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# Next-Generation Smart Nanocomposite Coatings for Metallic Corrosion Protection: From Passive Barriers to Active and Self-Healing Systems

Huwaidah Ibrahim Ahmed <sup>1</sup>, Mohammed RASHEED <sup>2,\*</sup>

<sup>1, 2</sup> Production Engineering & Metallurgy College, University of Technology- Iraq, Baghdad, Iraq.

\*Corresponding Author: [rasheed.mohammed40@yahoo.com](mailto:rasheed.mohammed40@yahoo.com)

## Abstract

A lot of attention has been paid to the development of advanced corrosion-resistant coatings because of the growing need to protect metals in a way that is long-lasting, useful in many situations, and good for the environment. Conventional protective coatings mostly use passive barrier mechanisms, but their long-term effectiveness is often limited by electrolyte penetration, mechanical damage, interfacial degradation, and aging in the environment. Recently, progress in nanotechnology has made it possible to create smart nanocomposite coatings that have the ability to improve passive barriers, stop active corrosion, respond to stimuli, and heal themselves. This review takes a close look at how polymeric, ceramic, and organic–inorganic hybrid coatings have changed over time. It looks at how functional nanomaterials like graphene and graphene oxide, MXenes, hexagonal boron nitride, metal oxide nanoparticles, layered double hydroxides, and metal–organic frameworks have been added. The connections between nanofiller properties, dispersion, interfacial interactions, coating structure, and mechanisms that prevent corrosion are given a lot of attention. A lot of information is given about advanced self-healing methods that use microcapsules, inhibitor-loaded nanocontainers, reversible polymer networks, shape-memory effects, and photothermal activation. Furthermore, the principal structural, morphological, chemical, mechanical, and electrochemical characterization techniques are evaluated, with particular attention to electrochemical impedance spectroscopy, potentiodynamic polarization, and quantitative assessment of self-healing efficiency. Comparative analysis highlights the advantages and limitations of different coating architectures, emphasizing the importance of long-term durability, controlled inhibitor release, and reliable recovery of protective functionality. The major challenges associated with nanofiller agglomeration, chemical stability, manufacturing scalability, environmental compatibility, and performance standardization are also addressed. Lastly, new directions for research are shown in areas such as multifunctional architectures, smart corrosion monitoring, data-driven material design, and long-lasting coating technologies. This review provides a holistic view of the transition from conventional passive coatings to adaptive, self-governing and self-healing nanocomposite systems for next-generation metallic corrosion protection.

**Keywords:** Smart nanocomposite coatings; protection of metal corrosion; functional nanofillers Self-healing coatings; active and passive protection.

## 1. Introduction

One of the biggest problems in modern engineering is corrosion, which reduces the durability, stability and efficiency of metals. Metal components in spacecraft, vehicles, the ocean, energy infrastructure, chemical processing plants and medical devices are continually subjected to conditions that promote electrochemical breakdown. Metal surfaces can experience localized or general corrosion when in contact with water, dissolved oxygen, chloride ions, acidic solutions and industrial pollutants. These processes slowly deteriorate the properties of materials, and so they become less reliable mechanically and require more repairs and replacements. Thus, one of the most important goals in the fields of materials science and surface engineering is the development of novel protective technologies to reduce corrosion damage and prolong the service life of metal components [1, 2].

Protective coatings have been used in the past to prevent contact of metal surfaces with the harsh environments by providing an unbroken physical barrier. Normal polymeric systems such as epoxy, polyurethane, acrylic and polyester coatings prevent corrosion by blocking the passage of water molecules, oxygen and dissolved ions. Ceramic and inorganic coatings, such as oxide based protective layers, enhance chemical stability, heat resistance and hardness. But their effectiveness depends a lot on how well they stick, how thick they are, how many holes they have, and how stable their structure is. Over time, normal coatings can develop tiny defects due to a variety of causes including mechanical stress, differential thermal expansion, environmental aging, and chemical degradation. When the harmful substances reach the coating–substrate interface, electrochemical corrosion reactions can initiate, resulting in localized failure, underfilm corrosion or coating delamination [1, 2].

The development of nanotechnology provides new opportunities to improve the performance of coatings by adding functional materials with nanometric size. In general, nanocomposite coatings are composed of a polymeric, ceramic or hybrid matrix, in which nanoparticles, nanosheets, nanotubes or nanostructured carriers are dispersed. These add-ons may alter the structure of the coating on the inside and affect its barrier properties, mechanical strength, surface wetness, thermal stability and chemical reactivity. Nanomaterials with high aspect ratio or high specific surface area are very important because they can alter diffusion pathways and surface interactions even at low concentrations. But the improvements depend not only on the addition of nanoparticles but also on the distribution, concentration, orientation and compatibility of the filler with the coating matrix [3].

Two-dimensional nanomaterials have attracted much attention because the layered structure of the materials can greatly facilitate the transport of corrosive species through a coating. Graphene and graphene oxide are two of the most studied candidates, which have high aspect ratios and good mechanical properties. Graphene protective layers can prevent diffusion and strengthen polymeric matrices but, being electrically conductive, can result in galvanic corrosion if the conductive pathways touch a metallic substrate. MXenes provide a broader selection due to tunable surface chemistry and layered structures, but the oxidation sensitivity and electrical conductivity should be considered. Hexagonal boron nitride, in contrast, is a good substitute, being electrically insulating and stable at both high and low temperatures [4]. These variations

show the significance of selecting nanofillers based on their physical barrier properties and their ability to interact with different chemicals [5].

In addition to the traditional barrier enhancement, the active corrosion protection has been more and more important in the current research [6]. Functional substances can react in active coatings, when harmful substances penetrate the protective layer [7]. Such systems may contain corrosion-blocking agents, ion-exchange compounds, functional metal oxides or nanostructured reservoirs that release protective species under certain chemical conditions [8]. Layered double hydroxides and metal-organic frameworks are particularly attractive as their structures allow for the incorporation of inhibitors and control of chemical flow [9]. When the proper functionalization is present, inhibitors can be delivered in response to changes in the pH, ionic composition, or conditions of the area that induce corrosion [10].

In the transition from passive to active protection, smart coating systems with additional adaptive functions have been designed [11]. These coatings are capable of localized inhibitor delivery, damage detection, surface passivation or recovery of protective functions. Self-healing coatings constitute a major category in this area [12]. They work by delivering encapsulated healing agents, through reversible polymer interactions, externally prompted molecular rearrangement, and shape-memory aided crack closure [13]. These strategies can be useful in alleviating the effects of localized mechanical damage, but their effectiveness is determined by the nature of the damage, the circumstances under which they heal and their ability to reinstate the relevant protective properties [14–16].

Numerous studies have demonstrated that functional microcapsules and nanocontainers can be loaded with healing agents and corrosion inhibitors. These carriers can be located in an intact coating due to corrosion or mechanical damage, and become active on a change of environment. Other areas of interest have included photothermal activation, reversible polymer chemistry and multi-functional protective architectures that can sense and report on themselves. The major challenge is however to distinguish between the temporary mitigation of corrosion by the released inhibitors and the actual restoration of barrier integrity. Therefore, electrochemical, chemical, morphological and mechanical measurements have to be done before and after damage for a reliable evaluation [12, 14, 17–21].

Despite considerable progress in the research, the application of smart nanocomposite coatings in industry is still limited due to some issues to be resolved. Some of these issues include non-uniform nanofiller dispersion, poor long-term stability, unknown environmental compatibility, complexity of manufacturing, and lack of widely accepted methods to measure self-healing performance. In addition, performance improvements seen during short-term laboratory testing may not directly translate to performance under combined mechanical, thermal and chemical exposure. To overcome these problems, we need to have a better understanding of the relationship between the coating composition, microstructure, corrosion protection mechanisms, environmental conditions and functional durability [13, 14, 22–32].

This review critically discusses the state-of-the-art smart nanocomposite coatings for corrosion protection of metals, emphasizing the evolution from passive barriers to active and self-healing systems. First, it reviews the main coating matrices and functional nanofillers. Then, it discusses

the mechanisms of passive and active protection. Subsequently, smart coating technologies are scrutinized in detail, including intrinsic and extrinsic self-healing, stimuli-responsive inhibitor delivery, shape-memory behavior, and corrosion sensing. The characterization methods, performance comparison, environmental issues, business problems, and future research directions are discussed finally. The main aim is to identify material design strategies and evaluation criteria that may back up corrosion protection technologies that are sustainable, multi-purpose and eco-friendly.

## 2. Advanced Nanocomposite Coating Materials and Functional Nanofillers

Nanocomposite coatings serve as protection due to the interrelationship between the continuous coating matrix and the mixed functional nanomaterials. The matrix controls the film formation, adhesion, flexibility, chemical resistance and environmental stability. The nanofillers, however, can modify the diffusion pathways, mechanical properties, surface chemistry and electrochemical functionality. Therefore, the choice of the proper combination of matrix material and nanofiller is important to achieve reliable protection in some cases [1-5].

### 2.1. Polymer-Based Protective Coatings

Among corrosion protection systems, polymeric coatings are one of the most popular types. This is because they are easy to work with, can be applied to a variety of metals, and can be used in a variety of industrial settings. One of their main jobs as protectors is to make a continuous film that stops metal surfaces from interacting with harmful chemicals. Epoxy resins are very important when it comes to regular polymeric materials because they stick well, don't react with chemicals, and can create very strong protective networks [2, 24].

Many things, like pipelines, storage tanks, marine equipment, and industrial buildings, are protected with epoxy coatings. The way they work as barriers comes from the way they connect polymer networks, which stop electrolytes from moving. Still, polymers can absorb water and change their properties after being exposed to it for a long time. Microcracks can also be caused by changes in temperature and mechanical stresses, especially in materials that are very cross-linked or brittle. Aggressive ions can reach the substrate and start localized corrosion once these flaws are linked together.

The incorporation of inorganic nanoparticles may improve the performance of an epoxy coating by altering the packing of the polymers, reducing the defect density and improving the coating toughness. For example, nanosilica particles can modify the coating hardness, its damage resistance and its interaction with other materials. Their efficiency depends mainly on particle size, concentration, surface modification and dispersion quality. While sticking particles can lead to stress concentrations and pathways for electrolyte penetration [25, 26], evenly distributed nanoparticles may contribute to the compactness of the coating structure.

Polyurethane coatings are another important class of coating due to their flexibility, resistance to abrasion and tunable mechanical properties. The molecular architecture of polyurethanes can be modified to provide a range of balances between hardness and elasticity, which is beneficial for substrates that are likely to be deformed, impacted or expand on heating. However, the chemical

stability of polyurethane formulations is dependent on their specific chemistry, and some systems may breakdown over time due to environmental or moisture-related damage.

When durability in severe environments, ease of processing and appearance of surface are important acrylic and polyester coatings are often used. Waterborne acrylic systems are very attractive, as they can reduce the use of organic solvents. However the effectiveness of their corrosion resistance depends on the nature of the film formation, the types of polymers used and the quality of the surface adhesion. Functional oxide nanoparticles can be added to enhance the protection and to add more electrochemical activity. Waterborne acrylic coatings with nanocerium have been investigated to show that barrier protection and chemically active ingredients can be combined into environmentally friendly formulations [27].

Conductive polymers, e.g. polyaniline and polypyrrole, provide an alternative route, as they can take part in electrochemical reactions at the interface between the metal and the coating. Under the right conditions, their redox properties could aid in surface passivation or modify interfacial corrosion behavior. However, the electrical conductivity may also lead to bad electrochemical interaction if the coating structure and substrate compatibility are not properly addressed. Thus, conducting polymers should not always be considered as better than protective matrices which do not conduct electricity [23]. For polymer-based nanocomposite coatings, optimization of the polymer network and the interactions between nanoparticles and the matrix should be performed simultaneously. The nanofillers should most likely improve corrosion protection by remaining well dispersed, assisting surfaces to bond well together and not alter how the material cures, how tough it is or how chemically stable it is over time.

## 2.2. Ceramic and Inorganic Coatings

There is a lot of research being done on ceramic and inorganic coatings for applications that need to be chemically stable, have high hardness, be resistant to heat and protect from harsh conditions. The typical materials are silicon dioxide, titanium dioxide, aluminum oxide, zirconium oxide and cerium oxide. To prevent corrosion, a chemically stable layer must form on the surface, which prevents the metal substrate from coming into direct contact with the environment [2, 27]. The sol-gel processing is useful for inorganic protective coatings because the compositions of precursors, hydrolysis, condensation and film formation can be controlled. This process involves chemical reactions between molecular precursors to form an inorganic or a hybrid network. The finished products can be deposited by dip, spray or spin coating and then dried and cured in a controlled manner. Sol-gel processing is a powerful technique for producing thin films with uniform thickness and for embedding a functional ingredient into the coating structure [2].

Silica coatings can be used to protect the surfaces from chemicals and to improve their stability. However, during the drying and curing of the material the formation of dense inorganic networks can cause shrinkage. Excessive shrinkage or thick coatings may create residual stresses and microcracks, which can affect the barrier performance. Therefore, it is necessary to find the optimal precursor concentration, curing conditions and coating architecture to minimize the structural defects.

Titanium dioxide and aluminum oxide are attractive because of their chemical and mechanical properties. Zirconia containing systems can offer better resistance in some chemical and thermal conditions. The performance of these materials however strongly depends on the way they are prepared, their porosity, phase stability and adhesion to the substrate. Also, some oxide nanoparticles can be photocatalytically active, which should be considered when they are mixed with organic materials, since the photocatalytic reactions can accelerate polymer degradation under light exposure.

An interesting fact about cerium oxide is that in addition to its structural role, it can also help stop corrosion. Under appropriate electrochemical conditions, compounds containing cerium might favor the formation of a local protective film. Such behavior is consistent with the physical barrier presented by the polymer or inorganic matrix surrounding it. However, the mechanism of protection is dependent on the chemistry, concentration and release behavior of the cerium and its environment [27]. There's a big problem with a lot of ceramic coatings, they don't respond very well to mechanical deformation. Brittle inorganic layers can crack or lose their adhesion when the substrate is bent, impacted or the temperature changes. This has resulted in hybrid systems that combine the stability of ceramics with the flexibility of polymers.

### 2.3. Organic–Inorganic Hybrid Coatings

Organic–inorganic hybrid coatings mix polymeric and inorganic components to obtain the best trade-off between flexibility, mechanical strength, chemical stability and corrosion resistance. These systems can be prepared by sol-gel methods, polymer-particle blending, silane coupling reactions or formation of interconnected organic and inorganic networks [1, 2]. The organic phase generally provides flexibility, film formation and adhesion. The inorganic part gives strength to the structure, stabilizes the chemicals and gives more resistance to permeation. The interaction between organic and inorganic parts has a large effect on the final performance. Weak interactions can produce small holes or help particles separate, but proper chemical bonding can assist stress transfer and prevent the formation of defects.

Silane coupling agents are often used to improve the compatibility between inorganic nanoparticles and organic polymer matrices. Functional silanes are able to chemically bond to the particle surfaces and polymer networks, resulting in better particle dispersion and more stable interfaces. This method is particularly effective for epoxy and sol–gel hybrid coatings with silica [25, 26]. Active corrosion inhibitors can also be incorporated into hybrid architectures. Zheludkevich et al. showed that nanocontainers loaded with inhibitors can be incorporated into hybrid sol–gel films for corrosion protection. The method used a protective coating that combined the physical barrier properties of the matrix with the localized release of inhibitor in response to changes related to corrosion [12].

So from a materials design point of view, what's the best thing about hybrid coatings? Well, they allow you to combine functions that go well together without each having to possess all the properties you want. The formulation, however, may become more complicated because the organic and inorganic parts may have different curing properties, thermal expansion, moisture affinity and chemical stability.

## 2.4. Graphene, Graphene Oxide, and MXene Nanofillers

Advanced corrosion-resistant coatings based on two-dimensional nanomaterials are now routinely fabricated. This is because their high aspect ratios can alter the diffusion paths in the not-so-thick protective films.

Graphene is a flat layer of carbon atoms bonded together in a hexagonal pattern. The multilayer structure and good mechanical properties make it suitable for reinforcing polymer matrices and hindering the transport of harmful substances. When the graphene nanosheets are homogeneously distributed and oriented nearly parallel to the metal surface, the electrolyte species trying to penetrate them will have longer diffusion pathways instead of reaching the coating–substrate interface directly [3].

Graphene oxide contains oxygen-containing functional groups that can help chemical modification and can improve compatibility with some polymer matrices. These groups can help interactions with polymer chains or coupling agents, but they can also increase the hydrophilicity of the filler, which may affect water uptake. Reduced graphene oxide generally has less oxygen groups and has different electrical and chemical properties that should be considered when formulating.

A big problem with systems built out of graphene is electrical conductivity. Galvanic corrosion may occur when an electrolyte contacts the interface of a conductive network that is electrically connected to a metallic substrate. Hence, the durability of graphene-based coatings has to be verified by testing under damaged and long-term exposure conditions instead of just the initial barrier properties [3].

MXenes are a unique family of two dimensional nanomaterials typically derived from transition metal carbides, nitrides or carbonitrides. Surface functional groups on their structures may alter their interactions with polymers and other nanoparticles.  $Ti_3C_2T_x$  is one of the most studied MXenes due to its layered structure and surface chemistry which allow for its functionalization in many ways.

MXene nanosheets could make the diffusion path more wavy and that will change the chemical behavior of the coating and change the mechanical behavior of the coating. But the fact they oxidize so easily is a big problem, especially when they are being processed, or left out in the air and water for a long time. Also, due to their electrical conductivity they might have electrochemical compatibility issues as those occurred with graphene based systems [4]. Thus, surface modification, combination with insulating nanoparticles and controlling the filler content are all effective ways to improve the stability of MXene coatings. In the future, scientists will need to make a careful balance between barrier properties of nanosheets and their ability to resist oxidation, improve dispersion and maintain unwanted electrical connections.

## 2.5. Hexagonal Boron Nitride and Metal Oxide Nanoparticles

Hexagonal boron nitride is a layered inorganic material that possesses strong in-plane bonding, high thermal stability and good electrical insulation. It has the appearance of graphene but its

electrical properties render it far more useful in applications where galvanic corrosion may be an issue with conductive nanofillers [5]. The addition of h-BN nanosheets to polymeric coatings can render the diffusion path more tortuous and help to mechanically strengthen the coatings. However, the efficiency of h-BN is dependent on the nanosheet size, orientation, concentration, and compatibility with other materials. Poor dispersion could lead to clumping and hole formation, which would diminish the expected improvement in barrier protection.

It is possible to functionalize h-BN surfaces to enhance compatibility with polymer networks. h-BN can be combined with responsive elements or self-healing chemistry to generate multifunctional formulations. Wang et al. explored a BN-based waterborne coating approach with corrosion protection, cross-linking and self-healing functions [28]. This demonstrated that the design of the whole coating architecture was more important than merely depending on one filler. Another type of nanofiller are metal oxide nanoparticles which can be used in many ways. Hardness, density and mechanical durability can be modified by silica nanoparticles. Some regions can be prevented from corrosion by cerium containing systems. Other oxides such as  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  can also possess surface-functional or reinforcement properties depending on the coating matrix and the environment.

The protective effects of oxide nanoparticles are highly dependent on volume fraction. Particles can occupy free space or improve the interaction between polymers and particles, if the right amount of filler is added. If it is too concentrated, things stick together, the fluid thickens and the continuity of the protective matrix is broken. This means that the optimization has to check the barrier properties, the mechanical behavior and the filler dispersion [25–27].

## 2.6. Layered Double Hydroxides and Metal–Organic Frameworks

The combination of lamellar structure and ion exchange properties makes layered double hydroxides a special class of nanostructured materials. Their positively charged hydroxide layers are balanced by charge-balancing anions that can be exchanged with other species in the environment. This structural feature makes LDHs good candidates to prepare active protective coatings that can host corrosion inhibitors or react with harmful chloride ions [6, 7]. The presence of LDHs in a coating can be advantageous for passive protection due to their layered structure and for active functionality due to their anion exchange capability. Under suitable conditions, aggressive ions can help to exchange or release inhibitor species stopping corrosion in specific areas.

In contrast, the delivery of inhibitors is dictated by the LDH chemical composition, interlayer species, morphology, loading concentration, and compatibility with the matrix. One of the most difficult things is to ensure that there is enough inhibitor storage in processing and long term exposure, and also that it can be released efficiently when corrosion occurs. Metal-organic frameworks (MOFs) are crystalline porous materials composed of metal nodes and organic linkers. Their chemistry and porosity can be finely tuned allowing the incorporation of functional molecules and the construction of responsive protective systems [8–10].

MOFs can serve as inhibitor storage, multifunctional fillers or components of hybrid nanocarrier systems. By altering their chemical structure, surface functionality and pore size you can alter

how the inhibitors are loaded and released. On the flip side, not all MOFs are stable enough to handle water or harsh chemicals. Protective performance can be degraded by hydrolysis, structural degradation or interactions with coating components.

So when you are considering the choice between LDH and MOF based carriers, you need to think about the chemistry of the inhibitor, how stable are the carriers in different environments, how fast do they release the drug, how well do they work with coatings and how easy are they to make. Both material types are promising for future active and smart coating technologies, but more research is needed on their long-term durability and potential for scale-up in industry. The properties presented in Tables 1 and 2 are general properties, and vary with type of coating, test substrate and testing environment.

**Table 1.** Classification of major coating matrices and their protective characteristics

| Coating category         | Representative materials                                                                | Main advantages                       | Principal limitations                        | Refs.          |
|--------------------------|-----------------------------------------------------------------------------------------|---------------------------------------|----------------------------------------------|----------------|
| Polymeric                | Epoxy, polyurethane, acrylic                                                            | Adhesion, flexibility, processability | Aging, water uptake, cracking                | [2], [24]      |
| Ceramic/inorganic        | SiO <sub>2</sub> , TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , CeO <sub>2</sub> | Chemical and thermal resistance       | Brittleness and shrinkage                    | [2], [27]      |
| Organic–inorganic hybrid | Silane–epoxy, sol–gel hybrid                                                            | Combined flexibility and stability    | Interfacial complexity                       | [1], [12]      |
| 2D-filled polymer        | Graphene, GO, MXene, h-BN                                                               | Diffusion-path modification           | Dispersion and material-specific instability | [3]–[5]        |
| Active nanocomposite     | LDHs, MOFs, functional silica                                                           | Inhibitor storage and release         | Loading and release control                  | [6]–[10], [26] |

**Table 2.** Functional nanofillers and their expected contributions to corrosion protection

| Nanofiller       | Principal function                        | Important advantage                | Major concern                     |
|------------------|-------------------------------------------|------------------------------------|-----------------------------------|
| Graphene         | Tortuous diffusion barrier                | High aspect ratio                  | Conductive galvanic pathways      |
| Graphene oxide   | Barrier and surface functionalization     | Polymer compatibility              | Moisture affinity and aggregation |
| MXene            | Layered barrier and functional interface  | Tunable surface chemistry          | Oxidation and conductivity        |
| h-BN             | Electrically insulating barrier           | Reduced conductive coupling risk   | Restacking and dispersion         |
| SiO <sub>2</sub> | Mechanical reinforcement                  | Coating densification              | Agglomeration                     |
| CeO <sub>2</sub> | Passive and possible active protection    | Corrosion inhibition potential     | Chemistry-dependent behavior      |
| LDH              | Ion exchange and inhibitor delivery       | Corrosion-responsive functionality | Carrier stability                 |
| MOF              | Inhibitor storage and responsive delivery | Tunable porosity                   | Hydrolytic stability and cost     |

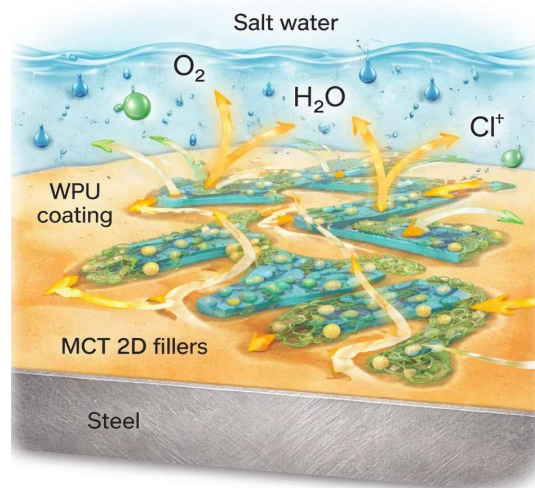


**Fig. 1.** This is a chart of the classification of polymeric, ceramic/inorganic and organic-inorganic hybrid coating materials with functional nanofillers for protection of metals from corrosion.

### 3. Corrosion Protection Mechanisms: From Passive Barriers to Active Systems

Several protective mechanisms are effective at the coating surface, in the coating matrix and at the coating–metal interface for good performance of advanced nanocomposite coatings. Most traditional coating systems are based on physical isolation. Multifunctional nanocomposites, meanwhile, can combine mechanical reinforcement, surface passivation, diffusion resistance, and electrochemical inhibition. Making sense of experimental results and finding links between nanofiller properties and long term corrosion resistance require understanding these processes [1, 3, 6].

#### 3.1. Passive Barrier Protection and Diffusion Resistance

Most organic and inorganic protective coatings function primarily through passive barrier protection. It does this by preventing or slowing down the interaction between the metal base and corrosive agents like water, oxygen, chloride ions and strong chemicals. In a perfect world the protective layer would create a continuous, not easily permeable barrier, with good adhesion and few holes. In practice, however, coatings contain molecular-scale voids, microscopic flaws, and edges through which water and dissolved ions can slowly permeate [1, 2].

Nanofillers can greatly alter the transport behavior of coating matrices. High aspect ratio nanosheets like graphene, MXenes and h-BN can create indirect diffusion pathways by forcing diffusing species to move through non- or semi-permeable architectures. This effect is a general term of the tortuous diffusion-path mechanism. Its effectiveness depends on the size, location, concentration and dispersion of the nanosheets [3-5].

For example, nanosheets that are nearly parallel to the metal substrate can form overlapping barriers, which increases the distance between the coating surface and the metal substrate. Conversely, randomly dispersed or agglomerated nanosheets can form relatively open pathways for transport and thus reduce the effectiveness of protection. The barrier performance is also

related to the degree of mixing between the filler surfaces and the surrounding polymer, as poor interfaces can create more diffusion channels. A simplified steady state form of Fick's first law can be used to demonstrate the relationship between permeation and coating thickness:

$$J = -D_{eff} \frac{dC}{dx} \quad (1)$$

where (J) represents the diffusive flux, ( $D_{eff}$ ) is the effective diffusion coefficient, (C) is the concentration of the penetrating species, and (x) is the position within the coating.

For smooth coating with mostly linear concentration difference, the flux magnitude can be expressed as:

$$|J| = D_{eff} \frac{dC}{L} \quad (2)$$

where (L) is the coating thickness and ( $\Delta C$ ) is the concentration difference across the coating.

From these equations it follows that the rate of penetration can be reduced either by decreasing the effective diffusion coefficient or by increasing the diffusion distance. However, actual polymeric coatings may deviate from the Fickian transport behavior due to the water induced swelling, heterogeneous interface and concentration dependent diffusion behavior. Thus simple transport models should be regarded only as conceptual descriptions, not as exact predictors of coating lifetime. Another important factor is the concentration of the nanoparticles. More filler may initially decrease permeability by complicating the diffusion pathways. However, if the concentration is higher than the ideal value, aggregation may decrease the porosity, disrupt the cross-linking of polymers, or lead to defects. Hence, optimization is often used to determine the best coating composition instead of maximum nanoparticle incorporation.

### 3.2. Active Corrosion Inhibition and Surface Passivation

Active corrosion protection differs from passive corrosion protection by the inclusion of chemical or electrical processes to inhibit corrosion after harmful species have reached weak areas of the substrate. Active coatings may include corrosion inhibitors or functional components which interact with the surrounding environment to prevent metal dissolution, cathodic reactions, or corrosion product propagation [6–10]. Anodic metal dissolution can be one of the forms of electrochemical corrosion of iron-containing metals. In a simplified form, it can be represented as:



Oxygen reduction is a usual cathodic reaction in neutral or alkaline air:



When an electrolyte comes in contact with the substrate, these reactions happen at the same time and cause electrochemical corrosion. The specific reactions depend on the type of substrate, the

availability of the oxygen, the pH, the chemistry of the electrolyte and the electrochemical conditions in the area. The active coating systems are designed to stop one or more of these processes. Corrosion inhibitors can adsorb to the metal surface, form protective complexes, aid in the formation of barrier compounds or alter the mechanism of local electrochemical reactions. Some of the inhibitors mainly inhibit anodic dissolution, and others interfere with cathodic reactions or both.

Surface passivation is very important for metals which can form protective oxide or hydroxide layers. In such cases the active species may help to retain the passive film in position or give rise to the formation of protective deposits in certain places. Compounds containing cerium have received a great deal of interest due to their ability to inhibit corrosion by precipitation and chemical reaction with surfaces [27]. If you have a lot of the inhibitor and it's concentrated then active inhibition works much better. This can mean that if not enough inhibitor reaches the corroding area, the protective response may not be as strong as it could be. In contrast, too much release may deplete the reservoir too quickly or affect the properties of the coating. Hence, for long term active protection, controlled inhibitor delivery is generally preferred to uncontrolled leaching.

### 3.3. Nanofiller Dispersion, Interfacial Adhesion, and Mechanical Reinforcement

Nanofillers may affect not only the electrical and permeability properties of protective coatings, but also the structure and mechanical properties of these coatings. These effects are very important, because microcracking, abrasion, interfacial debonding, or local mechanical damage are common modes of coating failure. The protective layer is strongly adhered to the metallic substrate and hence the electrolyte is prevented from penetrating the interface. So chemical compatibility and surface preparation are very important for long-term corrosion resistance.” Modified nanoparticles can interact with polymer chains and may improve stress transfer, compact the matrix, and reduce the probability of cracks forming. For example, the potential of silica nanoparticles in order to improve the epoxy coatings has been studied. Enhancement of mechanical performance can indirectly prevent corrosion by postponing damage-related failure [25, 26].

However, hardness is not always a good indication of resistance to corrosion. Harder coatings can be more brittle and more prone to cracking. Likewise, increased stiffness may hinder local deformation of the material, but also hinder the material's ability to accommodate substrate bending or thermal expansion. We have to think about the area around each nanoparticle that acts as a boundary. If the surface doesn't wet well or contains chemicals that don't mix, microscopic holes can form that allow water to build up. So a blend of naturally non-permeable particles can have poor corrosion resistance if the fillers are not dispersed well enough. The right particle functionalization, mixing conditions and curing procedures are important to make long-lasting nanocomposite coatings.

### 3.4. Synergistic Passive–Active Corrosion Protection

One of the most important advances in modern coating technology is the combination of passive and active protection in one material system. This process physically hinders the movement of

electrolytes and prevents chemicals from acting locally after damage to the coating or partial barrier failure [6–12]. For example, a typical multifunctional coating may consist of high aspect ratio nanofillers to stop diffusion and nanocontainers loaded with inhibitors that respond to changes in corrosion. The passive barrier retards the passage of aggressive species during the initial exposure time. If there are flaws or the electrolyte gets to the metal, the active parts can release inhibitors that slow the corrosion reactions in that area.

LDHs are well suited to such architectures since they can serve as barriers and simultaneously exchange ions. Similarly, MOF-based systems can provide porous frameworks for incorporation of inhibitors and control of their release [6–10]. To show real synergy, however, you have to do more than just compare the multifunctional formulation to an unchanged coating. In the right experiments you should compare a matrix not filled with anything, a matrix filled with only barrier fillers, a formulation filled with only active carriers and the combined system. The experiment is designed to test if the coating is more effective when assembled than when its components are applied separately. Moreover, longtime testing in the environment is required, as the passive and active functions may not fail simultaneously. A formulation may be very effective initially, but then become less effective when the inhibitors are depleted or the carriers break down or the polymers age. This means that the most promising systems are those that keep the barrier resistance during normal operation and only turn on active features when there are localized corrosion events.

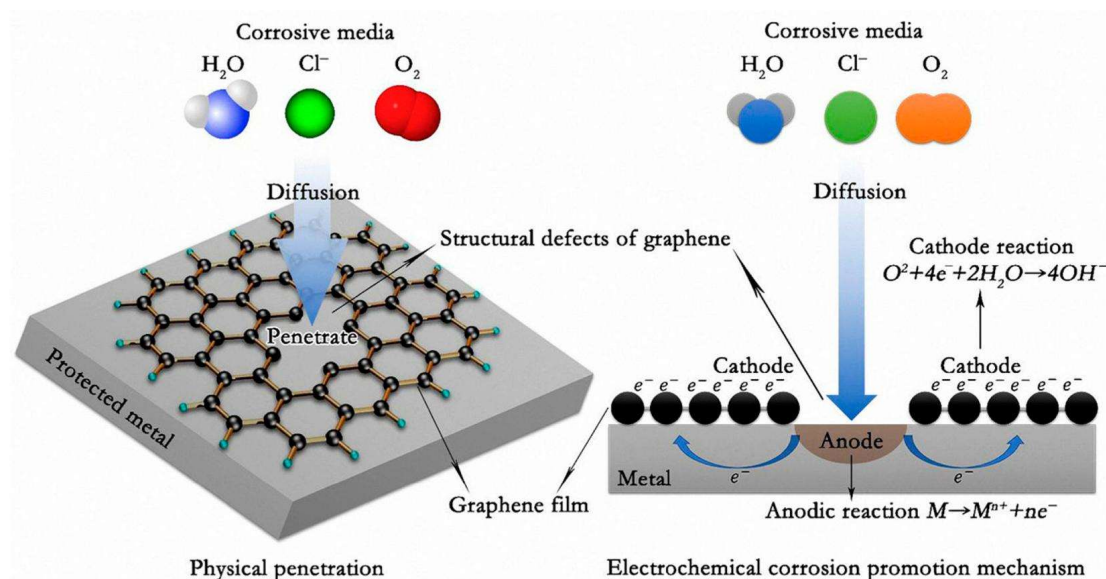


**Fig. 2.** Schematic illustration of corrosion protection mechanisms: (a) conventional barrier failure, (b) nanofiller-enhanced passive protection, and (c) active corrosion inhibition through controlled inhibitor release.

**Table 3.** Comparison of principal corrosion protection mechanisms in nanocomposite coatings

| Mechanism                | Protective action                                      | Representative components                      | Main limitation                 | Refs.          |
|--------------------------|--------------------------------------------------------|------------------------------------------------|---------------------------------|----------------|
| Passive barrier          | Restricts water, oxygen, and ion transport             | Polymer matrices, graphene, h-BN               | Damage sensitivity              | [1]–[5]        |
| Active inhibition        | Suppresses electrochemical reactions                   | Inhibitors, LDHs, MOFs                         | Inhibitor depletion             | [6]–[12]       |
| Surface passivation      | Promotes or stabilizes protective interfacial films    | Cerium compounds, suitable inhibitors          | Environment-dependent chemistry | [23], [27]     |
| Mechanical reinforcement | Improves resistance to damage initiation               | SiO <sub>2</sub> , oxide particles, nanosheets | Brittleness or agglomeration    | [25], [26]     |
| Passive–active synergy   | Combines transport resistance and localized inhibition | Hybrid carrier–nanosheet systems               | Formulation complexity          | [6]–[12], [29] |

#### 4. Smart and Self-Healing Nanocomposite Coating Technologies

Smart nanocomposite coatings possess advantages over traditional corrosion barriers due to their ability to respond to mechanical damage, chemical changes, environmental stimuli or detectable signals related to corrosion activity. They can perform functions such as the delivery of inhibitors, repair of physical damage, reversible chemical bonding, changes in surface properties or detectable signals associated with corrosion activity. Self-healing coatings are particularly important since scratches and microcracks are common locations where coating failure initiates [11–16]. However, the term ‘self-healing’ should be appropriately used. Some systems restore coating continuity via movement of the polymer or polymerization of a healing-agent, while others primarily prevent corrosion at damaged areas by releasing inhibitors. Both can restore protective performance, but in very different ways.

##### 4.1. Extrinsic Self-Healing: Microcapsules and Nanocontainers

Extrinsic self-healing systems rely on the incorporation of healing agents or corrosion inhibitors in separate reservoirs embedded in the coating matrix. These reservoirs can be microcapsules, hollow particles, porous silica structures or other useful containers. Most of the microcapsule based coatings work on the mechanical breakage. As the crack proceeds through the protective layer, microcapsules in the vicinity of the crack can break and release contained healing material. The released material could flow into the damaged area and cure or polymerize, thus partially patching the barrier. Liu et al. presented a study on epoxy-based microcapsules for self-healing anticorrosion coatings, showing the possibility of incorporating chemically compatible healing agents into polymeric protective systems [17].

The functionality is highly dependent on the shell size, the shell strength, the viscosity of the healing agent and the concentration of the capsules. The capsules need to be robust enough to

survive the coating preparation and curing process, and yet still react appropriately when they are seriously damaged. If the capsule walls are too weak they may open prematurely in processing. Too strong localized scratches may not start the healing process. We also need to improve the quantity of microcapsules. A higher loading may mean more healing agent is available, but the coating may not be as compact or strong. So the effective formulations must balance the ability to repair with the ability to act as a barrier first. Nanocontainers are a similar, but different, approach. When chemicals change, these systems usually release chemicals that prevent corrosion rather than releasing materials to physically fill cracks. Zheludkevich et al. developed nanocontainer coatings loaded with inhibitors that responded to environmental changes induced by corrosion. It exhibited enhanced protection in damaged zones [12]. The main drawback of many extrinsic systems is limited number of healing agents. If a capsule or reservoir is empty, it may not protect as well if used again in the same place. A further important research aim is the development of systems that release substances slowly and safely.

#### 4.2. Intrinsic Self-Healing: Reversible Polymer Networks

Intrinsic self-healing coatings can repair due to the reversible interactions embedded in the polymer matrix. Intrinsic systems join connections across damaged regions at the molecular scale [13, 15] while extrinsic systems require separate supplies of healing agents. These processes may involve reversible covalent bonds, hydrogen bonds, ionic interactions, metal-ligand coordination or supramolecular associations. After damage, polymer segments may start to interact again across the broken interface. The intrinsic healing is most effective if the temperature is appropriate, the network structure is good and the damaged area is of a certain size. Highly rigid polymer networks are initially very mechanically stable, but molecules are only able to be slightly mobile. In contrast, more mobile polymers might be more easily healed but would have lower mechanical strength or barrier stability.

Thus, a major challenge for materials design is to achieve the right balance between network rigidity and reversible functionality. Dynamic polymer chemistry means that the wound heals again and again because the useful functional groups remain in the coating. But repeated repair is no guaranty. Time, aging, irreversible bond cleavage, environmental contamination, and the loss of the ability to move chains around can all slow healing. Therefore, intrinsic self-healing systems should be evaluated after several damage-healing cycles, not only after one successful repair event.

#### 4.3. Stimuli-Responsive Coatings and Controlled Inhibitor Release

Stimuli-responsive coatings are developed to change their behavior in reaction to specific chemical or physical modifications. Possible stimuli include changes in pH, chloride ions, temperature, moisture, light and mechanical stress [11, 12, 18]. The local electrochemical reactions can change the chemical conditions around a damaged metal surface, so that the pH-responsive inhibitor delivery is very important for the protection of metal against corrosion. If these conditions are met, it is possible to produce functional nanocarriers that free protective molecules more readily. Jin et al. investigated a coating system that utilized dendritic mesoporous silica nanoparticles loaded with benzotriazole and polydopamine. The functional

carrier design was intended to allow for control over the inhibitor delivery and to provide corrosion protection [18].

The performance of stimuli responsive systems depends on the sensitivity and selectivity of the release mechanism. If the carrier responds to normal changes in the environment, it may release its contents before corrosion takes place. Conversely, a carrier which is too demanding a stimulus may not respond at the beginning of the corrosion. In an ideal world, inhibitor release should be limited during normal operation and should start up fast enough when a localized corrosion process starts. Release kinetics can be studied by time-dependent measurements of inhibitor concentration under controlled conditions. These measurements should be compared with the electrical behavior of the chemicals to find out if the release does really protect. Just because it has a coating with a carrier loaded with an inhibitor doesn't mean you should call it "corrosion-responsive". There has to be evidence of some relevant triggering process and a corresponding functional response.

#### 4.4. Shape-Memory and Photothermal Self-Healing Systems

Shape-memory-assisted self-healing coatings are based on materials that can revert to a pre-determined shape upon application of the appropriate stimulus, usually heat. This behavior may contribute to reducing the size of cracks or scratches and enhancing the contact between damaged polymer surfaces [15]. Shape recovery can be especially helpful when major coating defects make molecular-scale healing impossible. Shape memory may be useful in chemical or physical repair because it can physically bring damaged areas closer together. However, plugging geometrical fractures does not necessarily heal chemical bonds or stop electrolytes from penetrating. So, further measurements regarding adhesion, mechanical integrity and electrochemical resistance are necessary for the characterization of the recovered region. In photothermal self-healing systems, the light-absorbing parts can convert the incident radiation into localized heat. This increase of temperature can cause movement of polymer chains, breaking and re-forming of bonds or flow of healing agents [16].

Lai et al. investigated ultraviolet resistance and self-healing photothermally activated protective coatings. This demonstrated the potential of combining environmental protection and externally controlled repair [19]. "The great thing about photothermal systems is they can help localized healing that is externally induced. The fact is they can only be used if they can get enough light, use the right amount of energy, keep the right temperature and work with the substrate. Another distinction lies between spontaneous self-healing and externally triggered repair. A coating that must be intentionally heated or irradiated may still be useful for technology, but it shouldn't be called fully autonomous."

#### 4.5. Self-Reporting and Corrosion-Sensing Coatings

Coatings that can "report" damage or corrosion add an extra functional capability by sending signals that can be picked up. Changes in color, fluorescence, chemical response, or other properties that can be measured may be these signals [20, 21]. These kinds of coatings might help find localized corrosion early, before it causes major structural damage. As an example, functional microcapsules might have markers inside that change color when the chemistry in the

area changes or come out when the coating gets damaged. Having sensing and protective functions work together is especially useful for structures that need to be inspected regularly or regularly for preventative maintenance. A multifunctional system could theoretically identify coating defects and initiate a protective response at the same location.

However, sensing and healing should be considered as two separate concepts. A visible signal is not a proof of corrosion inhibition and an efficient release of the inhibitor does not imply an accurate detection of the corrosion. The reliability of sensing systems is based on parameters such as sensitivity, selectivity, environmental robustness, and resistance against false responses due to temperature, humidity or unrelated chemical changes. Future smart coating systems may combine sensing with controlled delivery of the inhibitor and even self-healing of the polymer, thus creating multi-functional architectures able to both identify and respond to local degradation.

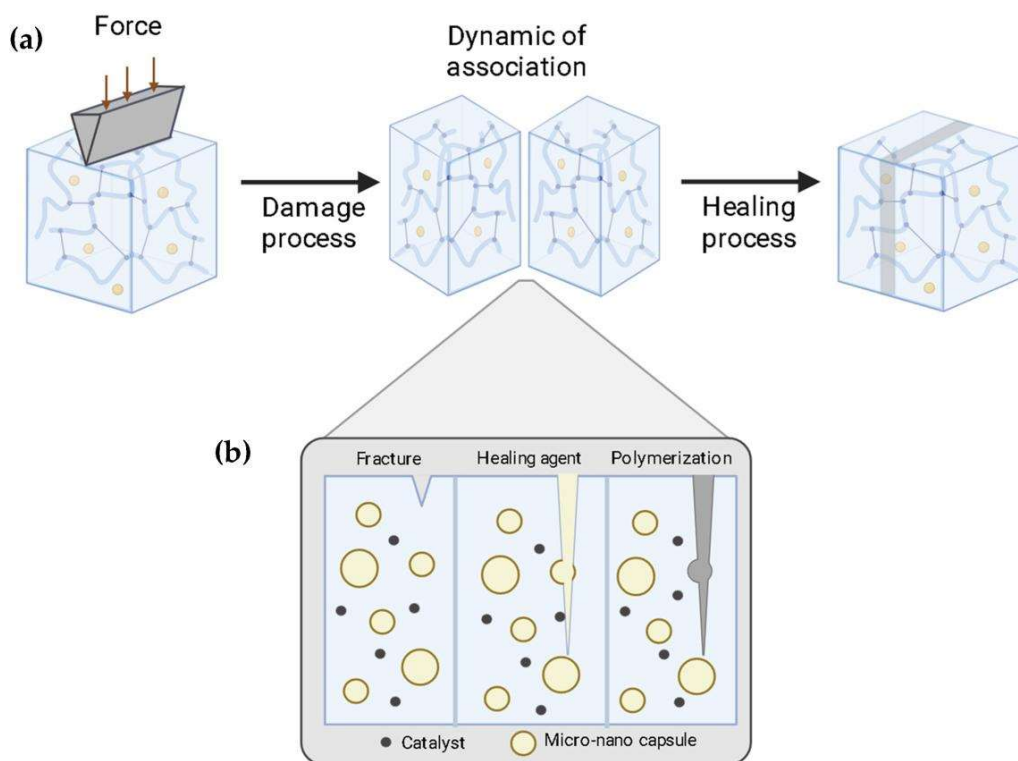


**Fig. 3.** Schematic illustration of self-healing mechanisms in nanocomposite coatings: (a) extrinsic healing through encapsulated agents and inhibitor release and (b) intrinsic healing through reversible polymer interactions.

**Table 4.** Comparative characteristics of smart and self-healing coating technologies

| Technology             | Activation mechanism              | Protective response             | Principal limitation           | Refs.            |
|------------------------|-----------------------------------|---------------------------------|--------------------------------|------------------|
| Microcapsule-based     | Mechanical rupture                | Healing-agent release           | Finite supply                  | [17], [20]       |
| Nanocontainer-based    | pH or ion-induced response        | Localized inhibitor delivery    | Carrier depletion              | [12], [18]       |
| Intrinsic polymer      | Reversible molecular interactions | Network restoration             | Healing-rate limitations       | [13], [14]       |
| Shape-memory-assisted  | Temperature or other stimulus     | Crack closure                   | Incomplete barrier restoration | [15]             |
| Photothermal           | Light-induced heating             | Activated healing               | External energy requirements   | [16], [19]       |
| Self-reporting         | Damage or corrosion response      | Detectable warning signal       | Sensor reliability             | [20], [21]       |
| Multifunctional hybrid | Combined mechanisms               | Protection, repair, and sensing | Processing complexity          | [11], [28], [29] |

## 5. Performance Evaluation, Industrial Challenges, and Future Perspectives

We have to study the structure, electrical and chemical responses, durability under pressure, environmental stability and performance of the new nanocomposite coatings. The incorporation of functional nanomaterials into coatings has been demonstrated in many studies to improve their corrosion resistance, but direct comparisons are still difficult, since the coating performance depends heavily on the experimental conditions, the composition of the substrate, the concentration of the nanofiller and the coating preparation method. A good evaluation should, therefore, use many techniques to describe something and to distinguish between short-term benefits and long-term protective features [14, 22, 30–32].

### 5.1. Structural, Morphological, and Chemical Characterization

A characterization of the structure and shape of nanocomposite coatings is necessary if one is to understand the internal structure and distribution of functional materials. The effectiveness of a protective coating depends on its continuity, porosity, filler dispersion, surface adhesion and resistance against microstructural degradation. Diffraction, microscopy, spectroscopy and surface analysis can be used to examine these properties in combination. X-ray diffraction (XRD) is widely used to identify crystalline phases and to confirm structural changes in inorganic nanofillers. XRD can be useful to identify metal oxide phases or layered double hydroxides or crystalline nanomaterials embedded in protective matrices, etc. Changes in the position of the peaks, their width or their intensity can tell you how the structure has changed, how far apart the layers are or how crystalline the material is. The amorphous nature of the polymer and the low concentrations of crystalline additives can make it more difficult to interpret the meaning of diffraction patterns in polymer-based nanocomposites [4, 6]. SEM and FESEM are powerful tools for investigating surface structure, defects in coating, distribution of nanoparticles, and corrosion changes. Cross-section views can provide information about the

coating thickness, the quality of the seal at the interface and any local defects that may lead to premature failure of the material. Energy-dispersive X-ray spectroscopy (EDS) gives additional information about the composition and distribution of elements and enables researchers to study the dispersion of fillers and the formation of corrosion products. But EDS alone does not give molecular bonding mechanisms or oxidation states. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) can show structures and particle boundaries at the nanoscale in more detail. You can use these methods to better understand graphene-based nanosheets, MXenes, h-BN, and functional nanocontainers. TEM analysis can show the sizes of particles, how nanosheets are stacked, how they stick together, or how surface treatment changes the structure. The electron microscopy can also provide information about the crystal structure of nanomaterials by using selected-area electron diffraction [3–5].

X-ray photoelectron spectroscopy (XPS) gives information on the chemical states and elements present on the surface. It is very useful to study the formation of oxides, the functionalization of nanoparticles and the chemical changes during corrosion. XPS can also be useful for studying the oxidation mechanism in systems with MXene or chemical environment of protective parts containing cerium. The combination of these methods allows for a more comprehensive understanding of structure-property relationships. However, the mere finding of a dense coating morphology or even uniform distribution of nanofiller is not sufficient to prove that its own protection against corrosion is better. Thus, electrochemical measurements and environmental exposure testing need to be connected with structural characterization.

## 5.2. Electrochemical Characterization: EIS and Potentiodynamic Polarization

The electrochemical characterization is required to evaluate the electrolyte penetration resistance of a coating and to understand the corrosion mechanisms at the metal–coating interface. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) are two of the most useful method as they provide us with complementary information on protective behavior [30–32]. Electrochemical impedance spectroscopy (EIS) measures the frequency dependence of the electrical response of an electrochemical system to a small-amplitude alternating potential or current. The resulting impedance data are usually presented in the form of Nyquist and bode representations. These plots can give you coating barrier properties, electrolyte penetration, charge transfer processes and interfacial wear and tear. This is the form we write the complex impedance in:

$$Z(\omega) = Z'(\omega) + jZ''(\omega) \quad (5)$$

where ( $Z'$ ) represents the real impedance component, ( $Z''$ ) represents the imaginary component, ( $j$ ) is the imaginary unit, and ( $\omega$ ) is angular frequency.

The impedance modulus is calculated using:

$$|Z| = \sqrt{(Z')^2 + (Z'')^2} \quad (6)$$

The low frequency impedance modulus is often used to compare protective coatings, as it reflects the combination of the coating resistance and the interfacial electrochemical processes. It is well known that a higher modulus of impedance generally indicates a more difficult passage of electrochemical current under the tested conditions. However, it should not be considered as a universal solution for corrosion protection, since similar impedance responses may be caused by different physical processes [30, 31].

EIS data are often interpreted by a method known as equivalent electrical circuit analysis. The condition of the coating affects some of the circuit elements, namely, solution resistance, coating resistance, coating capacitance, charge-transfer resistance, and double-layer response. Non-ideal capacitive behavior, e.g. if the surface is non-uniform and relaxation processes occur at different locations, is usually described using constant-phase elements.

Long term monitoring of EIS is very useful, as it can show how the coating behaves and changes with time. When a coating is first immersed, it may show a high impedance because its barrier structure is intact. As water and ions pass through the matrix, the resistance of the coating can decrease and more electrochemical processes can be observed at the interface. Consequently, time-dependent impedance analyzes usually yield more information than initial measurements alone [30–32].

Potentiodynamic polarization provides additional information by monitoring the current density as a function of the electrode potential. In favorable electrochemical conditions, corrosion potential and corrosion current density can be estimated. The inhibition efficiency can be calculated as:

$$\eta_{PDP}(\%) = \frac{i_{corr,ref} - i_{corr,coat}}{i_{corr,ref}} \times 100 \quad (7)$$

where ( $i_{corr,ref}$ ) is the estimated corrosion current density for the reference specimen and ( $i_{corr,coat}$ ) is the corresponding value for the coated specimen.

This equation has only a meaning when the estimates are derived from similar electrochemical conditions and correct kinetic interpretations. Intact, very resistive coatings may not generate polarization curves suitable for normal Tafel extrapolation. Therefore, polarization data should be interpreted together with EIS, surface morphology and all other relevant information.

For self-healing coatings, electrochemical measurements are very important, because they may show if the damaged areas regain their original protective function. However, an increase in impedance after healing does not necessarily mean that the crack has physically closed. It can also exhibit inhibitor adsorption, formation of protective precipitates or variations in the corrosion products [14]. A normalized impedance recovery index can be expressed as:

$$\eta_{healing}(\%) = \frac{|Z|_{healed} - |Z|_{damaged}}{|Z|_{initial} - |Z|_{damaged}} \times 100 \quad (8)$$

where the impedance values correspond to the initial state of being intact, damaged and healed, under the same frequency and similar conditions.

The value that comes out of this is the recovery versus the loss of impedance due to damage. It does not mean the full recovery of the structure or mechanical properties of the coating.

### 5.3. Comparative Corrosion Protection and Self-Healing Performance

To find the best systems, you need to look at how well different types of polymeric coatings, passive nanocomposites, active protective formulations and self-healing systems work. In contrast, papers dealing with corrosion often use dissimilar substrate materials, coating thicknesses, exposure times and electrolyte mixtures. So, you should not just put numbers from different studies in order without looking at how they were normalized and tested [3, 14, 31]. Initial barrier coatings can work pretty well if they stick well, don't have many holes, and dry properly. Their biggest problem is that their barrier properties gradually fail after long exposure in the environment. Electrolyte ingress and the initiation of underfilm corrosion can result from small cracks, water uptake and interfacial degradation.

Nanocomposite coatings with inorganic particles or nanosheets uniformly dispersed could make things less likely to breach or penetration. Epoxy systems filled with silica have been investigated for example to increase their strength and reduce the likelihood of rust [25, 26]. High aspect ratio fillers such as graphene-based coatings are promising as they can produce winding diffusion paths. However, the electrical conductivity can be a problem if defects in the coating are in electrical contact with the substrate [3]. Mxene coatings can also be used for layered barrier engineering but have to deal with additional issues such as being stable against oxidation and being able to conduct electricity [4]. In contrast, coatings with h-BN form nanosheet barriers which are not electrically conductive. This could decrease the possibility of conductive galvanic paths. But the best protection from corrosion is determined by the dispersion of the nanosheets, the surface chemistry, and how well the polymers work together [5, 28].

Another way, which can become very important after the coating has been damaged, is the use of active coatings with LDHs, MOFs and inhibitor-filled nanocontainers. In contact with the substrate, these systems can decrease the rate of corrosion reactions in the area [6–12]. With self-healing systems, they can repair some damage and get back to protecting you. But how well the body heals itself dictates how much improvement you get. Extrinsic systems are constrained by the quantity of healing agent that is available. Intrinsic systems, however, depend on reversible chemistry and mobile molecules. To compare barriers, the best way is therefore to consider their initial effectiveness, their healing after being damaged and their longevity. Table 5 shows a comparison by mechanisms instead of rankings of performance on experiments.

**Table 5.** Comparative performance and functional characteristics of advanced corrosion-resistant coatings

| Coating system                 | Dominant mechanism                 | Main performance advantage        | Critical limitation          | Refs       |
|--------------------------------|------------------------------------|-----------------------------------|------------------------------|------------|
| Conventional epoxy             | Physical barrier                   | Established industrial protection | Long-term aging and cracking | [2], [24]  |
| Silica/epoxy                   | Barrier and reinforcement          | Improved matrix characteristics   | Nanoparticle agglomeration   | [25], [26] |
| Graphene/polymer               | Tortuous diffusion barrier         | High-aspect-ratio reinforcement   | Galvanic corrosion risk      | [3]        |
| MXene/polymer                  | Layered barrier                    | Functional surface chemistry      | Oxidation and conductivity   | [4]        |
| h-BN/polymer                   | Insulating barrier                 | Reduced conductive coupling risk  | Dispersion limitations       | [5], [28]  |
| LDH-functional coating         | Active inhibition and ion exchange | Localized corrosion response      | Inhibitor release control    | [6], [7]   |
| MOF-functional coating         | Functional inhibitor storage       | Tunable carrier architecture      | Chemical stability           | [8]–[10]   |
| Microcapsule-based coating     | Extrinsic repair                   | Local crack response              | Limited healing reservoir    | [17], [20] |
| Intrinsic self-healing coating | Reversible bonding                 | Potential repeated healing        | Healing kinetics             | [13]–[15]  |
| Hybrid smart coating           | Combined mechanisms                | Multifunctional protection        | Cost and complexity          | [11], [29] |

#### 5.4. Mechanical Durability and Long-Term Environmental Stability

Metal parts are often subjected to mechanical and environmental stresses. Therefore, mechanical durability is an important property of protective coatings. Wear and tear, impact, bending, thermal cycling and vibration can lead to microcracks or loss of adhesion between surfaces that can allow electrolytes to pass. Some mechanical properties can be improved by using nanoparticle reinforcement, e.g. hardness and resistance to localized deformation can be improved. But making something stiffer can also make it less flexible, meaning it can't deal with breaking as well. Thus mechanical improvements are not necessarily good; rather they should be judged in light of their application [25, 26]. Adhesion of surfaces is very important since separation can result in moisture buildup and underfilm corrosion. The better the adhesion, the lower the probability of early delamination, but the quality of the surface preparation is determined by the substrate's composition, cleanliness, surface roughness and reactivity with chemicals.

New problems arise if the environment is stable over time. Water, UV light, heat or swelling can break down protective coatings and also alter the way polymers bond together. Another problem is that nanofillers can chemically change or lose their ability to stick to surfaces when they are exposed to air. Oxidation of MXene based systems is a significant problem as it can change the properties of the nanomaterial and its surrounding interface [4]. Similarly, carriers loaded with

inhibitors may slowly lose their active ingredients if they travel at high speed or are exposed to the environment. This cycle is started by corrosion and the performance of coating may not be good. Therefore it is important to repeat the electrochemical tests and compare the coating before and after exposure to different environments. The test is carried out by soaking it in water for a long time, varying between wet and dry conditions, changing the temperature, exposing it to UV light, testing its resistance to abrasion and adhesion, and causing controlled mechanical damage. These types of tests can give you a better idea of how long protective gear will last than just putting it in water for a short period of time.

### 5.5. Environmental Sustainability and Industrial Scalability

Corrosion resistant coatings are now made because they are better for the environment. Traditional protective systems sometimes use organic solvents, hazardous additives or energy-intensive processing. So, people are more interested in formulations that use water, inhibitors that are safe to the environment and synthetic routes that generate the least chemical waste and pollution.

Waterborne polymer coatings can be more eco-friendly if they contain less volatile organic solvents. But how well they protect depends on the chemistry of the polymers, how they harden, how long the film lasts, and how well they don't let water in [27,29]. Nanomaterials could be used for better working of eco-friendly formulations but their impact on production and disposal should also be considered. For this reason, the environmental performance of a coating should be evaluated over its entire life cycle, not only because it does not contain any common solvents or harmful pigments.

The production of some advanced nanomaterials may require harsh chemicals, specialized equipment, or large amounts of energy. The wear and tear, maintenance or disposal may also release nanoparticles that could be a problem for the environment and workers. Another big problem in the industrial world is scalability. In the laboratory, formulations are often prepared by mixing, ultrasonication, surface functionalization or multistep deposition procedures. Although these methods can produce good quality coatings for the sake of experiments, the question remains whether they are reusable or cost-effective at a large scale. Raw materials should be uniform, viscosity reproducible, coating should be stable enough to store, cure the same way every time and be compatible with standard application methods for commercial production of coatings. Therefore, the addition of multifunctional nanocarriers should be weighed against the complexity and cost of fabrication.

Finally, the economic viability of smart coatings depends on the fact if their added features lead to measurable improvements in service life, reduced maintenance and/or improved operational reliability.

### 5.6. Current Challenges and Limitations

Despite much progress, many scientific and technological problems still limit the widespread application of multifunctional nanocomposite coatings. A major problem is getting the nanofiller to disperse. Aggregation can alter the viscosity of a coating, reduce its compatibility with other

surfaces and cause small defects. This problem is crucial to take into account when studying two-dimensional materials because the nanosheets tend to reconfigure and/or connect to form clusters. Another problem is that functional components have to be stable. Long-term exposure to MXene oxidation, inhibitor depletion, carrier degradation and polymer aging may gradually reduce its protective efficacy.

It is also still difficult to assess behavior that contributes to healing itself. There are many different ways of characterizing things written about, but it is difficult to compare them due to differences in scratch geometry, healing conditions, immersion time and performance indicators [14]. Another problem is that it is difficult to understand what the real protection mechanism is. Barrier improvement, adsorption of inhibitors, protective precipitation or a combination of these processes may improve impedance. Without proper controls it is not possible to determine reliably the contribution of each component. Similarly, claims of total self-healing may be unfounded when measurements reveal only partial electrochemical recovery and no evidence of physical or mechanical repair. The formulation complexity can also increase when you want to combine several functional parts. Too many nanosheets or carriers or microcapsules could ruin the coating and cost more to produce. Therefore, future research should aim not only to improve each laboratory performance metric, but also to identify strong links between material composition, mechanisms, durability, compatibility with the environment, and manufacturing requirements.

### 5.7. Future Perspectives and Emerging Research Directions

Integrated structures combining high initial barrier resistance with corrosion-responsive inhibition and repeatable self-healing are under development, which are expected to make great progress in smart nanocomposite coatings in the future. Multilayer coating systems are a fascinating idea. In these systems, different layers do different jobs that complement each other. For example, an adhesion-promoting layer could stabilize the interface, a nanosheet-reinforced layer could prevent electrolyte penetration, and a responsive outer layer could detect damage or deliver inhibitors to specific sites. These types of architectures may overcome some of the compatibility issues that arise when trying to incorporate all the functional materials into one coating matrix. Another important direction is the development of advanced nanocarriers, capable of controlled inhibitor release and enhanced chemical stability. LDHs, MOFs and modified mesoporous structures can be used as engineering carriers which can respond selectively to environmental changes induced by corrosion [6–10, 18].

Another important goal is to heal itself over and over. Many of the microcapsule systems used today are not fully healable, as the contents are exhausted upon activation. Intrinsic polymer networks and hybrid architectures that combine reversible bonding with functional reservoirs may allow for better long term recovery. Future research should also concentrate on the integration of active protection and corrosion sensing. Multifunctional coatings that can detect local degradation and trigger a protective response can contribute to condition based maintenance and improved structural reliability [20, 21]. AI and data-driven materials design are new tools that can help us understand the relationships between nanofiller chemistry, polymer composition, processing conditions, and coating performance. But predictive models work well only if there are standardized datasets, accurate descriptions of the material and measurements

from experiments done under similar conditions. Sustainability for the environment has to be a central theme for the development of future coatings. Besides electrochemical and mechanical properties, the choice of waterborne matrices, green preparation methods, environmentally safe inhibitors, and life-cycle assessment should be considered.

Finally, more attention should be devoted to standard tests for long-term durability. The main aim is to not only demonstrate the improvement in immediate corrosion resistance, but also to develop reliable protective systems that can perform as desired in actual industrial environments.

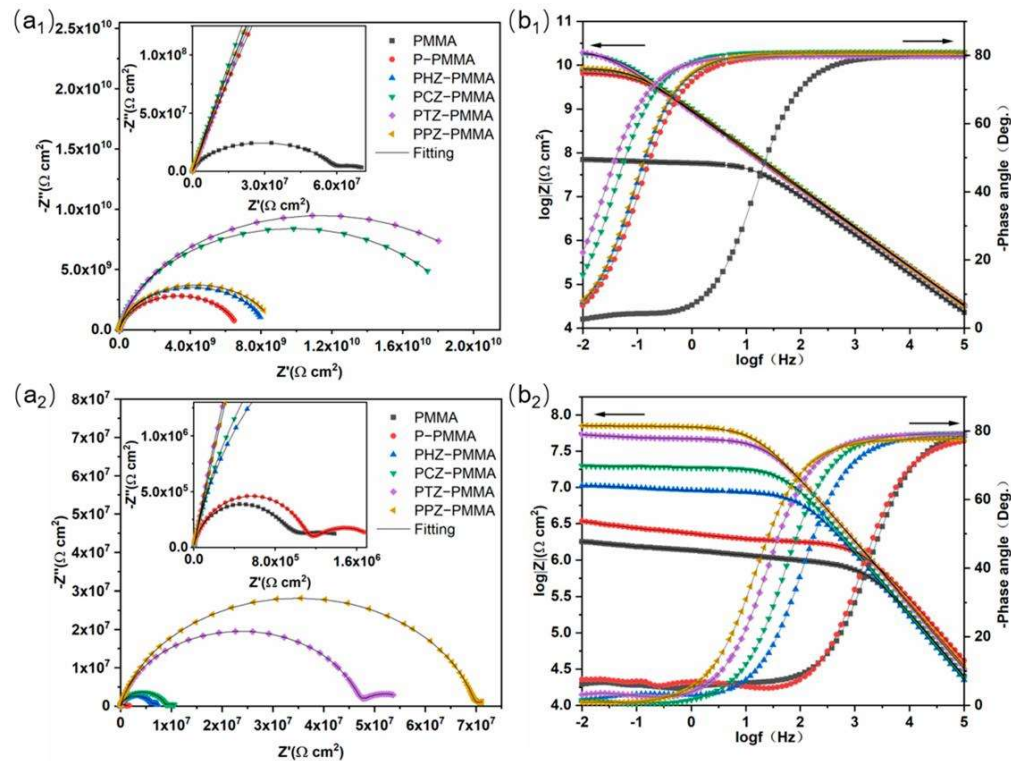


**Fig. 4.** Integrated characterization and performance evaluation of nanocomposite anticorrosion coatings using structural, electrochemical, mechanical, and long-term durability testing.

**Table 6.** Characterization techniques recommended for evaluating nanocomposite anticorrosion coatings

| Technique          | Principal information                       | Relevance to coating performance             |
|--------------------|---------------------------------------------|----------------------------------------------|
| XRD                | Crystalline phase identification            | Nanofiller structure and stability           |
| SEM/FESEM          | Surface and cross-sectional morphology      | Coating defects and corrosion damage         |
| EDS                | Elemental composition and distribution      | Filler dispersion and corrosion products     |
| TEM/HRTEM          | Nanoscale morphology and interfaces         | Nanofiller geometry and aggregation          |
| FTIR               | Chemical functional groups                  | Polymer chemistry and functionalization      |
| XPS                | Surface chemical states                     | Oxidation, surface modification, passivation |
| EIS                | Frequency-dependent impedance               | Barrier integrity and interfacial corrosion  |
| PDP                | Current–potential response                  | Corrosion kinetics where valid               |
| Contact angle      | Surface wettability                         | Water–surface interactions                   |
| Adhesion testing   | Coating–substrate bonding                   | Delamination resistance                      |
| Hardness/abrasion  | Mechanical characteristics                  | Resistance to damage initiation              |
| Healing assessment | Functional recovery after controlled damage | Self-healing capability                      |

**Table 7.** Major challenges, possible research strategies, and expected benefits

| Current challenge                   | Proposed research strategy                            | Expected benefit                     |
|-------------------------------------|-------------------------------------------------------|--------------------------------------|
| Nanofiller agglomeration            | Surface functionalization and dispersion optimization | Improved coating uniformity          |
| MXene degradation                   | Stabilization and hybridization                       | Improved environmental durability    |
| Conductive galvanic pathways        | Insulating interlayers or filler modification         | Reduced galvanic corrosion risk      |
| Uncontrolled inhibitor release      | Stimuli-responsive carriers                           | More efficient inhibitor utilization |
| Limited repeated healing            | Dynamic polymer networks                              | Improved repair capability           |
| Short-term testing emphasis         | Long-term and cyclic exposure                         | More reliable durability assessment  |
| Limited reproducibility             | Standardized protocols and reporting                  | Improved comparison across studies   |
| Environmental concerns              | Safer chemistry and life-cycle assessment             | Lower environmental impact           |
| Industrial manufacturing complexity | Scalable formulation and deposition methods           | Greater commercial feasibility       |

## 6. Conclusions

Next-generation smart nanocomposite coatings are a big step forward in corrosion protection technology as they enable the combination of normal barrier resistance with active electrochemical inhibition, damage responsive functionality and the ability to heal itself. Traditional protective systems have some problems such as easy damage by mechanical forces, aging from the environment, and initiating corrosion in some areas. This has led to the creation

of these coatings. The incorporation of functional nanomaterials into polymeric, ceramic and organic-inorganic hybrid matrices can result in mutually compatible properties. Graphene, graphene oxide, MXenes, hexagonal boron nitride, metal oxide nanoparticles, layered double hydroxides and metal-organic frameworks can be used to improve the durability of coatings. But their effectiveness depends a lot on the amount of filler used, its dispersion, how well it sticks to the metal, its chemical stability and how it interacts with the metal.

The move from passive protection to active systems is important as active systems have mechanisms to arrest localized corrosion following electrolyte penetration. The functionality of protective responses can be regulated by nanocontainers with inhibitors, ion-exchange materials and responsive polymer architectures. However, the reliability of such systems depends on the ease of obtaining inhibitors, the release rate, stability of the carriers and compatibility with the environment. Self-healing technologies provide us more ways to extend the work of coatings after they have been damaged by mechanical forces. Conversely, extrinsic systems encapsulate healing agents or inhibitors whereas intrinsic systems allow for reversal of chemical or physical interactions within polymer networks. Shape-memory-assisted and photothermal techniques provide more opportunities for controlled repair. However, each of these mechanisms needs to be considered independently as geometric crack closure, chemical corrosion inhibition, and electrochemical recovery do not always lead to the same level of structural recovery. It is important to fully describe the coating so as to understand the relationship between the composition, microstructure, mechanical integrity and electrochemical behavior. Mechanistic interpretation can be aided by techniques such as XRD, FESEM/EDS, TEM, FTIR, XPS, EIS and potentiodynamic polarization. Extra attention should be given to long term durability, controlled damage testing and repeatability in similar environmental conditions.

Although science has made great progress, the application of nanofillers in industry is still difficult due to their aggregation, chemical instability, poor healing capability, high manufacturing cost, and lack of standardized performance evaluation. So, the most important things for future work should be multifunctional coating architectures, environmentally friendly materials, controlled inhibitor delivery, repeatable healing mechanisms and manufacturing technologies that could be used by many people. The most promising direction is the development of smart protective coatings, which are capable not only to retain high passive resistance in normal operation, but also to ensure a targeted active protection and functional recovery in the event of damage. If these mechanisms are coupled with accurate characterization, long-term durability testing, and environmentally friendly manufacturing methods, it may be possible to develop the next generation of corrosion-resistant coatings for metal structures working in harsh industrial conditions.

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