



Review Recent Trends and Progress in Corrosion Inhibitors and Electrochemical Evaluation

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Abstract: Science and engineering research studies are currently concentrating on synthesizing, designing, producing, and consuming ecologically benign chemical species to replace harmful chemicals. This is due to the increasing demands of conservation knowledge and strict ecological regulations. Numerous environmentally friendly substitutes produced from natural resources, including biopolymers, plant extracts, chemical pharmaceuticals (drugs), and so on, are now frequently used as inhibitors to replace dangerous corrosion inhibitors. Many compounds have been extensively used. A range of methods, including physisorption, chemisorption, barrier protection, thin-film growth, and electrochemical procedures, will be used to provide corrosion resistance. The various kinds of corrosion inhibitors (CIs), the mechanisms underlying inhibition, and the evaluation procedures have all been covered in-depth. This review provides an overview of the relevant literature in which researchers and scientists used different types of CIs, the effect of CIs on metals, and information about designs and mechanisms used to minimize corrosion in a variety of equipment composed of alloys or metals, along with electrochemical evaluation studies. This review will provide scholars with fresh insights to advance the discipline.

Keywords: corrosion; inhibitors; self-healing; electrochemical; corrosion efficiency

1. Introduction

Corrosion has become a worldwide phenomenon that affects many areas, such as industries (oil and gas). Corrosion is caused by corrosive species commonly found in the air, leading to the deterioration of metal through electrochemical and chemical processes. This degradation occurs when the metal is exposed to atmospheric moisture, and it is dependent on both time and temperature [1]. It damages the beauty and glaziness of the metal materials; for example, cracks have appeared in certain areas of the Taj Mahal, India, etc. The steel inside the building is corroded and causing fractures because most metals rapidly undergo corrosive degradation through the reactivity of components in the surrounding environment because they are thermodynamically unstable in their pure form [2–4]. Different countries have conducted surveys on national cost corrosion. According to this survey, the economy of the US was reduced by \$70 billion, which is 4.2% of the gross national product, due to corrosion. The government of India spends approximately 3.5% of the country GDP per year on corrosion losses [5]. Due to the abovementioned factors, it is important to prevent corrosion. When metallic sections corrode quickly and must be replaced, it becomes a high-cost process. Furthermore, the procedure of addressing



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). corrosion is risky and dangerous, posing the potential to harm personnel or even lead to fatalities. This issue impacts health, safety, economy, technology, and culture.

Corrosion in industries is mainly due to acid-based cleaning and rust removal on various equipment, like metal pipes, wheels, and various machineries [6]. In the field of corrosion prevention, it has been shown that inhibitors have been the subject of the most research. Corrosive damage to metallic materials is prevented through inhibition, involving the use of chemical compounds. These compounds, known as corrosion inhibitors (CIs), reduce corrosion rates and impede the diffusion of corrosive ions in a corrosive environment caused by chemical elements within the corrosion system [7]. While increased corrosion protection is needed, the major driving force is that CIs that previously worked extremely well can now no longer be used due to their risks to health. Chromium-based corrosion inhibitors, such as hexavalent chromates (CrVI), were widely used for their effectiveness in preventing corrosion. However, these inhibitors have been found to be toxic and carcinogenic, posing serious health and environmental risks, and currently no alternatives have been identified that are both safe and effective in reducing corrosion.

Depending on the morphology of metal damage, corrosion is categorized into general corrosion, pitting corrosion, crevice corrosion, intergranular corrosion, environmentally induced fracture, de-alloying, galvanic corrosion, erosion, and corrosion based on the metal damage's morphology [8]. Atmospheric corrosion is one of the most common forms of corrosion. Infrastructure, transportation, energy, and other industries are all significantly impacted by atmospheric corrosion, which is influenced by a variety of environmental conditions. An important environmental factor is relative humidity. Rainfall can have an impact on how metallic materials react to air corrosion [9–11]. When steel is exposed to corrosive environments, it begins to deteriorate over time due to fatigue. Seawater environments speed up the development and progression of crack growth. In offshore structures, this has been discovered to be a significant failure mechanism [12].

There are a few ways to prevent corrosion on metal, as shown in Figure 1, including coating [13], alloying [14], cathodic protection [15], anodic protection [16], organic coatings [17], and, more recently, researchers are using a laser technology [18] for surface treatment of metal is to improve the properties of metals, such as their roughness, hardness, and corrosion resistance. Rust-preventative fluids are widely utilized to provide temporary corrosion protection throughout production operations, storage, and shipment, among the many options available to prevent corrosion of metals [19].

Depending on the types of base fluid, rust-preventative fluids can be categorized as solvent-based, oil-based, and water-based rust preventatives by adding corrosion inhibitors, film-forming agents, and other additives to a base fluid [20]. Most commonly, corrosion can be controlled by implementing specific corrosion "probing" techniques or devices in infrastructure, plants, buildings, bridges, and other engineered systems. In order to stop the contact of water with the steel surface, which causes corrosion, film-forming inhibitors are employed in industries to build a molecular layer directly on the top of the steel and an additional layer of the aliphatic tail in hydrocarbons.

Hazardous Cis, such as chromate-based and phosphate-based Cis, are no longer permitted due to their toxicity as a result of increased environmental awareness and legal changes. Green chemistry is gaining popularity among researchers due to its inexpensiveness and, moreover, it is safe for living organisms as well [21]. CIs that are favorable to the environment are growing in popularity because they contain a variety of active components that can be employed in organic compounds to attach to metal surfaces and produce a protective coating that stops further corrosion. As such, CIs developed from natural resources are an excellent option [22–24]. Nowadays, researchers are employing various techniques to develop environmentally friendly corrosion inhibitors (CIs). These CIs are designed to be more environmentally friendly by utilizing less toxic and biomassderived nanoparticles due to their favorable physicochemical characteristics [25]. The high surface-to-volume ratio of nanomaterials and their additives compared to those of typical macroscopic materials makes them effective corrosion inhibitors. Nano-compounds provide hardness, straightness, durability, optical properties, and thermal stability, in addition to stopping surface reactions and reducing the corrosion rate by blocking active sites on metal surfaces [26]. Numerous plant extracts have been studied as secure environmental corrosion inhibitors [27–29]. However, more research has to be performed on this green CIs area. This review presents a comprehensive analysis of the multi-faceted influence of corrosion across diverse domains, while also addressing distinct categories of corrosion inhibitors (CIs). It further elucidates the practical implementation of these CIs, the methodologies employed for evaluating their performance, and offers insights into the prevailing trends within this research domain.



Figure 1. Corrosion prevention methods.

2. Mechanism of Corrosion Inhibition

Chemical corrosion occurs when there is a non–conductive liquid where there is the absence of current and electron flow, and it also occurs in dry gases. Electrochemical corrosion takes place in a solution when the surface potentials of the metallic materials and the electrolytes are different. The metal oxidizes and transforms into an ion at the anode. The mechanism of CIs chemisorbed on the metal surface to produce a corrosion protection layer through the inhibition effect or the combination of inhibitor ions with the metallic surface is described below. The inhibitor causes the metal's surface protection layer to form an oxide layer. The inhibitor leads to a complex product when it reacts with a potentially corrosive component in an aqueous environment [30]. Figure 2 depicts the scheme of electrochemical corrosion.

$$M \rightarrow M^{n+} + ne$$

The cathode is the other component, where depolarization occurs predominantly through the reduction of hydrogen cations and oxygen molecules.

$$O_2 + 4 H^+ + 4 e \rightarrow 2 H_2O$$

 $2 \ H^{+} + 2 \ e \rightarrow H_{2}$



Figure 2. Scheme of electrochemical corrosion.

The development of a thick corrosion layer on the iron substrate in the atmosphere is explained by Evans and Taylor with cyclic electrochemical mechanisms. This cyclic mechanism involves oxidizing iron metal to produce iron (II) compounds that fill the corrosion layer pores. When the metal is enclosed by a thick water film, it is oxidized by dissolved oxygen into iron (II) species and into iron (III) oxyhydroxide, and the iron is also oxidized into Fe (II). The phenomena that take place within a thick corrosion layer (CL) have only been briefly electrochemically characterized in a few investigations. Using the carbon paste electrode (CPE) technique, Emmanuel et al. [31] investigated the metal's electrochemical behavior/CL system in the presence and absence of corrosion inhibitor as well as the impact of corrosion inhibitor on the electrochemical activity of various iron (III) oxyhydroxide phases of CL. The oil and gas sectors have found that using CI is an efficient way to reduce corrosion because the fuel gas comprises a variety of contaminants, including gases, such as nitrogen, oxygen, carbon dioxide, and water vapor. When water evaporates from a stream of fuel gas to form an aqueous phase, corrosive species, like H^+ , H_2CO_3 , and HCO_3 , will be obtained when CO_2 dissolves into the water and leads to corrosion in metals and metal alloys [32]. In the presence of O_2 , CO_2 inhibitors exhibit a significant decrease in inhibition performance. According to Singh et al. [33] in the presence of 100 ppb O₂ at 40 °C (1 bar CO₂, pH 5.5), the inhibitory efficacies of all imidazoline-based, quaternary ammonium-based, and amine-based processes were significantly reduced because the N atoms interact with oxygen and the inhibitor volatilizes from the metal surface. According to Wang et al. [34], in a coexisting O_2 and CO_2 environment, the corrosion prevention efficacy of 8×10^{-5} mol L⁻¹ amides was only 80.3%, whereas it was 98.3% in a CO_2 -saturated solution. Although it is evident that the presence of O_2 can considerably reduce the ability of CO₂ CIs to inhibit, the processes underlying this effect are not entirely understood.

3. Types of Corrosion Inhibitors

CIs are majorly classified into organic, inorganic, and green CIs, based on the active inhibitor molecules that retard the corrosion process. The application of different CIs is depicted in Figure 3. Furthermore, composite CIs have also been developed. These include biopolymerbased corrosion inhibitors, carbon-based corrosion inhibitors, silane-based composite coatings, sol-gel-based composites, micro-arc oxidation, and layered double hydroxides. Furthermore, composite CIs have also been developed, such as biopolymer-based corrosion inhibitors [35], carbon-based corrosion inhibitors [36], silane-based composite coatings [37], sol-gel-based composites [38], micro-arc oxidation, and layered double hydroxides [39].



Figure 3. Applications of corrosion inhibitors in various areas.

3.1. Organic Corrosion Inhibitors

Organic corrosion inhibitors (OCIs) are commonly employed in industry due to their efficiency over a wide temperature range, compatibility with protected materials, relatively low toxicity, and superior solubility. These substances have cathodic and anodic inhibitory effects. Cathodic corrosion inhibitors reduce the corrosion potential and impede or postpone the reactions that take place at the cathode (oxygen reduction and hydrogen evolution). Anode corrosion inhibitors work with the metal cation to form an insoluble hydroxide, obstruct the active sites on the metal surface, and shift the corrosion potential toward positive values. This reduces the rate of corrosion by stopping the metal's further oxidation process (dissolution) [40]. By moving water molecules away from the metal surface and forming a pressurized barrier, the bulk of organic inhibitors are absorbed onto the metal surface. The transit of the electron from the inhibitor to the metal is facilitated by the presence of p electrons and non-bonding electrons (a single pair) in the inhibitor molecule [41]. Heteroatoms with lone electron pairs are necessary for efficient organic corrosion inhibitors, such as those found in nitrogen, oxygen, sulfur, and phosphorus, as well as moiety with electrons (aromatic rings and multiple bonds), which can interact with free orbital d metal and facilitate the adsorption process [42,43]. The annual corrosion rate employing an organic inhibitor is shown in Figure 4 as a function of time. Some inorganic inhibitors are only partially soluble in some conditions. As a result, protection may be less effective if the inhibitor is less soluble, and it may be distributed unevenly.

The number and location of inhibitor containers, as well as the coating matrix, have been presented as factors influencing anticorrosion efficiency [44]. OCIs will protect the metal by forming a hydrophobic layer on its surface. The quality of an OCI is determined by its molecular structure (electronic structure), nature of metal surface affinities, electrolyte, and polar substituents, and chemical composition. However, this type of organic barrier protection is susceptible to damage from mechanical impacts that create holes during application, exposing the metal substrate to the environment. Additionally, when water and hostile species penetrate into the coating and make their way to the metal substrate, they can cause corrosion products to occur which can lead to the coating delamination or blistering and the material losing its barrier protection [45]. In contrast, metal surfaces can be guarded by using hybrid or organic corrosion inhibitors. In particular, functional groups on amines with an aliphatic tail are known to create an adsorption-derived barrier that prevents the entry of species that are corrosive, such as active anions or water molecules. It



is very desirable for the inhibitor to have a longer release because it can provide long-term resistance and increase its viability for practical applications.

Figure 4. Annual corrosion rate with organic inhibitors in relation to time and for various acid molarities [41].

Heterocyclic compounds are found to be good CIs because of their high inhibition effectiveness, cost-effectiveness, and the possibility of recyclization. Due to the electronwithdrawing nature of the -CN and NO₂ substituents in OCIs, it was anticipated that the efficiency would decrease due to the +R (the effect is referred to as the +R effect if the replacement group contains a lone pair of electrons to donate to the associated pi bond or conjugate system of pi bonds) and -I (the -I effect, also known as the negative inductive effect, happens when the substituent pulls electrons out) effects. Note that the highest occupied molecular orbital (HOMO) is associated with a metal inhibitor, whereas the lowest occupied molecular orbital (LUMO) is associated with a metal to restrict electron transfer. Organic molecules interact with metallic surfaces via donor-acceptor interactions. According to this observation, Ph-CN and Ph-NO₂ should have better anticorrosion properties than pure benzene, in which only the aromatic ring participates in charge sharing. In this case, the increase in inhibition and efficiency can be attributed to an increase in the molecular size and electron donating ability of the -CN and $-NO_2$ heteroatoms [46]. Zhenquiang et al. [47] designed a CI with different methods with the CI carrying more polar heads and alkylene linkers. As such, the adsorption of the CI on copper surfaces could increase by two or more polar groups. The chelating action of heterocyclic molecules as corrosion inhibitors is based on the formation of an insoluble physical diffusion barrier on the electrode surface, which could prevent metal reaction as well as dissolution. With this, they employed a benzothiazole heterocyclic ring as a polar head to design a new CI. Schiff bases (CSBs) made of chitosan were examined as CIs by Antony et al. [48]. According to this study, CSBs are stable and do not hydrolyze in the majority of experimental conditions. Three primary reactive functional groups are present in chitosan (CH), including amino (–NH₂), 1-hydroxyl (–CH₂OH), and 2-hydroxyl (>CH–CH₂OH) substituents at C-2, C-3, and C-6, respectively. CH and CSBs are effective for covering and safeguarding metal surfaces, such as steel and mild steel (MS) due to their polymeric composition. Verma et al. [49] used Ch-Cr-SB as a corrosion-resistant coating for AZ91E alloy in a 3% NaCl solution in their study. The anticorrosive potential of Ch-Cr-SB was investigated at various concentrations. The results show that increasing Ch-Cr-SB concentration increases the effectiveness of its corrosion protection or decreases the rate of corrosion, while increasing temperature has the reverse effect. Kim et al. [50] developed triethanolamine (TEA), an organic corrosion inhibitor covered with an epoxy finish and encapsulated. The sustained anticorrosion ability, made possible by its self-healing capability, was examined to enhance the alloy's ability to resist corrosion. According to EIS studies, the inhibition efficiency (IE) was 85% when metal experienced mild corrosion. When the local pH level starts to change, the inhibitor layer starts to form, which triggers the release of TEA. Moreover, it also shows self-healing properties. In the next section we discussed more about self-healing techniques. Samples embedded in nanocapsules show suppression of corrosion activity and provide long-term anticorrosion performance, especially in chloride-rich environments [51]. Verma et al. [52]. gave a comprehensive review on isatin and its derivatives as a new, efficient, and green N-heterocyclic class of organic corrosion inhibitors. The intolerable toxicity of current, albeit very successful, corrosion control techniques has increased the demand for novel, safe, and environmentally friendly corrosion inhibitors. The substantial expansion in technological skills related to the development of new organic corrosion inhibitors coincides fortunately with this demand. Although they have advantages in preventing corrosion, they also have some drawbacks that must be taken into account. Because of factors, like temperature changes, contact with corrosive substances, or extended exposure to the environment, organic corrosion inhibitors frequently offer only short-term protection that may deteriorate over time. It could be necessary to periodically reapply and monitor these inhibitors [53].

3.2. Inorganic Corrosion Inhibitors

Inorganic corrosion inhibitors work by preventing the system's anodic and cathodic components from reacting to cause corrosion. The salts of zinc, copper, nickel, arsenic, and other metals are the most commonly used inorganic corrosion inhibitors. A point to be made is that, in comparison to other substances, arsenic compounds are highly regarded [54]. Furthermore, they can be subdivided into cathodic and anodic CIs based on charges and the application. It is possible that not all metals or forms of corrosion respond well to inorganic corrosion inhibitors. Depending on the particular corrosion mechanism, the atmosphere, and the metal substrate, their efficacy can vary [55].

3.2.1. Anodic Corrosion Inhibitors

The term "passivation inhibitor" also refers to anodic inhibitors. They lead to a lower anodic response. They support the metal surfaces that are preventing the anode reaction, specifically. They also create a coating that is adsorbed on metal surfaces. Typically, these inhibitors react with the corrosion product first generated to form the previously noted cohesive and insoluble film. The anodic reaction is affected by the corrosion inhibitors and corrosion potentials of the examined metals. When corrosion inhibitors interact with the metal ions on their anode, they generate insoluble and impermeable metallic ions hydroxide coatings. When using anodic inhibitors, it is crucial to take into account the high inhibitor molecule concentrations in the solution. The film generated cannot completely cover the metal surface if the inhibitor concentration is minimal. Localized corrosion results from this. Anodic corrosion inhibitors include nitrates, molybdates, sodium chromates, phosphates, hydroxides, and silicates [56].

3.2.2. Cathodic Inhibitors

The cathodic corrosion inhibitors stop the metal surfaces from undergoing the cathodic reaction during the corrosion process. These inhibitors have metal ions that precipitate as

insoluble compounds at the cathodic sites. Here, a dense, adherent coating forms on the metal surface, limiting the diffusion of reducible species in these regions. Because of the oxygen diffusion and electron conductivity in these regions, these inhibitors have higher cathodic inhibitors because they react with the water's hydroxide ions to generate insoluble hydroxides. In order to safeguard the metal surfaces' cathodic sites, the generated insoluble hydroxides are deposited there. Oxides and salts of antimony, arsenic, and bismuth that are deposited on the cathodic area in acid solutions can be used as additional examples of cathodic inhibitors. These inhibitors are well known for reducing the emission of hydrogen ions [56].

3.3. Green Corrosion Inhibitors

The usage of green corrosion inhibitors is becoming more and more popular today due to traditional inhibitors being costly and harmful to the environment. For this reason, researchers have become interested in corrosion inhibitors that are economical, cost-effective, and highly effective in preventing corrosion.

Roots, chitosan, oil, flour, yeast, natural honey, leaves, herbs, and phytochemicals from plants including other substances are examples of green corrosion inhibitors. In a corrosive environment, green inhibitors treat the surface of metals or alloys by being added in very small quantities. Plant extracts are thought to be rich in naturally occurring chemical compounds that, when added to many industrial systems, reduce the rate of corrosion by adsorbing useful species on metal surfaces. Figure 5 shows the natural sources of green CIs. The report claims that some organic and biodegradable compounds are powerful inhibitors [3]. Both nonpolar chemicals with aromatic rings, aliphatic chains, heterocyclic rings, and functional moieties, as well as polar molecules with oxygen and nitrogen, are abundant in plant extracts. These substances can absorb on the metal surface and prevent corrosion without affecting the environment, unlike inorganic substances [57]. Heikal et al. [58] prepared a CI by using spinach extract as a green CI and tested it on OPC-fly ash composite cement pastes. One of the main components for the synthesis of imidazoline is the lauric acid that can be derived from vegetable oil. Wu et al. [59] developed CIs by adding CO₂ saturated oil to lauric acid; when this was applied to metal samples, the IE increased to 98.6%. Pomelo peel was used by Sun et al. [60] to develop CIs. They investigated N80 rusting in 3.5 wt.% NaCl saturated with CO₂ solution by employing the weight loss technique (WL). The efficiency of corrosion inhibition increased as the extraction solution's concentration increased. The efficiency reached a maximum of more than 87%.



Figure 5. Various sources for natural green corrosion inhibitors.

3.4. Composite-Based Corrosion Inhibitors

Many types of research conducted in this field suggest that CIs are toxic to both the environment and to living organisms. Therefore, it is essential to design inhibitors in such a way that they are less toxic but still cost-effective. To enhance the performance of CIs, it is preferred to design them using different materials, such as composite materials or materials based on polymers. Some authors have used various organic compounds, including thiol, dithiol, fatty acids, and some other heterocyclic compounds containing N, S, and atoms as metal corrosion adsorptive inhibitors. A few of these are polymer-based inhibitors. Corrosion takes place depending on the metals. In recent decades, new varieties of corrosion inhibitors based on organic and organometallic compounds have been researched.

Although they provide benefits, they also have some drawbacks that need to be taken into account. Multiple components must be carefully chosen and prepared in order to create efficient composite corrosion inhibitors. Finding the proper ratio and interaction between the various elements can be difficult. Depending on the precise composition, application techniques, and ambient circumstances, composite corrosion inhibitor performance may differ. If not adequately addressed, inconsistent performance may be a cause for concern [61].

3.4.1. Biopolymer-Based Corrosion Inhibitors

Organic materials known as biopolymers are made by the cells of both plants and animals. Due to their natural (animal and plant) origins, the usage of biopolymers is acknowledged as an environmentally friendly substitute for a variety of biological and industrial applications. Biopolymers, in contrast to synthetic polymers, are also biodegradable and non-bioaccumulative. Polysaccharides (starch, cellulose, chitosan, etc.), polypeptides, nucleic acids (RNA and DNA), natural rubber, lignin, and others are examples of common biopolymers. The use of eco-friendly biopolymers would be favored due to rising ecological awareness and environmental restrictions. It has been extensively demonstrated that chitosan has an anticorrosive impact on metals and alloys, such as copper, as well as aluminum and its alloys [62,63].

Corrosion inhibitors based on chitosan are regarded as environmentally beneficial due to their natural origin. In general, chitosan that has been modified with different organic compounds performs better in inhibiting corrosion than pure chitosan [3]. Rbaa et al. [64] developed a CI using a biodegradable polymer that is synthesized from oligosaccharide, chitosan, and an epoxy glucose derivative. This property will optimize chitosan's corrosion inhibition by increasing the number of oxygen atoms while also retaining its ecological properties. Chitosan was employed by Duda et al. [65] to generate a nitrogen-doped graphitized carbon layer for AA 6061's corrosion prevention. Thise resulted in high corrosion resistance with an efficiency of 99.91 \pm 0.10% in the acidic condition of 0.5 M H₂SO₄ and 2 ppm HF. Umoren et al. [66] used chitosan–copper oxide (CHT-CuO) by changing the amount of chitosan (0.5, 1.0, and 2.0 g) as a CI for X60 carbon steel in an acidic media of 5 wt.% HCl. The resulting corrosion IE was CHT_{1.0}–CuO (90.35%) > CHT_{0.5}–CuO (90.16%) > CHT_{2.0}–CuO (89.52%).

3.4.2. Carbon-Based Corrosion Inhibitors

Graphene (Gr), graphene oxide (GO), reduced graphene oxide (rGO), CNTs, and CNS are among the carbon derivatives that have been regarded as the best anticorrosive additives due to their high water solubility, good biocompatibility, and low toxicity [67]. According to molecular dynamics simulation, the hydrophobic coating that CNTs can create on the surface of carbon steel via functionalized groups limits the diffusion migration of corrosive media. In order to stop the corrosion of an aluminum current collector used in lithium-ion batteries, Hongyu Cen and colleagues [68] reported functionalized carbon nanotubes (FCNTs) synthesized using a hydrothermal method and adopted as a corrosion inhibitor of carbon steel in CO₂-saturated NaCl solution. They showed that functionalized

carbon nanotubes (FCNTs) can effectively inhibit carbon steel corrosion, and their IE is close to 90% at the concentration of 100 mg L^{-1} .

CNSs attracted researchers' interest due to their sphere shape and other unique features. Figure 6 shows encapsulation of CIs on a carbon nanosphere for the development of a carbon-based anticorrosive coating.



Figure 6. Schematic representation of anticorrosive coating by encapsulating CIs on a carbon nanosphere.

A detailed discussion on the usage of encapsulated CIs is presented later in Section 4 of this article. A unique hollow porous carbon nanosphere made of graphite (GCN@M16) with corrosion inhibitors infused in it was proposed for fabrication and investigation by Liu et al. [69]. The prepared CI strengthened their corrosion resistance capabilities while also acting as a lubricant and empowering them as corrosion inhibitors. The prepared CI was put to the test on copper metal in HCl, a media known to be corrosive. After applying GCN@M16 or M16, the corrosion phenomenon can be suppressed. Figure 7 clearly shows the surface microtopography of copper that has been immersed in HCl solution in the presence and absence of 5.0 wt.% GCN. The copper plates appear to become rougher on the surface when M16 or GCN@M16 is added to the HCl solution, indicating the existence of corrosion as well. This is shown in Figure 7d,e, but there are no longer any obvious deep cracks. The color of each corrosion solution after 30 days is also shown in Figure 7b–e.

3.4.3. Silane-Based Composite Coatings

The technology of organosilane, one of many coating systems, has advanced significantly in recent years. It has attracted the interest of researchers in recent years due to its low volatile organic content, strong anticorrosion, and adhesive qualities on metal substrates. A class of organic–inorganic compounds with silicon as its base called silanes is biocompatible. Silanes easily hydrolyze in aqueous solutions to create silanol groups (SiOH), which allow them to connect to any hydrated metal surface (metal-OH) by creating silicon (Si)–oxygen–metal linkages. Additionally, the silanol groups might engage in siloxane linkages for self-cross-linking (SieOeSi), which would result in the creation of a protective layer chemically attached to metallic substrates [70].

Due to its low density, lightweight nature, good castability, and recyclability, the aerospace, defense, and automobile industries extensively utilize magnesium (Mg) and its alloys. Among the coatings presently available, silane coating has gained extensive use in the anticorrosion sector due to its cost-effectiveness, environmental friendliness, and ease of application. However, the significant utilization of magnesium alloys is hindered by their susceptibility to corrosion. As a result, various surface modifications have been employed to protect magnesium alloys from corrosion. These include polymeric coatings [71], micro-



arc oxidation (MAO) coatings [72], chemical conversion coatings [73], silane coatings [74], and composite coatings.

Figure 7. SEM images show polished copper (blank), copper submerged in 5 mol HCl, and corrosive media, copper immersed in 5 mol HCl + 5 wt.% GCN, and corrosive media, and copper immersed in 5 mol HCl + 5 wt.% M16 [69] (**a**–**f**).

Jeyaram et al. [75] synthesized silane coating material via the sol-gel method using 3-glycidyloxypropyl trimethoxy silane as the precursor and (3-aminopropyl) trimethoxysilane as the cross-linking agent, and applied it on a mild steel substrate; this resulted in the formation of oxide layer, forming a passivation layer to enhance the corrosion resistance. P-aminothiophenol-doped 3-glycidoxypropyltrimethoxysilane-based sol-gel matrices (PATP-GPTMS) were synthesized by Balaji et al. [76] using condensation and hydrolysis processes. The PATP-GPTMS sol-gel produced via a self-assembly process was applied on polished copper (Cu) surface. Furthermore, in a 3.5% sodium chloride (NaCl) media, the ability of PATP-GPTMS/Cu coatings to prevent corrosion has been investigated. All of the findings showed that in an aqueous 3.5% NaCl media, the PATP-GPTMS/Cu coating improved the protection of Cu against corrosion. Flamini et al. [77] successfully deposited hybrid films based on polyaniline and polysiloxane moieties on commercial aluminum alloy using N-(3-trimethoxysilylpropyl) aniline (AnSi) as a primer for corrosion inhibition. Numerous studies have investigated how a silane layer affects the corrosion resistance of Mg alloys [78]. According to Toorani et al. [79] after introducing a threelayer coating, i.e., PEO/silane/epoxy, the impedance data fitting results show that the silane layer has a good impact on enhancing the protective qualities of the epoxy coating. The change diagrams of R_{coat} and R_{ct} values over the duration of immersion in 3.5 wt.% NaCl solution for the coated samples show this. The R_{coat} and R_{ct} values throughout the immersion period were greatly improved by the silane layer. Kaseem et al. [80] also investigated the surface characteristics of WO₃-MgO oxide layers formed on AZ31 Mg alloy by micro-arc oxidation. Impedance studies in 0.05 M NaCl corrosive media were carried out to better understand the impacts of WO₃ concentrations on the corrosion behavior of Mg in all samples. The results of the Nyquist plots revealed that samples containing

WO₃ had larger semi-circle loop diameters, which suggested greater resistance to the corrosive environment.

Due to their capacity to improve the adhesion, toughness, and performance of many materials, including metals, ceramics, and polymers, silane-based composite coatings, also known as silane coatings or silane-modified coatings, have become increasingly popular. They do, however, have limitations, just like any other technology. When applied and cured, silane coatings might be sensitive to the surrounding environment. Humidity and temperature variations can have an impact on the curing process, which could result in poor adhesion and coating integrity [81]. For the best adherence, silane coatings require meticulous surface preparation. To guarantee successful bonding, the substrate surface must be cleaned of contaminants, such as oils, greases, and oxides. Poor coating adherence and performance might result from inadequate surface preparation [82].

3.4.4. Sol-Gel-Based Composites

The migration of water and electrolytes through the sol-gel topcoat can cause corrosion processes at the metal-oxide contact. Pre-emptive healing occurs when water and other corrosives are trapped, and/or when the hybrid sol-gel releases inhibitors that specifically target and stop the corrosion reactions. As shown in Figure 8, self-healing chemicals could also repair damage to the topcoat caused by weathering and/or other factors [83].





The slow condensation processes of molecular precursors in a liquid medium that produce an oxide network are known as the sol-gel method. Sol-gel protective coatings have been shown to offer higher corrosion resistance, better oxidation control, and superior chemical stability for metal substrates. Additionally, the sol-gel process has the potential to replace hazardous pre-treatments and coatings that have typically been used to increase metals' corrosion resistance and is an environmentally beneficial method of surface protection [84]. Samiee et al. [85] developed eco-friendly sol-gel-based saline silane-based composite coatings reinforced with praseodymium cations (Pr³⁺) and benzimidazole that have a synergistic self-healing effect. In aluminum matrix composites supplemented with SiC particles, López [86] and colleagues developed mono- and multi-layered silica coatings achieved through a sol-gel technique for their corrosion protection. To replace the current three- or multi-coat methods, a colored sol-gel topcoat that Wenjin Yan and his coworkers developed over a zinc primer enhanced production while preserving the protective sacri-

ficial properties. However, the cerium (III) system in the sol-gel coating finally attained the maximum impedance and proved to be the most effective choice. Molybdate and cerium (III), two corrosion inhibitors, were added to sol-gel coatings to provide inhibitive protection in addition to the barrier protection [87]. For the purpose of preventing corrosion in the AZ91D magnesium alloy, Zhang and his team [88] developed a unique composite film using the sol-gel method. Electrochemical tests were performed in a 3.5 wt.% NaCl neutral solution to evaluate the anticorrosion properties of the sol-gel-coated and untreated samples. The outcomes showed that composite films with ace inner film and a mag outer film had improved corrosion resistance.

Sol-gel-based composites have drawn interest due to their adaptability and capacity to produce customized materials with a variety of uses. They do, however, have some restrictions that must be taken into account. When numerous drying and annealing phases are necessary, the sol-gel process can be time-consuming. This might affect turnaround time and production efficiency [89]. Sol-gel materials may shrink significantly while drying and curing, which can cause cracks and other flaws in the finished composite. In order to reduce these problems, proper processing methods are necessary [90].

3.4.5. Micro-Arc Oxidation Coatings

Micro-arc oxidation (MAO), also known as plasma electrolytic oxidation (PEO), is a surface treatment process that is used to enhance the corrosion resistance and wear resistance of metals, particularly lightweight metals, like aluminum and magnesium. It involves the formation of a ceramic oxide layer on the metal's surface through controlled electrochemical reactions that occur during a spark discharge process. It is a new, environmentally friendly coating process that can create ceramic coatings on metals, including aluminum, magnesium, titanium, and their alloys [91]. On the surface of the metal, a thick and dense oxide layer develops during the micro-arc oxidation process. The metal is well shielded from corrosive substances including moisture, salts, acids, and alkalis by this oxide layer, which serves as a physical barrier between the metal and its surroundings [92]. A homogeneous and regulated coating thickness is made possible by micro-arc oxidation throughout the entire metal surface. Any locations with insufficient coverage could become susceptible to corrosion and, hence, uniformity is essential for providing constant corrosion protection [93]. Micro- and nano-sized holes are frequently present in the oxide layer formed through micro-arc oxidation. Corrosion inhibitors or sealants can be efficiently trapped and retained in these pores, increasing the material's resistance to corrosion. Additionally, the intricate porous structure might slow down corrosive substances' passage through the covering, which will lessen corrosion [94]. The corrosion and wear resistance of the micro-arc oxidation coating on a novel glass microsphere-reinforced magnesium alloy composite was studied by Lin Liu and colleagues. Figure 9 illustrates the MAO coating process [95]. To protect the AZ91D magnesium alloy against corrosion, waterborne polyurethane (PU) coating's ability to adhere to and resist corrosion on an aluminum alloy surface was studied by Wang et al. [96]. This study showed that MAO treatment and silane coupling agent modification of the MAO layer considerably improved the adhesion and corrosion resistance of MAO-PU composite coatings on 7050 aluminum alloy.

MAO coatings have a number of benefits, but there are some drawbacks that must be taken into account. The MAO process can make it difficult to achieve uniform coating thickness over intricate geometries. Varying coating thickness might result in inconsistent performance and aesthetically undesirable outcomes [97]. In comparison to the main material, MAO coatings may be relatively fragile. Reduced impact resistance and susceptibility to cracking or chipping under mechanical stress can both be caused by this brittleness [98].

3.4.6. Layered Double Hydroxides

Layered double hydroxides (LDHs), also known as anionic clays, are a family of two-dimensional nanomaterials that serve as a typical example of the anion exchange mechanism. Their general formula is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_{2}]^{x+}$ ($A^{n-}_{x/n}$)·mH₂O, which resem-

Power supply

bles the layered structure of brucite, and they have recently taken on a significant role not only because of their distinctive two-dimensional structure, but also because of their anion exchange capabilities. LDH's crystallinity, morphology, and conductivity (depending on the LDH composition) can improve the electrochemical performance of materials used as a electrodes for batteries [99], fuel cells [100], supercapacitors [101], and other energy conversion and storage devices. Due to its distinctive structure, it has the capacity for controlled release and selective absorption, which is advantageous and important in the field of anticorrosion [102–104].



Figure 9. Schematic diagram of the micro-arc oxidation coating process [95].

LDHs loaded with corrosion-inhibiting anions (such as nitrite, nitrate, and 2-benzothiazollythiosuccunic acid) have been examined as effective additives for steel corrosion prevention because of their unique anionic exchangeability [105]. The combination of the organic inhibitor and the LDHs nanocontainer shows significant promise for the prevention of corrosion. The layered hydrotalcite structures were divided into nanosheets with a single layer, and then these exfoliated nanosheets were restructured, using an organic inhibitor to synthesize the MgAl-LDHs loaded with 5-aminoindazole (AIA). In the 3.5 wt.% NaCl solution, the AIA LDHs as-synthesized showed controlled release behavior and effective anticorrosion performance on the copper [106]. Using MgAl-NO₂ LDHs, Jinxia et al. [86] created CIs to prevent corrosion of the steel reinforcing in concrete. In contrast to chloridecontaminated simulated carbonated concrete pore solution, the results show that chloridefree simulated carbonated concrete pore solution has a noticeably greater MgAl-NO₂ LDH inhibition efficacy. In simulated carbonated concrete pore solution without chloride, MgAl-NO₂ LDH, IE is greater than 92%, but in the presence of chloride, the value is only less than 75%. LDH-C6(m2im)2-I and IL@LDH-C6(m2im)2-I are two coatings of MgAl-LDHs that have been modified using imidazolium-based dicationic ionic liquids. The two MgAl-LDH coatings were investigated for their surface morphologies and anticorrosion properties when submerged in 3.5 wt.% NaCl [107]. According to a survey of the literature, we can conclude that loading an inhibitor into LDHs can enhance the corrosion IE; however, the next stage could involve adding more inhibitors to LDHs.

3.4.7. Metal–Organic Frameworks

By altering the metal ions, organic ligands, or the interaction between the two, inorganic metals and organic ligands can be combined to form coordination polymers called metal-organic frameworks (MOFs). Previous studies have shown that aromatic rings and heteroatom-containing organic molecules, such as N, O, and S, are efficient corrosion inhibitors. Due to their significant loading capacity, biocompatibility, and simplicity of synthesis under mild conditions, the ability of the organic frameworks to perform sacrifices is improved with the inclusion of more electropositive metals. On the other hand, the organic structure produces a protective layer over the metal surface, slowing corrosion [108]. Zafari et al. [109] reported that the use of MOF-based CI names, such as s zeolitic imidazolate framework-8@{Mo₁₃₂} (ZIF-8@{Mo₁₃₂}), can act as a good green CI. The electrochemical results showed that there is much higher corrosion efficiency for ZIF-8@ Mo_{132} than the ZIF-8 structure. In another study from 2020, Cao et al. used composite material which consisted of inhibitor benzotriazole (BTA)-loaded MOFs and further loaded with tetraethyl orthosilicate (TEOS), and the resulting composite was further combined with graphene oxide (GO). The results showed that the BTA-OF-TEOS-GO incorporated into the epoxy coatings displayed the most excellent impedance values up to $8.6 \times 108 \text{ cm}^2$, indicating the most superior and long-lasting anticorrosion characteristics [110]. In another study, a hybrid nano-compound was developed by Kunyao et al. [111] by encapsulating BTA in Ce–MOFs and then adding TEOS to create a film to surround the Ce–MOFs. Figure 10 shows that Ce-MOFs@TEOS epoxy coating has the biggest impedance arc, while the epoxy coating has the lowest impedance arc, and this corresponds to the superior dispersion of Ce-MOFs@TEOS in epoxy coatings. However, because CIs have active corrosion properties, Wei et al. [112] investigated the CI efficiency of composite materials made of Cu-MOF/graphene, Cu-MOF/graphene oxide, Mn–MOF/graphene, and Mn–MOF/graphene oxide on carbon steel. The 3% Cu-MOF/GO and 3% Mn–MOF/GO composite coatings on the carbon steel surface had moderately high total polarization resistances at 55,097 and 55,729 cm², respectively. According to electrochemical tests and results, the carbon steel could be effectively protected against corrosion by these coatings.



Figure 10. Nyquist plots of different epoxy coatings after 2 h in a 3.5 weight% NaCl solution [111].

4. Encapsulation Technique for the Effective Corrosion Inhibition

CIs effectively resist corrosion through the formation of a passive coating on the metal substrate. Unfortunately, they spontaneously leak from coatings, which is one of the harmful concerns. Another critical issue is the homogeneity of the corrosion inhibitor dispersion in the matrix. For practical purposes, the accumulation of corrosion inhibitors would result in coating flaws, speeding up the progression of chemical corrosion and increasing the rate at which corrosion elements permeate the metal surface [113]. To address the aforementioned issues, inhibitors have been encapsulated in containers over the past ten years. Containers or carriers of corrosion inhibitors that operate as protectors must be able to withstand the premature loading release, retain core chemical activity, and improve dispersion. The schematic representation coating of encapsulated CI as depicted in Figure 11.



Figure 11. Schematic representation of nano-coatings on the metal surface.

Encapsulation is a technique for encasing active molecules in a carrier substance to aid the encapsulated system's intended use. As numerous subsequent studies in this area have demonstrated, using intelligent nanocontainers to transport corrosion inhibitors offers effective substitutes for conventional corrosion protection techniques. Smart nanocontainers in protective coatings provide anticorrosion qualities either as an autonomic response to fluctuations in the coating integrity or as a stimulated response to changes in the external environment. Carbonic nanoparticles, such as fullerenes, graphene sheets, carbon quantum dots (CQDs) [114], carbon nanotubes (CNTs), and carbon nanosphere (CNSs), have attracted researchers to use as a nanocontainer because of their unique properties [115]. Small-sized NPs acting as rolling spheres enter the frictional area to reduce the range of contact between the friction pair and convert sliding friction into rolling friction. Spherical NPs, in particular, have a flexible anti-friction mechanism that dominates the lubricant industry. Because of these reasons, CNSs have garnered the attention of researchers because of their tribological application [69,116]. Table 1 shows the different nanomaterials and encapsulated materials as CIs. Haddadi et al. [117] doped a mesoporous CNS with walnut extract (WE) and used ot as a CI in a saline environment (3.5 wt.% NaCl); the IE was 92.7%. Ghazi et al. [118] used sodium montmorillonite clay particles as a microcontainer of benzimidazole and zinc corrosion inhibitors in an organic coating to create a controlled release inhibitor system with a cation exchange mechanism. Thin et al. [119] synthesized the thiourea-modified polyepoxysuccinic acid (CNS-PESA) and used it as CI for cooling the water system of the factory. CNS-PESA gives 22.4% IE compared to polyepoxysuccinic acid.

Nanostructured	Encapsulated CI	Metal Sample	Corrosive Media	Reference
Carbon hollow spheres	2-mercaptobenzi midazole	MS	5 wt.% HCl	[56]
Polyaniline microcapsule	2-mercaptoben zothiazole	Carbon steel	3.5 wt.% NaCl	[113]
Mesoporous polyaniline (mPANI) hollow nanospheres	1H-benzotriazole	MS	3.5 wt.% NaCl	[117]
f-MWCNT	Poly (o-anthranilic acid) and GO	Stainless steel 316	2 M HCl	[120]
Hollow mesoporous organosilica	2-mercap tobenzimidazole	Copper alloy	3.5 wt.% NaCl	[121]
Carbon nanodots	Polycarbazole	Plain CS specimen	5 wt.% NaCl	[122]
Mesoporous polyaniline hollow spheres	Benzotriazole	Carbon steel	3.5 wt.% NaCl	[123]
Polyaniline (PANI) microcapsule	2-mercaptobe nzothiazole	MS	3.5 wt.% NaCl	[124]
Acid-modified halloysite nanotubes	Praseodymium ions (Pr)	AZ31 magnesium alloy	3.5% NaCl	[125]

Table 1. List of encapsulated corrosion inhibitors with nanostructured material.

5. Corrosion Monitoring Techniques

Corrosion monitoring programs are now being used more and more in a variety of huge infrastructures, including pipelines, refinery facilities, offshore structures, bridges, buildings, etc., as well as in electronic devices, instrument panels, big computers, and biological implants. To keep track of corrosion activity, a variety of corrosion monitoring approaches can be used. These methods range in complexity from simple to complex, relying on a variety of sensing concepts, from the most basic corrosion coupons to sophisticated, computer-controlled electrochemical probes [126]. The corrosion coupons, such as electrical resistance (ER), linear polarization resistance (LPR), potential monitoring (PM), zero resistance ammeter (ZRA), and ultrasonics are the techniques for corrosion monitoring that are most frequently employed in industry. New electrochemical methods are beginning to emerge, including electrochemical noise (EN), harmonic impedance spectroscopy (HIS), and electrochemical impedance spectroscopy (EIS). All of the abovementioned techniques are used to monitor the corrosion activity. However, even though these techniques have advantages, there are also some disadvantages.

The prolonged reaction time of the ER sensors is their primary flaw. The thickness of a sensor element affects the sensitivity of an ER sensor; a thicker sensor element has a slower reaction time. A significant change in resistance can only take place after enough corrosion has occurred [127]. In order to acquire reliable (useful) data, the linear polarization resistance monitoring method must not be used with gasses or water/oil emulsions since electrode fouling will occur [128]. In particular, a measuring resistor rather than an ammeter with zero resistance is used to connect the two corroding electrodes. Each electrode experiences corrosion events that cause current variations, which could cause a dip across the measurement resistor. Consequently, while utilizing the ZRA approach, the potentials

of the two electrodes differ. The electrochemical impedance method is found to be the most effective technique because it is advantageous among all the abovementioned techniques.

5.1. Electrochemical Impedance Method

Since the EIS approach can explain the electrochemical mechanisms taking place at an electrified interface in just one measurement, it is widely applicable. The invention of certain devices, such as the first potentiostat and the revolving disc electrode, has benefited EIS. It also allows for a better understanding of intermediate adsorption on electrode surfaces. In a multistep mechanism involving electrochemical reactions coupled with adsorbed reaction intermediates, and coupled with homogeneous or heterogeneous reactions, the intermediate adsorption on an electrode surface is more thoroughly analyzed with EIS [129]. The ability to conduct measurements at various potentials is a special benefit of EIS [130]. The measurement system contains the sample, electrodes, corrosive media, and a potentiostat, as shown in Figure 12. Recently, Siva et al. [131] reported the anticorrosion behavior of pure acrylic and inhibitor-loaded dendrimer-like mesoporous silica nanocontainers (DMSN) with the help of EIS (PARAST 2273 software). The obtained impedance spectra were depicted in the form of Bode plots. The Bode plot's single sloped line indicated the presence of a single time constant.



Figure 12. Schematic diagram of the electrochemical impedance measurement system.

The second slope appeared after prolonged exposure to NaCl solution on the coating, which suggests propagation of the corrosion process. They observed capacitance and resistance values with immersion time. Based on these results, they concluded that the charge transfer reaction's two-time constants were on the impedance curve. The lowered resistance values discovered during this evaluation were associated with corrosion-induced deterioration of the acrylic cover [131]. Manasa et al. [132]. carried out EIS studies after immersion of substrates (matrix sol-coated and HN-sol-coated and self-healing (SH)-coated substrates) in 3.5 wt.% NaCl over various time periods, resulting in different Nyquist graphs for all the samples. As the exposure time increases, the impedance values of SH-coated substrates increase more than those of the other substrates, and these findings suggest that the applied coating is acting as a good passivate for the metal. While the EIS value of the other two coatings decreased on a high duration of exposure to corrosive media, this shows that the barrier protection lasts only for a shorter time [133]. The efficiency of epoxy and sphere-like PANI-SiO₂ reservoirs (PSR) coating is evaluated by EIS by Siva et al. [134] They studied EIS on a MS surface in 3% NaCl after coating epoxy resin and with/without PSR. As the time of exposure to NaCl media increased, there was a decrease in the coating resistance: initially it was $6.03 \times 109 \ \Omega \ cm^2$, while after 30 days it reached $1.13 \times 105 \,\Omega$ cm², indicating the corrosion rate. Furthermore, after ten days of evaluation, the impedance showed that a charge transfer reaction had occurred, which is caused by iron breakdown and the presence of two-time constants [135].

Some of the recent developments in the corrosion inhibitor-related literature are mentioned below. The carbon steel Nyquist plot displays, as shown in Figure 13, a slightly depressed semi-circular curve, indicating that the charge transport mechanism controls carbon steel corrosion in the 1 M HCl solution primarily. The capacitance loop of the oxide layer that covers the surface of carbon steel is coupled to the first time constant, which appears in the mid-frequency region. The second time constant, which is low frequency, was attributed to an inductive loop that was produced either by the surface dissolution of the carbon steel oxide layer or relaxation of the relaxing of the adsorbed extract Eruca sativa seeds. After the extract was included into the mixture, the diameter of the semi-circle increased, and the corrosion of carbon steel was delayed by decreasing the constant phase element (CPE) values and raising the polarization resistance, Rp. Larger Rp values and lower CPE values were, thus, associated with the effectiveness of the investigated extract. As the extract concentration rose, this rise became more pronounced, demonstrating that the extract adsorbed on the surface of the carbon steel.



Figure 13. Nyquist plots for carbon steel corrosion at 1 M HCl in the absence and presence of different concentrations of Eruca sativa seed extract at 25 °C [133].

Nyquist plots of Al-Pure in 1.0 M HCl solution in the absence and the presence of various concentrations of o–CANB are given in Figure 14. It is clear from the figure that the impedance diagram yields a semi-circle shape. This indicates that the corrosion process is mainly controlled by charge transfer. A Randles circuit served as the comparable circuit that best fit the experimental results. One of the simplest and most used circuit models for electrochemical impedance is the Randles equivalent circuit. According to Yagan et al. (2006), it consists of a solution resistance Rs connected in series to a parallel combination of a resistor, Rct, the charge transfer (corrosion) resistance, and a double-layer capacitance, Cdl, or the electrode capacitance. Because the value is very little compared to the value of Rct, the Rs values in this situation can be disregarded. Figure 14 depicts the Randles cell's analogous circuit.

In 0.05 M NaCl solution at three distinct pH levels, electrochemical impedance spectroscopy measurements were made to track the evolution of surface condition as it was linked to the high frequency time constant of Mg. The thickness of the MgO layer was determined by fitting the EIS findings under the presumption that the high frequency time constant only comes from the surface coating. The results were extrapolated and compared to the real surface state, which was determined using local measurements and transmission electron microscopy. The surface film on Mg was investigated at different pH values of NaCl solutions. As shown in Figure 15. EIS confirms the different corrosion activity of Mg in solutions with pH 3, 5.6, and 11. Interestingly, TEM characterization indicates that the surface film formed on Mg in the pH 3 solution is the thickest compared to that in the pH 5.6 and pH 11 solution. This experimentally observed tendency is consistent with the calculations based on the HF capacitive loop in the EIS plots [137].



Figure 14. Impedance plot obtained at 35 °C in 1.0 M HCl at various concentrations of o-CANB [136].



Figure 15. Nyquist plots of high frequency time constant in electrochemical impedance spectra of Mg [137].

Like any analytical technique, EIS has advantages, but it also has drawbacks and limitations. EIS data can be complicated and difficult to interpret, particularly in systems where several electrochemical processes are taking place at once. An understanding of electrochemical theory and proficiency in impedance data analysis are necessary for the interpretation. EIS experiments can take longer than other electrochemical approaches. The method entails using a range of frequencies and assessing the effects at each frequency, which may extend the experimental period. Equipment with the ability to detect impedance across a broad frequency range, such as potentiostats or galvanostats, is often needed for EIS investigations. Depending on the environment, access to this equipment might be restricted [138,139].

5.2. Self-Healing Study Using A Scanning Vibrating Electrode Technique

Extrinsic self-healing corrosion protection coatings have gained a lot of interest because of their ability to stop the spread of damage by releasing corrosion inhibitors from micro/nanocarriers. The main storage sites for the healing agents are micro/nanocarriers or microvascular networks, which essentially decrease undesired interactions with the bulk coating and also make on-demand and controlled release possible. After unwanted external damage, self-healing materials have the ability to actively heal, extending the lifespan of organic coatings. Metal structures are typically shielded from corrosion by organic coatings, which are typically applied to the surface in liquid form and allowed to dry into a solid surface. Metallic coatings are applied by plating the target's surface with a thin layer of metal. Nanofibers, nanotubes, and electrospun nanofibers are a few examples of the many different types of carriers that are used to encapsulate corrosion inhibitors or self-healing chemicals. The problem of damaged coatings and under-film corrosion is addressed by coatings with encapsulated corrosion inhibitors as a form of self-healing technique. Corrosion inhibitors, as self-healing materials released from the damaged part of coatings, react with a metallic surface to form a passivation layer on the damaged metallic surface, thereby inhibiting the transportation of corrosion factors to the metal substrate and hindering further electrochemical reactions on the metal substrate. The scanning vibrating electrode technique (SVET) gives information about the corrosion initiation in a specified small area. SVET is run by non-instructive scanning and vibrating probe measurement, and also maps the electric field obtained in a plane that is above the electrochemically active surface. This helps quantify the local electrochemical and corrosion events in real time. The action of CI coating for the protection of corrosion is also studied in this method [140]. The coating structure can incorporate self-healing capabilities using a variety of methods. For instance, some polymers have the ability to absorb water and swell, covering and safeguarding the substrate surface under the damaged area [141]. The sol-gel approach is another way to make organic coatings capable of self-healing gel techniques as explained in the paper [142]. Owing to the abovementioned properties of SVET, many researchers have used this technique for the analysis of the coating's ability to resist corrosion. We discussed some of the studies performed using this method. By using the scanning vibrating electrode approach, the self-healing and corrosion protection abilities of the smart coatings are assessed. The vibrating electrode moves over the coated surface to sense the current flow that is naturally produced by the corrosion process. Therefore, a 3D current density map is plotted using the measured current density for a given area. In these graphs, the current flow is directly proportional to the spikes which appear on the 3D graph. The spikes are directly proportional to the corrosion rate [131]. According to the studies carried out by Manasa et al. [132] the different current density maps were obtained according to the exposure time of corrosive media on the scribed area. The experimental results showed that there was an increase in the anodic current (AC) in the scribed area of the bare substrate, which indicates accelerated corrosion and an absence of barrier protection. However, the matrix sol-coated substrate exhibited a decrease in AC current for 12 h before increasing. Current results confirm that these coatings provide good barrier protection. Due to a change in pH of the local scribed area because of the attaching of a Cl⁻ ion, the anodic current flow decreases after 12 h and is completely suppressed after 24 h. Further corrosion of metal will stop after the formation of the passive layer after cationic inhibitors are released from halloysite nanotubes which are mixed with an epoxy monomer matrix. As such, this confirms the self-healing mechanism using the SVET technique [133]. SVET has its own important role in waterborne coatings. Due to strict laws regarding emissions of volatile organic compounds, the market share of waterborne coatings has significantly increased during the past few decades. Waterborne coatings will have the internal ability to repair corrosion damage on their own or by using external components, such as water incorporating self-healing components. For innovative coating goods, sunlight, heat, or mechanical pressure are particularly attractive. Typically, nanocontainers or microcapsules that contain inhibitors or healing agents are impregnated into self-healing coatings. Due to

their size and pore volume, mesoporous silica nanoparticles (MSNs) are excellent nanocontainers. The spontaneous leakage of minute molecule inhibitors from mesoporous is a drawback of these approaches. To overcome these unwanted features researchers have been looking for chemicals that are adhesive in nature to fabricate corrosion inhibitor coatings. One of the most flexible techniques for functionalizing virtually all nanomaterial surfaces is the use of polydopamine (PDA). The adhesive abilities of catechol and amines in mussel adhesive proteins served as its inspiration. This is because PDA has great properties, like increasing wettability [143] and reconstruction of cracked polymer networks [144]. These promising techniques gained the attraction of researchers for the application of PDA into coatings or on metals. Based on a shape memory polymer (SMP) epoxy coating, polyaniline/benzotriazole (PANI/BTA) nanocapsules, and shape memory polymer (SMP) epoxy coating, a three-action self-healing coating was created to help prevent corrosion on carbon steel. As shown in the Figure 16. Additionally, the thermo-responsive SMP coating's ability to minimize scratch size upon heating helped to lessen the quantity of corrosion inhibitors required to completely cover the steel surface.



Figure 16. Saline-responsive triple-action self-healing coating for intelligent corrosion control [145].

Measurements using electrochemical impedance spectroscopy (EIS) were used to examine how well the coatings containing various amounts of PANI/BTA nanocapsules self-heal. Furthermore, scanning electrochemical microscopy was used to show the combined inhibitory effects of PANI, BTA, and SMP coatings. According to the findings, the healed 0.5 wt.% PANI/BTA coating had a high self-healing efficiency of over 96% and displayed a good self-healing characteristic [145].

Although SVET provides insightful information, it also has several drawbacks and restrictions. For monitoring local electrochemical currents and scanning the vibrating electrode, SVET requires specific equipment. It can be difficult to set up and maintain the equipment, and instrumentation and electrochemistry knowledge may be necessary. The electrochemical activities taking place at the material's surface are the main focus of SVET. It might not offer information about self-healing processes that take place in the majority of the material. Comprehensive SVET tests might take a while to complete since the vibrating electrode needs to be scanned across the sample surface, especially over long periods of time [146].

5.3. Localized Electrochemical Impedance Spectroscopy

LEIS, a scanning probe approach, is a nondestructive electrochemical testing technique. The sample can also be directly observed in a solution of a suitable electrolyte in this technique [147]. The most commonly used method for examining the surface of metals or semiconductors is EIS. It cannot, however, be utilized to analyze local changes, such those brought on by corrosion. Localized electrochemical impedance spectroscopy (LEIS), which was created by merging the direct current (DC) and alternating current (AC) approaches, is a much better instrument for analyzing the local changes on the electrode surface [148].

Similar to the previously mentioned global EIS approach, a global voltage is applied in LEIS; however, a local potential difference is recorded at a mobile probe or dual-probe setup. The local current can be calculated using this potential difference. The majority of contemporary LEIS instruments have a sensitivity of about 1 nV. The LEIS technique's resolution is claimed to be between 30 and 40 m, with this resolution depending on the probe's size and/or spacing (if twin probes are employed) [149]. Figure 17 demonstrates the basic setup for LEIS technique [150].



Figure 17. Block diagram of the LEIS setup [150].

There are two primary types of this method. The first method involves moving the probe tip over the sample in a grid-like pattern while immersed in an electrolyte and applying a fixed frequency potential disturbance. Usually, to identify any intriguing occurrences, such as a low impedance defect, this method is used. The second variation of the experiment can be carried out once a region of interest has been located. Here, the probe is positioned above the region of interest, and all of the impedance spectra are obtained over a certain frequency range. While the processing and graphing of the data after it has been acquired are similar to those of EIS, 3D graphs are frequently used to depict location-dependent information gained using the LEIS technique [151].

For use in regenerative medicine and personalized medicine, Boena Osiewicz and colleagues investigated novel methods to change the surface of the biomedical Ti-13Zr-13Nb alloy. They anodized the alloy in 0.5% HF electrolyte at 20 V for 120 min to produce first-generation oxide nanotubes (ONTs) layers on a Ti-13Zr-13Nb alloy. The 1G ONTs' in vitro corrosion resistance was tested using an open-circuit voltage in a saline solution at 37 °C compared to a Ti-13Zr-13Nb substrate. The distributions of the local impedance modulus |Z| values over the surface of the Ti-13Zr-Nb alloy before and after electrochemical oxidation in 0.9% NaCl solution are shown in Figure 18 (before and after). For Ti-13Zr-Nb that has not been anodized and after electrochemical oxidation, the average value of impedance irregularities is around 1.6 k and 13, respectively. This leads to the conclusion that, compared to the Ti-13Zr-Nb alloy with a 1G ONTs layer, the surface of the non-

anodized Ti-13Zr-Nb alloy exhibits a significantly heterogeneous distribution of impedance values. It was discovered that under the suggested circumstances, anodizing the surface of the Ti-13Zr-13Nb alloy's surface made porous ONTs significantly more resistant to pitting corrosion [152].



Figure 18. Ti–13Zr–13Nb LEIS maps recorded at EOC in saline solution at 37 °C: the non-anodized alloy (**a**), the anodized alloy (**b**), the non-anodized alloy (**c**), and the anodized alloy (**d**) [152].

LEIS frequently calls for specific hardware and setup, such as scanning probe microscopy in conjunction with impedance measurement methods. The size of the measurement electrode or probe has a big impact on LEIS's spatial resolution. It may be difficult to analyze extremely small or highly localized regions of interest due to this constraint. The LEIS experimental setup can be very intricate and necessitates exact alignment of the probing electrode or tip. In particular, in time-constrained research contexts, this complexity might result in higher experimental difficulties and lengthier setup periods, thus, restricting the efficiency of measurements [153].

5.4. Scanning Electrochemical Microscopy

Scanning electrochemical microscopy (SECM) is a technique in which the current that flows through a very small electrode tip (generally an ultramicroelectrode with a tip diameter of 10 pm or less) near a conductive, semiconductive, or insulating substrate immersed in solution is used in the SECM technique to characterize processes and structural features at the substrate as the tip is moved close to the surface. To probe the diffusion layer, the tip can be moved perpendicular to the surface (the z direction), or it can be scanned uniformly across the surface (the x and y direction). In an electrochemical cell, which often also includes other electrodes (such as auxiliary and reference) the tip and substrate form a component [154].

Collection modes, where products electrogenerated at the substrate are detected at the tip (kept at constant potential or operated in the cyclic voltammetry mode), and feedback modes, where the impact of the substrate on the tip current is monitored, are among the modes of operation that have been taken into consideration. For the study of structures and operations in micrometer- and sub-micrometer-sized systems, SECM is a useful instrument. It can examine chemical processes at liquid–liquid, liquid–air, and solid–liquid interfaces as well as electron, ion, and molecule transfers. Research into a wide range of phenomena, from metal corrosion to adsorption to metabolism in single living cells, is made possible by this adaptability [155]. SECM is an electrochemically based scanning probe microscope (SPM) method. Figure 19 illustrates how the movement of a microelectrode (ME) in close proximity to the interface being studied enables the application of a variety of experimental techniques that can be divided into amperometric and potentiometric operations depending on either sensing faradaic currents or probing potential values due to concentration distributions caused by the corrosion process [156].

SECM is used to characterize the topography and redox activities of the metal/electrolyte solution interface because to its high spatial resolution and electrochemical sensitivity in comparison to other local probe techniques that only characterize morphologically. Due to its direct detection of chemical species in localized corrosion processes with high spatial resolution, it would be more beneficial [157].

The ASTM standard D1141-98 (2013) was examined by Singh et al. to see whether guar gum-grafted 2-Acrylamido-2-Methylpropanesulfonic acid (GG–AMPS) might reduce the corrosion of carbon steel. The localized corrosion activity was identified by SECM. According to the technique, the produced current increased as the probe was lowered towards the surface of the carbon steel. This might be because the probe made direct contact with the conductor-acting metal surface shown in Figure 20a. When the identical probe was brought closer to the steel surface with GG–AMPS coating, a lower current was seen as a result of the insulating qualities of the steel surface's (Figure 20b). In conclusion, the steel acts as a conductor without the GG–AMPS coating layer and the probe only detects a lower current. On the contrary, the steel acts as a strong insulator with the coating layer present, and the probe records a higher current. Compared to synthetic seawater, the Ecorr values for the GG–AMPS coating also exhibit variances. At 600 mg/L, the GG–AMPS coating has the highest inhibitory efficacy of 92.5% in aggressive media [158,159].

With the use of the SECM, Izquierdo et al. discovered a new technique for measuring pH during the corrosion process; they used antimony tips because their dual-function characteristics of this material allow the combined amperometric/potentiometric operation of the SECM. Using an antimony microelectrode as the tip of a scanning electrochemical microscope greatly enhances the information obtained on corrosion reactions because it enables the spatial distribution of pH to be imaged (quasi) simultaneously with the instrument's regular amperometric operation in the generation-collection mode. Silva et al.

used amperometric and potentiometric probes for the detection and characterization of reactive sites on the 2098-T351 Al-alloy (AA2098-T351) using SECM and the alloy surface to study the distribution of reactive sites and the local pH changes associated with severe localized corrosion (SLC) on the alloy surface [160].

Figure 20. SECM 3D pictures of (**a**) blank steel and (**b**) steel with GG–AMPS coating submerged in synthetic saltwater [158].

Like any other analytical technique, SECM also has some limitations. The interactions between the probe and the sample surface can be affected by the presence of the electrolyte, because SECM measurements are normally carried out in an electrolyte solution. This can make it more difficult to interpret the findings, particularly when working with materials that are extremely insulating or diverse [161]. The SECM technique's chemical selectivity may be constrained by the fact that measurements are frequently predicated on observing a particular electrochemical response. The methodology may not be as chemically flexible as other analytical methods, despite changes that can be made to improve selectivity [162].

5.5. Tafel Polarization Techniques

To study the kinetics and processes of corrosion reactions, Tafel polarization studies are a common technique in the fields of corrosion research and electrochemistry. These investigations shed important light on the rate of corrosion, the propensity for corrosion, and the behavior of different materials in corrosive environments. A material exposed to a corrosive environment can benefit from having its corrosion rate, propensity for corrosion, and other electrochemical properties described. The Tafel equations, which link an electrode's current density to the applied potential, serve as the foundation for this approach. Researchers and engineers can precisely calculate the corrosion rate of a metal using the Tafel polarization method. A polarization curve (Tafel plot) can be produced by measuring the current density at various applied potentials. The rate of corrosion is determined by the slope of this curve at the corrosion potential. A steeper slope denotes a faster rate of deterioration [163].

Ferritic steel's corrosion behavior was examined by Eskinja et al. [164] under conditions similar to those seen in oil fields. Separate Tafel polarization measurements were used to verify the correctness of the results. Through the use of weight loss and Tafel polarization techniques, Diki et al. [165] examined the corrosion inhibition of MS by 7-(ethylthiobenzimidazolyl) theophylline (7-ETBT) in 1 M HCl medium between the temperatures of 298 and 318 K. By combining a self-powered cathodic protection based on a triboelectric nanogenerator (TENG) and a green corrosion inhibitor of zinc gluconate (ZnG), Cui et al. [166] developed an anticorrosion system. Using Tafel polarization curves, they assessed the performance of the synergetic anti corrosion system. Rathod et al. [167] extracted Garcinia livingstonei leaves and used them as a green CI in 1 M HCl medium; the inhibition effect was studied by employing Tafel polarization methods. By using Tafel polarization techniques at room temperature, Edison et al. [168] examined the corrosion inhibition and adsorption behavior of spermidine on MS in 1 M sulfuric and 0.50 M hydrochloric acid. The Tafel plots of MS in HCl and H2SO4 with and without spermidine are shown in Figure 21. Anodic Tafel slope (a), cathodic Tafel slope (c), corrosion potential (Ecorr), corrosion current (Icorr), and polarization resistance (Rp) were all deduced from the Tafel plots. After adding spermidine to the electrolytes, the corrosion current decreases. Additionally, the corrosion current value drops as inhibitor concentration rises, suggesting that the inhibitor forms a non-conductive layer on the MS surface and reduces the corrosion current while enhancing the IE. Additionally, no structural changes were seen in the anodic and cathodic branch Tafel plots when spermidine was present, indicating that the inhibitor had no effect on the corrosion mechanism.

Figure 21. MS Tafel polarization graphs in varied spermidine concentrations in (**a**) 1 M HCl and (**b**) 0.50 M H₂SO₄ [168].

6. Recent Trends and Developments in Corrosion Inhibitors

Nowadays, a variety of environmentally acceptable substitutes made from natural resources, such as biopolymers, plant extracts, and chemical medications (drugs), are frequently used in place of hazardous corrosion inhibitors. A number of biopolymers are also frequently utilized as environmentally safe corrosion inhibitors in both their pure and modified forms. Substances synthesized by multicomponent reactions (MCRs), as well as microwave (MW) and ultrasonic (US) irradiations, are also thought to be environmentally safe. Recently, environmentally friendly methods have received a lot of attention. These methods include the use of rare earth metals (REM), polyfunctional compounds, synergistic use of organic and inorganic compounds with REM, and encapsulation of inhibitors. These methods are obviously associated with low to no toxicity and high levels of protection effectiveness [169]. In particular, Monte Carlo simulations, molecular dynamics, and density functional theory (DFT) have lately become powerful computational chemistry methods for corrosion monitoring. Contrary to expensive experimental methods, computational modeling uses computer software to anticipate inhibitory efficiency and is also environmentally friendly [170]. The primary purpose of a DFT study is to compare the relative inhibitory effects of a number of molecules with identical chemical structures. High inhibitory efficiency instruments are typically related with greater EHOMO, softness (s), and dipole moment (m) values as well as lower ELUMO, electronegativity (c), and hardness (h) values [170]. The organic compound N, N, 1-tri(oxiran-2-ylmethoxy)-5-((oxiran-2-ylmethoxy)thio)-1H-1,2,4-triazol-3-amine (TTA) is used as a CI in the corrosive media 1 M HCl in carbon steel C38. The inhibition studies were performed using EIS, PDP, and theoretical calculation conducted via DFT and MD simulations [171]. Papaver somniferum (P. somniferum) seed

extract was used to test the iron alloy's corrosion resistance in 0.5 M sulphuric acid. Notably, at 500 mg/L concentration, Hany et al. [172] used a soyabean oil-based CI on steel alloy and efficiency was tested by DFT. Toghan et al. [6] synthesized nanocrystalline cellulose (CEL) and nanocrystalline cellulose (NCC) and tested it as a CI. The anticorrosive properties of CEL and NCC polymers were intended to be displayed via density functional theory (DFT) parameters. Somniferum demonstrated 95% corrosion resistance efficiency. Adsorption and phytochemical studies were carried out via DFT. Papaver somniferum has three phytochemicals, namely papaverine, narcotine, and thebaine. The optimized HOMO and LUMO orbitals of the aforementioned phytochemicals are shown in Figure 22 [173]. Highly concentrated acidic solutions are used in a variety of industrial operations [174–176]. Acid pickling is one of the most significant and well-known acidic processes, and it involves removing rust and other surface impurities from metal plates, wires, pipelines, and other metal equipment from various industrial sectors, including heat exchange, heat transfer, cooling system, and boiler industries. Most of the previously employed industrially useful corrosion inhibitors are not ecologically friendly due to their harmful nature and manufacturing using risky chemicals and solvents. However, the use of environmentally friendly materials derived from eco-friendly synthetic techniques and natural resources should be encouraged due to rising ecological consciousness and severe environmental restrictions. The adoption of environmentally friendly biopolymer-based CIs would be recommended due to increasing ecological awareness and environmental awareness and environmental restrictions [177–179].

Figure 22. Optimized structures, total charge density, and frontier molecular orbital density distributions (HOMO and LUMO). Bond length, counter and Mulkin charge images obtained by DFT/B3LYP/6-31 G+ (d,p) method for papaverine (1), thebaine (2), and narcotine (3) [173].

There have been numerous reports on the anticorrosive properties of chitosan's for metals and alloys [178,180]. Chitosan-based corrosion inhibitors are regarded as environmentally beneficial due to their natural origin [65,181,182]. In general, the corrosion prevention efficacy of chitosan that has been modified with different organic compounds is

higher than that of pure chitosan. Rhiam R et al. [177] applied Ch-Cr-SB as a metal's anticorrosive agent AZ91E alloy in a corrosive medium of 3% NaCl. The obtained results showed that the corrosion rate lowers when the Ch-Cr-SB concentration rises. In another study, Verma et al. [183] employed ChTSB as an anticorrosive layer on MS with the inhibitory potential demonstrated by WL, EIS, SEM, EDX, and AFM. The WL technique indicates that the inhibition performance is 86.94% at 1500 ppm concentration and 33 K. Zhao et al. [184] developed, for the first time, green CIs based on chitosan for the carbon dioxide corrosion of P1110 steel. Efficiency also rises when inhibitor concentration does. At 100 mg/L, both CHC and CAHC achieve their highest levels of corrosion inhibition effectiveness in a NaCl solution of dioxide, which, respectively, are 85.55% and 93.44%, demonstrating that both inhibitors have a sufficient inhibiting effect on carbon corrosion. An eco-friendly Schiff base (salicylaldehyde-chitosan Schiff base) was coated on a metal with a corrosive medium of 3.5% NaCl saturated with carbon dioxide at a 65 $^\circ$ C temperature. Weight loss, EIS, and potentiodynamic polarization (PDP) techniques were used to assess the inhibitory effect. According to the PDP findings, SCSB functions as a mixed-type inhibitor and successfully slows down corrosion at a concentration of 150 mg/L, with an IE of 95.2% and a corrosion rate of 0.444 mm/y. EIS measurements imply that the prevention of corrosion is a kinetic process [180,185].

7. Summary and Future Perspectives

However, the shortcomings of the current corrosion inhibitors are becoming more apparent, such as their short sustainability, rapid decomposition, and substantial environmental pollution. Therefore, it has been a long-standing goal to create new corrosion inhibitors that have long-lasting strength, high efficacy, and low toxicity. However, having a complete understanding of the innovative composition and inhibition instruments is the key to producing a high-efficiency corrosion inhibitor. It takes a lot of effort, innovation, testing, and laboratory examination to be able to recognize possible compounds that might be used as corrosion inhibitors with the ability to make the adsorption process fully active for inhibition. Additionally, three crucial conditions must be met in order for corrosion inhibition to be effective, namely high-impedance corrosion, long-term consistency, and environmental compatibility.

The review paper covers the following themes and subtopics: organic, inorganic, anodic, and cathodic corrosion inhibitors, as well as their design and mechanisms. We also investigated corrosion monitoring techniques, such as EIS, SVET, SECM, and LEIS. More attention was paid to self-healing procedures, encapsulation investigations, and the design of CIs. In this review, we focus on all the important areas with respect to corrosion inhibitors, including types of corrosion inhibitors, such as organic, inorganic, anodic, and cathodic, along with design and mechanism. Recent developments in CIs, encapsulation investigations, and self-healing methods have received more attention. Future developments in the field of corrosion inhibitors are likely as businesses look for more efficient and sustainable ways to avoid corrosion. As corrosion inhibitors, nanomaterials have shown promise thanks to their large surface area and distinctive characteristics. There is a good chance that scientists will develop more sophisticated nanomaterials that can offer improved corrosion protection while also being more effective and affordable. Future corrosion inhibitors might include intelligent components that can detect the beginning of corrosion and release inhibitors as necessary. Self-healing coatings might potentially advance, having the capacity to independently fix minor damage before corrosion worsens. Corrosion inhibitors may be made to perform several tasks, such as having antibacterial, UV, or flame-retardant qualities. As a result, companies would have access to more adaptable coatings that provide defense against a variety of dangers.

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Abbreviations

Corrosion inhibitor	(CIs)
Corrosion layer	(CL)
Organic corrosion inhibitors	(OCI)
Mild steel	(MS)
Micro-arc oxidation	(MAO)
Plasma electrolytic oxidation	(PEO)
Layered double hydroxides	(LDHs)
Metal–organic frameworks	(MOFs)
Benzotriazole	(BTA)
Electrical resistance	(ER)
Linear polarization resistance	(LPR)
Potential monitoring	(PM)
Zero resistance ammeter	(ZRA)
Electrochemical noise	(EN)
Harmonic impedance spectroscopy	(HIS)
Electrochemical impedance spectroscopy	(EIS)
Constant phase element	(CPE)
Scanning vibrating electrode technique	(SVET)
Mesoporous silica nanoparticles	(MSNs)
Localized electrochemical impedance spectroscopy	(LEIS)
Scanning electrochemical microscopy	(SECM)
Microelectrode	(ME)
Scanning probe microscope	(SPM)
Density functional theory	

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