalyst particles and the polymer electrolyte membrane. Detachment of the membrane, also known as membrane delamination, can be caused by the corrosion of the carbon support and can result in protons being unable to reach the platinum nanoparticles. This inevitably leads to lessening of the Pt utilization and catalytic activity of the MEA.

For a TPB site to exist, the catalytic metal must be bound onto the carbon support. The metal is usually deposited onto the support as dispersed platinum nanoparticles. To maximize the surface area and to increase the utilization of the active metal, these platinum particles usually are uniformly dispersed with particle diameters ranging from 3 to 8 nm for typical Pt/C catalysts. Poor adhesion to the carbon support or degradation of the support can lead to platinum particles being unanchored from the carbon. Unanchored platinum usually leaves the cell or migrates within the MEA by the assistance of water
entering and leaving the cell (Figure 3.1b). Platinum agglomeration is a well-studied phenomenon that can also be aggravated by carbon corrosion. As carbon oxidation weakens the mechanical strength of the support between platinum nanoparticles, the platinum metals aggregate and become unevenly distributed on the support surface.

The carbon support not only anchors the polymer membrane and the platinum nanoparticles, but is the pathway for electrons to arrive at the active site. Destruction of active sites can occur by the corrosion of this pathway and separation of the carbon electrical network. This mechanism is illustrated in Figure 3.1c.

For other structures of carbon, for example, doped, graphitic, or nanostructured carbons, the degradation of the support can also lead to structural changes of the support that can lead to changes in electronic properties or other characteristics. For example, nitrogen-doped carbons have been known to have enhanced bond strength between adjacent carbons and platinum. Corrosion of the nitrogen-doped support can change the properties of these platinum–carbon interactions and lead to a more rapid decay of the active sites during operation.

These mechanisms of degradation all lead to performance degradation in the overall PEMFC. Ongoing degradation through carbon corrosion is a serious issue for the longevity of the fuel cell and in the severest cases cause catastrophic failure of the MEA.

Oxidation of carbon to CO$_2$ at standard conditions is thermodynamically possible at potentials greater than 0.207 V vs. the reversible hydrogen electrode (RHE) by Equation 3.1 (Tang et al., 2006).

\[
C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-, \quad E^0 = 0.207 \text{ V vs. RHE} \quad (3.1)
\]

\[
C + H_2O \rightarrow CO + 2H^+ + 2e^-, \quad E^0 = 0.518 \text{ V vs. RHE} \quad (3.2)
\]

\[
CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-, \quad E^0 = -0.103 \text{ V vs. RHE} \quad (3.3)
\]
Carbon can also oxidize to carbon monoxide through a two-electron pathway at 0.518 V at standard conditions and be further oxidized to carbon dioxide through the addition of water (shown in Equations 3.2 and 3.3, respectively).

As it now stands, there is no widely accepted mechanism which details the oxidation and CO₂ generation of surface carbon species. Stevens and Dahn (2005) proposed a four-step mechanism shown in Equation 3.4 that hypothesized this oxidation process and assumed water to be the source of oxygen (Stevens et al., 2005).

\[
R-C\rightarrow R-C-\overset{\text{OH}}{\text{OH}} R-C\overset{\text{=O}}{\text{=O}} R-C\overset{\text{OOH}}{\text{OOH}} R-H + \text{CO}_2
\]

(3.4)

The reduction of O₂ to H₂O (Equation 3.5) is the desired process in a H₂/O₂ PEMFC and produces twice as many electrons as the reduction to hydrogen peroxide (Equation 3.6). The H₂O₂ can be further reduced to H₂O depending on the catalyst type and its kinetics, as shown in Equation 3.7.

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}_2, \quad E_0 = 1.229 \text{ V vs. RHE}
\]

(3.5)

\[
\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2, \quad E_0 = 0.67 \text{ V vs. RHE}
\]

(3.6)

\[
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}
\]

(3.7)

The reduction to H₂O₂ is also disadvantageous to the MEA because peroxide radicals within the cell can attack and degrade the polymer electrolyte membrane and the carbon support. These attacks on the carbon support have been reported to proceed by the following reactions (Maass et al., 2008):

\[
\text{C} + \text{H}_2\text{O}_2 \rightarrow \text{C-O}_\text{ad} + \text{H}_2\text{O}
\]

(3.8)

\[
\text{C-O}_\text{ad} + \text{H}_2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

(3.9)

Equation 3.8 describes oxygen from the peroxide adsorbing onto the carbon surface to form a carbon–oxygen intermediate. This intermediate is reacted as in Equation 3.9 to release the carbon from the support and form CO₂ which is released from the cell as a gaseous effluent. Therefore, ensuring the catalyst is efficient in catalyzing the direct pathway of O₂ to H₂O is critical to the stability of the overall electrocatalyst.

### 3.2.3 Kinetics of Carbon Support Degradation

The rate at which the carbon support corrodes is heavily influenced by catalyst type and operating parameters of the cell. Several experiments suggested that the temperature and platinum loading can heavily influence carbon corrosion rates. Stevens and Dahn carried out a series of experiments to examine the effect of platinum loading and operating temperature on the thermal combustion of the carbon support (Stevens et al., 2005). Platinum was loaded onto Black Pearl 2000 carbon black with nominal loadings ranging from 5 to 80 wt% with platinum particle sizes ranging from 1.5 to 5.1 nm, respectively. The weights of the samples were recorded over time to determine the carbon loss due to corrosion of the carbon support. From their results they determined that the base carbon (carbon without any loaded platinum) displayed no weight loss over thousands of hours at a temperature of 195°C. By increasing the platinum loading, carbon corrosion rates were observed to increase. This was attributed to platinum
particles catalyzing the carbon corrosion reaction, thus converting surface carbon to gaseous products (carbon monoxide (CO) and carbon dioxide (CO₂)). The temperature of the samples in the oven were also studied through the temperature range of 160–205°C and it was found that increasing temperature generally led to increased rates of carbon weight loss. Although the rates of degradation studied in this research do not accurately reflect the rates that occur in PEMFC operating conditions, it is proposed that a more thermally stable catalyst will also be a more electrochemically stable catalyst operating at PEMFC conditions.

Several kinetic models have been proposed to describe the rate of carbon corrosion in Pt/C electrocatalysts. Stevens et al. used a simple model to account for the fractional mass loss in carbon as a function of time, α(t) (Stevens et al., 2005):

\[
\alpha(t) = \left[\frac{100}{100 - \%Pt}\right] \left[\frac{m_i - m_t}{m_i}\right]
\]

(3.10)

where %Pt is the mass percentage of platinum, \(m_i\) is the initial dry mass of sample, and \(m_t\) is the mass of the sample at time \(t\). For their modeling, they applied a first-order kinetic model to the degradation:

\[
\frac{d\alpha}{dt} = k(1 - \alpha)
\]

(3.11)

where \(k\) is the standard exponentially activated rate constant. In their reasoning, they describe that not all carbon within the sample may be adjacent to platinum particles to combust catalytically over an infinite period of time, and thus a slight modification to the equation yields:

\[
\alpha = \alpha_{\text{max}}(1 - e^{-kt})
\]

(3.12)

where \(\alpha_{\text{max}}\) represents the maximum fraction of carbon that can combust catalytically over infinite time. By using the two parameters \(k\) and \(\alpha_{\text{max}}\), the degradation rates and reactivity of different carbon supports were compared.

Hu et al. also report the modeling of MEA and carbon corrosion based on four electrochemical and one chemical reactions taking place within the MEA (Hu et al., 2009). The two-dimensional model considers coupled transport of charged and noncharged species. The model was set up to solve for the local fuel starvation case and the start-up and shut-down case with the Butler–Volmer equation governing the kinetics of each half-cell reaction:

\[
i_{\text{Rxn}} = i_{0,\text{Rxn}} \left[\prod_{\text{Reactant}} \left(\frac{C_k}{C_{k,\text{ref}}}\right)^{n_k} \right] \left[\exp\left(\frac{\alpha_s F \eta}{RT}\right) - \exp\left(\frac{\alpha_c F \eta}{RT}\right)\right] \left\{\frac{S}{V}\right\}_{\text{eff}}
\]

(3.13)

where \(C_k\) is the concentration for species (mol m⁻³), \(F\) is Faraday’s constant (96,487 C mol⁻¹), \(i\) is the volumetric current density (A m⁻³), \(i_0\) is the exchange current density (A m⁻²), \(R\) is the universal gas constant (8.314 J mol⁻¹ K⁻¹), \(S/V\) is the surface-to-volume ratio (m² m⁻³), \(T\) is temperature (K), and the subscripts a, c, eff, and ref denote the anode, cathode, effective transport parameter, and reference state, respectively.

Owing to the numerous parameters and complexity of carbon support oxidation, many other papers (Meyers and Darling, 2006; Hu et al., 2007, 2008; Takeuchi and Fuller, 2007, 2008; Bi et al., 2008; Franco et al., 2008; Franco and Gerard, 2008; Gidwani et al., 2008) not reported here describe models such as the ones proposed to investigate the different parameters effecting carbon corrosion and fuel cell degradation.
3.3 Effect of Operating Conditions

In PEMFCs, understanding the relationships between the fuel cell’s durability and performance with different operating conditions is an important task before the realization of their commercialization can occur. Much of the performance and durability testing with PEMFC benchmarking takes place under idealized conditions that will not accurately reflect those experienced in reality. Environmental real-world conditions may irreversibly aggravate problems in the fuel cell and exacerbate degradation mechanisms such as catalyst support corrosion. In the following section, the effects of several operating conditions to catalyst support degradation are reviewed. The discussion will focus on carbon black supports that have been most commonly studied in the literature; however, the concepts mentioned could be applicable to many noncarbon black supports as well.

3.3.1 Global Fuel Starvation

Fuel starvation is a general term that refers to the deprivation of fuel in parts of the electrode or the entire fuel cell. When insufficient fuel is being supplied to the cell for a certain operating voltage, gross fuel starvation occurs. However, even with sufficient fuel being supplied, localized fuel starvation can occur where insufficient fuel is provided to localized regions along the catalyst layer due to poor cell design, water blocking/flooding or poor operating conditions of the cell. The consequences of gross fuel starvation include carbon support corrosion. Several authors have experienced negative operating voltages as the anode potential increased to positive potentials. In these scenarios, the carbon support is being consumed in place of the fuel which leads to quick catalyst support degradation and decreased durability for the PEMFC (Meng, 2008; Takeshita et al., 2008; Takeuchi and Fuller, 2008).

Gross fuel starvation and its effects were confirmed by Ballard through experiments that replaced H₂ with N₂ at the anode of an operating fuel cell. The anode potential rose to >1.23 V vs. RHE thereby allowing carbon corrosion to occur and the overall cell potential to achieve negative potentials. In experiments led by Taniguchi et al. cell potentials reached −2 V and the anode potential rose to 2.2 V as seen in Figure 3.2 (Taniguchi et al., 2004). Carbon corrosion was confirmed by the presence of CO₂ being detected in the effluent gas. Current densities at 0.7 V were recorded after 3 and 7 min of mimicked gross fuel starvation and resulted in 25 and 50% lower currents in Pt–Ru/C catalysts. Transmission electron microscopy (TEM) was used to observe changes in the average platinum particle sizes on the carbon support after simulating gross fuel starvation. The mean particle size increased from 2.6 to 5 nm at the anode and 2.8–4 nm at the cathode.

For fuel cell stacks consisting of multiple cells, gross fuel starvation can lead to several stacks operating with insufficient fuel, thus those respective stacks must degrade the carbon support to maintain the current being output by all the cells connected in series. To avoid this consequence, careful monitoring of the voltage and fuel distribution of each cell is necessary (Fowler et al., 2002). The implementation of such a control scheme certainly adds to the cost and complexity of the overall fuel cell stack.

It is important to understand the detrimental effects caused by gross fuel starvation as the anodic current that would have been supplied by the oxidation of hydrogen or the fuel is now being supplied by the oxidation of the carbon support to form carbonaceous species such as carbon monoxide and carbon dioxide. Gross fuel starvation results in irreversible damage to the carbon support and the loss of active site loss as the carbon corrodes.

3.3.2 Local Fuel Starvation

Carbon corrosion can also arise from a nonuniform distribution of fuel on the anode side (partial hydrogen coverage) and from crossover of reactant gas through the membrane. Local fuel starvations can cause this type of carbon corrosion. Because of its complexity and consequence to the durability of the fuel cell catalyst layer, local fuel starvation is both a widely studied and researched phenomena.
Unlike gross fuel starvation happening when there is insufficient fuel being supplied to the electrode to generate the required current for the cell, local fuel starvation occurs when sufficient gas is supplied to the cell but the current distribution is not homogeneous and the fuel supplied is unevenly distributed across the membrane and electrode surfaces. This uneven distribution of gas in the cell with sufficient gas supply leads to uneven partial pressures and uneven current distribution. Postmortem thickness and morphology studies on a degraded MEA caused by carbon corrosion under a local H₂ starvation operation in a PEMFC were carried out using optical microscopy, SEM, and TEM (Natarajan and Van Nguyen, 2005a,b). Samples used for the postmortem studies were selected and indexed with the aid of a limiting current density distribution map that was premeasured from the degraded MEA using an electrochemical diagnostic technique. It is clear from the observations in this study that PEMFC operating conditions that cause local H₂ starvation will cause corrosion of the carbon support. This carbon corrosion resulted in a collapse of the electrode’s porous structure, loss of mass transport in the electrode, and subsequent degradation of fuel cell performance. Further investigation is underway to fundamentally understand how carbon corrosion causes the collapse of the porous electrode structure and how it affects fuel cell durability (Natarajan and Van Nguyen, 2005a,b).

3.3.3 Load Cycling/Startup and Shutdown Cycling

Carbon corrosion and catalyst layer degradation may be aggravated by load cycling and startup conditions which may cause ambient air to replace hydrogen fuel in the anode (Roen et al., 2004; Paik et al., 2007). When the fuel cell is shut down or stopped, ambient air/oxygen may replace hydrogen in the gas channels through Brownian motion or via the cathode side by membrane crossover effects. When the fuel cell starts up, a transient fuel–air front is created in the anode layer that may lead to localized or complete fuel starvation (Ofstad et al., 2008). This resulted in dramatic carbon losses and performance decreases brought upon by decreased ECSA and structural changes due to carbon corrosion (see Figure 3.3).

To investigate further into these causes and effects, many reports have carried out detailed analysis to understand what reactions occur during start-up. Reiser et al. (2005) as well as Meyers and Darling...

![Figure 3.2](image-url)
Meyers and Darling (2006) modeled the behavior of the degradation assuming a maldistribution of hydrogen occurring at start-up. Their work has allowed them to determine the conditions that favored cathode carbon oxidation and the potential profile drops occurring between the electrode/electrolyte in the fuel–air anode. They concluded that this air–fuel boundary present in the anode might create locally favorable reverse-current conditions, which they called “the reverse-current decay mechanism” shown in Figure 3.4. This mechanism allowed for a reverse-current within the fuel cell and carbon cathode catalyst to degrade rapidly due to the cathode high interfacial potential that was calculated at 1.44 V vs. RHE.
The effects of load cycling on the carbon support degradation must be carefully monitored during PEMFC operation. Mitigation techniques for sensing oxygen in the anode or a purging stage prior to operation may be implemented after long periods of downtime to avoid the problems associated with startup and increase the lifetime of these fuel cells.

### 3.3.4 Cold Start-Up

The U.S. DOE targets for 2010 for automotive applications intend to have PEMFCs capable of surviving temperatures of $-40^\circ$C and starting operation from temperatures of $-20^\circ$C. The main concern with cold temperature and cold temperature start-up is the formation of ice resulting in structural changes that might occur to the catalyst, MEA and/or gas diffusion layers (GDLs). Ice formation has also been said to impede oxygen transport to the catalyst sites and in severe cases, render entire cells inactive (Mao and Wang, 2007). A study by Cho et al. to examine the effect of cold temperatures was conducted using MEAs that were made to be cycled between $80^\circ$C and $-10^\circ$C (Cho et al., 2004). In a previous study conducted by Cho et al. they hypothesized that the thermal cycling caused the pore sizes to increase in the catalytic layer that resulted in an increase in contact resistance due to structural changes within the cell catalyst layer (Cho et al., 2003).

Oszcipok et al. found similar results with Cho’s in their investigation of starting up the MEA from $-10^\circ$C (Oszcipok et al., 2005). They observed 5.4% loss in current at 450 mV per freeze–thaw cycle, and consecutive losses in ECSA after each start-up from $-10^\circ$C. However, contradictory results were obtained by Knights et al. who experienced little performance loss for a fuel cell subjected to 55 freeze–thaw cycles (Knights et al., 2004).

Three primary mechanisms of MEA degradation occurring in cold start have been put forward by Wang et al.: (1) interfacial delamination between the membrane and cathode catalyst layer, (2) Pt particle growth and Pt dissolution in perfluorosulfonic acid (PFSA) ionomer, and (3) cathode catalyst layer structural damage and hence densification. The interfacial delamination and catalyst layer densification appear to be closely related to each other, and the key parameter to affect both is the ice volume fraction in the cathode catalyst layer after each cold-start step. Eliminating or minimizing these two degradation processes could improve the MEA cold-start durability greatly. However, there is not much research directly relating the effect of cold start-up with carbon support degradation. More work has to be done to understand the full effects of cold start-up on catalyst support degradation.
3.3.5 Relative Humidity

Stevens et al. conducted various studies to determine the effect of carbon type and humidification on the carbon degradation (Stevens et al., 2005). They conducted two sorts of studies in which (1) the catalyst durability was studied \textit{ex situ} and degraded in an isothermal oven at 125°C and 150°C, and (2) the \textit{in situ} MEA durability was studied by a 1.2 V potential hold for 50 h. For both carbons tested (Vulcan XC-72 and Black Pearl 2000) using both methods (\textit{in situ} and \textit{ex situ}), the carbon support was degraded faster with increased humidity introduced into the environment. This agreed with many reports in previous studies (Bi et al., 2009). Figures 3.5 and 3.6 show typical carbon corrosion rates (increase in the amount of CO₂ released from the outlet of the fuel cell) and cell performances at varying inlet humidity at different temperatures. Stevens et al. hypothesized that this increased degradation effect was due to an alternate pathway through a water–gas type of reaction.

Sun et al. (2007) and Hottinen et al. (2003) studied the humidity conditions and the effects of humidity on local fuel starvation and learned that when the fuel cell membrane was under-humidified the current densities increased monotonically across the flow channel due to the progressive hydration of the membrane and increased proton conductivity of the Nafion membrane. In a cell operating with an over-hydrated membrane, the current distribution decreased monotonically due to increased partial pressure and decreased as water content increased in the catalyst layer due to blockage of active sites or water flooding. Thus, water content within the membrane strongly affects the current distribution within the fuel cell and can aggravate localized fuel starvation.

Cai et al. also described studies to evaluate the effect of gas humidity on two Tanaka fuel cell catalysts (Pt/Vulcan and Pt/High surface area carbon (HSC)) at 250°C for up to 30 h (Cai et al., 2006). The Pt/Vulcan demonstrated 11% loss of its initial carbon mass when water was present but no observable mass changes when there was no water present. The Pt/HSC, however, demonstrated no changes in mass regardless of whether there was water or not. This effect was explained by both HSC having a

![Figure 3.5](https://example.com/figure3.5.png)

**FIGURE 3.5** Monitored mass-spectrographic profiles of MEAs at different temperatures running corrosion tests at 1.4 V with humidified N₂. (Reprinted from \textit{Journal of Power Sources}, 193, Lim, K. H. et al. Effect of operating conditions on carbon corrosion in polymer electrolyte membrane fuel cells, 575–579, Copyright (2009), with permission from Elsevier.)
higher Brunauer–Emmett–Teller (BET) surface area than the Vulcan support and oxygen present in the system that adsorbed onto the carbon surface, thus causing mass increase that counteracted the loss of carbon.

The effects of relative humidity on the MEA performance are widely studied and the direct relationship between humidity increase and carbon corrosion are well noted in previous literature. The inevitability of humidity and water moisture in a fuel cell prompts for alternative operating methods or alternative catalyst supports which are more stable in a wide variety of PEMFC atmospheres.

### 3.3.6 Impurities

Feed stream impurities mainly in the hydrogen fuel fed to the anode electrode can cause both temporary and permanent performance degradation in PEMFCs. Steam reformation to produce hydrogen fuel inevitably leads to the presence of these impurities such as CO, H₂S, NH₃, organic sulfur–carbon, and carbon hydrogen compounds. The effects of these impurities in the fuel gas supply to the PEMFC have been well documented and studied in peer-review literature (Garzon et al., 2009).

The presence of CO in the hydrogen feed can poison the catalyst layer by binding onto platinum active sites rendering them useless for fuel cell reactions. Many studies detail the effects and mechanism by which CO is able to degrade the PEMFC, as well as, prevention and recovery strategies (Angelo et al., 2008). In a process known as O₂/air bleeding, 0.5–1% of oxygen gas is fed into the fuel cell together with the anode feed stream in order to mitigate the poisoning effect of CO at the anode. The O₂ in the anode feed stream is able to oxidize adsorbed CO on the platinum particles freeing active sites for the hydrogen oxidation reaction (HOR) (Franco et al., 2009). This oxygen however, can result in further problems for the cathode carbon support if the cell undergoes cell reversal as described previously. In a report by Franco et al. they reported a 600-h test using CO as a competing degradation species method to O₂ in the anode caused by O₂ crossover from the cathode (Franco et al., 2009). Their simulated model and experimental results suggested that the effect of CO in the anode was strongly dependent on the current-cycle mode and could be utilized to reduce oxygen gas crossing over from the cathode and mitigate carbon support degradation caused by cell reversal. In order to capitalize on their findings, Franco et al. suggested the use of CO-tolerant catalysts at the anode.

![Graph](source)

**FIGURE 3.6** MEA polarization curves of before and after corrosion experiments using nonhumidified N₂, humidified N₂ at temperatures of 30°C, 60°C, and 90°C. (Reprinted from *Journal of Power Sources*, 193, Lim, K.H. et al. Effect of operating conditions on carbon corrosion in polymer electrolyte membrane fuel cells, 575–579, Copyright (2009), with permission from Elsevier.)
The direct effect of contaminants entering the fuel cell gas feeds (both fuel and air streams) and affecting the corrosion of the support are not well reported although there is extensive study on the effect of performance overall by various impurities. Garzon et al. reported the effects of direct injection of various sulfur compounds, carbon monoxide, nitrogen oxides, ammonia, and salts into the fuel stream of the fuel cell (Garzon et al., 2009). In this work, they found that sulfur compounds such as H$_2$S and SO$_2$ could lead to severe performance losses in the fuel cell. Figure 3.7 demonstrates this loss in cell performance through MEA polarization curves after different periods of hydrogen sulfide exposure. Increased anode overpotentials were experienced leading to lower fuel cell efficiencies and higher cathode potentials. A consequence of high cathode potentials is the acceleration of platinum surface area loss and carbon support corrosion.

Other impurities have been experimented with in detail and have been reported to affect MEA and PEMFC performance; however, the exact interaction between the MEA and the impurity is not entirely known. The direct relationship with the carbon support may not be a factor when considering many of the impurities reported in literature which would degrade the MEA.

### 3.3.7 Oxidant Starvation

The effects of support degradation caused by air starvation are much less significant than that of fuel starvation. Similar to fuel starvation, oxidant (air) starvation can occur at the cathode whereby oxygen does not reach the catalyst layer to complete the electrochemical half-cell reaction of protons and oxygen to produce water. Common causes of oxidant starvation include a sudden change in the oxygen demand brought upon by start-up or a load change in the fuel cell. Water flooding at the cathode may also block the active sites at the cathode and therefore restrict gaseous oxygen from reacting. This water

![Fuel cell performance after hydrogen sulfide exposure](image)

**FIGURE 3.7** MEA polarization curves before and after 1 h and 2.5 h of hydrogen sulfide exposure. (Reprinted from Garzon, F. H. et al. 2009. *ECS Transactions* 25: 1575–1583. With permission from The Electrochemical Society.)
flooding typically comes about by three pathways: (1) water condensation from the humidified gas reactants, (2) water generation at the cathode active sites as a product from the electrochemical reaction, and (3) transport via electroosmotic drag associated with proton transport across the membrane. In experiments conducted by Taniguchi et al., air starvation led to a greater loss of ECSA, larger platinum particle sizes, and decreased activity of MEAs compared to MEAs operating under normal conditions (Taniguchi et al., 2008). During oxidant starvation, it was noticed that the cell terminal voltage rapidly changed to negative voltages, termed cell reversal. The electrode potential of the air-starved cathode electrode quickly dropped to less than 0 V while the anode potential decreased to about 0.1 V (Taniguchi et al., 2008).

Natarajan and Van Nguyen (2005a,b) also investigated cell performance over four hours using different oxidant flow rates at different temperatures. The reported results were comparable with Liu et al.’s results (2006a,b) indicating that during oxidant starvation, uneven current distributions could be observed resulting in a drop in both the reaction rate and current density experienced downstream of the gas inlet channel.

Although the result of severe oxidant starvation can lead to damage of the carbon support, it is not often studied or focused on due to the relative small effect it has when compared to fuel starvation. Oxidant starvation in PEMFCs is not considered a limiting factor in increasing the durability of PEMFCs.

### 3.4 Degradation Protocols

With the emphasis now on fuel cell durability as one of the main barriers holding back the commercialization of fuel cell technologies, it is important for researchers to know the tools and diagnostic methods available for accurate durability assessment. There is an arsenal of characterization techniques to evaluate catalyst degradation; however, there is no single approach that can be used to classify the severity of degradation nor is there one specific criteria used to assess the stability of the PEMFC catalyst. It is vital for the researcher to understand the wide variety of assessments available and to distinguish the capabilities and limitations of each testing method. The understanding of the individual degradation mechanisms of the catalyst support as well as the effect of the support degradation on the neighboring components of the cell is also important to synthesize new materials or develop new techniques to increase the longevity of the PEMFC. Fuel cell technology and energy organizations have established principle guidelines and set cost and durability targets based on the ongoing research that are meant to steer future endeavors toward high-stability and low-cost fuel cells. The following section outlines durability targets, diagnostic methods, and testing procedures that should be understood by those researchers in the field of PEMFC.

#### 3.4.1 Fuel Cell Programs and Durability Targets

The U.S. DOE, New Energy and Industrial Technology Development Organization (NEDO), and the European Hydrogen and Fuel Cell Technology Platform (HFP) are among the main governing bodies recognizing the need to develop fuel cell technologies. Each of the organizations has identified PEMFC technology as an area for future development for vehicles and stationary power applications. Rollout plans and/or cost and durability targets have been set as guidelines for maturing technologies. The following sections detail more about the individual organizations and elaborate on the expectations set.

##### 3.4.1.1 U.S. Department of Energy

The U.S. DOE Hydrogen, Fuel Cell & Infrastructure Technologies Program (HFCITP) was developed in recognition of America’s growing dependence of foreign oil. The program teams up with industry, national laboratories, universities, government agencies, and other partners to overcome challenges to commercialization of hydrogen and fuel cell technologies. The DOE has set stringent targets for PEMFCs for stationary and automotive applications. They stress durability and cost as main barriers for
commercialization. According to their targets set for 2010, the U.S. DOE aims at having fuel cell systems for automotive applications operate for at least 5000 h, which is equivalent to 150,000 driven miles, with less than 5% performance lost by the end of life. The projected cost per kilowatt for a fuel cell after mass manufacturing in 2005 is $75 kW$$. The DOE expects that in order for fuel cells to be competitive with internal combustion engines the price per kW must be less than $50. DOE set targets for 2010 and 2015 are $25 kW$ and $15 kW$$ respectively (Borup et al., 2007).

For stationary fuel cell applications the durability requirements for fuel cells is more rigorous. By 2005, stationary PEMFCs have been able to undergo 20,000 h of operation however, market requirements will demand even greater lifetimes over a broad range of temperatures (–35–40°C). By 2011, U.S. DOE expects to see stationary fuel cells maintain lifetimes up to 40,000 h at a cost less than $750 kW$$ (Borup et al., 2007).

3.4.1.2 New Energy and Industrial Technology Development Organization

In Japan, NEDO is seeking development and advancement in PEMFCs for practical applications. The program collaborates with sectors of government, industry, and academia to promote hydrogen energy education and technology application in areas of automobiles, stationary power, and portable information devices. In response to growing environmental concerns and the promising advantages of PEMFCs, NEDO promotes the following four development areas under the Strategic Development of PEMFC Technologies for Practical Applications: (1) Development of technology on basic and common issues, (2) development of elemental technology, (3) development of basic production technology, and (4) development of technology for next-generation fuel cells. The NEDO program also recognizes the need for durable, highly efficient, and cost-effective fuel cell systems and by the full dissemination phase of PEMFCs (2020–2030) NEDO expects to see operating lifetimes for over 100,000 km (Borup et al., 2007).

Similar to the U.S. DOE, NEDO has set ambitious targets for PEMFCs for automotive and stationary power applications. By 2015, the targets set for automotive PEMFCs are as follows: Greater than 5000 h of operating life with at least 60% efficiency based on the lower heating value, an operation temperature of the cell in between 90°C and 100°C and a stack cost of approximately 10,000 Yen kW$$. By 2020, operation cell temperatures are expected to increase to 100–120°C without a humidifier to avoid further complexity to the fuel cell system and must be able to operate with external temperatures of –40°C. Lifetime targets for degradation are expected to be less than 10% at end of life. For stationary power fuel cells, the set targets by NEDO are 40,000 h lifetime for 2010 and increased to 90,000 h by 2015.

3.4.1.3 European Hydrogen and Fuel Cell Technology Platform

The HFP focuses on the acceleration and development for cost reduction necessary to competitively market fuel cells for transportation, stationary, and portable power applications. Their Hyways Project Roadmap aims for a mass market rollout by 2020 for European class vehicles with efficiencies of at least 40% on the New European Drive Cycle (NEDC) at a cost of 100 Euros kW$$ and lifetimes of 5000 h for automobiles and 10,000 h for buses. The goals for stationary power systems mainly target residential power systems which the HFP hopes to see tangible market penetration by 2020. By 2009–2012, these systems are expected to maintain 34–40% electrical efficiency, a total fuel efficiency of 80%, >12,000 h of operation and cost less than 6000 Euro per system stack (Borup et al., 2007).

3.4.2 Diagnostic Methods

To test the degradation of fuel cell catalyst and assess the carbon support degradation effect on fuel cell performance, many diagnostic tools are available. These tools may test the morphology of the catalyst support directly or may evaluate the carbon corrosion indirectly through the fuel cell overall performance. Common parameters analyzed to evaluate the electrocatalyst degradation include measurement of the catalyst layer areas (cross-sectional and surface area), the ECSA, fuel cell current density, surface morphology, and elemental composition of material or effluent gas.
The morphology of the catalyst can be an important parameter when examining fuel cell catalyst degradation. Scanning electron microscopy (SEM) is often utilized to assess the thickness of catalyst layers and to determine surface morphology of the electrode. SEM (an example is shown in Figure 3.8) can also be useful in determining particle size distribution if the agglomerates or particles are relatively large (>20 nm) (Fujii et al., 2006). For smaller particle sizes or higher-resolution surface morphology analysis, TEM is often utilized. Platinum particle size distributions deposited on carbon supports can be seen through TEM as well as crystalline lattice parameters that are often conducted. SEM and TEM coupled with energy dispersive x-ray (EDX) analysis can become a powerful method to determine elemental composition of the surface of an electrode material.

Atomic force microscope (AFM) and optical micrography have also been used to characterize degradation of the catalyst layer. X-ray computer tomography (X-ray CT) was used by Garzon et al. (2007) and Lau et al. (2009) to conduct 3-D noninvasive scans of the catalyst layer before and after testing of the electrocatalyst. The morphology of the catalyst layer was observed through electron probe micro-analyzers for surface images and cross-sectional elemental distribution of Pt. X-ray photoelectron spectroscopy (XPS) is a powerful tool in determining the structure of the support and changes in chemical bonding structure over corrosion periods. This characterization is utilized by Zhang et al.

**FIGURE 3.8** SEM cross-sectional images in backscattering mode of (a) initial MEA and (b) MEA after 24 h of electrochemical cycling. (Reprinted from Chen, S. et al. 2010. *Journal of the Electrochemical Society* 157: A82–A97. With permission from The Electrochemical Society.)
and illustrated in Figure 3.9 (Zhang et al., 2009). Such experimental techniques are useful for destructive and nondestructive methods for characterizing morphological changes to the catalyst layer through different stages of the fuel cell tests.

Electrochemical techniques are often used to evaluate the performance of the fuel cell catalysts and to observe changes of the catalyst over the operation life. Catalyst degradation can be inferred by decreases in performance and changes in the ECSA of the catalyst that can be measured by estimating the charge area under the hydrogen desorption peak in a typical cyclic voltammetry (CV) experiment in acidic conditions (Gallagher et al., 2007). Typically, to electrochemically test the degradation of the fuel cell electrocatalyst, two commonly used routes are taken: accelerated durability test (a.k.a. the accelerated stress tests (AST)) or the life test. The more reliable and accurate method to test the degradation of fuel cell electrocatalysts is to run the test according to real operating conditions of the fuel cell; however, these tests are time consuming, costly, and infeasible in some cases as real-world fuel cell lifetimes are expected to reach over 40,000 h of operation lifetimes. ASTs have become increasingly popular due to their simplicity and ability to assess catalyst degradation (Makharia et al., 2006). Furthermore, ASTs can be used to test full fuel cells (in situ testing) or electrochemical half-cells (ex situ testing). In situ testing is more useful for testing the system as a whole and assessing how different components interact with one another, whereas tests using an electrochemical half-cell are more useful for isolated electrochemical testing focused on the catalyst performance (Dross and Maynard, 2007). Ex situ testing will not be able to detect membrane degradation issues, stack problems, water flooding, fuel crossover, and temperature effects.

Therefore, knowing the variety of evaluation methods and their applicability to determining the stability of a catalyst support or MEA is extremely helpful. It should be noted that there are other protocols for assessing support degradation but these techniques may vary by circumstance and are not heavily reported upon. The following section will discuss protocols and testing procedures utilized by many research labs as standardized testing for catalyst support durability.

### 3.4.3 Degradation Testing Procedures

To test the durability of PEMFC catalyst under real-world conditions and time periods is infeasible if not impossible. Fuel cell lifetimes are expected to meet the DOE’s target of 5000 h of operation for
automotive applications and 40,000 h for stationary application. Therefore, ASTs are developed to assess the degradation of these fuel cells under specified conditions. Several reports give detailed experimental conditions for assessing the durability of carbon-supported catalysts; however, the accuracy and effectiveness of these experiments to simulate real-world conditions is still in question. Table 3.1 gives commonly used examples of types of durability tests described by many peer-reviewed papers.

Lim et al. conducted durability experiments of Johnson Matthey Co. 40 wt% platinum catalysts with a focus on the effects of humidity, cell temperature, and gas-phase O\textsubscript{2} (Lim et al., 2009). Their degradation method was to hold the potential of their in-house-fabricated MEAs at 1.4 V for 30 min at various cell temperatures and varying humidity and measure the effluent CO\textsubscript{2} levels using online mass spectrometry.

Li et al. published a paper in which their degradation method of the catalyst support was to cycle the potential from 0.1 to 1.4 V at 10 mV s\textsuperscript{-1} scan rate (Liu et al., 2006a,b). They conducted a differential electrochemical mass spectroscopy (DEMS) study to analyze the CO\textsubscript{2} and platinum levels exiting the cathode during potential cycling. In their study, they claimed that the carbon support corrosion and the fuel cell degradation were further aggravated by multilayers of PtO and higher Pt oxides formed during cycling.

Zhang et al. conducted degradation tests by measuring the change in OCV with MEAs prepared from commercial Pt/C catalysts (Zhang et al., 2010). They reported ECSA losses of up to 60% after 254 h of operation. OCV degradation they observed was similar to OCV degradation trends reported in other literatures where the OCV greatly declined after a couple hours of operation and leveled off slowly with increased operation. The OCV can be recovered back to higher values through intermittent operation or after running a simple electrochemical recovery process. The thickness of the catalyst layer, as well as, the membrane was shown to decline with decreasing ECSA.

Due to the nature of PEMFC catalysts and their complexity usually involving precious metals or alloys, it is hard to evaluate the degradation method of the electrocatalyst and differentiate between carbon corrosion and other factors contributing to activity loss (e.g., platinum sintering or migration). It is therefore necessary in most cases to employ additional methodologies besides electrochemical measurements to determine the relative activity loss due to carbon corrosion. Such methods are mentioned in the previous sections; however, common techniques for characterizing carbon corrosion are SEM imaging of the MEA thickness and online CO\textsubscript{2} mass spectrometry.

In order to synchronize the efforts by various research groups and provide common metrics for evaluating the durability of fuel cell catalysts, the DOE has proposed specific conditions to evaluate and test the different components of the MEA. Tables 3.2 through 3.4 describe these metrics in full detail for different specific components, namely the electrocatalyst, the carbon support, and the MEA as a whole. These degradation and testing procedures provide a standard form of measurement for accessing the stability of the MEA, the electrocatalyst, and the catalyst support. The metrics do not give an accurate measure of the lifetimes that the MEA would experience in reality, but rather give a comparative measure between different catalysts across different research laboratories.

### TABLE 3.1 Commonly Used Carbon Corrosion Degradation Protocols

<table>
<thead>
<tr>
<th>General Methods</th>
<th>Experiment Protocol</th>
<th>Reference Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential holding</td>
<td>Hold cell at 1.4 V for 30 min using Johnson Matthey Co. 40 wt% platinum catalyst varying the gas inlet humidity and cell temperature</td>
<td>Ye et al. (2008); Lim et al. (2009); Ko et al. (2010)</td>
</tr>
<tr>
<td>Potential cycling</td>
<td>Cathode potentiodynamic cycling between 0.1 and 1.4 V vs. the anode electrode. 10 mV s\textsuperscript{-1} scan rate</td>
<td>Liu et al. (2006a,b)</td>
</tr>
<tr>
<td>Open circuit operation</td>
<td>Hold at open-circuit voltage (OCV) for 256 h with intermittent discontinues in operation 100 sccm min\textsuperscript{-1} and 50 sccm min\textsuperscript{-1} of air/H\textsubscript{2}, respectively</td>
<td>Zhang et al. (2010)</td>
</tr>
</tbody>
</table>
3.5 Mitigation Strategies

More of the current research regarding PEMFC catalyst supports focus on novel treatment processes, techniques, or different materials that allow for a more stable and active catalyst for PEMFC technologies. Based on the strict targets set upon by the DOE for fuel cell lifetimes, researchers have recognized the importance of stabilizing the support to impede corrosion mechanisms or to find novel materials that are able to avoid corrosion problems. This task of modifying the catalyst support has proven difficult for many laboratories who realized that an alteration of the catalyst stability will often affect other parameters to hinder its ability to succeed as a high-performing support. This section reviews possible strategies that have been used to either modify the carbon black as a more enduring support or replace it with another material able to prolong the lifetime of the overall catalyst.

<table>
<thead>
<tr>
<th>TABLE 3.2 Electro catalyst Potential Cycle and Metrics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cycle</strong></td>
</tr>
<tr>
<td><strong>Number</strong></td>
</tr>
<tr>
<td><strong>Cycle time</strong></td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
</tr>
<tr>
<td><strong>Relative humidity</strong></td>
</tr>
<tr>
<td><strong>Fuel/oxidant</strong></td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
</tr>
<tr>
<td><strong>Metric</strong></td>
</tr>
<tr>
<td>Catalytic activity</td>
</tr>
<tr>
<td>Polarization curve from 0 to ≥1.5 A/cm²</td>
</tr>
<tr>
<td>ECSA/cycle voltammetry</td>
</tr>
</tbody>
</table>

*Activity in A mg⁻¹ at 150 kPa abs backpressure at 900 mV iR-corrected on H₂/O₂, 100% RH, 80°C.*

Polarization curve per the U.S. Fuel Cell Council (USFCC) "Single Cell Test Protocol" Section A6.

<table>
<thead>
<tr>
<th>TABLE 3.3 Catalyst Support Potential Cycle and Metrics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cycle</strong></td>
</tr>
<tr>
<td><strong>Total time</strong></td>
</tr>
<tr>
<td><strong>Diagnostic frequency</strong></td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
</tr>
<tr>
<td><strong>Relative humidity</strong></td>
</tr>
<tr>
<td><strong>Fuel/oxidant</strong></td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
</tr>
<tr>
<td><strong>Metric</strong></td>
</tr>
<tr>
<td>CO₂ release</td>
</tr>
<tr>
<td>Catalytic activity</td>
</tr>
<tr>
<td>Polarization curve from 0 to ≥1.5 A/cm²</td>
</tr>
<tr>
<td>ECSA/cycle voltammetry</td>
</tr>
</tbody>
</table>

*Activity in A mg⁻¹ at 150 kPa abs backpressure at 900 mV iR-corrected on H₂/O₂, 100% RH, 80°C.*

3.5.1 Surface Modifications of Carbon Supports

Carbon supports typically undergo chemical or physical activation prior to platinum impregnation. The alteration of surface groups and functionalities on the carbon support can strongly influence the carbon–metal interaction that can directly affect the metal particle size, metal particle distribution, surface morphology of the carbon, and surface impurities that may be present. These parameters have been known to influence the catalytic metal stability and activity of the resulting catalyst. Common surface modifications strategies include chemical oxidation of the carbon or thermal activation to modify the surface structures.

3.5.1.1 Heat Treatments

One common approach to improve catalytic activity and durability of the catalyst is a heat-treatment process. Proper heat treatment of carbon support can increase the stability of Pt/C catalyst. Different types of heat treatments have been reported for fuel cell catalyst treatment, such as, oven/furnace heating, microwave heating, plasma thermal heating, and ultrasonic spray pyrolysis.

Continued efforts have been carried out to determine the effect of heat treatment on the individual components of the fuel cell catalyst. For a platinum-based catalyst, heat treatment has been known to have a significant impact on the metal particle size, particle size distribution, particle morphology, and dispersion on the support. A heat-treatment process could also be used to remove impurities present in the metallic catalyst (Bezerra et al., 2007). These effects help to increase the ECSA of the catalytic metal and generally improve the performance of these types of catalysts. Figure 3.10 illustrates the results obtained by Chen et al. who plotted the heat-treatment temperature of Vulcan XC-72R carbon black with specific corrosion rate seen in platinum alloy cathode catalysts at 1 V in H₃PO₄ at 180°C.

Separate studies carried out by Han et al. (2007) and Antolini et al. (2002) showed that typical Pt/C catalyst could be affected by heat treatments. In Han et al.’s study, they heat treated 20% Pt/C catalysts at several temperatures for varying durations and found that the average platinum particle size grew exponentially with increasing heating temperature and linearly with time. Antolini et al. showed that the heating rate was also an influencing factor in the heat-treatment process (Antolini et al., 2002). Platinum particles crystallinities, distribution and morphology were studied. Two different samples were treated at 15 and 45°C min⁻¹. The slow heating rate yielded more homogeneous particle sizes distribution and greater platinum crystallinity. The optimum pyrolyzation temperature was found in the range of 400–550°C.

### Table 3.4 MEA Chemical Stability and Metrics

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Steady State OCV Single Cell 25–50 cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total time</td>
<td>200 h</td>
</tr>
<tr>
<td>Temperature</td>
<td>90°C</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>Anode/cathode 30/30%</td>
</tr>
<tr>
<td>Fuel/oxidant</td>
<td>Hydrogen/air at stoics of 10/10 at 0.2 A cm⁻² equivalent flow</td>
</tr>
<tr>
<td>Pressure, inlet kPa abs (bara)</td>
<td>Anode 250 (2.5), cathode 200 (2.0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metric</th>
<th>Frequency</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-Release or equivalent for nonfluorine membranes</td>
<td>At least every 24 h</td>
<td>No target—for monitoring</td>
</tr>
<tr>
<td>Hydrogen crossover (mA cm⁻²)ᵃ</td>
<td>Every 24 h</td>
<td>≤20 mA cm⁻²</td>
</tr>
<tr>
<td>OCV</td>
<td>Continuous</td>
<td>≤20% loss in OCV</td>
</tr>
<tr>
<td>High-frequency resistance</td>
<td>Every 24 h at 0.2 A cm⁻²</td>
<td>No target for monitoring</td>
</tr>
</tbody>
</table>

ᵃ Crossover current per USFCC “Single Cell Test Protocol” Section A3–2, electrochemical hydrogen crossover method.
Proper heat treatment of carbon support can increase the stability of Pt/C catalyst. For catalysts using carbon black as support for the catalytic metal, the heat-treatment process is understood to provide two main functions for the stability: (1) Removal of oxygenated functional groups and (2) graphitization of the carbon support surface. The carbon surface of most carbon blacks is functionalized with various oxygen-containing functionalities which indubitably affect the surface chemistry of the carbon support (Bleda-Martinez et al., 2006; Colmenares et al., 2009). Heat treatments can thermally decompose these surface oxides to $\text{H}_2\text{O}$, $\text{CO}$, $\text{CO}_2$ at temperatures from 100°C to 900°C. Studies show that the greater concentration of surface oxides on the carbon support leads to poorer platinum dispersion. By removing these acidic functionalities more $\pi$ bonding formations ($\text{C}=$) are present thus leading to better platinum dispersion, higher ORR activity and higher stability under fuel cell operating conditions.

Graphitization inevitably changes the electrochemical properties of the carbon and leads to a more corrosion-resistant support. This increased metal-support interaction is related to the increasing strength of the $\pi$ sites on the support upon pregraphitization, which acts as anchoring centers for platinum (Stonehart, 1984; Prado-Burguete et al., 1991). Higher pyrolyzation temperatures are necessary for the graphitization using polymer and aromatic compounds (de Bruijn et al., 2008). At temperatures of 1630°C, large aromatic molecules will condense into graphene, and at temperatures greater than 1730°C, aromatization occurs to form a graphitic structure. The temperature selected for the heat treatment plays an important role in the extent of graphitization and the number of defects formed within the surface of the carbon support. Graphitization yields a thermally, and electrochemically stable carbon support material which has been used extensively in carbon nanotubes and nanocrystalline graphene structures to improve the stability and durability of fuel cell carbon catalyst supports.

### 3.5.1.2 Surface Treatments and Coatings

Surface chemistry of the carbon support plays particular importance in the activity and stability of the resulting electrocatalyst in PEMFCs. Surface treatments typically include the use of oxidizing agents such as $\text{HNO}_3$, $\text{O}_2$, $\text{O}_3$, and $\text{H}_2\text{O}_2$ that can modify the functional sites on the carbon from basic to acidic. These groups usually exist in the form of oxides such as quinone, ether, anhydride, carbonyl, phenol, lactone, and carboxylic groups. Although the effects of these surface treatments may vary in the literature, it has been proposed by Torres et al. that $\text{HNO}_3$-treated carbons leave strong acid functionalities whereas carbons treated with $\text{O}_3$ and $\text{H}_2\text{O}_2$ result in weak acid functionalities (Torres et al., 1997). According to their temperature-programmed desorption results, carbons with more weak acid functionalities display a
stronger interaction with the catalytic metal precursor \((\text{H}_2\text{PtCl}_6)\) during impregnation than those with strong acid functionalities. This strong interaction would favor the dispersion of Pt on the carbon surface and hence yield higher catalytic activity. However, several other papers contest this by saying that basic sites are more likely to be the centers for adsorption of \(\text{PtCl}_6^{2-}\) and that the oxidation treatment reduces the number of basic sites (Antonucci et al., 1994; Coloma et al., 1994; Roman-Martinez et al., 1995; Guerrero-Ruiz et al., 1998).

In a study made by Roman-Martinez et al. the relationship between support surface and the platinum precursor are studied (Roman-Martinez et al., 1995). It was found that there was a negative effect of the degree of surface oxidation on the final platinum dispersion seen after the resulting impregnation with two different platinum precursors \(\text{H}_2\text{PtCl}_6\) and \([\text{Pt(NH}_3]_4\)\(\text{Cl}_2\). This was a result of either the preferred anchorage of platinum precursor on the functional sites or a repelling electrostatic interaction by the oxidative groups. This discrepancy between reports suggests that different impregnation methods and surface functional groups on the carbon surface have not been fully explored with respect to the resulting platinum dispersion.

The treatment of carbon supports with \(\text{HNO}_3\), however, has led some research groups to speculate that nitrogen functionalities are added during the activation process which benefit the anchorage of platinum metals to the carbon surface. Nitrogen functionalities have also been claimed to have inherent catalytic ability to the ORR and thus, \(\text{HNO}_3\) is a common chemical pretreatment for the carbon support. Along these lines, nitrogen doping of the carbon support through the coating of carbon blacks has also been testified to and reported on in the next section—Novel Carbon Support Materials (Li et al., 2009).

Conductive polymers, such as polyaniline, polypyrrole, polythiophene, polyaniline, and so on, have interesting properties that make them suitable for use in PEMFCs (Heeger, 2001; Shirakawa, 2001). Their electroconductivity and noncarbon functionalities allow some of them to perform effectively as alternative carbon catalysts or with carbon supports to enhance their catalytic effects. Huang et al. utilized polypyrrole as a conductive polymer support for a platinum catalyst active for the ORR (Huang et al., 2009). Their results show significant resistance to carbon corrosion and improved conductivity over traditional Pt/C catalysts. They report that the platinum on polypyrrole catalyst (Pt/Ppy) has well-dispersed platinum particles of about 3.6 nm in diameter. CV scans up to 1.8 V revealed that there was little carbon support corrosion on the Pt/Ppy and a twofold increase in activity than Pt black at 0.9 V.

Various metals/metallic oxides have been coated onto carbons with the aim to improve the platinum tolerance to poisons, increase the platinum utilization and to avoid carbon corrosion of the catalyst support. Sn, Ru, Ti, and Co metals as well as their oxides have been reported on in fair amounts as being transition metals capable of increasing the platinum utilization by removing hydroxide species that would be present on the platinum such that the platinum can further catalyze the ORR. Although these materials have been coated onto the carbon as a support, there are alloying characteristics that occur with the impregnated platinum which result and thus will not be touched up in this section. However, many of these oxides and metals have been used as stand-alone catalyst supports without the use of a carbon substrate, and are discussed further in Section 3.5.3.

### 3.5.2 Novel Carbon Support Materials

With the introduction and expansion of the field of nanotechnology many novel materials and morphologies are being recognized as having similar but different properties than the bulk material. This observation has been extremely well noted for graphitized carbon structures which include CNTs, CNFs, graphene, and porous carbons. Most of these novel carbon structures have been noted to have higher chemical stability and mechanical strength, but also properties such as high aspect ratio, high electrical conductivity, and favorable surface properties. Because of this, these nanostructured carbons have been gaining tremendous popularity as alternatives for carbon blacks in a multitudinous variety of applications, especially for PEMFC catalyst supports. It is important to note, however, that although these catalyst supports differ in
structure and morphology than typical carbon blacks, they are still considered catalyst supports that are based on carbon and due to this, are prone to degradation at normal fuel cell operating conditions (with the exception of conductive diamond). Still, the use of these nanostructured carbon materials has been ever increasing and likely to continue expanding because of their relative success. The following sections review multiple studies incorporating different carbon support materials that have been developed to improve the performance and durability over typical platinum on carbon black catalysts.

3.5.2.1 Graphitized Carbons—Carbon Nanotubes, Carbon Fibers, and Graphene

In light of the durability problems with conventional carbon black catalyst support materials, much research has been geared toward novel nanostructured carbon materials. CNTs (Baughman et al., 2002) and CNFs have been receiving a lot of attention due to their unique properties as PEMFC catalyst supports. Compared to carbon blacks, they offer higher electrical conductivity, form ordered catalyst layers, and are synthesized to be purer than many of the furnace burned carbon blacks that may, for example, contain organo-sulfur impurities that risk contaminating the platinum metal. Specific interactions between the platinum catalyst and CNT/CNF also favor the nanostructured support. The graphitized carbon layers of these supports offer greater mechanical stability and delocalized π bonds which significantly increase electroconductivity resulting in higher reactivity (Li et al., 2008).

Another advantage of the graphitized carbon support is that carbon corrosion rates have been shown to correlate with the degree of graphitization of the carbon support with increased electrochemical and thermal durability seen in CNFs, CNTs, graphene, and other graphitized carbon structures (Li et al., 2006). Although graphitization of carbon supports is successful in slowing down the kinetics of carbon corrosion, it does not change the fundamental thermodynamics of the degradation and thus are still prone to durability issues.

CNTs of various diameters and morphologies have been used extensively in research to improve the durability and performance of Pt/C catalysts. For CNTs, the number of cylindrical shells can have an outstanding impact on the catalytic activity experienced by Pt/CNT catalyst. Chen et al. conducted a comparative study of different carbon nanotube supports including single-walled carbon nanotubes (SWNT), double-walled carbon nanotubes (DWNT), multiwalled carbon nanotube (MWNT), and carbon black (Chen et al., 2007). In terms of performance, DWNTs exhibited the highest activity for the ORR followed by MWNTs, SWNTs, and then Pt/C. They found that the durability of the CNTs with greater graphitization was increased dramatically and the structure of the tubes led to increased performance and higher ECSA values. This result was attributed to better electrochemical properties of the CNTs such as higher electroconductivity and higher mass transport capabilities being provided by a network of CNT structures. Wu et al. (2005) and Tang et al. (2007) however, realized contradictory results when testing different morphologies of CNTs for the methanol oxidation reaction (MOR). They found that SWNT supported platinum catalysts outperformed DWNT and MWNT as catalyst supports and attributed this increased activity to the higher specific surface area and higher platinum dispersion on the tubes. These conflicting results from the authors could be due to different structures and morphologies of the nanotubes used. Some reports in the literature claim SWNTs to be semiconductors depending on the structure and chirality that would decrease electron transfer rates over MWNTs. If this is the case, it would promote a more thorough investigation to determine the relationship between various structures and chiralities of CNTs and their catalytic performances.

Besides the number of cylindrical shells contained in the CNTs, another important factor is the type or number of defects on the CNTs/CNFs. Bamboo-type MWNTs, as opposed to hollow-type CNTs, are a class of carbon nanotubes in which the graphite planes are at an angle to the principle axis of the nanotube. These types of tubes form cone-shaped compartments at varying lengths along the tube and as a result have inherently higher defected edges that are exposed down the surface of the tube. Bamboo-type MWNTs have been shown to have higher electron transfer in electrochemical processes compared to hollow CNTs, where the graphite planes are parallel to the principle nanotube axis. This improved electron transfer has been shown to lead to enhanced catalytic activity which is a direct
The same parallels can be drawn when looking at different types of CNF structures. It was found that palladium supported on platelet type CNFs exhibited higher performances for the ORR than fish-bone-type CNFs which was a result of the greater edge to basal plane atoms of the platelet type CNFs. Tsuji et al. found similar results where they tested and compared the activity of platinum–ruthenium on different types of CNF structures: platelet, tubular, and herringbone, and found that catalysts prepared on platelet-type CNFs exemplified higher onset reduction potentials and current peak potentials for the ORR than the other structures (Tsuji et al., 2007).

Although it can be concluded from the above evidence that greater edge plane exposure and number of defected sites usually have a positive impact on catalytic activity of the carbon nanostructured supports, it is also known that the corrosion of carbon materials is initiated at these edge planes. This relationship between catalyst support enhancement and carbon corrosion needs to be kept in mind when developing novel nanostructured carbon catalysts. Unfortunately, the influence of defects in CNTs and CNFs on the durability of these structures is still not quite known and little research is published in this area.

Graphene-type carbon nanostructures, however, have not demonstrated similar promising results as carbon support structures compared with CNTs and CNFs (Antolini, 2009). Studies performed with platinum deposited onto graphene structures show low performance. Several explanations have been offered to explain why graphene sheets do not bond as well as their CNT/CNF counterparts. It has been argued that the delocalized electrons present in graphitized carbons are capable of three-dimensional mobility in CNT/CNF networks whereas on graphene sheets, electron mobility is hindered due to the planar, two-dimensional structure. This hindrance of mobility is exacerbated when the transport of gases and protons are considered to the catalyst active site to form a TPB. Platinum particles deposited on the graphene sheets become buried when layers of graphenes are stacked between one another—a problem not experienced by CNTs or CNFs that typically form a wire mesh network.

To further enhance the durability and performance of Pt/CNT structures, doping the CNTs has shown to have some interesting effects on the electrochemical properties of fuel cell catalysts (Acharya et al., 2009). A first principle study conducted by Yu-Hung Li et al. (2009) investigated the adsorption of platinum onto un-doped CNTs as well as CNTs doped with nitrogen or boron. The study confirmed the experimental results of many studies in that nitrogen-doped carbon nanotubes have increased reactivity for platinum adsorption on the surface of CNTs as well as higher binding energies when platinum adsorbs onto carbon atoms neighboring a nitrogen atom within the graphitic sheet. This study showed that the nitrogen incorporated into CNT structures simply mediated the enhancement of platinum adsorption onto the surface of CNTs by activating neighboring carbons and providing “donor-like” behavior due to an extra valence electron.

By the same study, boron was tested as a dopant for carbon nanotube structures and it was found that the binding energy of platinum bonded directly to boron within the graphitic sheet of the CNTs was higher than the binding energy of platinum adsorbed onto un-doped CNTs (Li et al., 2009). Unlike the case of nitrogen doping where the increased binding energy was due to the activation of the neighboring carbon atoms in the carbon graphite structure, the direct bond between platinum and boron is strengthened due to the hybridization of the platinum d-orbital with the boron p-orbital. In addition, it has been shown that the adsorption of platinum onto boron- and nitrogen-doped CNTs can be significantly increased with greater dopant content and different structures, for example, pyridinic nitrogen.

3.5.2.2 Porous Carbons

Recently, much study in the field of catalysis has sought interest in carbons with controllable pore diameters usually ranging from 2 to 50 nm. These mesoporous carbons can be classified into two categories, namely, ordered mesoporous carbons (OMCs) and disordered mesoporous carbons (DOMCs). OMCs can be synthesized by casting hard silica templates and impregnating a carbon source into the pores of the silica or by directly templating a triblock copolymer. OMCs are usually preferred over DOMCs.
Catalyst Support Degradation

because of their uniform pore diameters and interconnected pore chambers allowing for high specific surface area and better mass transport. DOMCs on the other hand are typically irregularly interconnected and exhibit wider pore distributions which results in lower conductivity.

As for optimal pore sizes, Yu et al. conducted studies on OMCs with pore sizes ranging from 10 to 1000 nm as a support for a PtRu catalyst used for the MOR (Yu et al., 2002; Chai et al., 2004) as seen in Figure 3.11. The optimal pore size observed for the catalyst was 25 nm leading to a 43% increase in activity compared to commercially available PtRu/C from E-TEK. They claimed that the pore size was optimal for high carbon support surface areas for catalyst dispersion and also large pore volumes for the formation of the triple phase boundary sites. The interconnected pore channels were also hypothesized to benefit the mass transport of gases to the reactant sites allowing for efficient flow of products and reactants.

Although the use of these OMCs have been utilized in recent years with great success as supports for PEMFC catalysts, not much work has been done on assessing the durability of these supports for long-term applications. And although these novel nanostructured carbons may display increased tolerance to the harsh operating conditions in fuel cells with respect to carbon blacks, carbon corrosion is still thermodynamically possible and not completely eliminated.

3.5.3 Noncarbon Supports

Several other materials are considered alternatives for carbon supports and are more durable and stable for a platinum support in fuel cell operating conditions. In light of the carbon corrosion problems faced by Pt/C catalysts today, many researchers have focused on novel materials which are able to operate efficiently in the harsh conditions of a PEMFC. An ideal catalyst support would be able to operate in high operating voltage, withstand low pH, be cost efficient, have high surface area, and be readily available. It would also be advantageous if the novel support material would be environmentally friendly and recyclable from an MEA. Much research has been documented reporting some of these materials such as tungsten oxide, indium tin oxide, tin oxide, tungsten carbide, W- and Nb-doped titania, and sulfated zirconia. It should be noted that although the supports presented in this section are reported as standalone noncarbon supports, it is common that some researchers will integrate the materials with a carbon support hoping to achieve added benefits of the noncarbon materials with the ease and conductivity of a traditional carbon support.

3.5.3.1 Tungsten Oxide

Tungsten oxide is an n-type semiconductor that has been used in electrochromic, photochromic, photocatalyst and gas-sensor applications. The inherent electrical conductivity of tungsten oxide stems

![Figure 3.11](https://example.com/figure311.png)
from its nonstoichiometric composition and oxygen vacancies in the crystal lattice. The good electrical conductivity and flexible material design allows tungsten oxide to be a good candidate as a PEMFC catalyst support alternative. However, what makes it attractive for PEMFC applications is the tolerance it exhibits to CO. Tungsten oxide has been used frequently as a CO-tolerant catalyst support especially for the MOR, ethanol oxidation reaction (EOR) and the ORR. CO tolerance is necessary when CO impurities are present in the inlet feed or during ethanol and methanol oxidation where CO may be an intermediate byproduct of the electrochemical reaction.

Chhina et al. conducted studies using tungsten oxide as platinum catalyst support materials (Chhina et al., 2007a,b). Thermogravimetric analysis and electrochemical testing showed that the tungsten oxide support material was much more resistant to oxidation than commonly used Vulcan XC-72R with and without deposited platinum. Tests showed that after repeated cycling tungsten oxide maintained its structural integrity much better than the widely used carbon support.

Maiyalagan et al. studied platinum supported on tungsten oxide nanorods that were synthesized using anodic alumina membrane (Maiyalagan et al., 2008). Their catalyst showed good activity for the MOR, which was attributed to a synergistic effect between the platinum and WO$_3$ and the ability of their catalyst to avoid poisoning that could have otherwise occurred from oxidation of methanol intermediates.

The durability of WO$_3$ is a problem since it has been found that tungsten dissolution can be observed. This dissolution hinders WO$_3$ catalyst supports from its application in fuel cells. It has been found, however, that with the addition of Ti$^{4+}$ into the WO$_3$ lattice framework, the stability improved and the catalyst experienced a decrease in ohmic resistance (Antolini and Gonzalez, 2009). Further research and understanding of these stability effects are necessary to adequately incorporate WO$_3$ as a catalyst support for PEMFC applications.

### 3.5.3.2 Indium Tin Oxide

Since the first report of transparent conducting CdO films in 1907, vast research and development has been carried out on transparent conductive oxides to tune their properties so that they can be effectively utilized in numerous applications (Hosono, 2007). Conductive oxide films have been found to be well suited for applications such as liquid crystal displays, transparent electrodes of solar cells, photodetectors, and smart windows (Wan et al., 2004).

Indium tin oxide (ITO) is a Sn(IV)-doped In$_2$O$_3$ n-type semiconductor on which a great deal of research has been conducted. The creation of electron degeneracy is fulfilled by introducing a tin dopant that allows for the simultaneous occurrence of high optical transparency (~90%) and high electron conductivity (Tahar et al., 1998a,b). In comparison, the electrical conductivity of ITO is much greater (1000 S cm$^{-1}$) whereas graphitized carbon exhibits electron conductivity of 727 S cm$^{-1}$. To meet economical and technological demands, most research reporting the synthesis of indium tin oxide describe the use of dc and rf sputtering, spray pyrolysis, chemical vapor deposition, and vacuum evaporation, although the use of a sol–gel technique has been recently reported (Mattox, 1991; Tahar et al., 1998a,b).

Chhina et al. conducted thermal and electrochemical stability studies on an ITO oxidation-resistant support as a replacement for carbon supports for fuel cell applications (Chhina et al., 2006). Chhina et al. compared their Pt/ITO catalyst with HiSpec4000, a commercially available Johnson Matthey 40 wt% platinum catalyst deposited onto Vulcan XC-72R carbon black. As a further means of comparison, their group synthesized platinum supported onto Vulcan XC-72R catalyst in-house using the same procedure as their Pt/ITO to impregnate the platinum onto the support. This allowed for a more accurate measurement between the two supports since the same platinum deposition method was used. Results of the ITO catalyst showed improved stability both electrochemically and thermally especially at elevated voltages and temperatures. Thermogravimetric analysis revealed that at 1000°C in an air-flowing atmosphere, both carbon-supported catalysts lost their support mass significantly (~55 wt% loss in mass), whereas the Pt/ITO catalyst maintained its mass with only 0.7 wt% loss. To determine the catalysts’ stability, 100 cycles of electrochemical potential step cycling were conducted.
with electrode coated with the three individual supported catalysts starting with a potential hold at 0.6 V for 60 s and then 1.8 V for 20 s. These electrochemical tests were conducted in 0.5 M H₂SO₄ at 30°C in a deoxygenated environment with the electrode rotating at 2000 rpm. Each catalyst was tested thrice for repeatability and the limits of error and normalized activity for the first 30 cycles for the three catalysts are plotted in Figure 3.12. It should be noted that cyclic voltammograms were obtained during the testing, before and after every 10 potential step cycles and hence, there is a slight increase in activity for cycles 11 and 21 where the activity would increase due to the CV. Based on the results, Chhina et al. concluded that the electrochemical stability of the ITO support was far greater than that of Vulcan XC-72R and led to a more durable catalyst at high-potential sweeps (Chhina et al., 2006). However, even though the stability was far greater for the Pt/ITO catalyst, the activity and ECSA were poor. XRD of the Pt/ITO showed that platinum particles deposited on the ITO support was around 13 nm, where the support particles themselves averaged 38 nm in diameter. Typically, carbon black particles range from 50 to 100 nm and platinum crystalline sizes range between 3 and 8 nm. Chhina et al. claimed that the ITO particle size was too small to optimally disperse platinum nanoparticles on the surface. Decreased platinum particle sizes tend to show greater catalytic activity in PEMFC catalysts as a result of increased ECSA. Chhina et al. proposed that with synthesis methods able to control the particle sizes of ITO, possibly a sol–gel method, it would help limit the agglomeration seen in the platinum deposits in the resulting Pt/ITO catalyst and help increase the activity to acceptable levels (Chhina et al., 2006).

Owing to the high electrical conductivity and the known stability of ITO, this material is particularly interesting for fuel cell catalyst supports. It has been proposed as an alternative material for the cathode support in PEMFCs that could avoid the corrosion problems experienced by conventional carbon supports. However, the application for PEMFC catalyst supports is novel and there are few reported works geared specifically toward fuel cell applications.

### 3.5.3.3 Titanium Oxide

Titanium dioxide or titania (TiO₂) has been considered a promising alternative catalyst support in low-temperature fuel cells because of its excellent corrosion resistance, good stability in acid, and tolerance to high potentials (Diebold, 2003; George et al., 2008). As an electrocatalyst support, TiO₂ deposited...
PEM Fuel Cell Failure Mode Analysis

with catalytic metals have shown good ORR performance for PEMFCs mainly attributed to good dispersion of catalytic metals on the surface of the support and to the metal–support interaction (von Kraemer et al., 2008). TiO₂ also exhibits proton conduction across the surface of the material that is greatly beneficial for a PEMFC catalyst support. This allows for greater utilization of the catalytic metal in the catalyst as more TPBs are formed between the catalyst and the support (García et al., 2007; Shao et al., 2009). Furthermore, TiO₂ is cheap, readily available, and nontoxic, making it widely accessible for use in PEMFCs.

TiO₂ is known to exist in mainly three crystalline forms, each with distinctive properties: anatase, rutile, and brookite. Anatase, the metastable state, and rutile, the stable form, are the only forms of interest for TiO₂ applications (Diebold, 2003; Antolini and Gonzalez, 2009). Pure stoichiometric TiO₂ exists in a distorted octahedral configuration and has a low electrical conductivity of only \(10^{-13} \text{ S cm}^{-1}\) at 298 K; however, substochiometric compositions or added n-type dopants such as vanadium, niobium, and tantalum can create oxygen deficiencies within the lattice structure thereby drastically increasing the conductivity of these materials.

The high electroconductivity (e.g., Ti₄O₇ having an electrical conductivity of 1000 S cm⁻¹), wide diversity of structures, and previously mentioned properties allow them to be used as PEMFC catalyst supports (Chhina et al., 2009a,b,c). Although Ti₄O₇ and Ebonex® are stable in acid, Chen et al. reported that they could still be oxidized under extensive polarization at high potentials (Chen et al., 2002). For this reason, they claimed that doping titania was the preferred method of enhancing the electrical conductivity and stability of these materials.

Chhina et al. examined the stability of such a catalyst support by comparing Pt/C and Nb-doped titania after the addition of 10 wt% Pt (Chhina et al., 2009a,b,c). They found that their Pt/Nb-doped titania was slightly outperformed by traditional Pt/C during MEA test studies; however, after a potential hold at 1.4 V for 60 h the performance of the Pt/Nb-doped titania remained nearly unaffected compared to Pt/C which showed a 50% drop in catalyst layer thickness from SEM images. Figure 3.13 shows the MEA polarization curves of commercial HiSpec4000 before and after 20 h of 1.4 V potential hold as well as the Pt/Nb–TiO₂ catalyst before and after the same durability test.

Nanostructured TiO₂ has also been utilized as PEMFC catalyst supports with dimensions well below 100 nm. Like other TiO₂ structures, these materials also inherit high stability, high surface areas, and moderate electrical conductivity. Titanium oxide nanotubes are of particular interest for fuel cell catalyst supports due to their abilities to form porous networks, disperse catalytic metals upon the surface

![Figure 3.13](image-url)  
**FIGURE 3.13** MEA polarization curves depicting Pt/Nb-doped titania and commercial HiSpec4000 catalyst before and after a 1.4 V potential hold for 20 h. (Reprinted from Chhina, H. et al. 2009b. *Journal of the Electrochemical Society* 156: B1232–B1237. With permission from The Electrochemical Society.)
of the material, as well as, allow for better mass transport, all of which increase the catalytic ability of the catalyst. Kang et al. evaluated these titanium oxide nanotubes as supports for catalytic metals for ORR (Kang et al., 2008a,b). They synthesized arrays of nanotube titanium oxide structures of approximately 1 µm long and 120 nm in diameter grown on titanium substrates. Deposition of bimetallic catalysts was carried out using a dual gun sputtering technique which deposited either Pt–Ni (Kang et al., 2008a) or Pt–Co (Kang et al., 2008b) onto the surface of the nanotubes. HRTEM determined that the Pt–Ni particles ranged in diameter between 5 and 10 nm (shown in Figure 3.14), while the Pt–Co particles were between 3 and 4 nm. HRTEM also confirmed the tube structure of the titanium oxide nanotubes as well as the crystalline phases of the Co and Pt. It was remarked that the TiO₂ catalyst support was of polycrystalline anatase phase. The initial ORR performance with PtNi/TiO₂NT was poor; however, an annealing procedure at 400°C in hydrogen reducing environment allowed for the ORR activity to be significantly improved (Kang et al., 2008a). No comparisons to similar carbon structures were made. Pt₇₀Co₃₀/TiO₂NT was also assessed for its ability to catalyze the ORR (see Figure 3.15). When compared with PtCo deposited on a TiO₂ film, the ORR activity of the Pt₇₀Co₃₀/TiO₂NT displayed a significant activity increase (Kang et al., 2008b). The nanotube structure of the titanium oxide was thought to provide better mass transport of oxygen to the catalysts, as well as, a higher surface area for better dispersion of the catalytic metal on the support.

**FIGURE 3.14** SEM images of (a) bare TiO₂NT, (b) platinum deposited onto TiO₂NT, (c) Pt/TiO₂NT after an annealing treatment at high temperature and, (d) a HRTEM of annealed PtNi/TiO₂NT. (Reprinted from Kang, S. et al. 2008a. Journal of the Electrochemical Society 155: B1058–B1065. With permission from The Electrochemical Society.)
Many structures of TiO₂ and substoichiometric TiO₂ exist which seem suitable for PEMFC catalyst supports. The added benefit of proton conductivity and improved durability in the catalyst support is advantageous over traditional carbon black supports; however, the performance of Pt/TiO₂ catalysts are lacking according to published research. More directed research with these types of catalyst supports might prove effective for high durability, low Nafion-loaded MEA applications.

### 3.5.3.4 Sulfur ZrO₂

Many metals such as titanium, zirconium, tantalum, and niobium have been known to provide high corrosion resistance in acid media. This is mainly due to their ability to passivate on the surface of the bulk material by forming metallic oxides (Antolini and Gonzalez, 2009). Thus, these oxide materials have potential as corrosion-resistant materials in PEMFCs. Zirconium oxide (ZrO₂) can be easily modified with sulfonic acid groups (SO₃⁻) to increase the acidity and proton conductivity (5 × 10⁻² S cm⁻¹ at 60–150°C) of the material. In fact, sulfated-ZrO₂ (S-ZrO₂) is the strongest solid acid among well-known super acids (Hₐ < −16). For these reasons, much research has been conducted with S-ZrO₂ in fuel cells as

---

**FIGURE 3.15** (a) Cyclic voltammograms and (b) ORR performance of Pt/TiO₂NTs, and Pt–Co/TiO₂NT catalysts. (Reprinted from Kang, S. et al. 2008b. Journal of the Electrochemical Society 155: B1128–B1135. With permission from The Electrochemical Society.)
a catalyst for conversion of organic compounds (Hino et al., 1979; Song and Sayari, 1996; Yadav and Nair, 1999), additive for Nafion composite membranes and liquid electrolytes (Zhai et al., 2006; Navarra et al., 2008), and catalyst supports for electrocatalysts (Zhang et al., 2007).

There are several advantages for the use of S-ZrO$_2$ as a catalyst support in PEMFC applications. Because of its hydrophilicity, it has been suggested that this type of fuel cell catalyst would be well suited for low-relative humidity conditions and possibly simplify fuel cell components to operate without the use of a humidifier. Due to the proton conductivity across the surface of the material, less Nafion ionomer needs to be cast to form the TPBs. Platinum utilization increases as the S-ZrO$_2$ support acts as both the platinum and proton conductor and better gas diffusion to the catalyst site results from the decreased blockage of Nafion ionomer (Liu et al., 2006a,b). It is believed that within porous carbon catalyst supports, platinum deposited within the pores may not have proton conductivity due to the perfluorosulfonated ionomer unable to penetrate into the pores. Thus, a TPB which is necessary for a catalyst active site will not be formed. Therefore, the S-ZrO$_2$ support has an additional benefit over porous carbon material supports in that by using the S-ZrO$_2$ as a support for platinum catalysts, the surface of the support can act as a proton conductor and platinum deposited anywhere on the surface of the support will provide immediate access to the electron and proton pathways thereby requiring less Nafion. Thus the use of S-ZrO$_2$ in fuel cell MEA components may potentially lower the cost of materials substantially, as the catalytic metals and membrane materials are among the most costly in a PEMFC. However, like most metallic oxides, the downside of their use stems from their relatively low electron conductivity and low surface areas that results in poor platinum dispersion.

To overcome the poor dispersion of platinum on S-ZrO$_2$, Suzuki et al. proposed an ultrasonic spray pyrolysis method to disperse platinum onto commercial S-ZrO$_2$ (Suzuki et al., 2007). The platinum precursor (H$_2$PtCl$_6$•6H$_2$O) and S-ZrO$_2$ supports were suspended in solution and mists of the solution were generated using an ultrasonic atomizing unit and allowed to pyrolyze at 650°C with air flow. With this synthesis technique, platinum particle sizes of ~8 nm were deposited. Single cell electrochemical tests showed that, compared to Pt/C, the Pt/S-ZrO$_2$ catalyst exhibited a slightly poorer ORR performance when Nafion was incorporated as a binding agent into the catalyst layer for both catalysts. However, when Nafion was not incorporated into the catalyst layer, but only in the electrolyte membrane, the cell performance of Pt/S-ZrO$_2$ was much greater. This substantiated the claim by Suzuki et al. that Pt/S-ZrO$_2$ could be used as a catalyst to reduce Nafion ionomer in the MEA (Suzuki et al., 2007).

The improved corrosion resistance demonstrated by S-ZrO$_2$ over carbon supports shows much promise for it to be a replacement for carbon as a catalyst support, and utilizing the ultrasonic spray technique, platinum particle sizes were adequate for ORR catalysis. However, like many of the other novel noncarbon supports, much more study is required to optimize this support and to determine the real-world performance of the catalyst on these types of supports.

### 3.5.3.5 Carbides

Although carbide materials contain carbon, their structure and properties differ drastically from traditional carbon blacks, and thus for the purpose of this text, they will be considered here as noncarbon materials. Boron carbide has been used considerably since the 1960s for catalyst supports in phosphoric acid and alkaline fuel cells (Shao et al., 2009). The platinum deposited onto these supports was shown to be more resistant to sintering than platinum on graphite or platinum black. There was also an enhanced catalytic activity effect by the platinum that was deposited onto the carbide support. By the 1980s, silicon carbide and titanium carbide were also tested as phosphoric acid supports in fuel cell catalysts. Silicon carbide showed poor electroconductivity and titanium carbide had low surface area (less than 1 m$^2$ g$^{-1}$) making both of them disadvantageous for electrocatalyst supports (Antolini and Gonzalez, 2009). Of all the transition metal carbides, tungsten carbides shows the biggest promise in PEMFC applications as it has an electronic density near the Fermi level most resembling platinum. This has attracted the use of tungsten carbides for either a catalyst or catalyst support for many researchers.
In addition to having inherent catalytic properties, tungsten carbides have shown to be resistant in both acid and alkaline media at anodic potentials. The electrical conductivity of WC is about $10^5$ S cm$^{-1}$ at 20°C, and the active sites are resistant to poisoning species such as carbon monoxide, numerous hydrocarbons, and hydrogen sulfide (McIntyre et al., 2002). Different phases of tungsten carbide allow for the material to be highly flexible with facile methods to change the surface properties and chemical composition. Tungsten carbide has little catalytic activity for the MOR on its own; however, in combination with a platinum catalyst, the support–catalyst system has a synergistic effect for the MOR and improves performance greatly (Zellner and Chen, 2005). Thus there are several reports that describe the use of Pt/WC to enhance MOR activity (Hwu et al., 2001; Ganesan et al., 2005, 2007; Zellner and Chen, 2005).

As for the stability of these types of support materials, according to Zellner and Chen W$_2$C and WC were the most important forms of tungsten carbides. They tested the stability of both materials in 0.5 M H$_2$SO$_4$ (Zellner and Chen, 2005) and confirmed that W$_2$C was thermodynamically unstable at low temperatures and that WC was stable at potentials lower than 0.6 V. This was in agreement with studies conducted by Chhina et al., who performed thermal and electrochemical stability of Pt/WC catalysts (Chhina et al., 2007a,b). Their group found that WC was a more stable catalyst support than Vulcan XC-72R after potential cycling between 0.6 and 1.8 V. The activity of the platinum deposited onto WC support remained after 100 cycles while the Pt/C catalyst was completely degraded after 20 cycles. Still the initial activity of the Pt/C catalyst was higher than that of the Pt/WC catalyst. This was attributed to the extremely low surface area of the WC support and poor particle size distribution of platinum. XRD analysis showed that the particle sizes of WC were ~36 nm, while the platinum deposited onto its surface was ~30 nm. Therefore, they concluded that better methods to synthesize WC with higher surface areas could drastically improve the catalytic activity. The same group conducted a follow-up study utilizing three different methods for WC synthesis to improve the platinum dispersion. Commercial WC was synthesized through a direct carburization of the tungsten metal with carbon or graphite at high temperatures (1400–2000°C) in hydrogen or a vacuum (Antolini and Gonzalez, 2009). With this method, however, additional phases of amorphous tungsten carbides may be generated. Chhina et al. presented three alternative synthesis routes of a WC catalyst support to increase the support surface area by aqueous tungstate dispersion on carbon, an incipient wetness technique to disperse tungstate on carbon and a DC magnetron sputtering of tungsten on carbon (Chhina et al., 2008). Of the three methods, DC magnetron sputtering showed to be the optimal method as the resulting WC support contained an outer shell of WC and a porous inner support of carbon. This outer layer was uniformly distributed with tungsten and had a relatively high surface area. Oxidation cycles of 0.6 and 1.8 V showed that the durability of the Pt/WC catalyst remained stable after 100 cycles, whereas commercial HiSpec4000 catalyst lost its activity in several cycles. The plot of the normalized activity of the Pt/WC over 30 cycles is shown in Figure 3.16. It is also important to note that tungsten carbide can be oxidized to form substoichiometric tungsten carbide which remains slightly conductive (Chhina et al., 2007a,b). Thus, these tungsten carbide supports have attracted much attention for PEMFC applications; however, better methods of platinum dispersion are required to improve the electrochemically active surface area and performance.

### 3.5.3.6 Conductive Diamond

Pure diamonds are nonconductive and generally have low specific surface area. However, by doping diamonds with a dopant such as nitrogen or boron, doped diamonds exhibit the electrical conductivity and chemical stability necessary for PEMFC applications. Several experiments have shown that these conductive diamonds exhibit a phenomenal stability being able to endure an extremely wide potential window. For instance, platinum and platinum alloy metals have been experimentally deposited onto doped diamond supports and were shown to have excellent activity for the ORR, MOR, EOR, and oxidation of ethylene glycol (Sp taru et al., 2008). The doped diamonds were found to act similarly to the commonly used sp$^2$ carbon, which illustrates their potential as fuel cell catalyst supports (Hupert et al., 2003). Moreover, no microstructural changes were found in nanocrystalline boron-doped diamonds when the platinum dispersed catalysts were stressed to 1.6 V.
Catalyst Support Degradation

The use of doped conductive diamonds as PEMFC catalyst supports is still unperfected as there are still several disadvantages when compared with typical sp² carbons. Diamonds typically exhibit low conductivity and low surface areas which is unfavorable for dispersing the catalytic metal uniformly onto the support. In several experiences the catalytic metal nanoparticles deposited onto the diamond surface were too large for PEMFC applications. Some researchers reported that using techniques such as magnetron sputtering and electrochemical deposition, platinum particle sizes between 10 and 300 nm were obtained (Montilla et al., 2002; Salazar-Banda et al., 2006). Finally, doping nanocrystalline diamonds with boron is not easily controllable to realize a homogenous dispersion.

To increase the surface area of conductive diamond supports, a technique called vacuum annealing is utilized in place of doping that anneals un-doped nanocrystalline diamonds to make a conductive diamond. These diamonds, also termed nanodiamonds, are advantageous as catalyst supports because they have high surface areas created by the crevices and surface boundaries between the nanocrystallites. These surface defects acting in favor of platinum deposition however cripple the stability of the material compared to pure diamond.

Much of the current research with conductive diamonds in PEMFC research is to develop platinum deposition techniques that can result in more uniform and smaller particle sizes on the conductive surfaces of diamond. However, conductive diamonds for catalyst support applications have often been used to examine the intrinsic properties of catalytic metals because of their inertness to electrochemical processes, lack of surface corrosion, and oxide formation. They remain strong candidates for fuel cell applications where catalyst integrity and durability are high priorities, and where typically carbon supports may fail due to the harsh operating conditions and high operating voltages.

3.6 Summary

Catalyst support degradation has been identified as a crucial PEMFC degradation mechanism, especially in automotive applications. Catalyst support degradation during long-term fuel cell operation under universal conditions is a complex process that occurs through many parallel mechanisms. Thermodynamically, carbon corrosion can occur at potentials greater than 0.207 V. However, studies have shown that increased voltages, humidity, load cycling, and impurities can cause structural and chemical changes to the carbon support or cause operational changes such as local/gross fuel starvation which accelerates carbon corrosion even further.
Extensive effort has been put into the study on methods to assess the structural damage brought upon by support degradation. The most popular methods include electrochemical tests such as CV and potential holding. Physical characterization can include TEM, and online mass spectrometry; however, SEM, AFM, XPS, EDX, and X-ray CT have been used as well to assess catalyst layer damage and structural changes. Typically, electrocatalysts will be operated in real time or operated through some AST to simulate long-time operation and a final or online assessment can be carried out. Several goals as well as protocols have been outlined by U.S. DOE, HFP, and NEDO to standardize support degradation testing and prioritize the needs of the fuel cell research industry.

The preferred strategy to reduce the negative influence of carbon corrosion on fuel cell performance is to use alternative, more stable materials as catalyst supports. Several strategies are reported to reduce the degradation that has been experienced in the previous literature. Further treatments steps to the carbon black such as heat treatments or oxidation treatments are commonly used to increase the graphitization or add additional functionalities to the surface of the support. This has resulted in slower kinetics of the corrosion, better dispersion of the catalyst metal and stronger Pt-support bonds to increase the performance and/or stability of catalysts in PEMFC environments. It has been proposed that new types of carbon with higher graphite components, such as CNTs, CNFs, and graphene, show greater stability than normal carbon black as support materials for PEMFCs; however, these are still prone to degradation. Other species of materials, such as tungsten carbide, tin-oxide, zirconia oxide and tungsten oxide, and integrating these materials with a carbon support to achieve added benefits of the noncarbon materials and maintains the ease and conductivity of a traditional carbon support 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 PEMFCs. In order to meet the targets set out by DOE and increase the operating lifetimes for automotive and stationary PEMFCs, more research must be conducted to understand and mitigate fuel cell degradation.

References


DOE cell component accelerated stress test protocols for PEM fuel cells. 2010.


Han, K. et al. 2007. Heat treatment and potential cycling effects on surface morphology, particle size, and catalytic activity of Pt/C catalysts studied by 13C NMR, TEM, XRD and CV. *Electrochemistry Communications* 9: 317–324.


Catalyst Support Degradation


Shirakawa, H. 2001. The discovery of polyacetylene film: The dawning of an era of conducting olymers (Nobel Lecture) Copyright (c) The Nobel Foundation 2001. We thank the Nobel Foundation, Stockholm, for permission to print this lecture. *Angewandte Chemie (International ed. in English)* 40: 2574.

Catalyst Support Degradation


