Review

Corrosion Performance of Electrodeposited Zinc and Zinc-Alloy Coatings in Marine Environment

Kranthi Kumar Maniam [1] **and Shiladitya Paul** [1,2,*]

1 Materials Innovation Centre, School of Engineering, University of Leicester, Leicester LE1 7RH, UK; km508@leicester.ac.uk
2 Materials and Structural Integrity Technology Group, TWI, Cambridge CB21 6AL, UK
* Correspondence: Shiladitya.paul@twi.co.uk

Abstract: Electrodeposited zinc and zinc-alloy coatings have been extensively used in a wide variety of applications such as transport, automotive, marine, and aerospace owing to their good corrosion resistance and the potential to be economically competitive. As a consequence, these coatings have become the industry choice for many applications to protect carbon and low alloy steels against degradation upon their exposure in different corrosive environments such as industrial, marine, coastal, etc. Significant works on the electrodeposition of Zn, Zn-alloys and their composites from conventional chloride, sulfate, aqueous and non-aqueous electrolyte media have been progressed over the past decade. This paper provides a review covering the corrosion performance of the electrodeposited Zn, Zn-alloy and composite with different coating properties that have been developed over the past decade employing low-toxic aqueous and halide-free non-aqueous electrolyte media. The influence of additives, nano-particle addition to the electrolyte media on the morphology, texture in relation to the corrosion performance of coatings with additional functionalities are reviewed in detail. In addition, the review covers the recent developments along with cost considerations and the future scope of Zn and Zn-alloy coatings.

Keywords: corrosion; marine; composites; electrodeposition; superhydrophobic coatings; zinc and zinc-alloys; electroplating; aerospace

1. Introduction

Steels are commonly used as structural materials in diverse fields (construction, marine, aerospace, automotive, mining) [1] as they possess interesting engineering properties such as (i) high tensile strength, (ii) melting point, (iii) hardness [2,3]. Among them, mild steel is one of the most widely used materials in various industrial applications such as automotive [4], oil and gas [5], marine (ship hull, naval architecture) [6], owing to its compatible functions and properties with diversified industrial functions. The formation of rust is one of the most widely recognized case of the corrosion, commonly observed with ferrous steel materials such as carbon steel, and can be visualized as a salt of the original metal with different phases (oxides, oxy-hydroxides) in reddish-brown color. The formation of rust scale affects the functional engineering properties of structures, materials besides appearance, strength and liquid, gas permeability (through pores), indicative of material deterioration by corrosion process [7].

Corrosion mitigation is an indispensable challenge, particularly in aggressive environments such as seawater, underground mining, aerospace, automotive to biomedical implants, etc. The annual global cost of corrosion is estimated to be around 2.5 trillion USD, which is ~3.4% of the world's gross domestic product (GDP) [8,9]. Corrosion protection of carbon steel and other low alloy steels has been a topic of interest for many years and are continuously being studied with more emphasis on identifying a suitable alternative to the conventional toxic cadmium coatings [10]. One of the recommended solutions to combat corrosion is to employ a metallic protective coating that can improve the corrosion

resistance of ferrous steel materials such as mild steel/carbon steel, low alloy steels, etc. [11]. These coatings protect the metal structures by acting either as a physical barrier or as a sacrificial coating [12]. Adherence of coating to the substrate surface and their internal strains are two key parameters that needs to be optimized in order to overcome in-service mechanical stresses such as vibration, friction, etc. [13]. An ideal coating should have higher corrosion resistance and pose minimal environmental threat. Proper selection of metal and its alloys as preferred coating material can be considered as a mitigation technique to combat severe corrosion. In order to choose an ideal metallic protective coating, it is important to consider the intended application and the exposure environment [11].

Considering the intended application and economics, zinc (Zn) is the most commonly used metal that is identified for corrosion protection due to its highly sacrificial nature with electrochemical potential less than that of the ferrous metals such as mild steel/carbon steel [14,15]. Zn is widely used to coat mild steel to prevent corrosion by at least 50%. Additionally, it is the fourth most common metal in use with annual production just below that of iron, aluminum and copper [16]. Moreover, Zn and the corrosion products of Zn are not as toxic as cadmium and are found to be most suitable for corrosion resistant coatings applications. Figure 1 lists the various applications in which zinc and its alloys are employed as protective coatings (either as composite or metallic layers) along with their primary requirements. Overall, zinc and zinc-alloy protective coatings cover a wide range of applications ranging from structural steelwork for buildings, offshore platforms and bridges with flat structures to nuts, bolts, sheet, wire, tubes.

Automotive	• fasteners, fluid delivery pipes, car body assembly, seat belt connectors • good adhesion, corrosion resistance, lubircation, coefficient of friction, scratch resistance
Aerospace	• hang glider airframes, fasteners, bolts, structural components (mild steel, aluminium) • high mechanical and thermal resistance, anti-icing, corrosion resistance, super hydrophobicity
Building and construction	• steel sheet roofs, cladding • corrosion resistance, mechanical resistance
Marine	• ship hull, subsea pipelines, offshore platforms, submarines • weather resistance, corrosion resistance (chemical, microbial), anti-bacterial, super hydrophobicity, anti-icing, anti fouling
Oil and gas	• carbon steel pipelines, drilling rigs • corrosion resistance, anti scaling, super hydrophobicity with self-cleaning, self-repairing, anti-icing, good stability
Window frame and door manufacturing	• garage doors, window frames, cover plates of locks, the external casing of handles, corner transmission (functional part in door handle), keypad case (for remote opening of doors) • weather resistance, corrosion resistance, aesthetical quality
Miscellaneous	• Supermarket trolleys, cable trays carrying electrical cables • Anti-fouling, corrosion resistance (chemical, microbial)

Figure 1. Figure shows the applications of zinc and its alloys along with their functional requirements in various industry sectors.

One of the key benefits in employing a Zn/Zn–alloy coating to protect the metal surfaces is that it offers a cathodic corrosion protection layer which dissolves and significantly delays the time until the substrate material can be attacked by the corrosive environment [17,18]. Generally, corrosion performance of Zn/Zn–alloy coatings are studied under different climatic conditions, regions depending on the nature of corrosivity and test condi-

tions as per different standards. The primary objective of performing corrosion studies is to evaluate the coating durability when exposed to a certain corrosive environment.

When corrosion studies related to the Zn-coated structural materials are performed during their exposure to different corrosive environments, one can expect an initial mass increase. This initial mass increase can be generally ascribed to the corrosion products that are formed on the coating surface as a result of Zn corrosion followed by a decrease in mass indicating the corrosion products separation from coating surface [19]. Such a transition during the initial period of studies (between 1 to 3 years) are reported to be uneven and can occur either sooner or later depending on the presence of certain aggressive constituents (such as carbon dioxide, chloride, sulphates, nitrates), and their relative concentrations. Considering such a scenario, conducting long-term corrosion studies of Zn/Zn–alloy protective coatings under atmospheric conditions deserve significant attention [20] as they provide information on the corrosion products, processes and their formation mechanisms on the coated surface. Studies covering the atmospheric corrosion of zinc in both short and medium term have been published by different groups [21]. A consolidated review on the corrosion performance of the electrodeposited Zn, Zn–alloy coatings performed in different environments such as urban, rural, sea (natural, synthetic), microbial corrosion has been not covered so far. The number of articles that have been published on the zinc-based coatings for different applications in the past 10 years range from 1200–1700 every year (based on the data from scopus), signifying the importance of the field. This review will cover the progress on the recent developments in Zn, Zn–alloy, composite coatings, electrodeposited on different commonly used industrial substrates and their corrosion performance along with future challenges and economics.

2. Corrosion Performance of Zinc and Zinc–Alloy Coatings

2.1. Zn Coatings

Zinc coatings offer flexibility in fabrication and good affordability owing to their sacrificial property [22]. As a consequence, these coatings were fabricated by different methods to protect the bare metallic structures against deterioration and degradation upon their exposure in different corrosive environments. Among the different techniques, electrodeposition is simple, economic and versatile in producing uniform, adherent coatings with variable thickness at processing temperatures <100 °C. On the contrary, other techniques such as hot dip galvanization, ion vapor deposition techniques require high processing temperatures and expensive equipment to produce Zn coatings, and are relatively expensive in electrodeposition besides achieving uniformity in coatings. For instance, the cost to produce a 35-micron thick hot dip galvanized coating is $1.76 /ft^2 in contrast to $0.1/ft^2 [23,24] for the electrodeposited Zn coatings, signifying the techno-economic benefit of electrodeposition. When Zn coatings are exposed to aggressive environments such as coastal, marine which contain rich amounts of chlorides, sulfates, etc., their corrosion resistance is significantly influenced. The factors that influence the corrosion resistance of the zinc coatings obtained via electrodeposition method include: (i) applied current density, (ii) deposition temperature, (iii) electrolyte pH, (iv) mode of current deposition, (v) additives (grain refiners, brightening agents). For instance, Zhang et al. [25] showed that increasing the applied current density to an optimum value during the electrodeposition of zinc increased the nucleation density, cathodic current efficiency and most importantly, improved the grain refinement of the Zn. Grain refinement favors the nucleation while controlling the growth, resulting in a compact deposit. Such features delay the corrosion by reducing the contact area between the corrosive environment and the coating surface [25,26]. The same study has shown a deposit deterioration when the Zn deposition is performed beyond the optimum. Deposition temperature might play a role in (i) controlling the average size of the crystallite, (ii) energy consumption during the process, (iii) current efficiency. Tuaweri et al. [27] reported an increase in current efficiency when employing the acidic sulphate-based electrolyte while achieving a relatively low energy consumption (per unit mass of the deposit) by controlling the temperature between

40–45 °C. Increasing the temperature influenced the rate of deposition and crystal size reduction of the Zn deposit owing to their high cathodic reduction and increased nucleation density while controlling their growth. Increasing the pH of the electrolyte dictates the conductivity which significantly influences the hydrogen ion concentration at the cathode in addition to the electrodeposition of Zn. While lowering the pH favors the conductivity increase and facilitate good deposition, it acidifies the solution below a certain pH. Acidification of the electrolyte solution elevates the hydrogen ion concentration of the cathode and as a result, hydrogen evolution reaction dominates the Zn deposition, thereby affecting the overall deposition process and the corrosion resistance of the Zn deposit. As a consequence, significant works were carried out with different types of deposition media with different pH such as acid chloride [28], acid sulphate [29], mixed bath (chloride and sulphate, sulfate–gluconate) [30,31], alkaline zincate baths [32] and acetate baths [33]. Amongst them, acid sulphate was demonstrated to perform better in terms of plating, non-toxic nature and wide operating current density ranges [34].

Many recent studies reported that the modes of deposition, direct current (DC), pulse mode (PC), pulsed cycle reversal mode (PCR), influence the structure and indeed, the corrosion resistance of the Zn deposits. Results from [35–37] showed that deposition of Zn via pulse mode resulted in more compact thinner deposits with (i) less porosity, (ii) better corrosion resistance than the direct current mode, with PCR being predominant. The key advantage with the PCR mode of deposition is that it facilitates the formation of Zn deposits with nano-grains and contributes to better hardness and corrosion resistance than the Zn deposited by other modes of deposition. Wasekar et al. [35] demonstrated this approach by depositing Zn employing different deposition techniques, DC, PC, PCR, and correlated this with the formation of corrosion products on Zn surface. The authors observed that different corrosion products were formed when Zn was deposited using different deposition modes. A compact ZnO was reported to be formed from the corrosion of Zn deposited from PCR. On the contrary, corrosion of the Zn deposited from the other two modes (DC, PC) was shown to form zinc hydroxy-chloride, a highly porous corrosion product. Obtaining Zn deposits with grains in the nanometer range via the PCR mode of deposition was demonstrated to be the key in achieving better corrosion protection properties with high hardness. Such a morphology might facilitate the formation of ZnO film easily via the controlled diffusion mechanism occurring through the grain boundaries.

A different approach that has been identified to improve the corrosion resistance of Zn deposits is the introduction of additives in the electrolyte. Additives can be organic or inorganic and they greatly influence the corrosion resistance of Zn deposits by modifying their structural characteristics, such as (i) surface composition, morphology (microstructure), (ii) grain size, (iii) crystal orientation, texture via controlling the reduction of metal ions [38–40]. They usually get adsorbed to the substrate that is being deposited via the non-bonding electron pairs present in nitrogen, Sulphur, oxygen, hydrophilic groups and (i) enhance the rate of nucleation while controlling the grain growth, (ii) aid the formation of fine, compact, refined deposit. One of the key advantages in obtaining a compact deposit via employing additives is the formation of crystallographic planes with closed packed structure. This contributes to the overall improvement in corrosion resistance of the Zn deposit [41,42]. For instance, Mouanga et al. [43] demonstrated an increase in the intensity of Zn crystal plane (1 1 2) with the addition of urea as an additive in a chloride-based zinc electrolyte. The study focused on the influence of 3 additives: (i) urea, (ii) thiourea, (iii) guanidine (which has same molecular structure but different electron pairing groups: oxygen, Sulphur and nitrogen), and studied the corrosion behavior in relation to the structural characteristics of the deposit. The study concluded that corrosion test results (performed by polarization, weight loss) showed an increase in the corrosion resistance for the Zn deposited in the presence of urea. This was attributed to the presence of oxygen in the molecular structure of urea to function as an effective additive. Though it has been demonstrated that the radical with more free electrons interacted more effectively with the metal substrate in controlling the morphology of the final deposit, the molecular weight of

the additive influences its adsorption capability. Ballesteros et al. [44] observed that the molecular weight of an oxygen group containing radical poly-ethylene glycol (PEG) had a significant influence on the final quality of the Zn deposit. When PEG with a molecular weight in the order of $<10^4$ was introduced into the Zn deposition bath, the results showed a greater adsorption of Zn(II) ions with the substrate than the ones containing the higher molecular weight PEG ($>10^4$). Issues were shown to occur on the addition of PEG with molecular weights $>10^4$, which decreased the number of oxygen pair electrons that can form an effective bond with the additive and affected the adsorption characteristics of the Zn(II) ions. The influence of additives towards improving the corrosion resistance properties of the deposits could be correlated with their ability to increase nucleation rate while retarding growth. Employing an additive may result in a higher cathodic overpotential than the non-additive containing electrolytes. High cathodic overpotential tends to increase the formation of new nuclei, increasing its nucleation rate, utilizing the free energy, thereby inhibiting the growth of Zn [45]. In general, the contribution from adding an additive (mostly organic) towards improvement in the corrosion resistance property of electrodeposited Zn coatings can be related to either of the following or their combination:

- texture
- composition
- morphology
- grain size

Electrodeposited Zn is composed of Zn with a hexagonal closed packed (hcp) structure with different crystallographic orientations representing different planes: basal, pyramidal, prismatic. These planes differ in terms of their packing density and significantly influence the corrosion rate. Zn crystals possessing low-index basal plane texture such as (0 0 1) possess high packing density and were reported to be significantly corrosion resistant relative to other orientations and different planes [46]. Based on the published literature, it was identified that promoting the presence of (0 0 2) basal plane via the additives contributed to the corrosion resistance property more effectively than the other crystal planes. For instance, Chandrasekar et al. [37] obtained a more compact Zn deposit with (0 0 2) as the dominant facet by employing polyvinyl alcohol (PVA) as the additive, and demonstrated a significant increase in the corrosion resistance. In this context, it is important to consider the influence of surface roughness over the crystal plane texture. Lowering the surface roughness results in a deposit with fine grain size which lowers the corrosion rate by providing a lower contact area between the deposit surface and the corrosive environment, indicating the predominant influence of grain refining over the crystal orientation/texture. Grain refining achieved via the addition of additives will produce a coating that accelerate the formation of ZnO passive films via the diffusional mechanism and elevate the corrosion resistance. Table 1 lists the most commonly used organic additives that are employed during the Zn deposition in different deposition media along with their functional role. These additives were demonstrated to be contributing towards the enhancement of corrosion protection by imparting additional functionalities to the deposit.

Besides many functions, additives such as thiourea [43] can also influence the compositional change in the Zn deposit with fine grains when added to the electrolyte. Despite its attractive grain refining property, such an addition incorporates sulfur in the deposit which made the neighboring regions anodic and decreased the corrosion resistance. Almeida et al. [47] performed a detailed investigation by studying the influence of glycerol on the corrosion resistance of the electrodeposited zinc obtained via the galvanostatic mode. Glycerol exhibit similar characteristics to urea, coumarin wherein the oxygen atoms double bonded with carbon act as radicals (free unpaired electrons) and favor the adsorption of the organic additive in the Zn deposit. Physical characterization revealed that addition of glycerol played the role of a grain refiner but decreased the intensity of (0 0 2) basal planes similar to the observations made by Chandrasekar et al. [37] and Nayana et al. [48] when the combinations of piperonal +PVA [37], cetyltrimethyl ammonium bromide (CTAB) + veratraldehyde (VV), formic acid (FA) + cyclohexylamine (CHA) [45] are employed as

additives. However, the electrochemical test results showed that these coatings possessed the best corrosion resistance. The authors ascribed this to the predominance of grain size over the texture by demonstrating the results from microhardness, surface measurements. An increase in compactness due to the grain refining was shown to exhibit better corrosion resistance despite the decrease in (0 0 2) basal plane.

Table 1. Table listing the additives that have been employed to improve the corrosion resistance property and impart addition functional properties to the Zn deposit.

System	Substrate	Additive	Functional Role [1]	References
Alkaline zincate	mild steel	Poly vinyl alcohol (PVA)	Texture	[37]
Alkaline zincate	mild steel	(PVA) + piperonal	grain refiner	[37]
Acidic sulphate	steel sheet	Gelatin	grain refiner, lowering the surface roughness	[49]
Acidic sulphate	steel sheet	polyethylene glycol (PEG)	grain refiner, lowering the surface roughness	[49]
Acidic sulphate	steel sheet	Saccharin	grain refiner, lowering the surface roughness	[49]
Acidic sulphate	steel sheet	tetrabutylammonium chloride	grain refiner, lowering the surface roughness	[49]
Acidic sulphate	steel sheet	sodium lauryl sulfate	grain refiner, lowering the surface roughness	[49]
Acidic sulphate	mild steel	cetyltrimethyl ammonium bromide (CTAB) + ethyl vanillin	grain refiner	[50]
Acidic chloride	carbon steel	Sodium benzoate	grain refiner	[51]
Alkaline zincate	carbon steel	trisodium nitrilotriacetic (NTA)	complexing agent	[52]
Acidic sulphate	mild steel	(CTAB) + veratraldehyde (VV)	grain refiner, texture, morphology	[48]
Acidic sulphate	glassy carbon	[3-(2-furyl) acrolein]	grain refiner	[29]
Acidic sulphate	mild steel	PEG	grain refiner, texture	[31]
Acidic sulphate	mild steel	CTAB	grain refiner, texture	[31]
Acidic sulphate	mild steel	Thiourea	grain refiner, texture	[31]
Acidic sulphate + gluconate	mild steel	PEG	grain refiner, texture	[31]
Acidic sulphate + gluconate	mild steel	CTAB	grain refiner, texture	[31]
Acidic sulphate + gluconate	mild steel	Thiourea	grain refiner, texture	[31]
Acidic sulphate	mild steel	Polyacrylamide	grain refiner	[36]
Acidic chloride	mild steel	(PEG) and syringaldehyde (SGA)	grain refiner, texture	[28]
Acidic chloride	carbon steel	Formic acid (FA) + cyclohexylamine (CHA)	Texture	[45]

[1] Functional roles are listed based on the conclusions reported by the references mentioned in the table.

2.2. Zn-Alloy Coatings

Though zinc coatings have proven to be acting as a sacrificial layer to protect the ferrous substrates from corrosion, they readily undergo rapid corrosion within a short period of time which significantly impact the overall performance and durable life of the coatings over the period of time depending on its interaction with the type of environment. To enhance the corrosion performance in a harsh environment such as marine, Zn is alloyed with iron group metals, namely cobalt (Co), nickel (Ni), iron (Fe), introduced during the last three decades, with an intention to impart additional functional properties and match the industry market requirements [4,18,53]. Few of these include hardness, uniformity, deformability, weldability, paintability, corrosion and wear resistance. With the ever changing demands from automotive, aerospace, fastener, building and frame and marine industry, active research in the field is being pursued [54]. An exhaustive research has been conducted for many years to explore the possibility of replacing the toxic cadmium coatings with similar corrosion resistant zinc–nickel alloy coatings [10,55–58]. It was demonstrated that Zn–Ni alloys with Ni content of 12 to 15 wt.% possessed excellent corrosion resistance properties with longer corrosion protection life, reduced corrosion rate while retaining the primary sacrificial anodic behavior. Numerous studies were conducted to support the fact that incorporating Ni in the Zn–Ni alloys enhances the corrosion resistance of the overall coatings [53,59–61]. Besides, studies with varying Ni contents concluded that Zn–Ni alloys tend to become nobler with increasing Ni content and tend to lose their sacrificial property (with respect to steel) when the deposit contains above 30 wt.% Ni. Such Zn–Ni coatings transit from active to passive owing to their increasing nobler character, show cathodic behavior and favor the corrosion of bare ferrous steel substrates. Incorporation of Ni could slow down the dissolution rate of Zn when present in the range of 12 to 15 wt.%, retarding the dissolution of zinc and delaying the corrosion of bare ferrous steel substrate. Zn–Ni coatings with 12–15 wt.% Ni are known as "γ"-phase coatings and exhibit the best corrosion resistance [62]. Despite their excellent corrosion resistance, Zn–Ni alloy coatings lack two properties: (i) phosphatability and (ii) paintability, rendering them weak in coating applications. As a consequence, zinc–iron (Zn–Fe) alloys were introduced and studied extensively on the deposition from chloride, sulfate (with moderate pH) alkaline baths [54,63] and extended to Zn–Co coatings. While electrodeposited Zn–X (X: Ni, Co, Fe, Mn) have gained significant attention, development of Zn–Mn alloys with Mn contents varying from 10 to 40 wt.% paced up rapidly. Alloying Zn with Mn (10 to 40 wt.%) could facilitate the formation of an insoluble passive barrier layer, which enhances the protective ability of the coatings, and impart better corrosion properties [64]. However, Zn–Ni alloy coatings are reported to be corrosion resistant amongst the other alloy coatings such as Zn–Fe, Zn–Co, Zn–Mn in a marine environment, with good mechanical properties, and considered as a potential alternative to toxic Cd coatings [65]. As the industry interest is shifting towards the development of lightweight materials, automotive industries shed some light on the development of Zn–Mn electrodeposits on base substrates such as aluminum (Al), magnesium (Mg). As the potentials of electrodeposited Zn–Mn alloys are in close proximity with reactive substrates: Al, Mg, they tend to serve more actively as a sacrificial anode and justify their ability to protect the surface from corrosion. Zn–Mn coatings offer excellent steel corrosion protection due to their good synergy, passive corrosion product layer, that are formed in corrosive environments [66] despite the fact that Mn is a thermodynamically less noble character than Zn. The synergistic effects can be attributed to the protective ability of Zn–Mn alloy deposits combined with the insoluble passive corrosion product layer. Obtaining Zn–Mn alloys by electrodeposition needs complexation because zinc and manganese have reversible potentials different by more than 0.4 V [67]. This motivated the scientific community to study Zn–Mn alloy electrodeposition, and previous results have shown that the coatings with increased Mn content offer salient benefits such as: (i) passive layer formation comprising oxides of Mn and Zn salts, (ii) monophasic structure. The formation of a compact, insoluble passive layer will not only control the anodic dissolution [68], but also favor the inhibition of dissolved oxygen reduction at the cathode [69].

Zn–Mn alloys with monophasic structure are reported to hinder the local corrosion cell formation that generally originates in dual phase structure, indicative of better corrosion resistance in the former [37]. Fashu et al. [70] demonstrated that crystal size influences the behavior of Zn–Mn alloy deposits during corrosion, with a smaller size showing the best results. Claudel et al. [71] demonstrated that Zn-Mn alloys with Mn contents up to 30 wt.% could be achieved on steel substrates by pulse plating with a faradaic efficiency up to 90% in contrast to 65% efficiency by direct current. Additionally, the deposits obtained were pore-free and homogeneous when pulse plating was employed. Obtaining a small crystal size with high Mn content is difficult to achieve, as increasing the Mn content could aid the increase in crystal size of the monophasic Zn–Mn alloys and affect its corrosion resistance. Bucko et al. [72] observed such a phenomenon while depositing Zn–Mn alloys and concluded that incorporation of a high amount of Mn in the Zn–Mn alloy and monophasic structure are not the only conditions that enhance corrosion resistance. There are certain factors that affect the corrosion behavior of Zn–alloy coatings. Deposition temperature is a parameter which influences the metal–alloy electrodeposition process, and has the capability to tailor the corrosion resistance, structural characteristics (micro/nano), mechanical properties and alloy composition of Zn–alloy coatings. Beheshti et al. [73] conducted an experimental study on the effect of deposition temperature in relation to the structural properties, phase composition and corrosion behavior of Zn–Ni alloy electrodeposits on API 5L X52 low carbon steel using an aqueous chloride bath. The deposition temperature was varied from 25–70 °C and the corrosion behavioral study was conducted via electrochemical characterization techniques: linear polarization resistance, immersion method using 3.5 wt.% NaCl solution, analyzed in relation to the surface morphology. The study demonstrated that the Zn–Ni alloy electrodeposited via chronopotentiometric (constant current) method at 25 °C exhibited a compact and dense morphology with good uniformity, less crack and highest corrosion resistance. Additionally, Ni content was reported to be within the range of 12 to 15 wt.%. Increasing the temperature beyond 25 °C resulted in an increase in Ni content, decreased the uniformity, compactness of the deposits and the corrosion resistance. This was attributed to the formation of more cracks in the Zn–Ni coatings with increasing temperature due to the internal stress resulting from hydrogen embrittlement, indicative of predominant hydrogen evolution reaction. Hydrogen evolution reaction is a cathodic reaction commonly observed in aqueous electrolyte media which competes with the electrochemical reduction reaction between Zn/Ni, facilitates the hydrogen to diffuse inside the coatings, resulting in a brittle deposit inducing crack. Additionally, deposition of Zn–Ni at higher temperatures shall increase the Ni content in the alloy, making the deposit nobler than the ferrous steel substrate. Zn–Ni deposits shall then lose their sacrificial ability, thereby accelerating the corrosion of the underlying less noble ferrous steel substrate. Therefore, optimizing the deposition temperature was shown to be an important parameter in improving the properties of Zn–Ni alloys in aqueous solutions such as (i) corrosion resistance, (ii) mechanical (crack formation control), (iii) phase composition, (iv) structural (uniformity, compactness).

Alloying Zn with cobalt (Co) in low contents (<3 wt.%) are considered a potential alternative to the conventional Zn–Ni systems owing to their (i) less noble character than steel, (ii) better corrosion protection properties than Zn coatings [74,75]. In addition, their possibility to achieve the desirable surface finishing properties such as brightness, decorative aspects with low Co contents (1–3 wt.%) in contrast to high Ni wt.% (12–18 wt.%) in Zn-Ni makes it an economically viable candidate to replace the toxic Cd coatings. Significant works has been reported from past 2–3 decades from different electrolytes such as (i) acidic-chloride, (ii) alkaline-sulfate, (iii) cyanide, and shown that the deposition follows an anomalous type similar to Zn–Ni. Among them, Zn–Co with Co content in the range of 1 wt.% was shown to exhibit superior corrosion resistance and is widely accepted by the various industry segments (automotive, marine, sanitary) [76,77]. One of the major hurdles with the current chemistries is the presence of carcinogenic compounds as cyanides, complexing agents which pose human threats, environmental challenges.

Replacing the electrolyte with acetate ones has shed some light on these alloy coatings and is shown to produce Zn–Co alloys with good corrosion protection properties. Selvaraju and Thangaraj [78] fabricated Zn–Co alloys via direct current electrodeposition on mild steel substrates and studied the influence of current density in relation to the corrosion resistance of the Zn–Co coating. It was demonstrated that Zn–Co deposited at 4 A dm^{-2} exhibited (i) better coverage with good throwing power, (ii) hardness with high corrosion resistance and (iii) reduced corrosion rate. The authors attributed the enhancement in corrosion resistance to the texture, morphology obtained with the acetate-based electrolyte and demonstrated its techno-commercial capability to replace the currently used electrolytes.

2.3. Zn and Zn–Alloy Composite Coatings

To enhance the strength, durability of zinc-based coatings for their application in harsh conditions, metal nanoparticles with better chemical stability than the matrix are often incorporated. These additions promote the development of microstructures with a uniform lower number of surface defects, facilitate the formation of stable passivation film with good adherence and resist further corrosion attack. Such coatings are referred to as composite coatings. Unlike alloys, composites are made from two or more different materials, which are physically distinct from each other by certain boundary/interface and contain 2 phases: (i) a continuous matrix phase, (ii) an insoluble reinforcement phase, bonded in such a way as to form a solid material. Alloys are obtained through a combination of two or more materials (metallic, non-metallic) which form a homogeneous solid solution at a certain temperature. Composites are reinforced materials that are tailored to either enhance the existing properties of a coating or impart additional functional properties that might be required for a specific application. Studies of composite coatings are shown to possess improved corrosion, mechanical properties than the traditional metallic coatings [79,80]. Therefore incorporating the metal nanoparticles into the metallic coatings broadens their range of applications and is reported to perform good while minimizing the addition of hazardous chemical agents (complexing, organic chelating) with elimination of chrome passivation. This could reduce (i) the environmental impact, (ii) economics, and as a result, these composite coatings are encouraged to substitute for the cyanide-based aqueous Zn/Zn–alloy coatings [81–83]. The development of Zn, Zn–alloy composite coatings by electrodeposition is motivated by the sacrificial ability of Zn in protecting bare steel against corrosion, thereby making it attractive to fabricate advanced novel matrix composite coatings with improved surface properties in oil and gas, marine, automotive, aerospace, etc. [84,85]. These applications are quite demanding with ever changing market dynamics, and hence, the Zn-based composite coatings technology attracts significant interest.

Zn-composites have been demonstrated as technically competitive in comparison to the Zn coatings in harsh corrosive environments such as marine, coastal, their overall corrosion protection life is mitigated by the early formation of their corrosion products [80]. It is important to optimize the conditions to obtain a composite coating with improved particle dispersion and microstructure as the quality of the composite based deposit is dependent on the deposition conditions besides particle loading, concentration and the way of particle incorporation [86–88]. Tuaweri et al. [88] studied the influence of applied current density, deposition time, particle concentration, agitation in relation to the current efficiency, deposit characteristics of Zn–SiO$_2$ composite coatings. The results showed that Zn–SiO$_2$ composite coatings displayed a higher cathode current efficiency at low current densities, SiO$_2$ concentration of 26 g L^{-1} under an agitated condition. With a further increase in time, Zn dendrites were shown to face certain struggle in building up through the dense SiO$_2$ layer, indicative of predominant dense SiO$_2$ as the top layer. Tuaweri and Ohgai [88–90] investigated the effect of time, current density on the composite growth, thickness and studied in relation to the increase in weight, thickness, microstructural characteristic of the Zn-SiO$_2$ deposit. It was shown that the composite thickness and its growth was not significantly affected on varying the current density. Though the coating became thicker with deposition time, cracks were reported to be growing with time. Such

a composite is prone to rapid corrosion owing to the rapid transport of corrosive species through the cracks formed at the surface. In order to achieve good composite coatings with enhanced properties, it is necessary to optimize not only the deposition conditions but also control the particle dispersion and distribution. Incorporation of particles (metal oxides, ceramics, borides, nitrides, carbides, etc.) into the matrix might tend to impede the grain growth, structural characteristics which subsequently shall result in the formation of small-sized crystals containing the microstructures [91–93].

By dispersing them in the Zn matrix, the defect prone regions of the composite coatings such as pores, gaps, microholes, crevices, etc., which represent the corrosion active defective sites, get covered up and form a compact layer, acting like a physical barrier in separating the corrosive species from the metal matrix [92,94]. Praveen et al. [95], Punith et al. [96] and Rekha et al. [97] reported on the corrosion performance of Zn composites containing nano-sized carbon particles. The test results conducted employing 3.5 wt.% NaCl electrolyte solution as the corrosive media showed that the Zn metal dissolution in the matrix took place at a steady rate in comparison to the Zn metal coatings and at higher anodic potentials. Zirconia (ZrO_2) is reported to exhibit high hardness and thermal stability with excellent wear resistance and a similar coefficient of thermal expansion to that of iron [98]. Considering the advantages of ZrO_2, Vathsala et al. [91] and Setiawan et al. [99] studied the influence on the corrosion resistance of Zn by incorporating ZrO_2 nanoparticles in the Zn metal matrix. The results demonstrated that incorporating ZrO_2 (i) influenced the kinetics of the electrode reactions, (ii) favored the formation of a stable passivation layer, (iii) enhanced the corrosion protection of the composite coatings. To improve the coatings' corrosion performance, it is necessary to optimize and establish the particle loading/incorporation. For instance, Malatji et al. [100] demonstrated that addition of Al_2O_3, SiO_2 to the Zn metal matrix beyond an optimum concentration of 5 g L^{-1}, resulted in the formation of agglomerates, decreasing the corrosion performance of the composite coatings significantly. Incorporating the agglomerates in the metal matrix could promote the initiation of surface defect sites, chemical heterogeneities in the final composite coatings that will directly (or indirectly) contribute to the overall corrosion degradation performance.

There are significant works reported on the Zn-alloy composite coatings: composite coatings prepared from Zn–Co [101,102], Zn–Ni [63,80], Zn–Fe [103] were identified to be excellent candidates for corrosion protection. Among them, Zn–Ni composite coatings attracted predominant interest owing to the chemical stability of Ni and mechanical properties [63]. Zn–Ni composite coatings incorporated with metal oxides (Al_2O_3, SiO_2, TiO_2, ZrO_2) and carbides (SiC) were formulated to enhance (i) corrosion resistance, (ii) good adhesion, (iii) hardness, (iv) wear resistance, (v) crack free surface [81,85]. For instance, incorporating Al_2O_3 in the Zn–Ni matrix with uniform distribution was shown to (i) minimize surface defects, (ii) achieve smaller crystallites, (iii) improve the grain growth, compactness in the final deposit [104]. It was also demonstrated that incorporating the metal oxide particles along with its size, influenced the crystallite size of the deposited Zn–Ni composite. Besides, the addition of second phase metal oxide particles shall also influence the Ni content in the electrodeposited Zn–Ni composite. Works from [104,105] demonstrated the addition of metal oxide particles: Al_2O_3, SiO_2 influenced the Ni content which increased up to 12.3 wt.% with a significant decrease in Zn up to 87.7 wt.% in the final Zn-Ni composite. Furthermore, inclusion of metal oxide particles into the Zn-Ni matrix shall influence the morphological features of the resultant composite coating. [106] reported on the morphological transitions of the Zn–Ni composite coating from spherical nodular like to cauliflower type morphology when Al_2O_3 was added into the matrix. Corrosion test results from [107] showed that the addition of Al_2O_3 particles in the concentration range of 5 g L^{-1} to the deposition electrolyte solution yielded a deposit which displayed (i) reduced corrosion currents, (ii) increased polarization resistance. These results in combination with the data obtained by [83,108] conclude in the fact that the Al_2O_3 imparts a corrosion inhibiting effect on the corrosion of the composite matrix owing to low electronic

conductivity, thereby perturbing the corrosion current when present. Similarly, the Zn–Ni composite matrix consisting of SiO_2 nano-sized particles was reported to be possessing excellent corrosion resistance when tested in 3 wt.% NaCl solution [100,105]. Table 2 shows the list of Zn and Zn-alloy composites that showed significant progressive developments in the past 10 years and have been focused upon in the recent reviews [109].

Table 2. Table listing the Zn and Zn–alloy composites that have been developed in the past 10 years.

Zn/Zn-X	Second Phase	Substrate	System	Mode of Deposition	E_{Corr}, V (SCE)	i_{Corr}, $\mu A\ cm^{-2}$	References
Zn	CeO_2	mild steel	chloride	direct current	−1.127	3.56	[110]
				pulse current	−1.147	0.69	
Zn	$TiO_{2.5}$	steel	sulfate	direct current	−1.052	2.7	[111]
				pulse current	−1.118	15.1	
Zn	SiO_2	mild steel	chloride	galvanostatic	−1.127	~1	[100]
Zn	Al_2O_3	mild steel	chloride	galvanostatic	−1.282	~1	[100]
Zn	ZrO_2	mild steel	sulfate	direct current	−1.034	4.45	[91]
Zn	SiC	mild steel	sulfate	direct current	−1.100	2.090	[112]
Zn	graphene oxide	mild steel	sulfate	direct current	−1.131	4.1	[113]
Zn–Ni	TiO_2	steel	citrate	galvanostatic	−0.90	176	[82]
Zn–Ni	Fe_2O_3	mild steel	sulfate	direct current	−1.1991	0.682	[114]
Zn–Ni	CeO_2	mild steel	chloride	reverse pulse current	−0.78	28	[115]
Zn–Fe	graphene	mild steel	sulfate	direct current	−1.087	19.20	[103]
Zn–Co	CNTs	mild steel	sulfate	direct current	−0.901	0.156	[102]

Considering the significant advances in the utilization of TiO_2 for development of Zn–Ni–TiO_2 composites to achieve better corrosion resistant, mechanical properties, Anwar et al. [82] studied the corrosion behavior analysis of the Zn–Ni–TiO_2 composite deposited via galvanostatic mode on mild steel substrates. Deposition was performed from citrate-based baths containing nano-sized TiO_2 as these baths are identified to be stable in nature and comparison was made with chloride (non-citrate)-based bath. The authors observed that the Zn–Ni–TiO_2 deposits from citrate-based electrolyte yielded the following: (i) formation of compact coatings, (ii) small sized crystals, (iii) uniform texture, (iv) reduced hydrogen evolution, (v) good corrosion resistance. In addition, they revealed the corrosion products that are formed on the γ-phase Zn–Ni composites upon exposure to seawater environment when conducted in laboratory. Their study demonstrated that ZnO (zincite), $Zn(OH)_2$ (Wulfingite), $Zn_5(CO_3)_2(OH)_6$(hydrozincite), $Zn_5(OH)_8Cl_2$ (simonkolleite) are the predominant products that are formed due to the corrosion which is aligned with the data proposed by Leygraf et al. [21]. Figure 2 shows the sequence of corrosion products that are formed on the Zn–Ni–TiO_2 composite surface upon exposure to corrosive media over a period of time recorded up to 72 h. It was shown that the immersion time had significantly influenced the composition of the corrosion products with simokolleite being the predominant. Though the initial corrosion resistance was shown to be lower, there was a significant increase in corrosion resistance on increasing the exposure time beyond 24 h owing to the formation of the robust, compact corrosion product layers (hydrozincite, simonkolleite). The authors observed the conversion of simonkolleite back to hydrozincite, and attributed this to the unstable nature of hydrozincite and demonstrated its conversion back to simonkolleite, which is represented as a reversible loop between hydrozincite and simonkolleite in Figure 2.
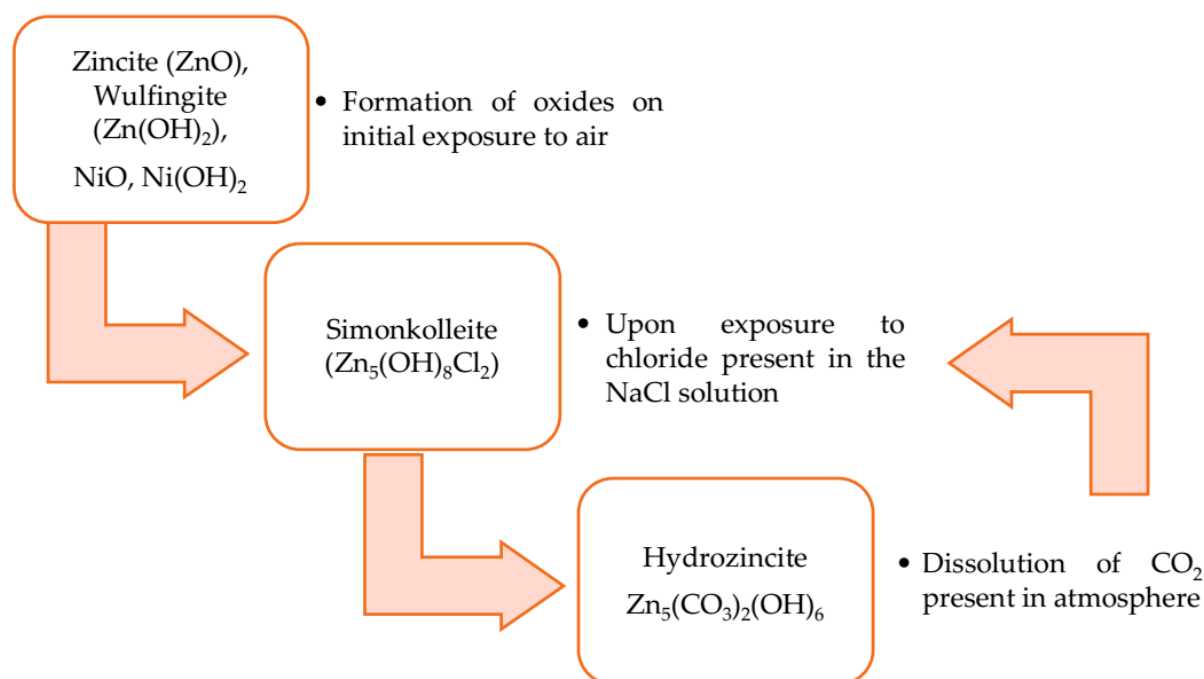
Figure 2. Figure depicting the schematic sequence of corrosion products that are formed on the surface of Zn-Ni-TiO$_2$, as reported in [82].

3. Recent Developments

3.1. Zn and Zn–Alloy Deposition in Ionic Liquids

Though there are significant works on the deposition of Zn and Zn-alloys on various substrates from aqueous solutions, there are certain challenging issues that remain to be critically solved. All the zinc alloys with an alloying metal from the iron group (nickel, iron, cobalt) are obtained under so called anomalous codeposition; that is, with preferential deposition of the less noble zinc. One of the possible reasons for the anomalous codeposition is the formation of zinc hydroxide followed by its adsorption on the surface during the hydrogen evolution reaction. This will hinder the reduction of respective alloying metal ions (Ni^{2+}) and control the overall alloy (Zn-Ni) composition as the high surface activity of zinc ions facilitates the easy replacement, inhibition of Ni ions and its nucleation, growth in the case of Zn–Ni alloy deposition. This combined with the hydrogen evolution affected the quality of the deposit drastically in terms of (i) visual appearance, (ii) crack formation, (iii) adhesion, (iv) brittleness, (v) throwing power, (vi) structural properties, (vii) corrosion resistance behavior. Besides, the optimization of the deposition parameters (current density, temperature, mode of deposition, bath agitation), electrolyte conditions (pH, concentration), additives are added either as complexing agents or levelers or brighteners or their combination which favor the anomalous deposition, formation of passivation layers (resulting due to corrosion). These shall circumvent the brittleness of the deposit by controlling the hydrogen embrittlement due to the evolution reaction and reduce the crack formation, thereby delaying the corrosion. Though there are significant research works carried out on the structural-property relation of the Zn–alloys, scientific understanding of the structural features (morphology, crystal size and orientation, alloy composition) in relation to their corrosion behavior has not been fully established. For instance, it is known that the rate of Ni deposition in the Zn–Ni alloy is hindered by the formation of zinc hydroxide. From the studies of [60,116], it was shown that the pH value measured near to the cathode surface doesn't form zinc hydroxide, indicating that the hindrance in the electroreduction of Ni ions did not occur via the hydroxide formation mechanism. The combination of Zn deposition and monolayer formation during the underpotential deposition and high overpotential of Ni resulted in anomalous Zn–Ni

deposition with controlled inhibition of the Ni ions' nucleation and growth process. Due to the ever-growing demand across a range of engineering and structural market applications, in deposition of Zn and Zn–alloys in non-aqueous electrolyte media, (i) ionic liquids and (ii) deep eutectic solvents were identified as an alternative technical competitive approach. Ionic liquids (ILs) are composed of single organic cation and an inorganic/organic anion while deep eutectic solvents (DESs) contain a combination of cations, anions. These media exhibit similar physical properties but differ in terms of synthesis, chemical properties. By employing ILs, it is possible to (i) eliminate the hydrogen gas liberation, (ii) tailor the redox properties, (iii) achieve the desired physical, chemical properties, (iv) control nucleation characteristics [117–121]. Their large electrochemical windows in combination with their good physico-chemical properties, thermal stabilities, low vapor pressures make them versatile for electrodeposition of Zn and Zn-alloys, enhance the coatings' corrosion resistance performance [122]. ILs offer an ideal alternative for the electrodeposition of Zn and its alloys such as Zn–Ni, Zn–Fe, Zn–Co, Zn–Mn in two ways. First is the hydroxide suppression mechanism that is responsible for the formation of anomalous deposits can be eliminated, and second is the elimination of hydrogen liberation owing to the absence of water in the non-aqueous bath [123]. The motivation for using ILs in Zn-alloy deposition such as Zn–Mn is due to (i) solution instability in aqueous media, (ii) low current efficiency, (iii) poor deposit morphology. Poor quality deposits and low current efficiencies arise in the case of Zn–Mn alloy coatings because these require higher negative potentials to reduce Mn, which results in drastic hydrogen gas liberation at the cathode [124]. One key benefit in using ILs is their ability to tune redox potentials via the metal speciation and promote better co-deposition of metal alloys: Zn–X (X: Ni, Co, Fe, Mn) without the need for a complexing agent, unlike aqueous electrolytes [125–128]. Since Zn and Mn co-deposits have a large difference in their redox potentials, employing an IL with a high electrochemical window shall favor the metals' co-deposition owing to their better tailoring properties. Table 3 shows the corrosion parameters obtained from the electrochemical characterization of the Zn and Zn–alloys deposited from ionic liquids.

Table 3. Table showing the corrosion parameters for the deposition of Zn and Zn-X alloys (X = Ni, Mn etc.) in ionic liquids (ILs).

System	Coating	Substrate	Mode of Deposition	Corrosion Test Method	E_{Corr}, V (vs Pt/SCE)	I_{Corr}, $\mu A\ cm^{-2}$	References
	Zn	Carbon steel	Potentiostatic	LPP	-0.289 [1]	0.68	[129]
	Zn–Mn (0.4–0.7) [3]	Copper	Potentiostatic	LPP, EIS	-1.021 [1]	1.075	
	Zn–Mn (0.4–1.0) [3]	Copper	Potentiostatic	LPP, EIS	-1.054 [1]	0.917	
ChCl–Urea	Zn–Mn (0.4–1.4) [3]	Copper	Potentiostatic	LPP, EIS	-1.098 [1]	1.175	[70]
	Zn–Mn (0.4–0.7) [3]	Copper	Potentiostatic	LPP, EIS	-1.062 [1]	0.989	
	Zn–Mn (0.4–1.0) [3]	Copper	Potentiostatic	LPP, EIS	-1.079 [1]	0.875	
	Zn–Mn (0.4–1.4) [3]	Copper	Potentiostatic	LPP, EIS	-1.109 [1]	1.251	
ChCl–Urea (1 wt.% H_2O)	Zn–Ni	Carbon steel	Potentiostatic	LPP	-0.414 [1]	0.82	
ChCl–Urea (3 wt.% H_2O)	Zn–Ni	Carbon steel	Potentiostatic	LPP	-0.478 [1]	1.3	
ChCl–Urea (5 wt.% H_2O)	Zn–Ni	Carbon steel	Potentiostatic	LPP	-0.801 [1]	2.1	[129]
ChCl–Urea (7 wt.% H_2O)	Zn–Ni	Carbon steel	Potentiostatic	LPP	-0.931 [1]	5.6	
ChCl –EG	Zn	Mild steel (AISI 304)	Potentiostatic	LPP, EIS	-1.040 [1]	6.57	[130]
[EMIm][Tf_2N]-	Zn–Mn	DP-1000 steel	Potentiostatic	LPP	-1.016 [1]	0.0119	[131]
Zn[Tf_2N]	Zn–Mn	DP-1000 steel	Potentiostatic	LPP	-0.776 [1]	0.0112	[131]
ChCl–Urea	Zn	WE43-T6 Mg alloy	galvanostatic	LPP	-1.420 [1]	38.68	[132]
ChCl–Urea	Zn–Mn (1–1) [4]	Steel	galvanostatic	LPP	1.110	1.06	[128]
ChCl–Urea	Zn–Mn (1–1) [4]	Steel	galvanostatic	LPP	1.040	3.2	[128]
ChCl–Urea	Zn–Mn (1–1) [4]	Steel	galvanostatic	LPP	1.045	3.6	[128]
ChCl–Urea	Zn–Mn (1–3) [4]	Steel	galvanostatic	LPP	1.130	0.90	[128]
ChCl–Urea	Zn–Mn (1–3) [4]	Steel	galvanostatic	LPP	1.040	0.82	[128]
ChCl–Urea	Zn–Mn (1–3) [4]	Steel	galvanostatic	LPP	1.046	5.3	[128]
ChCl –EG	Zn	Copper	galvanostatic	LPP	-1.197 [2]	7.987	[133]
NaOAc: EG [2]	Zn	Mild steel	galvanostatic	LPP	-1.066 [2]	1.01	[134]

[1] Linear potentiodynamic polarization (LPP) conducted in 0.1 M $NaNO_3$ (or) 3 wt % NaCl solution; EIS: Electrochemical impedance spectroscopy. [2] NaOAc: EG–Sodium Acetate: Ethylene Glycol. [3] Zn–Mn(0.4–X) indicate 0.4 M of $ZnCl_2$ + X M $MnCl_2 \cdot 4H_2O$ in the electrolyte solution containing choline chloride: Urea in the molar ratio 1:2. X: 0.7–1.4 [70]. [4] Zn–Mn(1–Y) indicate 0.1 M of $ZnCl_2$ + Y M $MnCl_2 \cdot 4H_2O$ in the electrolyte solution containing choline chloride: Urea in the molar ratio 1:2. Y: 0.1; 0.3 [128].

3.2. Superhydrophobic Zn and Zn–Alloy Coatings

In recent times, superhydrophobic coatings are considered a beneficial approach for corrosion protection of metallic structures for a variety of applications such as aerospace, marine, oil and gas and so on. Superhydrophobic surfaces are usually formed with a combination of low surface energy materials and rough microstructures. To create superhydrophobic surfaces to resist against corrosion, it is important to create rough microstructures [135,136]. On one hand, the rough microstructure surfaces trap the air within them when they are in contact with water, acting like an additional barrier and retard the corrosion rate on aircraft and ship surfaces. On the other hand, they exhibit self-cleaning, anti-fouling, anti-icing/de-icing properties which enable them to be suitable potential

candidates for protecting pipelines and other surfaces that are exposed to the marine environment besides corrosion [137]. Low surface energy substances (generally organic-based) are often added directly to the electrolyte solutions to achieve superhydrophobic coatings. With the addition of low surface energy materials to the electrolyte solution containing the metal ions, they tend to react with the functional groups of these substances during electrodeposition and form a coating with low surface energy and high-water angle on the cathode surface. The key advantage of such an addition is that superhydrophobicity can be obtained without the need for any surface modification after electrodeposition [138]. The high-water contact angle will directly influence the reaction between the corrosive species and the bare metallic substrates (generally mild steel) and prolong the life of the coatings by lessening their reaction time. On increasing surface hydrophobicity, it is possible to limit the metals' interaction with corrosive species, such as water and other ions such as Cl^-, SO_4^{2-}, CO_2, etc., and reduce the corrosion rate of the coatings deposited. For organic anticorrosive coatings, incorporating a superhydrophobicity property would impede the diffusive mass transport of water molecules and enhance the coating's protectiveness against corrosion of underlying metallic structures for longer periods [139]. In cases such as oil and gas, these coatings seem to be an economical solution to control the corrosion and fouling in pipelines for transporting oil and gas related products such as natural gas liquid products and liquid propane via subsea, and also, they have a high tendency to be used over different substrates [140].

Considering the likelihood of obtaining several surface morphologies with varied roughness and different microstructures, electrochemical deposition is considered to be the most versatile in terms of simplicity, scalability and cost effectiveness. Table 4 lists the Zn coatings prepared by electrodeposition that exhibit superhydrophobic properties. The most widely preferred mode to obtain a metallic coating is via the electrochemical deposition at the cathode. It is also possible to achieve coatings with superhydrophobic, corrosion resistance properties by anodic electrodeposition. For instance, Wang et al. [141] performed anodic electrodeposition and obtained a superhydrophobic coating on metallic zinc anode surfaces from the solution containing zinc tetradecanoate with platinum as the cathode. A corrosion resistant superhydrophobic Zn layer was formed on the zinc anode substrate by one-step potentiostatic deposition at 30 V for 2 h and room temperature. The authors demonstrated the possibility of obtaining the superhydrophobic coatings by oxidizing the Zn to Zn^{2+} initially, which resulted in the formation of a superhydrophobic Zn deposit film by combining with tetradeconate on the anode surface. Corrosion test results of the superhydrophobic Zn coatings showed an enhancement in corrosion protection of the substrate. The behavior of the air medium that is trapped between the pockets of the superhydrophobic surface was shown to be similar in the action of a dielectric film in a parallel plate type pure capacitor. Such a configuration would improve the corrosion resistance life of the substrate through circumventing the metallic pathway between the substrate and the electrolyte.

Table 4. Table showing the list of Zn coatings with superhydrophobic properties prepared by electrodeposition.

Coating	Substrate	System/Bath	Surface Energy Reducer Agent	CA°	Reference
Zn	steel	chloride	vulcanized silicone polymer	155 ± 1	[142]
Zn	X65 steel	sulphate	stearic acid	158.4 ± 1.5	[143]
Zn	X90 steel	sulphate	perfluoro octanoic acid	154.21	[144]
Zn	carbon steel	Sulfate-acetate	stearic acid	153	[145]
Zn	carbon steel	alkaline	stearic acid	158.7	[146]
Zn	copper	DES [1]	stearic acid	164.8 ± 0.6	[147]

[1] DES: Deep eutectic solvent consisting of chloine chloride:ethylene glycol (1:2).

In a study by Wang et al. [148], the zinc-laurylamine superhydrophobic complex film with corrosion resistant properties was obtained on a zinc substrate via the same anodic electrodeposition route. The corrosion resistance of the deposited film was investigated in a simulated marine environment. The results showed that the superhydrophobic film coating was corrosion resistant with a protection efficiency of ≥99% [149]. Obtaining structures similar to Micropogonias Undulatus scales on the coatings via electrodeposition could result in micro patterns with superhydrophobicity. Such micro patterns exhibit the similar skin surface topographical features that are observed with marine creatures (sharks and fish) [150]. Considering the advantages with electrodeposition in obtaining structures on various geometries from simple to complex, it can be assumed that such a pattern is achievable. Inclusion of micropatterns similar to the topographical features of marine creatures (e.g., Micropogonias Undulatus-like scales) is expected to boost the physical properties and contribute to the enhancement in the corrosion resistance of the mild steels [151]. A number of scientists and researchers have leveraged the benefits of zinc coatings fabricated by electrodeposition in improving the corrosion resistance [11]. Li et al. [144] fabricated a crater-like Zn structure on an X90 steel pipe surface with super-hydrophobic coating via 2 steps: (i) galvanostatic electrodeposition in sulfate electrolyte followed by (ii) chemical modification using perfluorooctanoic acid (PFOA). Contact angle measurement data showed a stable value of ~150 °C even after exposure to air for 80 days and the superhydrophobic coatings demonstrated good quality with self-cleaning properties and air stability. In addition, these coatings were shown to play a dual role acting as self-cleaning coatings on the one hand and exhibiting cathodic protection on the other hand, thereby enabling a double protection to the bare metal substrate. Imparting superhydrophobic properties to Zn coatings shall overcome the limitations of short corrosion life that are commonly observed with conventional Zn coatings under high humid conditions such as coastal and marine environments. Such a surface can resist the formation of a moisture film owing to its small tilt angle or high-water contact angle, which makes it difficult to hold the water molecules. Polyakov et al. [145] aimed at investigating the possibility of forming superhydrophobic Zn coatings and estimating their corrosion protection ability under salt spray chamber conditions, using 0.5 M NaCl test solution. Attempts were made by modifying the electrochemical pretreatment of carbon steel surface prior to deposition followed by 2-stage treatment in obtaining the Zn coatings with superhydrophobic properties. The 2-stage treatment involved the potentiostatic deposition of Zn dendrites from sulfate–acetate-based electrolytic solution followed by treatment with stearic acid (hydrophibising/surface energy reducing agent). The results showed that employing such an electrochemical pretreatment will play a vital role in preserving the superhydrophobic properties of the obtained coatings as the pretreated surface via galvanostatic method provides a polymodal surface with adequate roughness for creating

an anti-wetting surface. Additionally, corrosion test results from salt spray, 0.5 M NaCl confirmed that the coatings can withstand severe corrosion owing to the formation of a gas interlayer on the superhydrophobic coating surface which acted like an insulator or dielectric film, thereby preventing the Zn dissolution. This was justified by evaluating the average value of the wetting angle for the superhydrophobic coated with Zn/Stearic acid that was shown to be $\geq 151°$ after 148 h of exposure in the salt spray chamber. The authors also identified that ultrasonication of Zn coatings with stearic acid specimens had a positive influence on improving the superhydrophobic properties, preserving it for a long duration while possessing excellent corrosion resistance.

Subsequently, research has shifted towards the deposition of Zn, Zn–alloys with ferromagnetic iron group metals such as Fe, Co from ionic liquids resulting in the formation of superhydrophobic coatings. For instance, Li et al. [147] utilized the advantages associated with DESs, a class of ILs, in obtaining nanostructured deposits and synthesized hierarchical Zn structures via two-step electrodeposition from choline chloride: ethylene glycol-based DESs on copper-based substrates. It was observed and shown that the Zn structural coating was mainly composed of a combination of micro-slices containing pure, uniform, dense nano-concaves of Zn and zinc–stearate. Designing a superhydrophobic coating with micro- and nano-structural combinations was demonstrated to be highly adherent to the substrate and a promising potential solution. While nano-concaves generate van der Waals' forces and strong negative pressure, micro-slices control the surface wettability and the degree of super hydrophobicity. Development of such a unique structure shall not only endow the Zn-based coatings with high surface roughness but also with low surface energy and can be employed for applications such as self-cleaning, anti-icing and so on. Chu et al. [152] demonstrated the formation of Zn–Co alloy coating with superhydrophobic properties on AM60B magnesium alloy via electrodeposition from choline chloride-based ionic liquid and subsequent surface modification employing stearic acid as the surface energy reducer. The coating so obtained displayed improved corrosion resistance behavior and immersion test results. Additionally, the superhydrophobic coating exhibited high stability in aqueous solution and could maintain the rough surface textures even after mechanical destruction, indicative of mechanical scratch resistance. Development of superhydrophobic surfaces on lightweight metal alloy substrates such as Al, Mg provide a water-repellent surface and prevent the permeation of water into the substrate, thereby enhancing the corrosion performance of the coatings. Additionally, the scanning electrodeposition technique was developed recently, where the electrodeposition process takes place by holding the substrate stationary while the anode nozzle is kept in motion [153]. Such a technique shall overcome the difficulty associated with the plating complex shaped part such as cargo restraints (marine), propeller shaft housings (marine), wing flap bearings (aerospace). The unique structure and surface composition are expected to bestow the resulting Zn-based coatings on lightweight materials such as Al and Mg with several desirable properties. These include: (i) high surface roughness, (ii) low surface energy, (iii) reduced water-contact surface, (iv) flexibility for use in various applications, and they show a great potential in developing smart materials for corrosion protection of metallic parts in marine, aerospace, oil and gas subsea lines against chemical, mechanical, biological, physical corrosion causing agents.

4. Cost Considerations and Future Challenges

4.1. Economic Aspects

Electrodeposited Zn and Zn–alloy coatings have been demonstrated as low cost, scalable solutions to minimize the surface degradation of mild steel parts, structures (of reasonable size) in the marine environment. Their corrosion protection abilities combined with additional functionalities gained by incorporation of nanoparticles make them techno-commercially viable for such applications. While there were potential developments in the Zn, Zn–alloy coatings and composite coatings over the past decade, it is important to get an appreciation of the costs that are required for the fabrication of the material system. Figure 3 shows the cost comparison of the electrodeposited Zn, Zn–alloy and com-

posite coatings produced by different electrolytes: less toxic citrate, acetate; non aqueous ILs [33,82,127,134,154], which were selected based on their significant developments over the past decade, the number of works published by scientific community, and that were demonstrated to be techno-commercially viable solutions as corrosion resistant coatings. As can be seen, the Zn, Zn–alloy deposition from ILs seems to be more expensive while the Zn, Zn–alloy composites deposited from the aqueous system seem to be economical and are in line with the conventional Zn, Zn-alloy deposits. In addition, certain relatively low-toxic aqueous electrolytes such as citrate, acetate are less expensive than the sulfate. Hopefully, these electrolytes could live up to their primary aptitude and offer real, ecofriendly solutions to numerous technical challenges that are currently being faced with the conventional chloride, sulfate systems. With the rapid advancement in the applications of ILs at a relatively large scale, it becomes obvious that the bulk production of ILs may increase and reduce the costs by up to ~1 USD per kg. Additionally, certain advantages such as recycling large fractions of plating solutions combined with the possibility of bulk scale production illustrate their economic competitiveness in producing high quality Zn, Zn–alloy deposits and are expected to make potential savings in costs [155]. With ever-growing composites, it becomes more important to understand the composite properties, its intended application and corrosion behavior in a particular service condition. Therefore, judicious selection of the electrolyte combined with the properties and the costs required must be put into consideration. Development of Zn and Zn–alloy composites from aqueous media have been demonstrated not only to be technically competitive but also economically viable and are expected to overcome the challenges associated with marine applications such as (i) corrosion resistance, (ii) wear resistance, (iii) frictional drag, (iv) fouling. Minimizing the costs of the coatings developed while meeting the performance requirements for marine applications remains of significant interest while their service life remains a great challenge.
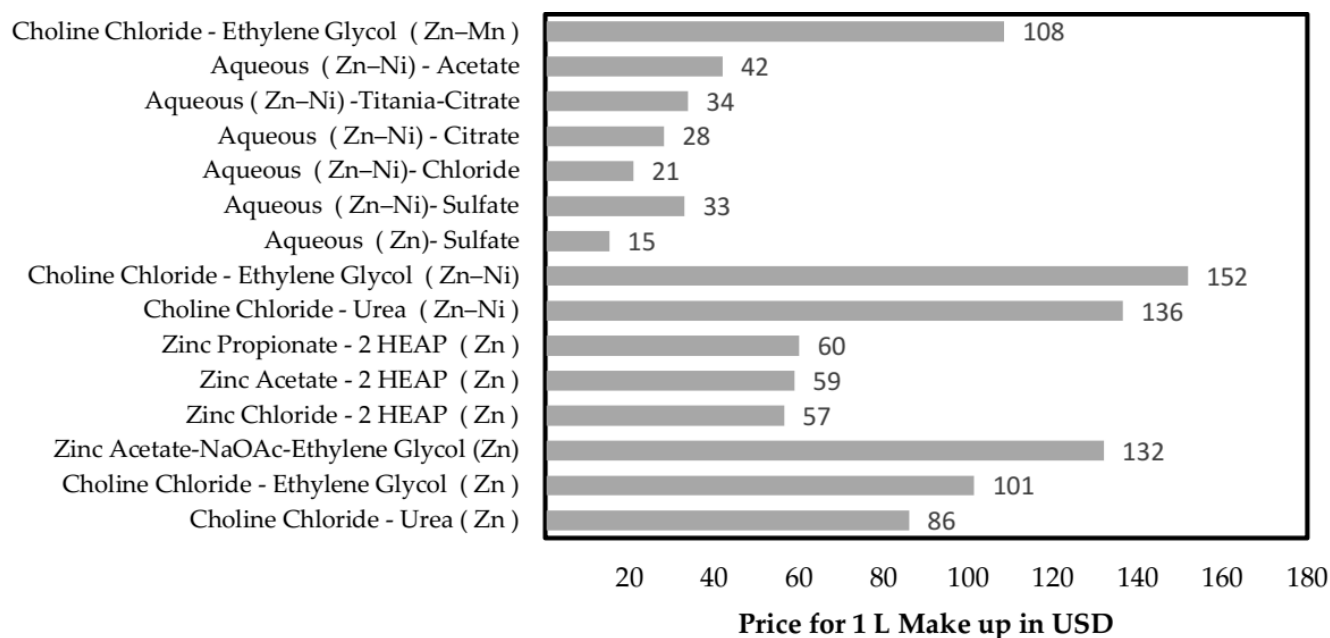

Figure 3. Plot showing the cost comparison of different electrolytes that were developed for the deposition of Zn, Zn-alloys and Zn, Zn-alloy composites considering the initial make up of 1 L solution [33,82,127,134,154]. NaOAc-sodium acetate; HEAP-2-hydroxyethyl ammonium propionate.

4.2. Future Challenges

Electrodeposition of Zn and its alloys, and composites, have significantly progressed, employing low toxicity aqueous electrolytes (e.g., citrate, acetate) and ILs over the past decade. These have shown promising applications with additional properties such as wear

resistance, superhydrophobicity and hardness in addition to corrosion resistance [63,78,81,119]. However, the globe continues to face challenges that are critical in materials deterioration, often resulting in failures of components during service. The conflicting choice of a compatible material envisioned for an explicit use and environmental hazards' control will be one of the key challenges that remains to be critically addressed by the researchers, scientists, industrial experts, etc., in the field. One of the cost-effective approaches to protect the metal parts that are being used in various applications ranging from automotive to marine is by choosing the right material and method. Electrodeposition of Zn and Zn-alloys have been demonstrated to fit the requirement owing to the sacrificial property offered by a relatively cheap Zn metal combined with the simple, cost effective method of fabrication. Electrodeposited Zn, Zn–alloy coatings combined with incorporation of nano-particles could not only protect surface degradation of mild steel in the marine environment but also impart the necessary additional properties such as superhydrophobicity, improved hardness, wear resistance, fouling resistance of mild steel components. As a consequence, these become the foundation for surface adhesion and corrosion property enhancement [11].

It is well known that Zn coatings are prone to atmospheric corrosion and result in the formation of different corrosion products depending on the nature of environment they are exposed to. The evolution of corrosion products on zinc surfaces when exposed to either sulfur-dominated or chloride-dominated environments are most commonly observed. Exposure to a sulfur-based environment might result in the formation of zinc hydroxysulfate ($Zn_4SO_4(OH)_6 \cdot nH_2O$) with different amounts of water depending on the moisture it is exposed to, followed by the formation of $Zn_4Cl_2(OH)_4SO_4 \cdot 5H_2O$. In aerosol dominated environments such as marine and offshore industries, the presence of high concentrations of NaCl or other chlorides favors the formation of Simonkolleite $Zn_5Cl_2(OH)_8 \cdot H_2O$ with Gordaite ($NaZn_4Cl(OH)_6SO_4 \cdot 6H_2O$) as the final product. The sequence of different corrosion products that are formed due to exposure to sulfur-rich and chloride-rich environment over the period is represented in the Figure 4 as shown below. In chloride rich environments such as marine, the aerosols are expected to have a high concentration of NaCl which initially form $Zn_5Cl_2(OH)_8 \cdot H_2O$. These will tend to form gordaite ($NaZn_4Cl(OH)_6SO_4 \cdot 6H_2O$) by interacting with sulfate, whose emission comes from the biological activity (microorganisms, sulfate producing bacteria), droplets containing sulphate. This is reported by many works as the main reason for the frequent detection of gordaite as the final corrosion product from a chloride rich environment [156,157].
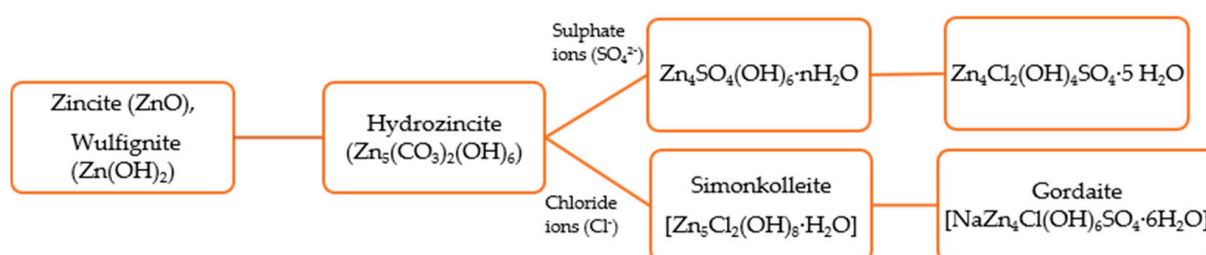

Figure 4. Figure showing the sequence of corrosion products that are formed on the Zn surface exposed to chloride and sulfate-based environment [21].

Considering the recent changes in the world's climatic conditions, it has been observed that the chloride-based environment is predominantly increasing relative to the sulfur-based environment [21]. Corrosion studies on Zn and Zn–alloy composites showed that the nanoparticle incorporation tend to lower the corrosion current, signifying a reduction in the corrosion rate for the coatings. The nanoparticles are thought to be capable of blocking the penetration path of the corrosive medium through the voids, gaps, crevices and holes within and on the surface of the coatings, besides incorporating additional functionalities such as brightness, uniformity, etc. In such cases, the transport of corrosive species to reach the metal substrate is further delayed, indicating improved corrosion

resistance. Most of the reports signify the corrosion protection offered by the Zn, Zn–alloy nanocomposite coatings was improved as compared to pure Zn, Zn–alloy coatings [80,109]. Though there are significant studies that reported on the atmospheric corrosion of Zn, especially on the development of corrosion products on their surface, such studies on the electrodeposited Zn, Zn–alloys from aqueous and non-aqueous media (such as ILs) remain scarce. Hence, it becomes very important to understand not only the chemical speciation of electrodeposited Zn, Zn–alloys surfaces developed from different electrolyte media such as aqueous, non-aqueous (ILs) in different environmental settings, but also from potential Zn–composite surfaces.

Different environments have different chemistries and include a variety of combination of anions such as Cl^-, OH^- and others found in marine environment. Understanding the nature of the zinc corrosion platina layer at different circumstances might require primary attention. The formation of porous or a compact ZnO layer either at the bottom or intermediate remains critical for the electrodeposited Zn, Zn-alloy metal structures and their composites fabricated using the less toxic citrate, acetate baths and ILs used in a marine environment. Surface methods such as scanning electron microscope (SEM) and X-ray diffraction (XRD) that are utilized for identification of corrosion products formed may not be a reliable indicator in determining the relationship between the corrosion performance of the layer formed and its full structural assembly. A prodigious deal of work is required in this area to produce a much superior understanding on the (i) formation of layered structures, (ii) conditions under which the various elements interact on the surface of electrodeposited Zn, Zn–alloys fabricated using the newly developed electrolytes. Finally, the role of each corrosion product layer towards the formation of a corrosion barrier needs to be elucidated with electrodeposited Zn, Zn–alloy and their composite coatings' surfaces [157]. This shall help to identify the environmental risks, service life of the coatings and contribute significantly when performing an assessment study such as life cycle assessment, atmospheric corrosion.

Superhydrophobic Zn coatings are considered as potential corrosion resistant coatings for marine applications and subsea pipelines in oil and gas, and incorporate several additional functions such as (i) self-healing, (ii) anti fouling, (iii) nominal involvement from external agents (e.g., UV light). There are limited studies on the Zn-based super-hydrophobic coatings synthesized by electrodeposition and the corrosion performance of these coatings has only been evaluated for shorter periods in laboratory. Hence, there is an imminent necessity to fabricate Zn-based superhydrophobic coatings that maintain corrosion protection capabilities and other properties such as wear, self-cleaning for a long period. Long term exposure to severe corrosive conditions would represent the marine environment where structures, subsea pipelines (e.g., X60, X80, X90 pipelines) and parts coated with Zn (combined with a polymer) are mostly used. In addition, the development of Zn superhydrophobic coatings could be extended to protect the industry grade carbon steel substrates that are generally used for transporting oil, gas through the pipelines. With respect to the corrosion studies, validation of the indirect lab corrosion measurements via the electrochemical characterizations, weight loss measurements while considering the factors that control the electrochemical corrosion rate become critically important. There is a wide growing interest in the development of Zn, Zn–alloy composites from the newly developed electrolytes with different surface structures that offer superhydrophobic properties combined with tribological properties for marine applications [158]. Studies on the evolution of corrosion products of such surfaces on exposure to simulated marine environment could provide an understanding of the service life of the coating and help the engineers, scientists, manufacturers to decide the service life of the ship hull.

5. Conclusions and Outlook

This review covered the developments in the electrodeposition of Zn, Zn–alloys and their composite coatings produced from different electrolyte media ranging from low toxicity aqueous citrate to halide free acetate- based ionic liquids. These electrolyte

media have shown a promising potential to develop coatings with improvement in their texture, morphology, phases in the case of Zn–alloys which showed good results in terms of corrosion resistance. Electrodeposited Zn, Zn–alloy composite coatings have been encouraged by the availability of newer and nanostructured materials such as TiO_2, Al_2O_3, CeO_2, etc., and have seen major progress for potential application in marine, automotive aerospace, heavy duty engineering and so on.

Some recent works on forthcoming applications such as Zn-superhydrophobic coatings offering improved corrosion resistance with mechanical and tribological properties have been reviewed. The review also covered the works that have been conducted to investigate the corrosion behavior of electrodeposited Zn and Zn–alloys in controlled laboratory environments. Recent developments in the electrodeposition of Zn and Zn–alloys using ionic liquids and composites with different nano-particle incorporations have been discussed. Despite the significant developments of the electrodeposition of Zn, Zn–alloys and Zn-composites using low toxicity aqueous electrolytes, halide free ILs, the evolution and roles of different corrosion products formed on such deposited surfaces in tropical marine environments still need a detailed investigation. Corrosion studies of the Zn–coatings produced by newly developed electrolytes in the tropical marine atmosphere could help the marine industry understand the challenges associated with the coatings. Understanding the relation between the tests performed at lab scale combined with the corrosion kinetics and chloride salt deposition rate remains of critical importance for predicting the corrosion behavior of the electrodeposited Zn-based coatings. Development of zinc-manganese (Zn–Mn) alloys have started receiving primary attention for their high corrosion resistance and formation of denser corrosion products and can be potential alternatives to the Zn–Ni, Co alloys. However, certain challenges associated with Zn–Mn electroplating such as the need for complexing agents and their corrosion behavior in real environments still require detailed investigation. In addition, studies of the formation of layered structures representing different corrosion products on the progressively developed Zn–alloy composites, Zn–alloys from ionic liquids and Zn-superhydrophobic coatings will be of greater significance. Considering future trends towards the development of superhydrophobic coatings, the combination of corrosion protection abilities along with mechanical, tribological studies should also be explored. To conclude, the role of each layer in creating a corrosion barrier needs to be explicated for the rapid pace of industrialization.

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