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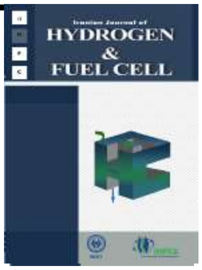

A review of the main mechanisms of catalyst layer degradation in a polymer electrolyte membrane fuel cell (PEMFC) and different performance recovery methods

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Abstract

This paper reviews over 100 articles on the subject of the mechanism of catalyst layer (CL) degradation and the effect of various types of contamination in the polymer electrolyte membrane fuel cell (PEMFC). Also, the recovery of PEMFC via different types of methods, the causes and fundamental mechanisms of cell degradation, and their influence on long-term performance of PEM fuel cells is discussed in this review paper. The most important mechanism of CL degradation in PEMFC includes the effect of different contaminations such as carbon monoxide, carbon dioxide, hydrogen sulphide, sulfur dioxide, N_2, NOx(NO, NO_2), SOx (SO, SO_3), and ammonia. In this study, the agglomeration of catalyst, reactant gas starvation, and oxide and hydroxide formation are investigated. As some of these CL degradations procedures are reversible, different recovery methods for retrieving the catalyst electrochemical active surface area (ECSA) are presented. Some of these recovery methods, including recovery by H_2 purge, direct and indirect zone, short circuit method, water steam, and the reduction method, are presented in this review article. The review results show that the high and effective performance of the PEMFC was achieved by applying ozone method, water steam, and reduction method. However, only H_2 purge and reduction methods are applicable to a stack of fuel cells. Therefore, in light of the facts outlined above, it is safe to conclude that the reduction method is one of the most effective methods for the recovery of reversible CL degradations. Finally, a flowchart of the studied cell degradation and its recovery is presented at the end of the paper. This review was focused on the degradation mechanism of the catalyst layer from different research aspects such as contamination's impact on the performance of a fuel cell, various mechanism approaches, and mitigation development. As the result, we hope that this brief overview provides a good perspective of the important issues that engineers and researchers in this field should address to extend the lifetime and durability of the next-generation of fuel cells.

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1. Introduction

Due to the increasing worldwide demands for energy supplies, the development of energy storage systems and conversion technologies such as fuel cells are considered to be a green power source in recent years [1]. Fuel cells can directly convert the chemical energy of different fuels into electricity without combustion. The main driving force for fuel cell research, development, and commercialization is the increasing concern about global pollution caused by energy emission, especially from transportation and stationary applications. Due to their high efficiency, zero emissions, silent operation, high reliability, and low maintenance fuel cells have been regarded as one of the most promising power generation technologies [2, 3]. Depending on the type of the electrolyte, fuel cells can be divided into different categories like polymer electrolyte membrane fuel cells (PEMFCs), solid oxide fuel cells (SOFCs), alkaline membrane fuel cells (AMFCs), and so forth [4]. The greatest advantage of PEMFCs over internal combustion engines in automobile vehicles is the fact that PEMFCs produce zero emissions when using hydrogen as the fuel and air as the oxidant. In other words, owing to the easy accessibility of hydrogen gas as the fuel, air as the oxidant, and the high efficiency of the system, PEMFCs are the most well-known energy source for electric vehicles engines throughout the world [4]. The schematic of a PEMFC [5] is illustrated in the Fig. 1.

The relatively short life of a PEMFC is a significant barrier to their commercialization in stationary and mobile applications. A longer life span for fuel cell components should be achieved to ensure high reliability, low maintenance costs, and to justify fuel cells as economical alternative energy systems [6]. The Department of Energy's (DOE) 2020 lifetime target requires PEM fuel cells to achieve 5000 h for mobile applications and 40,000 h for stationary applications [4].

Moreover, PEMFC is susceptible to degradation through several physical and chemical phenomena, which may be either reversible or irreversible [7]. In a PEMFC, corrosion of the membrane electrode assembly (MEA) is the most important degradation phenomena [6]. The extent of performance, durability, and degradation levels in a fuel cell change depending on the current and long-term operating. In general, the longer the fuel cell stack is operated

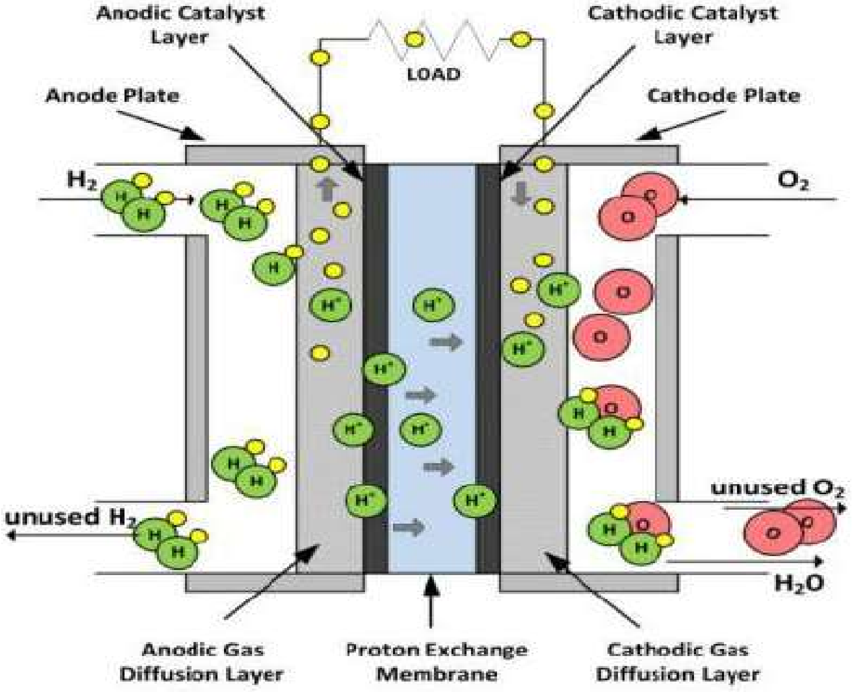

Fig. 1. Schematic of PEMFC [5]

in transient or cyclic condition, the stronger the corrosion and the deterioration [8, 9]. Degradation and corrosion of the electrocatalyst layer of the MEA can lead to serious performance losses and is the most important hurdle in the commercialization of PEMFCs. The material used for catalysts in both the anode and cathode is usually platinum (Pt) or nanometer-sized particles of platinum alloy[6]. In most of today's PEMFC designs the basic structure of the electrodes are similar; the anode and cathode are often exactly the same. Frequently, carbon paper or cloth is used to build the basic mechanical structure of the electrode, and very small particles of Pt catalyst are applied on the carbon surfaces [10].

Corrosion of the Pt catalyst means a loss and change in structure and distribution of the Pt on the carbon support along with a decrease in the electrochemical active surface area (ECSA) of the electrodes [11]. A variety of experiments assessing the ECSA of Pt-catalysts have reported that ECSA decreased with time [10, 12-14]. The loss of ECSA can be described by agglomeration, sintering, oxide formation on the surface of Pt, reactant gas starvation, contamination with different impurities such as CO, H_2S, NH_3, NO_x, SO_x, and so forth [6]. Some of these missing chemical ECSA are reversible so the system performance can be fully or partially recovered by some strategies like H_2 purge, Ozone treatment, oxidation method, short circuit method and etc.

In general, most of the published work has focused on different contaminations, their influence on PEMFC performance [15], and the effect of individual treatment methods. A general overview covering every aspect of fuel cell recovery has not yet appeared in the literature. Therefore, it is necessary to obtain updated and detailed information that is as broad as possible in order to identify the problems and to gain knowledge and a fundamental understanding of PEMFC recovery mechanisms. Then, based on validated mechanisms, effective control strategies can be developed to improve the reliability and durability of PEMFCs to accelerate the commercialization process of fuel cell technology.

In this paper, the different mechanisms of PEMFC catalyst layer (CL) degradation, their impacts on fuel cell performance and lifetime, and the different recovery methods are reviewed in a broad scope. Finally, recovery of a fuel cell stack that has experienced a drastic decrease in performance due to the formation of oxides and hydroxide layers is investigated.

2. Different mechanisms of CL degradation

In this section, different mechanisms of CL degradation in a PEMFC, such as the effect of contamination, agglomeration and reactant gas starvation, are presented.

2.1. Effect of different contaminations

Nowadays, different contamination sources for PEMFC have been recognized. They can be subdivided into three different groups:

1) fuel (hydrogen) contamination sources, 2) air contamination sources and 3) other contamination sources like trace amounts of metallic ions from corrosion of stack or system components (such as flow-field bipolar plates, seals, inlet/outlet manifolds, humidifier reservoirs, cooling loops, membranes and coolants can also cause fuel cell contamination [15]. Other impurities, such as silicon dissolved from the sealing gasket [16], have also been reported to have a contaminating effect on fuel cell performance. Table 1shows different impurities sources and typical contaminants.

The contaminants in Table 1 can cause negative effects on fuel cell performance in different ways. For anode and cathode CLs, the impurities from feed gases and system components can directly enter the matrix structure (reaction zone), poisoning the catalyst sites, changing MEA properties, such as hydrophobicity and hydrophilicity, modifying the proton transportation path, and affecting water management, thus, causing performance degradation. The contamination effects can also be divided into three major areas: 1) kinetic losses due to the poisoning of both anode and cathode

Table 1. Major contaminants identified in the operation of PEM fuel cells [15]

Impurity source	Typical contaminant
Air	N_2, NO_X(NO, NO_2), SO_X(SO, SO_3), NH_3, O_3
Reformate hydrogen	Co, Co_2, H_2 S, NH_3, CH_4
Bipolar metal plates (end plates)	Fe^{3+}, Ni^{2+},Cu^{2+}, Cr^{3+}
Battlefield pollutants	So_2, No_2, Co, propane, benzene
Sealing gasket	Si
Coolants, DI water	Si, Al, S, K, Fe, Cu, Cl, V, Cr
Membranes	Na^+, Ca^{2+}

electrocatalysts, 2) ohmic losses due to an increase in the resistance of cell components, and 3) mass transport losses because of changes in the structure and hydrophobicity of the CLs, PEMs, and GDLs [17-19].

According to the literature review, the most extensively investigated contaminants are carbon oxides, particularly CO, due to the popularity of H_2 production through a reformate process which can produce traces of CO and CO_2 in H_2-rich fuel for fuel cell applications [15]. Air stream contaminants, such as NO_x and SO_x, and trace cationic ions generated from the cell components have also been studied in recent years. Therefore, in this section, we will pay special attention to the effects of carbon oxides, sulfur-containing species, and ammonia on fuel cell performance. These contaminants degradation mechanisms were reviewed based on a literature survey.

2.1.1. Effect of carbon monoxide

Both carbon monoxide and carbon dioxide have become major concerns in PEMFCs using reformate H2-rich gas as fuel, particularly at conventional operating temperatures (<80 ◦C). It is well documented that CO binds strongly to Pt sites, poisons hydrogen electro-oxidation sites on the Pt surface and resulting in the reduction of surface active sites available for hydrogen adsorption and oxidation. With respect to this, Baschuk and Li [20] reviewed the CO poisoning of platinum electrocatalysts used in PEM fuel cells in terms of characteristics, mechanism, mitigation, and theoretical models. It seemed that the CO poisoning effect was strongly related to the concentration of CO, the exposure time to CO, the cell operation temperature, and anode catalyst types.

The proposed mechanism for CO adsorption can be expressed as follows [21]:

1) Dissociative chemisorption

$$H_2 + 2Pt \rightarrow 2Pt\text{–}H_{ads} \quad (1)$$

$$CO + Pt \rightarrow Pt\text{–}CO_{ads} \quad (2)$$

$$2CO + 2Pt\text{–}H_{ads} \rightarrow 2Pt\text{–}CO_{ads} + H_2 \quad (3)$$

2) Electro-oxidation reaction:

$$2Pt\text{–}H_{ads} \rightarrow 2Pt + 2H+ + 2e^- \quad (4)$$

Reaction (1) requires two adjacent bare Pt sites and therefore is quite slow. Reaction (4) is relatively fast. The adsorption of CO occurs not only at bare Pt sites through Reaction (2), but also at Pt hydride sites via Reaction (3). It is believed that a linear-absorbed CO species involves one adsorption site per CO molecule, while a bridge-bonded CO species requires two adjacent Pt surface sites [22, 23].

Also, the elimination of adsorbed CO can be described by the following reactions:

$$Pt + H_2O \rightarrow Pt\text{–}OH_{ads} + H+ + e^- \quad (5)$$

$$Pt\text{–}CO_{ads} + Pt\text{–}OH_{ads} \rightarrow 2Pt + CO_2 + H^+ + e^- \quad (6)$$

The poisoned Pt sites are ineffective for CO electrocatalytic oxidation since water cannot be readily adsorbed at Pt sites to produce oxygen-containing species via Reaction (5) at an electrode potential of 0.5 V versus NHE. Reaction (6) takes place at even higher electrode potentials (0.6 V versus NHE). Cheng and co-workers reported that at potentials below the oxide formation (Reactions (5) and (6)), a near-zero rate constant for hydrogen electro-oxidation was obtained using scanning electrochemical microscopy on a CO covered polycrystalline Pt in sulfuric acid solutions [15]. However, on a CO-free Pt electrode, the obtained rate constant was larger than 1 cm s^{-1} [24]. This clearly demonstrates that CO adsorption can significantly reduce the H_2-oxidation rate, resulting in a fuel cell performance drop. The effect of CO on average cell voltage drop [25] is depicted in Fig. 2.

2.1.2. Effect of carbon dioxide

Currently, almost 95% of hydrogen is generated by steam reforming of natural gas (CH_4), which produces a high level of carbon dioxide (25%) as a by-product [26]. Due to the similarity of direct CO adsorption, CO2 can lead to the production of Pt–CO_{ads}. This can be formed through a water-CO_2 gas shift reaction (WGSR) [27]:

$$2Pt + H_2 \rightarrow 2Pt\text{–}H_{ads} \qquad (7)$$

$$CO_2 + 2Pt\text{–}H_{ads} \rightarrow Pt\text{–}CO_{ads} + H_2O + Pt \qquad (8)$$

However, the exact structure and adsorption form

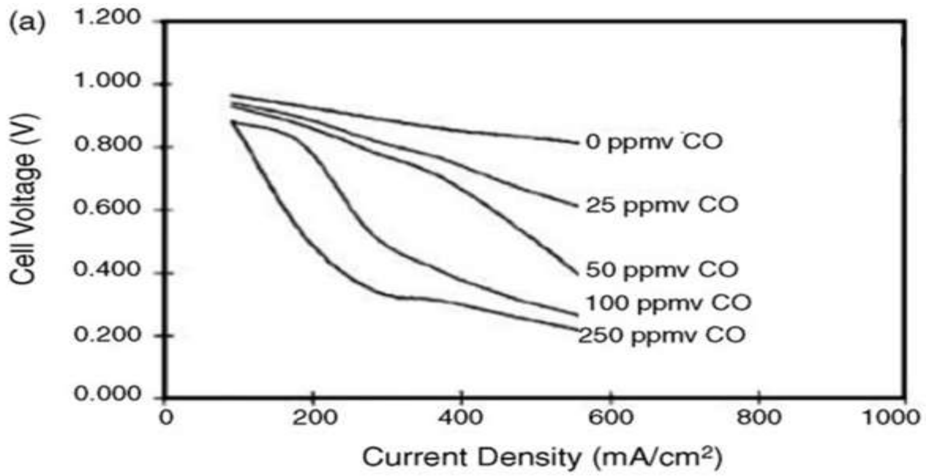

Fig. 2. Effects of CO concentration on cell performance [25]

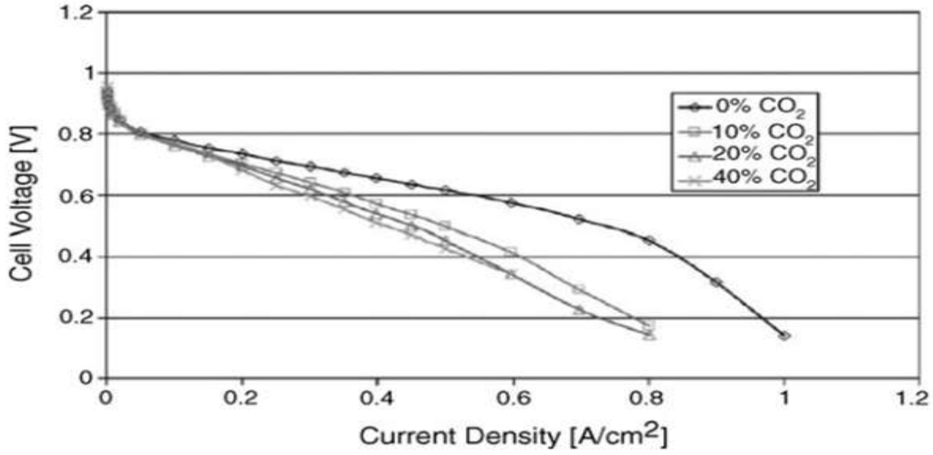

Fig. 3. Effect of CO_2 concentration on cell performance [24]

of surface species formed by CO_2 reduction has not yet been clarified. It could have a linear-, bridge- or triple-bonded CO structure [28-30]. The CO/COOH radicals [31], $COOH_{ads}$ and COH_{ads} [32, 33], have also been reported in different studies. All of these formed species lead to a loss of performance and cell voltage drop. In Rajalakshmi et al. observed a performance loss due to CO_2 contamination in anode fuel, especially at higher current densities (Fig. 3) [26]. Also, an increment in cell voltage drop was observed when the amount of CO_2 increased. Additionally, Bruijn et al. reported a performance loss of 30% occurred at 0.5 V with a 20% CO_2 content [27].

Adsorption species formed on the Pt surface from either Reactions (2) and (3) or reaction (8) can be electro-oxidized at higher electrode potentials (≥0.7 V versus NHE) via the “reactant pair mechanism” [34] and abandon the surface of the catalyst:

$$\text{Pt–CO}_{ads} + \text{Pt–O}_{ads} \rightarrow \text{CO}_2 + 2\text{Pt} \qquad (9)$$

$$\text{Pt–CO}_{ads} + \text{Pt–OH}_{ads} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^- + 2\text{Pt} \qquad (10)$$

2.1.3. Effect of hydrogen sulfide and sulfur dioxide

Sulfur-containing species such as sulfur dioxide and hydrogen sulfide are typically present as impurities in the fuel and air streams of a fuel cell. Even small amounts of S impurities can cause significant performance losses [35-37]. A trace amount of H_2S, when exposed to an anode or cathode, was found to degrade the cell performance significantly, mainly through the poisoning effect of the Pt catalysts [37]. The adsorption of S-containing species to the active sites of a catalyst occupys the polyatomic sites preventing the reactants, including oxygen and hydrogen, from being adsorbed at the catalyst surface. A loss of performance occurs as a consequence of S-containing species on the surface of the Pt . As illustrated in Fig. 4, it was found that a negligible amount of H_2S (1.2 ppm) can cause a cell voltage drop greater than 300 mV within 25 h at 100 mA cm^{-2} and 80 ◦C [38]. Also, a 0.1 ppm level of H_2S in the fuel stream can cause a 250 mV cell voltage drop within 300 h at 0.5 A cm^{-2} load. There are some points in this figure related to the simulation data in [38], and since this is not in the scope of this paper, we do not present any discussion about it.

Additionally, the adsorption mechanism of S-containing species on the surface of Pt can be described as follows [15, 39]:

$$\text{Pt} + \text{H}_2\text{S} \rightarrow \text{Pt–S}_{ads} + \text{H}_2 \qquad (11)$$

$$\text{Pt} + \text{H}_2\text{S} \rightarrow \text{Pt–H}_2\text{S}_{ads} \qquad (12)$$

$$\text{Pt} + \text{HS}^- + \text{H}^+ \rightarrow \text{Pt–HS}_{ads}^- + \text{H}^+ \qquad (13)$$

$$\text{Pt–HS}_{ads}^- + \text{H}^+ \rightarrow \text{Pt} + \text{H}_2\text{S} \qquad (14)$$

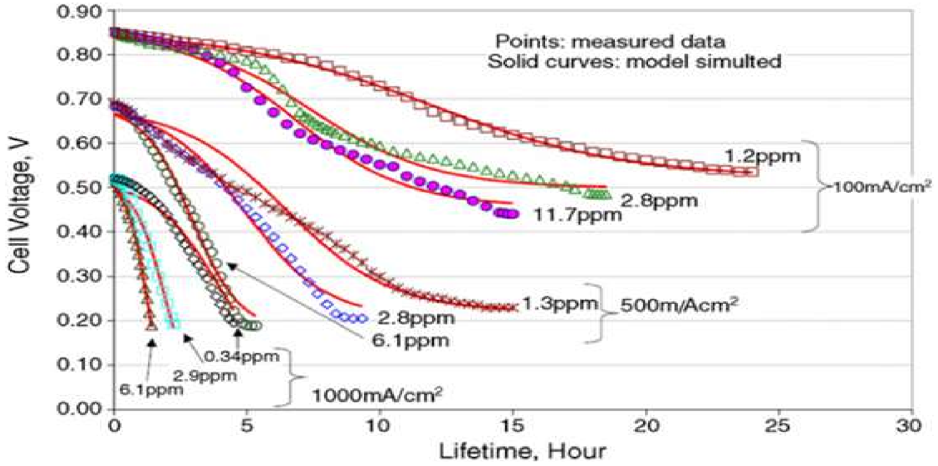

Fig. 4. Effect of H_2S contamination on cell performance and lifetime [36]

$$Pt+H^{+}\rightarrow Pt^{+}\text{–}H_{ads} \qquad (15)$$

The following reaction is also possible due to an electrochemical potential resulting from Reactions (14) and (15) [39]:

$$2Pt+H_{2}S\rightarrow Pt\text{–}SH_{ads}+Pt\text{–}H_{ads} \qquad (16)$$

With respect to SO_2, it was demonstrated that the final products of SO_2 adsorption on a Pt electrode would be a linear bridged adsorbed S species [40]. These two types of chemisorbed S species on Pt at 80 °C were reported to be responsible for catalyst poisoning. which electrochemical reduction SO_2 to S on Pt surface was also suggested [15]:

$$Pt + SO_2 + 2H^+ + 2e^- \rightarrow Pt\text{–}SO_{ads} + H_2O \qquad (17)$$

$$Pt\text{–}SO_{ads} + 2H^+ + 2e^- \rightarrow Pt\text{–}S_{ads} + H_2O \qquad (18)$$

2.1.4. Effect of Ammonia

Contamination by ammonia is another type of pollution which may occur in PEMFC. The extent of performance deterioration due to the existence of ammonia relies on the concentration level and exposure time [26, 41, 42]. It was believed that ammonia, contrary to other contaminants, could have a significant effect on the membrane of the PEMFC rather than the CL. It was also proposed that NH_3 might not be readily adsorb on the carbon fibers in the MEA; but rather, it might have been some reactions with protons in the membrane. Therefore, by staying in the membrane phase and decreasing the membrane conductivity, ammonia may form $NH4^+$ thorough the following reactions [41, 43]:

$$NH_3\ (g) \rightarrow NH_3\ (membrane) \qquad (19)$$

$$NH_3\ (membrane) + H^+ \rightarrow NH_4^{\ +} \qquad (20)$$

According to Halseid et al. [44], reaction (20) led to a linear decrease in membrane conductivity in a Nafion 117 membrane phase. Also, it is probable that this reaction occurs with the ionomer inside the catalyst layers [15]. However, as mentioned above, the main effect of ammonia is on the membrane. Table 2 summarizes all of the contaminations mechanisms of section 2.1.

2.2. Agglomeration of catalyst

Pt is used as the catalyst for both the hydrogen

Table 2. Catalyst layer degradation by different contaminants

Contaminant	Reversibility	Mechanism	Ref.
CO	Reversible	$H_2 + 2Pt \rightarrow 2Pt\text{–}H_{ads}$ $CO + Pt \rightarrow Pt\text{–}CO_{ads}$ $2CO + 2Pt\text{–}H_{ads} \rightarrow 2Pt\text{–}COa_{ds} + H_2$ $2Pt\text{–}H_{ads} \rightarrow 2Pt + 2H^+ + 2e^-$ $Pt + H_2O \rightarrow Pt\text{–}OH_{ads} + H^+ + e^-$ $Pt\text{–}CO_{ads} + Pt\text{–}OH_{ads} \rightarrow 2Pt + CO_2 + H^+ + e^-$	[14, 19-23]
CO_2	Reversible	$2Pt + H_2 \rightarrow 2Pt\text{–}H_{ads}$ $CO_2 + 2Pt\text{–}H_{ads} \rightarrow Pt\text{–}CO_{ads} + H_2O + Pt$ $Pt\text{–}CO_{ads} + Pt\text{–}O_{ads} \rightarrow CO_2 + 2Pt$ $Pt\text{–}CO_{ads} + Pt\text{–}OH_{ads} \rightarrow CO_2 + H+ + e^- + 2Pt$	[24-32]
H_2S & SO_2	Reversible	$Pt + H_2S \rightarrow Pt\text{–}S_{ads} + H_2$ $Pt + H_2S \rightarrow Pt\text{–}H_2S_{ads}$ $Pt + HS^- + H^+ \rightarrow Pt\text{–}HS_{ads}^{\ -} + H^+$ $Pt\text{–}HS_{ads}^{\ -} + H^+ \rightarrow Pt + H_2S$ $Pt + H^+ \rightarrow Pt^+\text{–}H_{ads}$ $2Pt + H_2S \rightarrow Pt\text{–}SH_{ads} + Pt\text{–}H_{ads}$ $Pt + SO_2 + 2H^+ + 2e^- \rightarrow Pt\text{–}SO_{ads} + H_2O$ $Pt\text{–}SO_{ads} + 2H^+ + 2e^- \rightarrow Pt\text{–}S_{ads} + H_2O$	[14,33-38]
NH_3	Irreversible	$NH_3\ (g) \rightarrow NH_3\ (membrane)$ $NH_3\ (membrane) + H^+ \rightarrow NH_4^{\ +}$	[14,24, 39, 40, 41, 42]

oxidation reaction (HOR) occurring at the anode and the oxygen reduction reaction (ORR) at the cathode. Usually, the Pt catalyst takes the form of small particles on the surface of somewhat larger carbon particles that act as a support. However, sometimes Pt lose its performance owing to the agglomeration phenomena. Agglomeration is a change of small narrow and uniformly dispersed Pt-particles to larger particles which are then distributed more widely [6, 13]. The agglomeration of the Pt particles and accordingly the loss of ECSA is affiliated with the long run operating conditions of the cell. Cell potential cycling is one of the most important factors contributing to platinum agglomeration and/or oxidation, and hence to a decrease in ECSA [6]. For instance, it was reported by Borup et al. [12] that after 1500 cycles from 0.1 to 1.0 V, approximately 40% of the performance loss was observed for the Pt catalyst in the temperature range of 60 to 120 °C. This amount of performance loss can be higher in higher cell potential. In general, higher potential levels accelerate agglomeration and cell degradation [6]. Therefore, it is better to operate the PEMFC in lower potential to maintain large ECSA for a long time and prevent cell performance loss.

Another parameter which has a significant effect in agglomeration of Pt particles in PEMFC is temperature. Since, increasing the temperature improves the reactions kinetics, different cell temperatures during operation can have an influence on the ECSA [45]. Generally, higher temperatures result in faster growth of Pt-nano particles [13].

In addition to the previous two parameters, the humidification level of reactants in PEMFC can play a significant role in agglomeration of catalyst particles. The higher the relative humidity (RH) of the gases, the higher the growth of the catalyst particles, especially during potential cycling [6]. Therefore, in order to enhance the lifetime of the catalyst, the RH should be maintained at a low level [6].

2.3. Reactant gas starvation

Starvation refers to an overall undersupply of reactants at the cell level [46-48]. In other words, fuel or oxidant starvation alludes to the operation of PEMFC in sub-stoichiometric reaction conditions [6]. There are several operational faults that can lead to gas starvation in a PEMFC: 1) poor water management with flooding [49, 50], 2) poor heat management during sub-zero temperature which may lead to the production of ice within the cell and block the pores of the gas diffusion layers [51, 52], 3) poor gas feeding management which can lead to non-uniform distribution of the reactant gases causing local or overall fuel and/or oxidant starvation [53, 54], 4) following a sudden load demand, the reactant feeding might not follow fast enough which causes transient starvation [55], and 5) defective PEMFC design with an unbalanced distribution of mass in the flow fields [11]. The main consequences when the PEMFC is starved of fuel or oxygenare catalyst loss, carbon-support corrosion, performance degradation, generation of hydrogen in the cathode or oxygen in the anode, and the cell voltage drops [55]. It was reported by Taniguchi et al. that fuel starvation is accompanied by the disappearance of the smallest particle size which leads to the decrease of ECSA and PEMFC performance losses [46].

In a PEMFC, high anode potential occurs in the fuel starvation phenomena [48]. Subsequently, the water present at the anode may split into hydrogen and oxygen thorough the following reactions:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \text{ (anode)} \qquad (21)$$

Also, in the absence of hydrogen, the following reaction can occur in the anode:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \text{ (anode)} \qquad (22)$$

Moreover, hydrogen can be produced at the cathode during oxygen starvation as follows: [56]:

$$2H^+ + 2e^- \rightarrow H_2 \qquad (23)$$

While the normal reaction is:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (24)$$

The presence of O_2 at the anode and H_2 at the cathode will lead to a negative potential difference between the cathode and the anode which is called cell reversal potential [57]. These phenomena accelerate the corrosion of carbon support in CL through reaction (22) [49, 57]. Also, the product of reaction (22) is CO_2 which is recognized as contamination for CL [58].

2.4. Oxide and hydroxide formation

Oxide and hydroxide formation mainly occur in PEMFC owing to the presence of oxygen and water in the cathode. Similar to the previous CL degradation mechanism, these type of reactions lead to performance loss and subsequently a potential drop in PEMFC performance. The mechanism of oxide formation can be described as follows [7]:

$$Pt + O^{2-} \rightleftharpoons PtO + 2e^- \quad E = 0.88V\ vs\ SHE \qquad (25)$$

Also, the mechanisms of platinum oxide and platinum hydroxide formation due to the presence of water are [7, 59, 60]:

$$PtO + 2H^+ + 2e^- \rightleftharpoons Pt + H_2O \ E_{Pt/PtO} = 0.980 - 0.059pH \qquad (26)$$

$$Pt + H_2O \rightarrow Pt - OH + H^+ + e^- \ (0.8 - 1.1Vs\ SHE) \qquad (27)$$

$$t - OH_{ads} \rightarrow (OH - Pt)_{3D\ lattice} \quad (place\ exchange) \qquad (28)$$

$$(OH - Pt)_{3D\ lattice} \rightarrow (Pt - O)_{3D\ lattice} + H^+ + e^- \ (1.1 - 1.4Vs\ SHE) \qquad (29)$$

$$\mathrm{Pt} + 2OH^- \rightleftharpoons \mathrm{Pt}(\mathrm{OH})_2 + 2e^- \quad E = 0.14V\ vs\ SHE \qquad (30)$$

A Pourbaix diagram can be used for studying the formation of different species, and Pt stability of bulk materials in aqueous environments in a PEMFC [61]. This diagram represents the most stable state of a material as a function of pH and potential [62]. A Pourbaix diagram is calculated from the first principles [63]. The Pourbaix diagram for Pt is illustrated in Fig. 5. As can be seen, this diagram is divided into sections by different colors. The gray and blue areas in the diagram indicate the area of OH^- and O_2 adsorption on the Pt surface, respectively. It is clear from the diagram there are three kinds of blue color and two kinds of gray color. The darker blue areas are attributed to the higher amount of O_2 adsorption, Pt, and O formation, which subsequently lead to more losses of ECSA. Also, the darker gray area is related to a higher amount of hydroxide formation on the surface of the catalyst. The red area shows the region of stable Pt^{2+} dissolution. The Pourbaix diagram indicates that by increasing the potential and pH, a greater amount of PtO and PtOH species will be generated in the PEMFC system.

From this section we can conclude that all of these contaminations procedures cause a loss of ECSA. However, some of them are reversible while others are not. The reversible degradation can be addressed by performance recovery methods that will be discussed in the next section. Table 3 listed different mechanism of CL degradation as a summary of section 2.

3. Different methods of PEMFC performance recovery

As previously mentioned, some ECSA losses and CL degradation are reversible. In other words, by applying recovery methods one can retrieve ECSA and prevent any performance loss in the PEMFC. This not only improves the life span and durability of the system but also will restore the PEMFC to almost its initial situation.

3.1. Recovery by H_2 purge

One of the most influential performance recovery methods is purging hydrogen to the PEMFC cathode. By purging hydrogen to the cathode, Pt oxide film that has formed on the surface of the catalyst can be reduced to Pt, which will modify the performance of

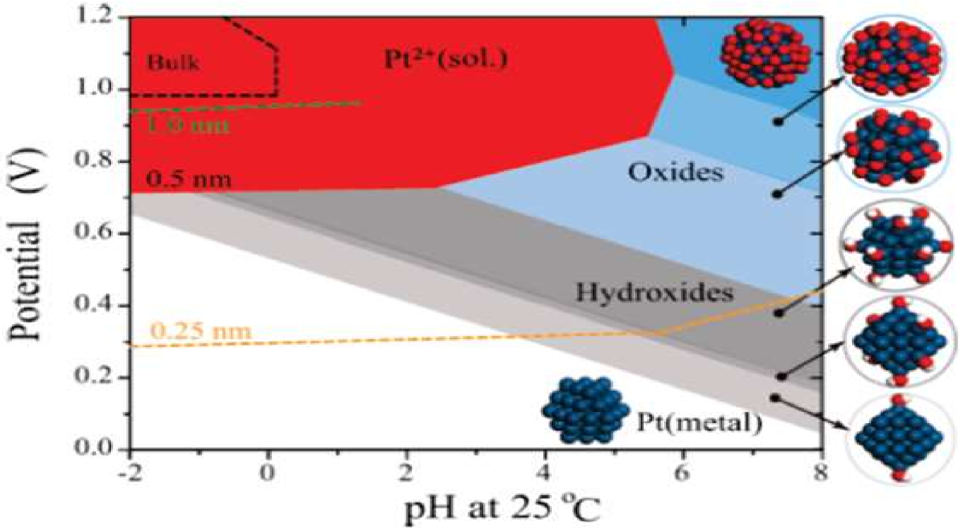

Fig. 5. Pourbaix diagram for Pt [59]

Table 3. Different mechanism of catalyst layer degradation

Degradation Method	Reversibility	Mechanism	Ref.
Contamination	Table 2	Table 2	Table 2
Agglomeration	Irreversible	High cell potential cycling	[5, 11, 12, 43]
High temperatures	Irreversible	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (anode) $C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$ (anode) $2H^+ + 2e^- \rightarrow H_2$ $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	[5, 10, 44-56]
High relative humidity	Reversible	$Pt + O^{2-} \rightleftharpoons PtO + 2e^- \quad E = 0.88V\ vs\ SHE$ $PtO + 2H^+ + 2e^- \rightleftharpoons Pt + H_2O \quad E_{Pt/PtO} = 0.980 - 0.059pH$ $Pt + H_2O \rightarrow Pt - OH + H^+ + e^- \quad (0.8 - 1.1Vs\ SHE)$ $Pt - OH_{ads} \rightarrow (OH - Pt)_{3D\ lattice} \quad (place\ exchange)$ $(OH - Pt)_{3D\ lattice} \rightarrow (Pt - O)_{3D\ lattice} + H^+ + e^- \quad (1.1 - 1.4Vs\ SHE)$ $\mathrm{Pt} + 2OH^- \rightleftharpoons \mathrm{Pt(OH)}_2 + 2e^- \quad E = 0.14V\ vs\ SHE$	[6, 57-61]

the stack through the following reaction [7]:

$$PtO + 2H^+ + 2e^- \rightleftharpoons Pt + H_2O$$
$$E_{Pt/PtO} = 0.90 \quad Vs\ SHE \tag{30}$$

By this reaction, the ECSA will recover to almost its initial value and an increment in stack potential will be observed [7]. The complete recovery method consists of three different steps: 1) supplying fully saturated H2 to the cathode of a degraded fuel cell stack for a predestined period, 2) sealing the fuel cell stack for a predetermined time and allowing the oxide layer to be reduced while the cathode is maintained around SHE potential under fully saturated conditions, and 3) repeating the above steps at least three times.

In order to verify the effectiveness of the H_2 purging method, Choo et al. [7] investigated this method on a 13.6% degraded stack which consisted of a few hundred unit cells. The results demonstrated that the initial degradation ratio of 13.6% at 0.6A/cm^2 declined to 11.3%, 10.0%, and 9.0% as the number of recovery increased. They believed that the generating power of the fuel cell stack partially recovered about 20-30% at 0.6A/cm^2 after applying the H_2 purging method [7]. Additionally, they were of the opinion that average potential of a few hundred cells enhances by a large margin after the first trial and the recovery rate seems to be slow down in the following recovery trials (Fig. 6). Also, this method is capable of removing sulfonated SO_3^- anion as well as oxide [64].

This method of recovery has several advantages and disadvantages. It can be applied to stacks while other recovery methods may not apply. Also, this method can be effective in short periods of time. However, the flammability, the high cost of preparing pure hydrogen, and only partial recovery are the drawbacks of this method.

3.2. Recovery by Ozone

Recovery by Ozone is a novel and effective method for the recovery of a degraded PEMFC. Ozone cleaning mechanisms can be generally divided into electrochemical and chemical processes [65]. The chemical process can be the incorporation of 1) a direct reaction of O_3 with the pollutant and 2) a series of complicated indirect chemical reactions including radical intermediates. These two types of reaction will be described comprehensively in the following sections [66].

3.2.1. The direct method

A direct reaction of ozone with contamination is an attack of O_3 on the surface of the catalyst in order to remove any impurities. This method does not require any intermediate, like water and oxygen, to recover the degraded CL in a PEMFC. For instance, when the sulfur is adsorbed to the vacant site of Pt, O_3 is able to attack the Pt-Sads and generate SO_2 and SO_3 via the ensuing possible reactions [66]:

$$Pt\text{-}S_{ads}+O_3(g) \rightarrow Pt\text{-}O+SO_2(g) \tag{31}$$

$$Pt\text{-}S_{ads}+O_3(g) \rightarrow Pt+SO_2(g) +O^{\cdot}(g) \tag{32}$$

$$Pt\text{-}S_{ads}+O_3(g) \rightarrow Pt+SO_3(l) \tag{33}$$

Subsequently, $SO_3(l)$ will react with the water present in a PEMFC and undergo rapid hydrolysis to generate sulfuric acid [66, 67]:

$$SO_3(l) +H_2 O(l)\rightarrow H_2 SO_4(l) \tag{34}$$

Therefore, the contaminated cell can be effectively recovered using only ozone without any intermediates. Kakati et al. studied the effect of ozone on the treatment of a degraded PEMFC which was contaminated with hydrogen sulfide [66]. They found that the PEMFC performance dropped dramatically after exposure to H2S. However, treatment of the poisoned CL rapidly restores the cell performance. They found that after applying only 300 s of ozone recovery at room temperature, the performance of

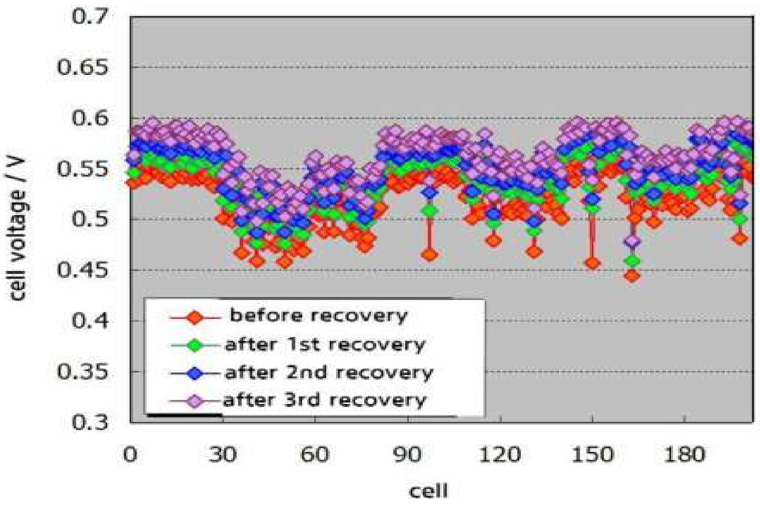

Fig 6. Cell voltage distribution according to recovery number at 600mA/cm^2 [7]

the PEMFC was retrieved to 87-97% of the fresh cell across the entire current density range. Their results are illustrated in Fig. 7.

3.2.2. The indirect method

The indirect process that occurs in the acidic aqueous environment of the ionomer includes the generation of some intermediates like radical species which then attack the adsorbed contamination on the surface of catalyst [66, 68]. Under acidic conditions, ozone reacts to produce an oxygen atom, followed by a subsequent reaction with water to produce two hydroxyl radicals [69, 70]:

$$O_3(aq) \rightarrow O_2(aq) + O^{\cdot}(aq) \quad (35)$$

$$O^{\cdot}(aq) + H_2O(l) \rightarrow 2OH^{\cdot}(aq) \quad (36)$$

In the case of sulfur contamination of a PEMFC, the $O^{\cdot}$ and$OH^{\cdot}$ radicals may have a reaction with $Pt\text{-}S_{ads}$ to generate a range of sulfur-containing species including SO_2. Furthermore, it is highly probable that in addition to the generation of SO_x, some other types of species likeSO_{ads} andSOH_{ads} are produced [66]. The mechanism for generation of these species is mentioned below:

$$Pt\text{-}S_{ads} + O^{\cdot}(aq) \rightarrow Pt\text{-}SO_{ads} \quad (37)$$

$$Pt\text{-}S_{ads} + OH^{\cdot}(aq) \rightarrow Pt\text{-}SOH_{ads} \quad (38)$$

Following these reactions, oxidation of sulfur oxides by an oxygen-containing species like $O^{\cdot}$, $OH^{\cdot}$, O_2, H_2O, etc. may occur, and that causes desorption of sulfur oxides from the catalyst surface which increases the ECSA. This reaction can be demonstrated as follows [66]:

$$Pt\text{-}SO_{ads} + [O] \rightarrow Pt + S_x O_y^{z-} + zH^+ \quad (39)$$

Where $S_x O_y^{z-}$ is the representative of the different arrays of species like SO_2, SO_3, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, etc. that can be produced through reaction (37). Additionally, the potential of more than 1 V is a prerequisite for oxidation of sulfur from the platinum catalyst indicating that the kinetics of these reactions are somehow slow and need a large overpotential to happen [66].

This method of recovery has several advantages such as full recovery of the system, short time period for recovery, and not needing an additional reagent in order to enhance the efficiency of this method. The disadvantages of this method of PEMFC performance recovery include not being applicable for the stack, being environmentally pollutant, and the production of some intermediates which inherently are a kind of contaminant.

3.3. Recovery by the short circuit method

The short circuit is a method of performance recovery with only a very limited number of publications on the implication of this method for enhancement of PEMFC performance [71]. This method consists of connecting two heads of a PEMFC circuit to each other. When the current short circuit is applied in the PEMFC control system the load resistance is nearly zero so the current in the PEMFC stack is at maximum, and the electrode reaction rate also tends to be the maximum [72]. The short circuit method has several advantages: 1) evaporation of the water in the MEA swiftly leads to the transfer of reactant gas to the CLs and an improvement of the PEMFCs performance [72], 2) additional water production [73], and 3) oxide stripping [74, 75].

Despite all of these studies and suggestion, there remains uncertainty about the mechanisms of performance improvement in PEMFC. In an investigation carried out by Gupta et al. [71], they refuted the first two theories. They stated that a typical short circuit period might be 100 ms every 10 s, and during the short circuit the current and subsequently the quantity of water produced during this time might double. However, the time during the short circuit is just 1% of the whole operating time. As a consequence, only 1% more water in total will be generated by the short circuit. Therefore, one cannot consider this to have a remarkable influence on the water management of the PEMFC, except perhaps the local concentration of water in the CL. The second theory can be discarded in the same way. They believed it is true that if the system runs at 0 V, all of the produced energy generated will be dissipated as heat internally and this causes a sudden increment in temperature at localized points which could evaporate water at those points. However, similar to the previous agruement, the short circuit represents just 1% of the total operating time. Conversly, since the generated heat during the remaining 99% of the operating time is less and the stack might be cooler, this leads to some detrimental consequence like flooding of the system [71]. Therefore, one can assume that the dominant mechanism in the short circuit method is removing oxides layers and other adsorbed species from the surface of Pt. The probable reactions in this process are [76-80]:

Adsorption: $2Pt+O_2 \rightleftharpoons Pt_2O_2$ (40)

Dissociation: $Pt_2O_2 \rightleftharpoons 2PtO$ (41)

Reduction 1: (42)
$PtO+H^+ +e^- \rightleftharpoons PtOH \quad E^0 = 1.1-1.4V\ vs\ SHE$

Reduction 2: (43)
$PtOH+H^+ +e^- \rightleftharpoons PtH_2O \quad E^0 = 1.1-1.4V\ vs\ SHE$

Desorption: $PtH_2O \rightleftharpoons Pt+H_2O$ (44)

Each of the reactions 40-44 have an equilibrium potential, so there will be an equilibrium coverage of species on the Pt surface that is a function of the operating potential at the cathode. Thus, at different potentials, there are various equilibrium concentrations of species, which means that there are more or less available vacant sites for oxygen to be adsorbed on the Pt. Therefore, if the reactions intermediates concentration builds up too high, since they can limit the current density at a given potential, they should be considered poisons to the reaction and catalyst [71]. Fortunately, as all of the adsorbed species on the surface of Pt are in dynamic equilibrium with each other, the equilibrium concentration for a specific potential require time to be established. Thus, by periodic perturbation of the system, such as applying short circuit, it is possible to achieve a time-averaged concentration of intermediate species which is different from the equilibrium concentration for a given potential[71].

Kim et al. [81] studied the effect of the short circuit on the performance recovery of PEMFCs. In their expermients, the short circuit was applied every two seconds and its performance was compared to that without short circuit control. As illustrated in Fig. 8, the performance was better at high load in comparison with low load. At the load of 3 A, the power output with short circuit control (98 W) did not show a great enhancement over that without short circuit (107 W). However, at a load of 9 A, the improvement was much better, with the output increasing from 218 to 252 W when the short circuit control was applied. Therefore, a 16% improvement of performance with short circuit was achieved.

Last but not least, the advantaes of the short circuit method are being applicable with a simple control system, extremely fast operation, and being cost effective. The disadvantes of this method include partial recovery and not being applicable for stacks because of high current generation which may lead to melting of electrical instruments.

3.4. Recovery by the water steam method

Recovery by water is an effective method for removal of the different contaminations mentioned in section 2.1. One of the main pollutants that can be removed from the surface of the catalyst by using this method is H_2S. As previosuly mentioned, H_2S can react with Pt and occupy one vacant site by the following reaction [82]:

$H_2S+Pt \rightleftharpoons Pt-S+H_2$ (45)

This reaction is very fast and reversible in a wide spectrum of concentration [83]. The adsorption

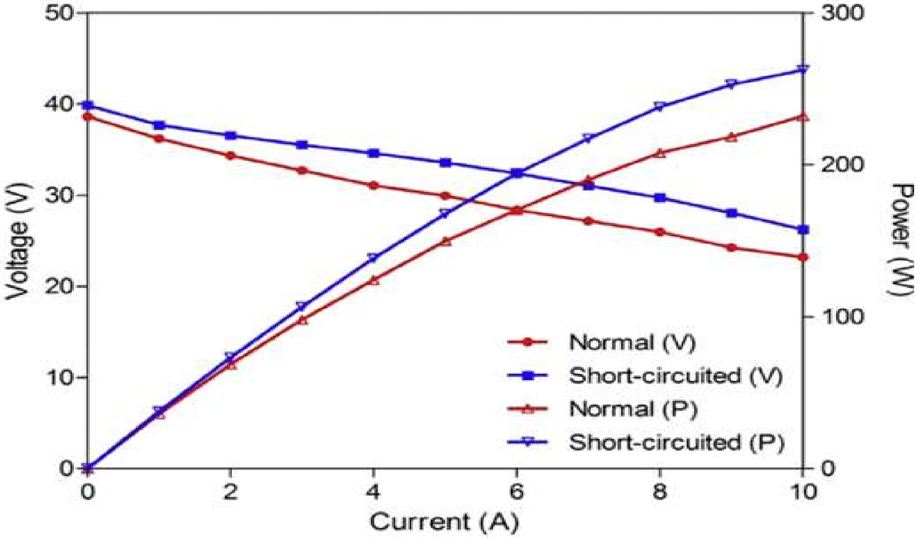

Fig. 8. Improvement in PEMFC performance using short circuit control [81]

isotherm in this reaction obeys the Temkin law. The coverage fraction of sulfur enhances with the ratio (P_{H2S}/P_{H2}) and decreases with temperature [82]. The above adsorption is linked to adsorption of water:

$$H_2O + Pt \rightleftharpoons Pt - O + H_2 \tag{46}$$

Which competes with sulfur binding for high water steam contents in the feed. Owing to the reversibility of sorption, natural regeneration of Pt surfaces by reducing the sulfur content of the feed is theoretically probable [84-86].

Regeneration of Pt surfaces was demonstrated to be effective upon encountering oxidizing atmosphere by injection of water steam at 700 ◦C or more:

$$Pt - S + H_2O \rightleftharpoons Pt - O + H_2S \tag{47}$$

Attention has to be paid to temperature level selection in order to prevent sintering of the catalyst, which may happen above 800 ◦C. Hydrogen sulphur is then oxidized with water to sulphur dioxide with the formation of hydrogen:

$$H_2S + 2H_2O \rightleftharpoons SO_2 + 3H_2 \tag{48}$$

The equilibrium of the reaction imposes a (P_{H2O}/P_{H2}) ratio of almost 200 to avoid back-formation of hydrogen sulfide and subsequent sulfurization of the platinum surface [83]. Hydrogen formation in reactions 43 to 46 lead to an increase of H_2 concentration in the system. Therefore, according to Le Chatelier's principle [87], the reactions 43, 44, and 46 will be reversed and the catalyst surface will be regenerated, and an improvement in PEMFC performance will be observed [82].

Jung et al. [88], studied the effect of water steam for recovery of a PEMFC that was contaminated by the coolant. The changes in the polarization curve after an injection of 2.5 µLmin^{-1} of coolant are shown in Fig. 9. After the injection of the coolant, the OCV decreased about 5.1% and recovered completely in constant current mode after water cleaning. The performance at 0.6 V decreased by 58.2% from the initial performance after coolant injection but recovered to 96.2% after recovery by water cleaning.

3.5. Recovery by the reduction method

This method of recovery is another effective method for recovery of performance loss in a PEMFC. To start the recovery in this method, one has to obtain cyclic voltammetry (CV) from the PEMFC in order to find the region of oxide formation and reduction processes. There are lots of reports for CV of Pt in the literature [89-95]. According to Garsany et al. [94], the CV of Pt (Fig. 10) consist of three separate potential regions: the hydrogen underpotential

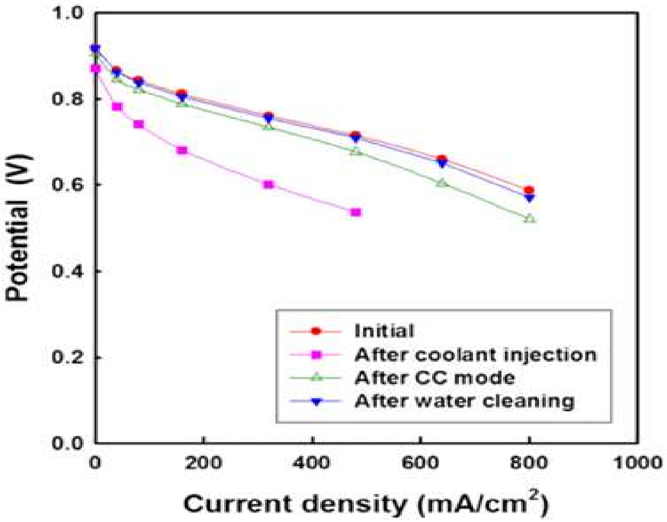

Fig. 9. Polarization curve changes of 2.5 μLmin^{-1} coolant injection in unit cell [88]

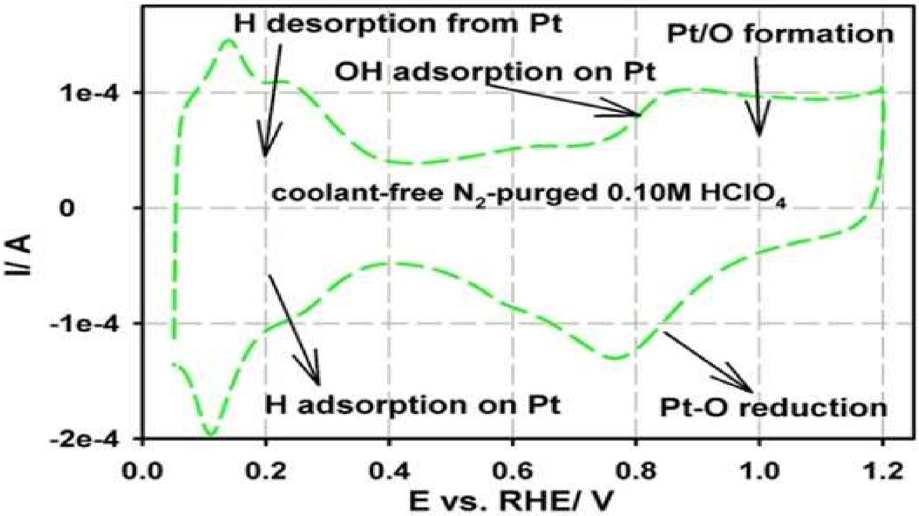

Fig. 10. Cyclic voltammetry of Pt [92]

adsorption/desorption region (Hupd, 0.05 V E 0.40 V) which is directly followed by the double layer potential region (ca. 0.40 V E 0.75 V) [96]. (2) the reversible adsorption of OH, and finally (3) an irreversible oxide formation peak was observed [97]. Additionally, an anodic current peak (of about 1×10^{-4}) was detected at the thermodynamic potential of E =0.90 V, which correspond to oxidation of the Pt surface [94]. During the reverse negative sweep from 1.20 V to 0.05 V, a peak at E = 0.80 V appears which is attributed to the reduction of the Pt surface.

According to Fig. 10, electrochemical reactions of Pt redox reactions may occur between 0.75 to 1 V vs RHE. The probable reactions that may occur in this range of potential are presented in the table of electrochemical series [98]:

$$Pt + O^{2-} \rightleftharpoons PtO + 2e^{-} \quad E = 0.88V\ vs\ SHE \tag{50}$$

$$Pt + H_2O \rightleftharpoons PtOH^{+} + H^{+} + 2e^{-} \quad E = 1.2V\ vs\ SHE \tag{51}$$

$$PtO + H_2O \rightleftharpoons PtO_2 + 2H^{+} + 2e^{-} \quad E = 1.01V\ vs\ SHE \tag{52}$$

$$Pt + 2H_2O \rightleftharpoons PtO_2 + 4H^{+} + 4e^{-} \quad E = 1.01V\ vs\ SHE \tag{53}$$

In addition, Schüring et al. [99, 100], listed the standard potentials of different platinum oxides in Table 4. As can be found from this table, the potential for PtO formations is in accordance with the CV of Pt, electrochemical series table, and Pourbaix

Table 4. Standard potentials of different platinum oxides [97, 98].

Electrode	Standard Potential	Electrode	Standard Potential
Pt/Pt-O	0.88	$Pt/PtO_2 . 4 H_2O$	1.06
Pt/PtO	0.9	Pt/PtO_3	1.5
$Pt/Pt(OH)_2$	0.98	Pt/PtO_2	>1.6
$Pt/PtO . 2H_2 O$	1.04	$Pt/Pt_3 O_4$	1.11
$Pt/PtO_2 . 2 H_2O$	0.96	$Pt(OH)_2/ PtO_2$	1.1
$Pt/PtO_2 . 3 H_2 O$	0.98	O_2	1.23

diagram. Also, Waje et al. were of the opinion that both PtO formation and PtO reduction is included in the cycling range such as 0.6-1.3 V vs. RHE [101].

After determining the potential of oxide formation and reduction, according to Stack Performance Recovery standard [102], the recovery of PEMFC performed as following:

(1) Nitrogen purge process in anode has to be performed. This cause PEMFC to work under OCV condition leading to decreasing of hydrogen concentration and its partial pressure in anode.

(2) As a consequence, according to Nernst equation [103], this will lead to a potential drop in the system as follows:

$$E = E_0 + \frac{RT}{nF} \ln\left(\frac{P_{H_2} P_{O_2}{}^{0.5}}{P_{H_2O}} \right) \qquad (54)$$

Where R is the universal gas constant: R=8.314472(15) J K^{-1} mol^{-1}, T is the temperature in Kelvin's, F is the Faraday constant, the number of coulombs per mole of electrons: F = 9.64853399(24)×10^4 C mol^{-1}. During this potential drop, it is necessary to have a small load on the system to enhance the voltage drop and also provide electron for reactions (50) to (53).

(3) After decreasing hydrogen concentration, Air purge must be performed. This help the system to oxidize any probbale contamination in anode path. However, since saftey issues are so important in PEMFC, we have to prevent the formation of any hydrogen and oxygen mixture in anode. Therefore, one have to firstly purge nitrogen to decrease hydrogen concentration significantly and then perform air purge.

(4) a minimum air-flow on the cathode side with a low overpressure of e.g. 10 kPa can be set to promote air diffusion process from cathode to anode for anode reactivation[102].This cause the crossover of oxygen from cathode and recovery of those catalyst particles which are so close to the membrane and did not have the chance of the recovered by air purge in the previous step. This process is illustrated in the Fig. 11.

(5) The next step is purging nitrogen to the anode decrease all hydrogen and oxygen concentration.

(6) Finally, we have to perform nitrogen purge on cathode. By this procedure the system will be recovered completely.

Table 5, tabulated the pros and cons of each recovery methods. Amoung these methods, only the H_2 purge and recovery by reduction method are applicable for stacks. Additionally, full recovery of the degraded PEMFC performance is possible only by utilizing the recovery by reduction and recovery by ozone method. Therefore, since the recovery by reduction method leads to both a full recovery of PEMFC performance and is applicable for a stack of the fuel cell, this method may be a better method in comparison with the others.

Last but not least, Fig. 12 illustrates the flowchart for studying the recovery of PEMFC that lost its performance owing to the formation of different arrays of oxides and hydroxides. According to this flowchart, the first step is is to obtain different documents such as the Pourbaix diagram, CV of Pt, and electrochemical series tables, which the reseacher completed in the detailed literature reveiw. After obtaining the Pourbaix diagram, it is necessary to specify the pH of the system to find the regions of formation of possible oxides and hydroxides in the PEMFC. Also, the oxide formation and reduction regions will be determined by studying the CV. After that, we have to obtain a CV for a real system. If the CV for a real system and the one found in the literature are the same, we can report the redox

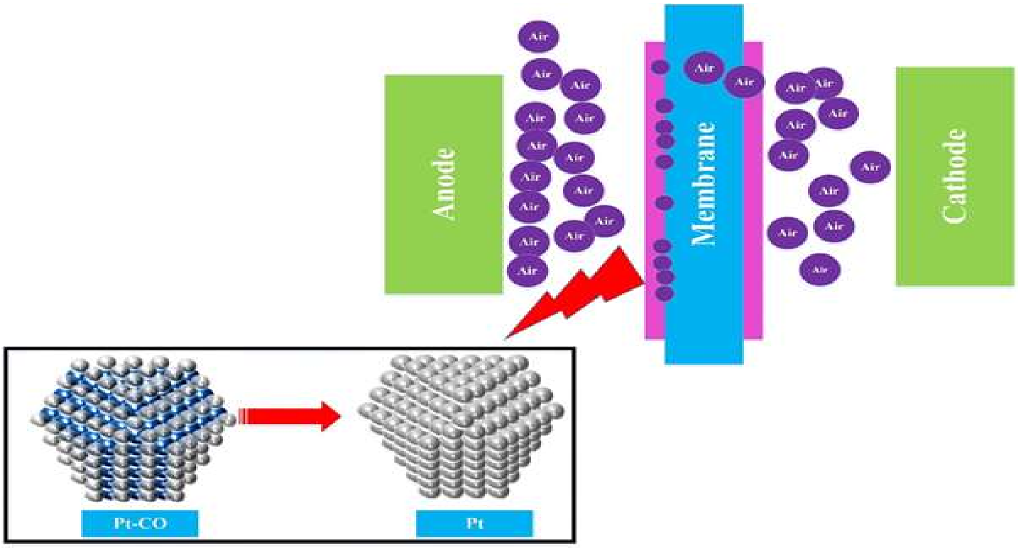

Fig. 11. Anode recovery by an over pressure from cathode

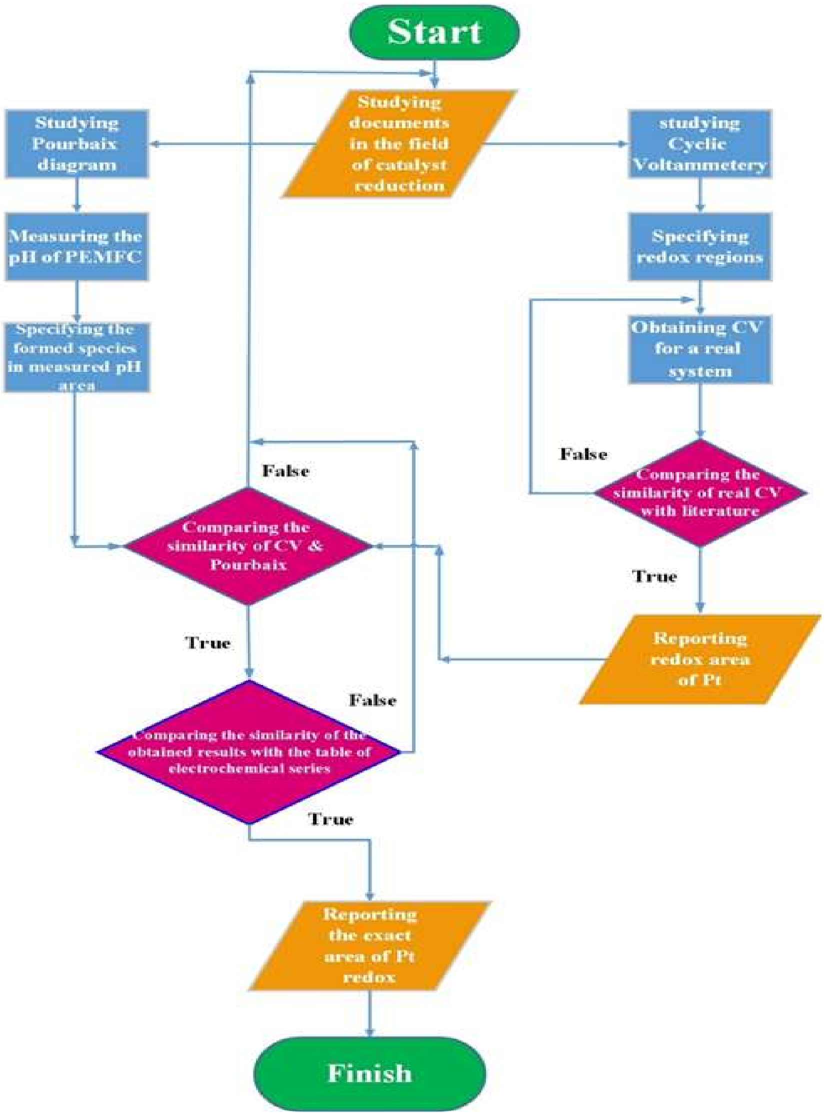

Fig.12. Flowchart for studying the recovery of PEMFC by reduction method

Table 5. Different recovery methods.

Recovery Method	Mechanism	Applicable for stack of PEMFC	Ref.
H_2 purge	$PtO + 2H^+ + 2e^- \rightleftharpoons Pt + H_2O \quad E_{Pt/PtO} = 0.90 \ \ Vs\,SHE$	Yes	[6, 62]
Direct Ozone treatment	$Pt - S_{ads} + O_{3(g)} \rightarrow Pt - O + SO_{2(g)}$ $Pt - S_{ads} + O_{3(g)} \rightarrow Pt + SO_{2(g)} + O^{\cdot}_{(g)}$ $Pt - S_{ads} + O_{3(g)} \rightarrow Pt + SO_{3(l)}$ $SO_{3(l)} + H_2O_{(l)} \rightarrow H_2SO_{4(l)}$	No	[64, 65]
Indirect Ozone treatment	$O_{3(aq)} \rightarrow O_{2(aq)} + O^{\cdot}_{(aq)}$ $O^{\cdot}_{(aq)} + H_2O_{(l)} \rightarrow 2OH^{\cdot}_{(aq)}$ $Pt - S_{ads} + O^{\cdot}_{(aq)} \rightarrow Pt - SO_{ads}$ $Pt - S_{ads} + O^{\cdot}_{H(aq)} \rightarrow Pt - SOH_{ads}$ $Pt - SO_{ads} + [O] \rightarrow Pt + S_xO_y^{z-} + zH^+$	No	[37, 64-68]
Short Circuit	$2Pt + O_2 \rightleftharpoons Pt_2O_2$ $Pt_2O_2 \rightleftharpoons 2PtO$ $PtO + H^+ + e^- \rightleftharpoons PtOH \quad E^0 = 1.1 - 1.4V\ vs\,SHE$ $PtOH + H^+ + e^- \rightleftharpoons PtH_2O \quad E^0 = 1.1 - 1.4V\ vs\,SHE$ $PtH_2O \rightleftharpoons Pt + H_2O$	No	[69-79]
Water Steam	$H_2S + Pt \rightleftharpoons Pt - S + H_2$ $H_2O + Pt \rightleftharpoons Pt - O + H_2$ $Pt - S + H_2O \rightleftharpoons Pt - O + H_2S$ $H_2S + 2H_2O \rightleftharpoons SO_2 + 3H_2$	No	[80-86]
Reduction method	$Pt + O^{2-} \rightleftharpoons PtO + 2e^- \quad E = 0.88V\ vs\,SHE$ $Pt + H_2O \rightleftharpoons PtOH^+ + H^+ + 2e^- \quad E = 1.2V\ vs\,SHE$ $PtO + H_2O \rightleftharpoons PtO_2 + 2H^+ + 2e^- \quad E = 1.01V\ vs\,SHE$ $Pt + 2H_2O \rightleftharpoons PtO_2 + 4H^+ + 4e^- \quad E = 1.01V\ vs\,SHE$	Yes	[87-101]

Table 6. Pros and cons of different recovery methods.

Recovery Method	Advantage	Disadvantage
H_2 purge	Fast process Applicable for stack of PEMFC	Partial recovery Flammability of system High cost of operation
Ozone	Full recovery of system not needing to additional reagent to enhance the efficiency of method	Not being applicable for stack of PEMFC being environment pollutant production of some intermediates which inherently are some of contaminations
Short Circuit	being applicable with a simple control system exrremly fast operation being cost effective	partial recovery Not being applicable for stack of PEMFC
Water Steam	Fast process Full recovery of system Low cost of operation	Not being applicable for stack of PEMFC Catalyst agglomeration Needing high temperature for recovery
Reduction method	Applicable for stack of PEMFC Full recovery of system Low cost of operation	Flammability of system

regions. If not, there will be some problems and we will have to find the points and strategies to solve them. The second step is to compare the obtained results from the Pourbaix diagram and CV of Pt. If the results are similar, we can move on to the third step which is to compare the specified potential of oxide formation and reduction in the second step with the potential of reactions of Pt that are mentioned in the electrochemical series tables. If the obtained results in the second and third steps are similar, we can report the exact area for Pt redox and reduce the platinum oxide and enhance the ECSA of the system. If the results are not analogous, we have to come back to the previous steps to find the errors.

4. Conclusion

This manuscript presents a brief overview of the main mechanisms of CL degradation in a PEMFC and its recovery by different methods. Different interacting mechanisms attributed to the loss of performance of a PEMFC and which negatively impact fuel cell durability are provided. It is important to understand these processes and interactions well to take the necessary steps to extend the lifetime of the next-generation of PEMFC's. The authors hope that this manuscript is a step towards understanding the vast work that has been performed and reported on mechanisms of CL degradation in the literature, and to help identify critical directions for further research. A summary of some of the key points are given below:

1) The main procedures for losing ECSA in the PEMFC were investigated. It was found that contamination by different impurities from different sources can play a significant role in decreasing ECSA and performance loss. CO, as a typical fuel contaminant, has been studied extensively. Other typical pollutants like CO_2, sulfur-containing species (H_2S, and SO_x), NO_x, and ammonia have also been investigated. Their individual effects on fuel cell performance and the mechanism of degradation have been discussed extensively.

2) The agglomeration of the Pt particles and accordingly the loss of ECSA is an irreversible process of CL degradation. This procedure is dependent on three main parameters including cell potential cycling, which is one of the most important factors contributing to platinum agglomeration. Temperature is the second parameter affecting the rate of agglomeration. Higher temperature leads to faster agglomeration and subsequently faster degradation of CL in PEMFC. Lastly, the humidification level of reactants in a PEMFC can also have a great effect on the agglomeration of catalysts. The higher the relative humidity (RH) of the gases, the higher is the growth of the catalyst particles.

3) Reactant gas starvation is another type of procedure that cause irreversible CL degradation. Poor water management with flooding, poor heat management during sub-zero temperature, poor gas feeding management, sudden load demand, and a defective PEMFC design are the main factors causing reactant gas starvation in the PEMFC. The main consequences of this procedure are catalyst loss, carbon-support corrosion, performance degradation, generation of hydrogen in the cathode or oxygen in the anode, and cell voltage drops.

4) Oxide and hydroxide formation, which mainly occur in PEMFC owing to the presence of oxygen and water in the cathode, are another type of parameters causing loss of ECSA. the region of oxides and hydroxides formation in PEMFC were identified by utilizing the Pourbaix diagram.

5) Different procedures of cell performance recovery or catalyst juvenilization processes were presented in this paper. These methods include recovery by H_2 purge, recovery by direct and indirect ozone, recovery by the short circuit method, recovery by water steam, and recovery by the reduction method. Also, the pros and cons of each procedure were discussed.

6) It was found that since the reduction method is applicable for a stack of fuel cells and also can leading to a full recovery of PEMFC, this method may be a better procedure in comparison with the other methods.

7) A flowchart of the studied degradation of CL and performance recovery is presented.

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