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REVIEW PAPER

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# A review of bipolar plates materials and graphene coating degradation mechanism in proton exchange membrane fuel cell

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**Summary**

Proton exchange membrane fuel cells (PEMFCs) have the perception to strongly reduce global emissions through an environmentally friendly perspective. Graphene has drawn global attention and has positioned itself as a potential material for bipolar plates application. This study reviews the application of graphene and summarizes the degradation of graphene coating that has become a significant issue in the improvement of PEMFC's performance. In the analysis, the degradation and its dissolution processes are presented. The need to improve the material selection focused mitigation on fabrication defects that act as initiation sites for graphene coating degradation is recommended. Finally, this review through recommendation endeavors to prevent graphene coating degradation and reduces high costs associated with the replacement of bipolar plates in the PEMFCs.

**KEYWORDS**

coating, degradation, Graphene, material, proton exchange membrane fuel cell

**Highlights**

- Graphene is used as a bipolar plates material.
- Metallic bipolar plates are often coated with graphene.
- Degradation of the graphene coating has been a great barrier in the proton exchange membrane fuel cell achieving an optimal performance.
- Graphene degradation follows different disintegration mechanisms.
- Improvement in the performance of graphene can be achieved through material selection.

## 1 | INTRODUCTION

Sustainable development and a green environment require cost-effectiveness and environmentally energy conversion systems. The proton-exchange membrane fuel cell (PEMFC) performs the primary function of converting the chemical energy of hydrogen and oxygen to electricity and water as the by-product for industrial and domestic applications. Notwithstanding, the significant cost of materials, for example, bipolar plates (BPPs) and catalysts, utilized in PEMFC limit its application. Stainless steel is among the metallic materials that have been examined as materials for BPPs. It was reported that oxide layers are formed on the stainless steel surface when used in an acidic PEMFC environment.[1] The formed oxide layer can reduce the corrosion rate and increase the thermal and electrical conductivity of the stainless steel material. Numerous researchers have examined the modification of stainless steel with carbon materials to fulfill the necessities of high corrosion resistance and low impedance.[2]

Graphene is a molecularly thin film of a honeycomb organization of $sp^2$-hybridized carbon particles, which have been used as a BPP material and deposited effectively on different steel substrates for BPP applications.[3,4] Other than its corrosion-resistant property, graphene additionally has phenomenal conductivity and hydrophobicity properties.[5] Modifying the base metal with carbon material or coating the substrate utilizing different deposition methods has been explored.[2,6] The chromium carburization process has been utilized to form a chromium carbon protective layer on the surface of stainless steel to increase corrosion resistance.[7] Other groups of researchers have used elements such as niobium (Nb) and titanium (Ti) to modify the behavior of the stainless steel for BPP application.[6] The overall results showed that irrespective of the modification made, utilizing stainless steel or other metals as BPP material requires employing material that will not form layers on the BPP surfaces or the substrate coated.

Several types of coatings have been used to modify the surface of the BPP and improve its corrosion-resistant.[8] The coatings are classified into two major groups: carbon-based and metal-based. While the carbon-based includes graphite, conductive polymer, diamond-like carbon, and organic self-assembled mono-polymers, the metal-based coating involves noble metals, metal nitrides, and metal carbides.[9,10] For the coatings to be used in different applications, it is required that the coefficient of thermal expansion of the base metal and the coating be as close as possible to eliminate the formation of micropores and microcracks observed in coatings as a result of unequal expansion that can occur during the fabrication.[11] Although much of these coatings have been used for different applications, graphene coating has stood out as a potential candidate for BPP application due to its high flexibility that eliminates chipping and cracks in coatings. Furthermore, graphene coating has antistatic capabilities, incredible hydrophobic properties, and solid qualities over ceramic and other coatings employed in the BPP applications.[12] Thus, researchers have examined the utilization of graphene for the fabrication and coating of metallic BPP surfaces.[3,13] Results have shown that graphene can provide the required conductivity and corrosion resistance for optimal performance of the BPPs.[14,15] Recently, graphene has drawn in a lot of exploration due to its extraordinary properties, like its high electrical conductivity, heat transfer rate, and explicit surface area.[16,17] As of now, most BPPs for power devices are made of graphene due to its excellent material properties.[3,18,19]

The corrosion resistance of the BPP also can be enhanced utilizing the electrochemical properties of graphene in coating the substrate material and has been investigated by authors.[18,20] Pu et al[18] deposited graphene on the BPP substrate to improve the performance through the provision of the anticorrosion graphene coating for the PEMFC environment. Chung et al[21] developed a graphene layer on a nickel/stainless steel surface, and during this interaction, the carbon molecules at first formed round carbon structures on the nickel grain boundaries. Ongoing examinations have shown that graphene can be utilized as a protective layer on metal surfaces to reduce oxidation and corrosion.[22,23] Krishnamurthy et al has utilized graphene developed on permeable nickel foam as effective electrodes in microbial fuel cells.[24] Some examinations have likewise shown that the inclusion of copper plates with graphene could successfully lessen transient air oxidation rates and increase that material's electrical and chemical properties.[25,26]

To understand the application of suitable material for the BPP utilized in the PEMFCs, it is valuable to examine the potential of the material structure and its behavior in the PEMFC environment. While there have been many studies on the application of graphene as a candidate for BPP fabrication, the degradation mechanism of this material especially in the PEMFC environment has not been detailed and reviewed in the literature. There is the other need to assess and review the graphene coating degradation mechanism and develop more robust and stable materials for BPP applications. The review aims to bridge the gap. The degradation mechanism of graphene integrates with the BPP substrate through dissolution and penetration of the coated layer on the steel substrates. The manufacturing defeats act as initiation sites for the degradation and affect the material's capacitance and performance. For a coating to be effectively used in BPPs, and the BPP becomes financially available for different applications, the degradation mechanisms of the materials ought to be reviewed and understood.

## 2 | BASIC PRINCIPLE OPERATION OF PEMFC

The basic work of the PEMFC is to convert chemical energy to electrical energy through the electrochemical reaction process that occurs in the fuel cell. The PEMFC comprises components such as anode, cathode, BPPs, gas diffusion layer (GDL), catalyst layer (CL), membrane, backplate, and gas flow channels as shown in Figure 1.

Within the fuel cell, hydrogen gas ($H_2$) is fed through the anode, and oxygen ($O_2$) or air is supplied through the cathode producing water and heat in the electrochemical reaction process. In the PEMFC arrangement, while the CLs conduct protons to and from the electrochemical reaction sites through the polymer material, the proton exchange membrane (PEM) designed with ionomers conducts protons coming from the anode side of the cell. The PEMFC consists of two electrodes namely, anode and cathode, that conduct electrons through the cell. The end plates (EDs) fasten the inner stacks to provide a seal between membrane-electrode assemblies (MEAs), thereby reducing the contact pressure between the cell and layers. The GDLs certify the uniform distribution of reactive gases on the surface of the electrodes and the transport of electrons to or from the external electrical circuit. Several pieces of research have been performed to understand the operation and performance of the PEMFC.[28] The transport of water within the fuel cell has been a critical area of study.[29] It was revealed that improper management of water in the fuel cell can result in the flooding and degradation of the PEMFC.

## 2.1 | Catalyst layer

The CL is covered behind the GDL within the fuel cell and needs to be designed not only to produce high rates of the anticipated reactions but also to reduce the amount of catalyst necessary for reaching the required levels of the PEMFC power output. Some of the functions of the CL are to maximize the active surface area per unit mass of the electrocatalysts and reduce the number of obstacles stopping the reactants from reaching the catalyst. The CL should also be able to enhance the transport of protons to the exact positions as well as ensure product removal from the cell. The above roles showcase the importance of CL in the PEMFC water management as having been reported extensively in the literature.[30,31] The CLs often are made of nanometer-sized particles of platinum spread on high-surface-area carbon support due to its conductivity requirement.[32]

## 2.2 | Proton exchange membrane

The PEM is also one of the important components in PEMFC. The PEM is semipermeable designed with ionomers to conduct protons coming from the anode side of the cell. The PEM performs the function of an electronic insulator and reactant barrier. Kraytsberg and Ein-Eli[33] reported that the PEM is the central control point of the PEMFC operation and needs materials that perform the necessary function in the PEMFC. An ideal PEM should be able to have high proton conductivity, excellent chemical resistance, high mechanical strength, and be durable. Material requirement for the PEM depends on the operating parameter of the cell and fuel permeability.[34] Nafion polymer has been used as the base component material for most PEM fabrications.[35]

## 2.3 | Electrode

The PEMFC consists of two electrodes namely, anode and cathode, that conduct electrons through the cell. In

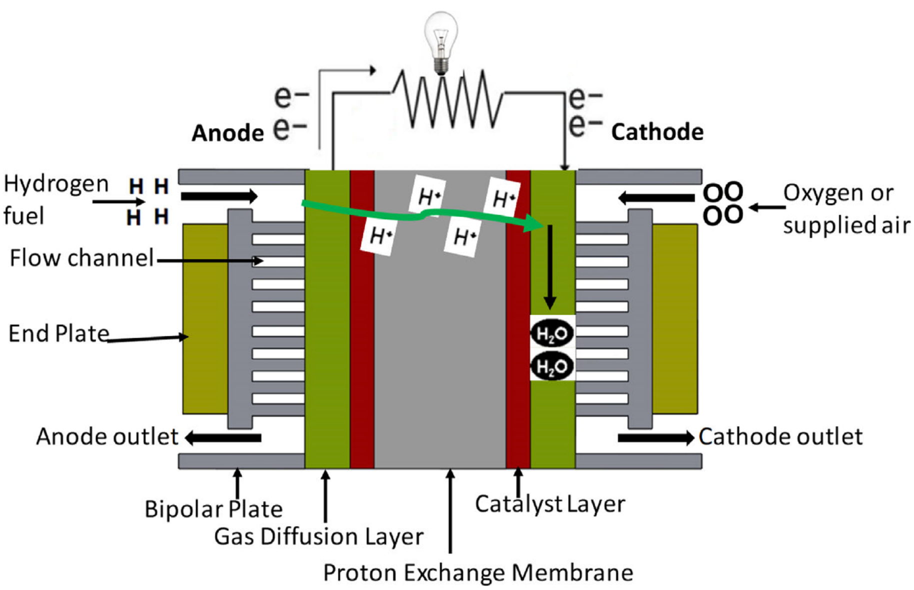


FIGURE 1 Drawing of a proton exchange membrane fuel cell (PEMFC) structural operation[27]

the PEMFC arrangement, the electrodes are separated by an electrolyte that conducts ions. Based on the design nature of the anode, a catalyst oxidizes the fuel introduced through the anode, typically hydrogen, turning the fuel into a positively charged ion and a negatively charged electron. As the electrolyte is precisely designed so ions can pass through it, the positively charged ion passes through the membrane, while the electrons pass through the external circuit to generate electricity.[36] The cathode conducts the electrons back to the external circuits to the catalyst site of the cathode, where they can recombine with the hydrogen ions supplied by the anode and oxygen to form water. While oxidation of fuel occurs at the anode surface, reduction takes place at the cathode surface in the electrochemical process. Wu and Jiang[37] revealed that materials with high thermal and excellent resistance to corrosion are required as electrodes to enhance the PEMFC performance and mitigate the degradation of the electrodes.

### 2.4 | End plates

The EDs fasten the inner stacks to provide a seal between the MEAs, thereby reducing the contact pressure between the cell and layers. To effectively perform the clamping task, the EPs need to have enough mechanical strength, lightweight, electrochemical properties, and provide electrical insulation. Because the EDs can prevent the gases from escaping from between the plates, the endplates often have holes for bolts and manifolds.[38] However, the challenges coming from the corrosion problems, thermal losses, and excessive weight have resulted in using alternative materials such as plastics to specifically address the corrosion and weight problems. Subsequently, composite materials have also been projected for endplates to improve their mechanical strength and achieve efficient fuel cell systems.

### 2.5 | Gas diffusion Layer

The GDLs certify the uniform distribution of reactive gases on the surface of the electrodes and the transport of electrons to or from the external electrical circuit. The GDLs are made of thin carbon fibers, porous, and hydrophobic materials. In the PEMFC setup, the GDL should be able to support the electrolyte and facilitate the evacuation of water to avoid flooding.[31] The GDLs also maintain a balance between the membrane hydration and water removal rate and provides effective heat management to the fuel cell. Recent studies have demonstrated the importance of the hydrophobic nature of the diffusion layer in overall PEMFC performance.[29]

### 2.6 | Bipolar plates

The BPPs are the primary backbone of the PEMFC power stack since they separate and conduct current between individual cells. They also enhance water and thermal management through the cell, while they provide channels for reactant gases and remove reaction products. The BPPs are commonly made of graphite or metals. While the BPPs supply hydrogen to the anode and oxygen to the cathode through the flow channels, they also provide the electrical conduction between the cells. Over the past decades, various materials such as stainless steel, graphene, aluminum, and titanium have been developed and used for BPP applications.[39]

## 3 | STAINLESS STEEL AS BIPOLAR PLATES MATERIAL

Metals offer numerous benefits to the BPP applications and some of the benefits include generally minimal cost, high strength, simplicity of production, and corrosion resistance.[40,41] Metallic BPP can be effortlessly manufactured for complex shape applications and can give a huge improvement in the energy component innovation.[40] Stainless steels are high-strength corrosion resistance materials utilized in corrosive conditions in light of a promising combination of mechanical properties, corrosion resistance, and cost viability when contrasted with other materials for BPP application.[42,43]

The fabrication process of the stainless steel can influence the corrosion behavior of the material and the synthetic organization of the stainless steel decides by and large their applications as BPP materials. However, it has been realized that stainless steel is inclined to the chemical attack in the PEM fuel cell environment delivering an oxide layer that regularly harms the membranes. The oxide film expands the interfacial contact resistance (ICR) resulting in a decrease in the fuel cell performance.[44,45] When utilizing uncoated stainless steel material for BPP applications, exposure of the BPP to a destructive environment brings about the gradual degradation of the BPP and needs to be addressed. The significant concerns have been the degree of degradation and the impact of the passivation film on the corrosion interaction.[46,47] As the formed oxide layer increases in thickness, the conductivity of the stainless steel material decreases as the operational time increases. Figure 2

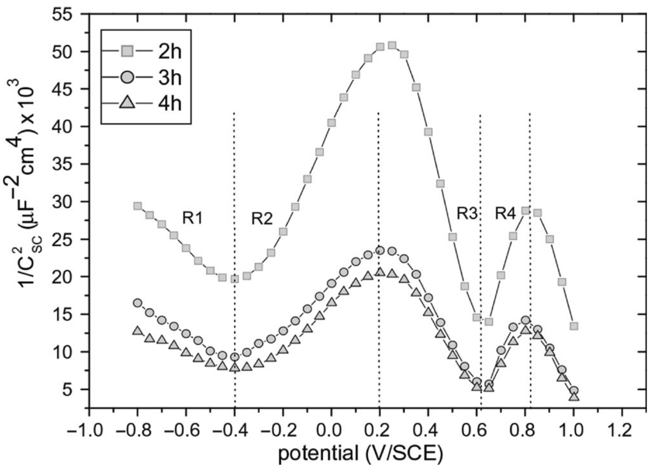


**FIGURE 2** Mott–Schottky curves showing the film formation at different exposure times[48]

shows film formation on the stainless steel metal at different durations.

Several types of research have been performed to comprehend the corrosion behavior of stainless steel as a BPP material and results reported.[49,50] Hermas et al[51] revealed that the corrosion rate of stainless steel increments as temperature rises, which influences the detached layer arrangement. Davies et al[52] investigated the corrosion behavior of three diverse uncoated stainless steel, in particular, 316, 310, and 904L. While the outcome showed that the corrosion resistance was high for all the samples, the alloying content of the materials, specifically, Grade 904L fabricated with a higher amount of chromium and nickel substance displayed enhancement in the contact resistance.[52] Hodgson et al[53] showed that 316 stainless steel presented decreased corrosion resistance in the fuel cell environment. The decreased corrosion resistance was credited to the thickening of the oxide layer formed on the material surface and the increasing contact resistance. Li et al[54] examined the corrosion behavior of type 316 stainless steel in mimicked electrode environment for PEMFC. The electrochemical test outcomes showed that the behavior of the 316 stainless steel was affected by the simulated environment. It was accounted for that the adsorbed hydrogen ions from electrode corrosion reaction on the steel surface may have corroded the steel material. On the other hand, Lee et al[55] performed four tests utilizing four stainless steel test samples. The tests were to confirm the huge improvement in corrosion behavior of the treated samples. It was tracked down that the produced oxide film had gotten enhanced with chromium (Cr) after the interaction and was ascribed to the improvement in the corrosion resistance. The authors detailed that the decrease in the oxide thickness leads to a decrease in both surface and contact resistance. Wang et al[56] considered the impact of oxygen and hydrogen on the corrosion behavior of 316L stainless steel in a PEMFC environment. The open-circuit potential (OCP) and potentiodynamic tests showed that corrosion of 316L stainless steel occurred in an $O_2$-containing environment. The potentiostat tests additionally showed that there is less corrosion in a simulated anode environment and were credited to the decrease in the H+ particles bringing about a negative current that provided cathodic protection to the 316L stainless steel. Recently, Kumar et al[20] studied the behaviors of two grades of stainless steel for BPP application. The magnesium-based stainless steel displayed more passive current density and better corrosion potential compared to nickel-based stainless steel. The authors revealed that the two BPP stainless steel materials require coating for better fuel cell performance. Despite many studies performed on the application of stainless steel as BPP material, corrosion of the BPP has been a great concern to the renewable energy industry and needs to be addressed by employing high corrosion-resistant material and coating of the BPP material substrates.

## 3.1 | Graphene as bipolar plates material

Graphene is one of the materials utilized for BPP applications. Graphene, a moderately new material found in 2004, has attracted a lot of interest because of its charming properties that incorporate high electrical conductivity, huge explicit surface area, high thermal conductivity, and thermal dependability.[57,58] The electrical conductivity of normal graphene depends on the method of fabrication, the processing parameters, sieving associated with the processing activity, and molecule morphology. Graphene is a translucent type of carbon that involves atoms covalently fortified by three close atoms, leaving one free electron unbonded to work with the exceptionally needed electrical conductivity of the plates. Through this structural arrangement, the graphene films often completely cover the surface of the substrate material as shown in Figure 3.

Graphene BPP is widely received to be the suitable material for BPP fabrication because of its high corrosion resistance in moist and acidic environments as well as great chemical stability inside a PEM fuel cell.[16] The delocalization of π-electrons in graphene makes it exceptionally hydrophobic, which enhances its water and gas management in the PEMFC.[46,58] More so, graphene has a few benefits like high contact resistance, low density, and high thermal conductivity.[58,60] Despite the vast applications of graphene, there have been worries over its poor mechanical strength, which is noted for diminishing the

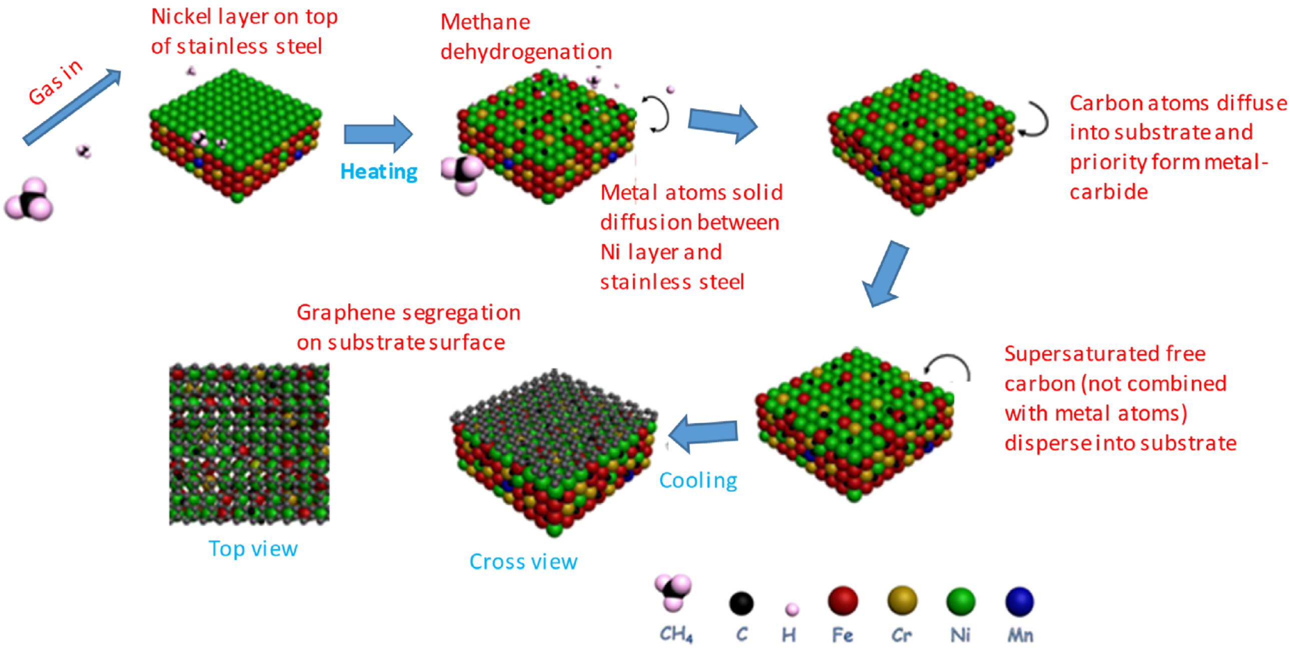


**FIGURE 3** The graphene formation mechanism on the metal substrate[59]

**TABLE 1** Functions of graphene in proton exchange membrane fuel cell (PEMFC)

| PEMFC component | Function | Refs |
|---|---|---|
| Bipolar plates | Provides excellent hydrophobicity to the fuel cell | 59 |
| | Enhances corrosion resistance of the BPPs | 62,63 |
| | Provides high electrical conductivity, heat transfer rate, and specific surface area | 18 |
| | Offers support to the metal catalyst | 3 |
| | Provides high output power density to the fuel cell due to its chemical inertness | 3,64 |
| | Contributes to the high capacitance value of the BPP | 65 |
| | Enhances the oxygen reduction reaction and improves the efficiency of the fuel cell | 13 |
| | Provides excellent charge transfer characteristics to the BPP | 62 |

thickness of the BPPs, resulting in low performance.[60,61] Notwithstanding, the bond energy in the planes is more than the bond amid layers, which results in a more fragile flexural strength and a high penchant for a crack during manufacture when compared with different materials used for BPPs.[19] To enhance the properties of graphene, consideration should be given to the level of crystallinity, size, morphology, and the permeation limit should be determined. Table 1 displays some of the functions of graphene in the PEMFC environment.

### 3.2 | Graphene coating fabrication and performance

Graphene coatings have been fabricated using several methods such as spray methods, electrochemical reduction methods, electrophoretic deposition (EPD), laser induction, chemical vapor deposition (CVD) methods, etc.[66,67] Among these methods, the CVD technique has been reported to be the most effective and commonly used method to fabricate graphene coating due to its ability to produce a high-quality coating and large area of coverage.[67] The CVD strategy can be utilized to fabricate a graphene coating on the outer layers of metals such as copper (Cu), nickel (Ni), magnesium (Mg), aluminum (Al), iron (Fe), etc.[68,69] The fabrication of the graphene coating involves the deposition of a layer of polymethyl methacrylate (PMMA) resist on the graphene surface to produce a PMMA/graphene/Cu interlayer. This process is followed by the dissolution of the copper foil using an etchant before depositing the PMMA/graphene on the target metal surface. The formed composite is dried, and the PMMA is dissolved using acetone resulting in the coverage of the metal surface with graphene coating.

Researchers have studied the fabrication and deposition of graphene on different metal surfaces and various results reported.[70] Pu et al[18] revealed that only a small amount of graphene coating could directly be deposited on the surface of bare stainless steel by the CVD method, while stainless steel coated with Ni could allow the deposition of a large area of graphene coating on the steel surface. Zhao et al[47] discovered that the area covered by the deposited graphene coating on the steel surface can be increased by using a mechanical transfer method to transfer the graphene coating onto the substrate of the target metal as shown in Figure 4.

While employing the mechanical method in the graphene coating preparation has shown significant improvement, intrinsic contamination of the graphene coating has been reported.[71] It was revealed that the residue of the transferred polymer may be responsible for the contamination which affects the optical, heat transfer, and wettability properties of the graphene coating.[72] A group of researchers has explored several avenues to reduce the contaminants and improve the coating ability of the graphene coating.[73] Some of the methods utilized include employing a new polymer transfer method, which increases the area covered by the graphene coating. In another study, Prasai et al[74] investigated the behavior of graphene coating on copper and nickel metals. The result showed that the corrosion rate was seven-time slower for graphene-coated copper than that of uncoated copper. Although the graphene coating provided significant protection to the copper metal, small cracks of the graphene coating were observed as shown in Figure 5A.

Although the bond strength between the graphene coating and the metal substrate is affected by the distance between the coating and substrate material, the strength of graphene coating has been shown to depend significantly on the metal substrate.[75] Ollik and Lieder[76] proposed that a high-quality graphene coating with a complete barrier effect is required to cover and create a strong bond between the metal and coating, thereby providing long-lasting corrosion resistance. In the comparison of the graphene coating with other metals, nickel was coated with graphene, and the result revealed that the corrosion rate of nickel covered with graphene coating was 20 times slower compared to uncoated nickel metal.

Another research study was performed to understand the effect of multilayers coating on the corrosion behavior of metal.[74] In the study, the corrosion resistance of the two-layer and four-layers graphene coatings was considered. The outcome demonstrated that the corrosion rate of nickel covered with four layers of graphene coating was better than the uncoated nickel in protecting the metal surface from corrosion. It was revealed that the performance of the graphene coating increases as the thickness of the graphene coating increases as shown in Figure 5B-D. Tiwari and Singh Raman[77] deposited single and multilayer of graphene coating on the copper substrate. Although the ultra-thin nature of graphene during some short-time exposures provides considerable resistance against corrosion, the problem of corrosion protection ability of the single-layer graphene coating can be

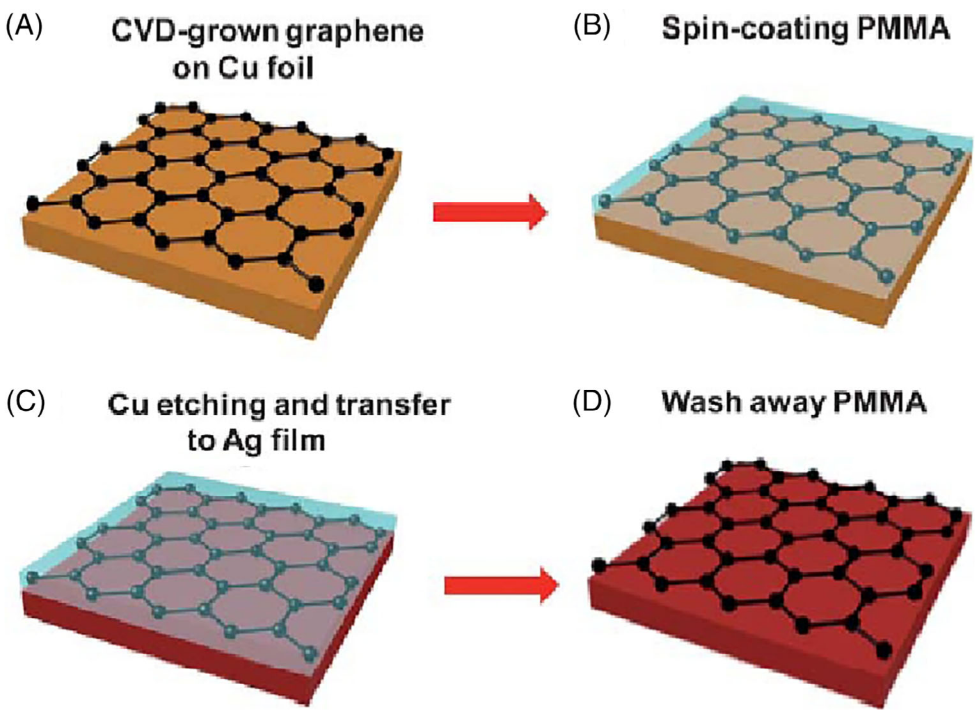


**FIGURE 4** Mechanical transfer method[47]

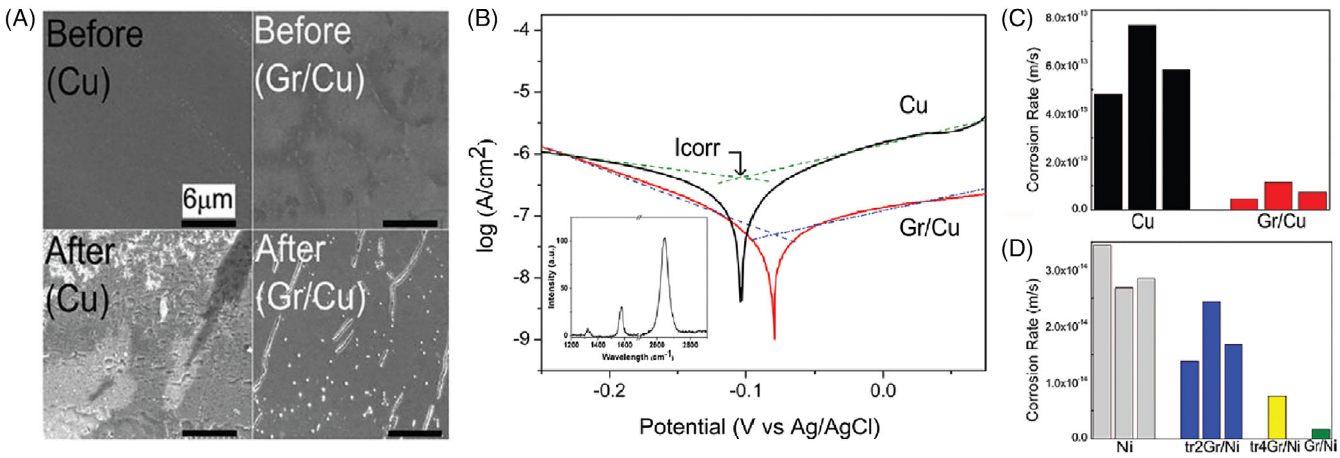


**FIGURE 5** (A) Comparison of the scanning electron microscopy (SEM) images of Cu and copper graphene-coated before and after corrosion, (B) result of Tafel fitting, (C) extract of corrosion rates of the Cu and graphene/Cu samples, and (D) corrosion rate of the bare Ni sample and Ni substrate covered with graphene[74]

overcome by applying multilayer graphene on the metal surface. However, the role of graphene coating in the defects experienced by the graphene coating is a challenge in developing an efficient and effective graphene coating.[77] The authors suggested that either development of defect-free graphene coating or the development of multilayer graphene coating can improve the corrosion resistance of graphene coating. Further in the study, the authors reported that multilayer graphene coating developed by mechanical transfer may not provide an effective corrosion resistance compared to the CVD technique since channels may be left for transport of corrosive ions through the metal substrates.[77] Subsequently, it was generally reported that the graphene coating prepared by CVD can provide effective corrosion protection not only to copper and nickel but to other metal substrates such as carbon steel, stainless steel, and alloys for BPPs.[18,63]

## 3.3 | Fabrication parameter for graphene coating

The process parameters and the types of substrates are the two major influencing factors especially for graphene coating by the CVD method. The carbon solubility and the catalyst also influence the quality of the graphene coating.[78] Parameters such as immersion time, temperature, precursor materials, and gas flow are also considered essential and have to be optimized during the fabrication of graphene coating. It was proposed that temperatures between 120°C and 180°C can be an effective reaction temperature for the fabrication of graphene coating.[79]

External factors can also influence the corrosion behavior of coating as coating deposited on the metal surface can contain some inhomogeneity that can appear on the coating in form of cracks, microvoids, contaminants, etc. It was demonstrated that each of the factors can affect the integrity of the coating and influence the transport of aggressive species through the coating and the coating–substrate interface, thereby affecting the degradation process of the coating.[79] Controlling the parameter can enhance the quality and efficiency of the produced graphene coating as well as improve its corrosion resistance. Optimizing the CVD process parameter is another attempt explored to improve the performance of the graphene coating since variation in the process parameters can influence defect density of the graphene and affect the coating corrosion resistance.[80] It was reported that process parameters such as graphene growth temperature, hydrogen volume flow, cooling rate, and annealing time can affect the graphene coating properties prepared by the CVD technique.[80,81] Among the process parameters, the effect of cooling rate and hydrogen flow on the quality of graphene coating prepared by the CVD method has been investigated.[82] It was discovered that the growth of graphene coating stopped when the cooling rate was slowed irrespective of the absence or presence of the hydrogen flow. On the other hand, the study observed a decrease in the wrinkles found on the graphene coating as the cooling rate was increased in the absence of hydrogen flow, and the coating was reported to provide durable corrosion resistance to the metal.[80]

## 3.4 | Addressing defect problems and improving the corrosion resistance of graphene coating

The single-layer graphene coating fabricated by CVD experiences different defects, which restrict the huge scope utilization of graphene as an excellent corrosion mitigation agent. Several techniques have been employed on a few enhancement measures to acquire an improved graphene coating, which provides improved protection to the metals.[83] One of the methods involves choosing adequate substrates or providing an enhanced binding at the interface as shown in Figure 6.

This was demonstrated in the detailed study performed by Weatherup et al[83] where the long-term protection of graphene coating on NI, Co, Fe, and platinum (Pt) was compared. The results revealed a strong interaction between the graphene and metal, which was found as the significant factor in the long-term protective behavior of the graphene coating. It was further understood from the study that passivating oxide formation could cover up the defects experienced during fabrication and prevent the oxidation process progression.

To address the problem of defects found in graphene coating, multilayer graphene coating has been recommended as an effective and long-lasting approach on the ground that the commonly matching defects cross over with one another and a spatial steric obstacle is formed.[22] Researchers have investigated the effect of multilayer coating on the performance of graphene coating.[74,77] While Tiwari and Singh Raman[77] studied the protection of multilayer graphene coating on the surface of copper and found it to be several times protective for the copper in sodium chloride solution, the explosive investigation performed by Yu et al[84] showed that multilayer prepared by CVD method has more protection compared to that obtained by the mechanical transfer method. The overall result demonstrated that multiplayer graphene coating has preferable oxidation resistance over single-layer graphene coating and can be ascribed to the overlapping effect of multilayer in forming a steric hindrance effect on the metal surface.

## 3.5 | Modification of stainless steel for the bipolar plate with graphene

Modification of the steel substrate can increase the corrosion resistance of the stainless steel and limit the formation of a thick oxide layer that is formed on the surface of the BPPs, thereby expanding the ICR during operation. This should be possible by either coating the substrate or modifying the base material with alloying components.[3,85] Studies have shown that uncoated stainless steel BPPs show oxide layers on the metal surface prompting a progressively decline in the performance of the PEMFC.[86] Consequently, it is required that some surface modification techniques or self-protective coating be applied to stainless steel to improve their protection against corrosion. To investigate the conceivable use of graphene as a successful material for corrosion resistance improvement of the BPP material, an extremely small graphene film was coated on the titanium substrate.[3,58] The electrical and contact resistance property of this coated material was considered in the test.[85] As per the simulated fuel cell, the graphene-coated Ti sheet showed an impressive diminishing of both corrosion current and interfacial contact resistance, making the graphene coating an excellent material for the BPP and a promising candidate for applications in PEMFC. Iqbal et al[62] studied the effect of coating copper BPPs with graphene on corrosion resistance. As displayed in Figure 7, the result

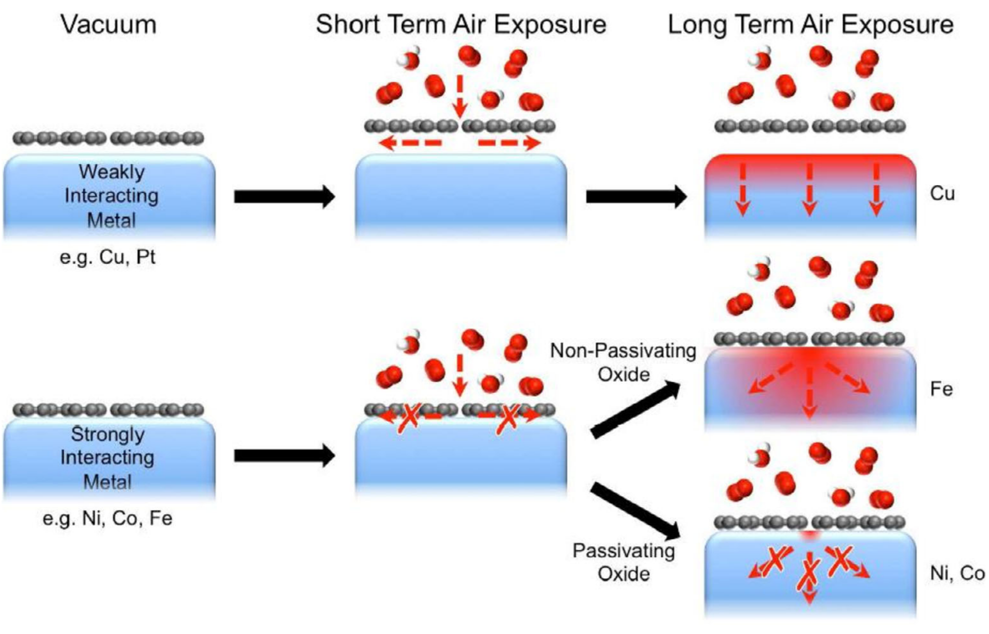


FIGURE 6 Mitigating graphene coating defects techniques.[83]

showed uniform monolayer graphene on the surface of the BPPs, which increased the corrosion resistance of the BPP as well as the PEMFC performance.

In a comparative report on the effect of graphene film on the corrosion performance of BPP, an examination of the conductivity and corrosion resistance of aluminum BPP in fuel cells was performed.[6] As indicated by the outcomes, a noteworthy decrease in the current density by four significant degrees under a simulated PEMFC environment was observed. The authors attributed the results to the significant decrease in the ICR between the sheet and carbon paper due to extra graphene coating on the metal substrate. The outcome showed that the graphene-coated 316L can be viably utilized as a BPP material since the materials showed negative (cathodic) current densities either in the PEMFC cathodic or in the anodic climate for the entire polarization tests. In this way, the graphene-coated SS316L might be utilized as a BPP material in the PEM fuel cell applications. In another study, a group of researchers explored the reaction of two stainless plates of steel when coated with graphene.[18] Multiple graphene layers were coated on the metal surfaces as shown in Figure 8.

Figure 8 shows the formation of multiple graphene coating that covered the steel surface. The authors[3] revealed that excellent corrosion resistance and high conductivity were achieved through a coating of the BPPs with graphene coating. Table 2 shows some of the applications of graphene as a material for BPPs.

## 4 | GRAPHENE-COATED COPPER BPP DEGRADATION MECHANISM IN PEMFC ENVIRONMENT

The corrosion mechanism of graphene-coated copper in the PEMFC environment can be considered through copper dissolution by analyzing the oxygen reduction in the presence of sulfuric acid potentials utilizing Equations (1) and (2).[63]

$$CU - -CU^{+} + e \tag{1}$$

$$CU^{+} - -CU^{2+} + e \tag{2}$$

Sulfuric acid is often used as an electrolyte for the PEMFC.[91] The acid concentration and interaction with the PEM fuel cell environment can affect the degradation and integrity of the fuel cell components.[92]

During the dissolution process, the cathodic reduction of oxygen is represented by Equation (3).

$$O_2 + 4H^{+}\, 4e + 2H_2O \tag{3}$$

When in immersed solution, the copper used as electrode forms a large capacitive loop, which is attributed to high-resistant copper oxide and the appearance of Warburg impedance as shown in Figure 9.

The appearance of Warburg impedance in the circuit displayed in Figure 9A shows the transport of oxygen

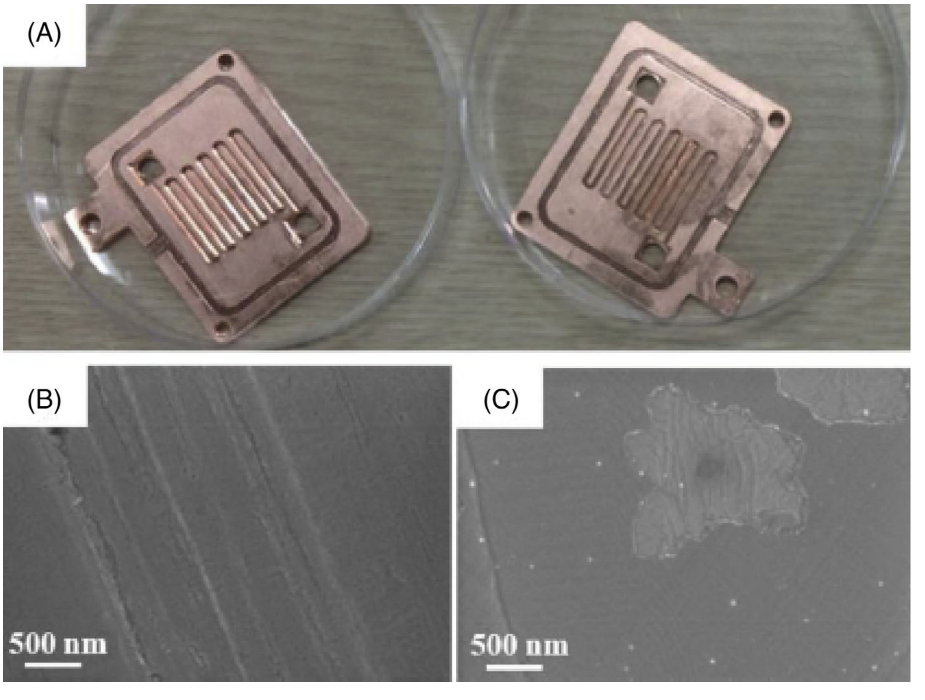


FIGURE 7 (A) The anode and cathode Cu bipolar plates (BPPs), scanning electron microscopy (SEM) micrographs of BPP surface, (B) without graphene, and (C) coated with graphene[62]

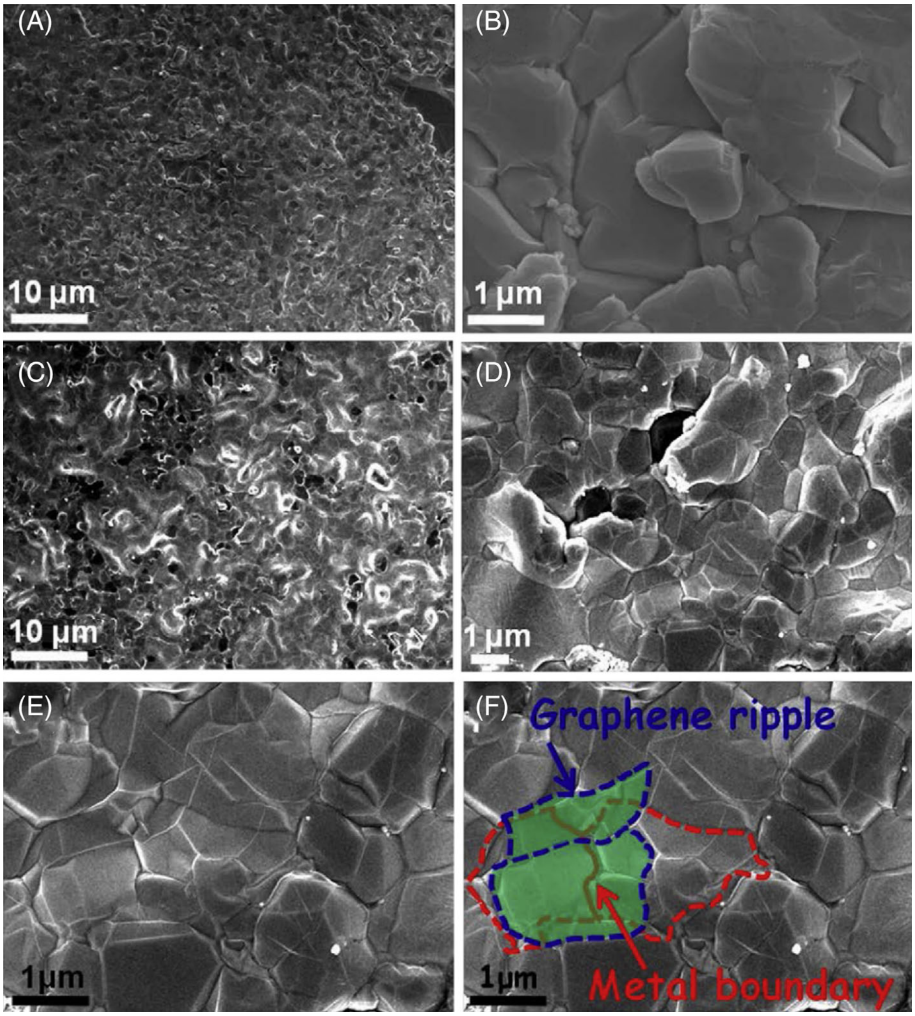


**FIGURE 8** Scanning electron microscopy (SEM) micrographs of (A,B) showing graphene and SUS304-900 immersed for 4 hours (C-E) showing graphene, nickel, and SUS304-900 immersed for 4 hours; (F) the red line shows the metal grain boundary, the blue line indicates the graphene ripples, and the green area shows the metal boundaries[3]

through the graphene-coated copper to the substrate material. The capacitance arc decreases as the copper dissolves further in the acidic medium resulting in the formation of porous copper sulfide as shown Figure 9B. The disappearance of Warburg impedance in the equivalent circuit displayed in Figure 9C indicates that charge transfer between the electrolytes and metal enhance further copper corrosion process. All through the PEMFC operation, electrons from the anode side of metal are transported to the graphene/electrolyte interface to react with oxygen. The oxygen is consumed on the surface of the graphene coatings resulting in a high oxygen concentration of graphene across the graphene coatings that reduces the supply of electrons at the metal surface.

The interaction of graphene coating with the metal and oxygen adsorption on the underlying metal surface is critical in applying the graphene coating and preventing the corrosion of the BPP.[19,65] Oxygen species formed during the corrosion process naturally do not like to be adsorbed on the graphene surface but embed into the graphene/metal interface.[93] During the active operation of the PEMFC, through the cathodic reaction process, the hydrogen ion present in the acid electrolyte is consumed resulting in increased pH of the electrolyte and a decrease in the copper dissolution rate. However, penetration of the coated layer by the electrolytes through the presence of defects can result in a decrease in the capacitance resistance (Rc), causing gradual degradation of the graphene coating. Hsieh et al[94] described electrolyte penetration as a capillary action in which corrosion ions diffuse through the graphene membrane. Ren et al[63] suggested this process can be accelerated in the presence of defects on the coatings. Nevertheless, proper fabrication of the graphene coating is necessary to minimize the component defeats that can ultimately provide initiation sites for degradation of the coating.

## 5 | PROSPECTS AND CLOSING COMMENTS

BPPs are one of the major components of PEMFC, and graphene has positioned itself as a suitable material for BPP. In this study, a systematic review is presented to assess the BPP materials requirements and applications of

**TABLE 2** Graphene application as the bipolar plate in proton exchange membrane fuel cell (PEMFC)

| Environment | Application | Outcome | Refs |
|---|---|---|---|
| PEMFC | Graphene coating on stainless steel | Enhanced corrosion resistance. | 18 |
| | Graphene coating on copper | Enhanced corrosion resistance. | 63 |
| | Graphene incorporated into metal material | Improved durability and fuel cell performance. | 62 |
| | Graphene-polybenzoxazine composites | Composite loading in the range of 10-60 wt% increased the thermal, electrical, and mechanical properties of the BPP. | 87 |
| | 3D graphene-coated nickel for BPP | Displayed low corrosion rate, enhanced power density, and weight reduction. | 88 |
| | Graphene coated on the copper BPP | Stable and higher current–voltage–power was achieved compared to uncoated graphene BPP. | 65 |
| | Graphene/$TiO_2$ hybrid coating for the BPP | Hybrid graphene coating acted as a protection for the copper against corrosion in an acidic medium. | 89 |
| | Graphene film deposited on the aluminum BPP substrate, | Graphene-coated aluminum showed lower current density and stable interfacial contact resistance compared to uncoated material. | 16 |
| | Graphene coated on titanium for BPP application | Graphene-coated titanium BPP showed high corrosion resistance and conductivity. | 90 |
| | Graphene deposited on the 304 stainless steel bipolar plates plate | Enhanced the current density of the graphene-coated BPP. | 13 |

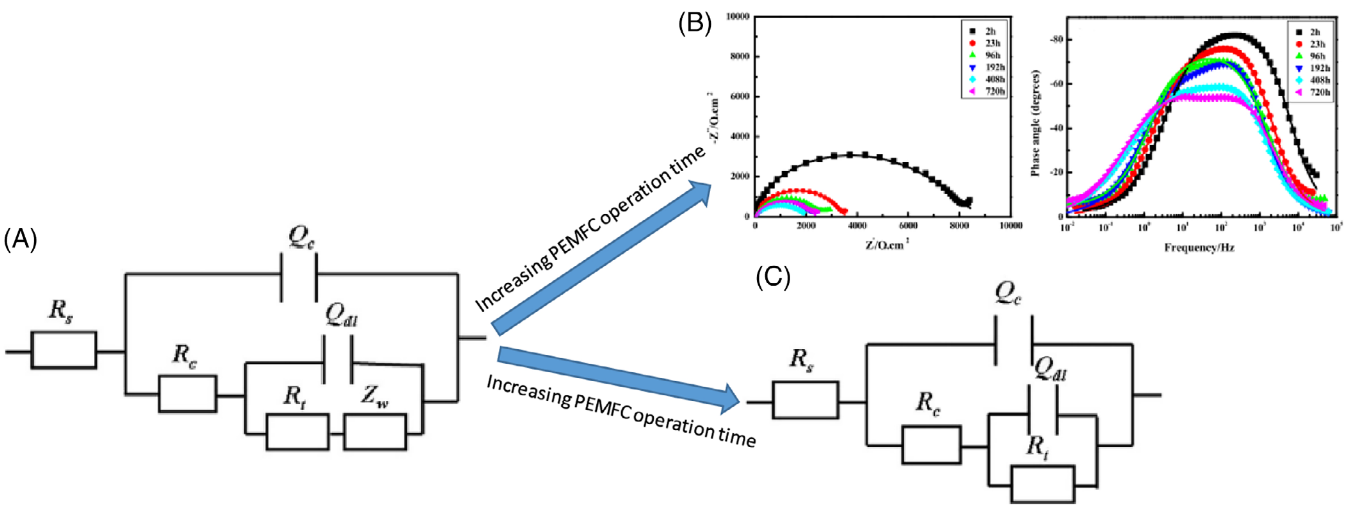


**FIGURE 9** Electrochemical impedance representation of graphene-coated copper degradation mechanism in proton exchange membrane fuel cell (PEMFC) environment[63]

graphene in the PEMFC with the view of understanding its degradation, which affects the overall fuel cell performance. It is likewise proposed in this review to utilize graphene and its coating to increase the performance of the PEMFC. Low resistance, high strength, and corrosion resistance of graphene make it a decent competitor to be utilized for low eroding and profoundly stable BPPs.

Graphene coating can segregate corrosion media from the base and give viable protection to metals. In this review, research on the corrosion mechanism of graphene coating has been explored and the effect of fabrication defects on the coating of metal is discussed. The behavior of mono-layer and multiplayer graphene-coated metal on corrosion resistance as means to reduce corrosion of metals used in different corrosive environments deliberated. In certain investigations, coatings of graphene on the metal substrate have been fabricated. Nonetheless, the mechanism of graphene distribution in the coating has not to be explored in detail and may provide more valuable information about the agglomeration of graphene coating with the metal substrate. Presently, CVD has been mostly used to fabricate graphene coatings due to large-scale manufacturing. Nonetheless, defects in graphene coatings may speed up the corrosion of substrate metals in the long term. The localized oxidation of graphene will diminish its mechanical strength and influence its service life. In this manner, it is important to further develop and enhance the CVD fabrication process to produce graphene coatings with an enormous coverage area, low defect density, and solid protection from mechanical damage. Graphene coatings have more fulfilling corrosion resistance than traditional coatings due to their "barrier" impact. Graphene hinders the entrance of corrosive substances and the proliferation of cracks. The scattering and systematic arrangement of graphene in coatings are basic to its safeguarding protection. To expand the scattering of graphene in coatings and its existence in polymer matrices, graphene alteration approaches can be utilized.

There are numerous difficulties ahead that must be settled before the effective application of graphene-based BPP in the PEMFC. Besides deliberate examinations of corrosion resistance of graphene as BPP material, it would be imperative to explore other benefits in terms of combining graphene with other nano-composites. Furthermore, the nature of graphene likewise assumes a significant part in the performance of the PEMFC. Various reports have affirmed fluctuating performance of the same composition of graphene, which might be somewhat ascribed to shifting characteristics of graphene as a result of fabrication techniques and process parameters. In like manner, the comparative and comprehensive methodology might provide the solution to the defeats that often occur in the fabrication of graphene and its coatings. Understanding the defeat-initiated degradation mechanism of graphene is necessary for an effective remedial approach during the fabrication process. The approach will provide improved performance of the PEMFC and the strength difficulties of graphene as BPP materials for reasonable applications. The flexibility and chemical stability of graphene and its coating make it to be a potential candidate and appealing for future industrial applications. We expect the corrosion mechanism described in this work to be considered in the plan of future graphene coating of BPP electrodes materials to enhance its corrosion resistance effectiveness.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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