

Review

Progress in Electrodeposition of Zinc and Zinc Nickel Alloys Using Ionic Liquids

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Abstract: Zinc (Zn) and zinc–nickel (Zn–Ni) electrodeposition has been widely used in many industries, such as automotive and aerospace, for corrosion protection of steel components owing to their excellent corrosion resistance. Conventional zinc and zinc–nickel electrodeposition is performed in different types of aqueous baths (acid and alkaline). Such electrolytes suffer from certain drawbacks such as hydrogen gas evolution, low coulombic efficiencies, and environmental toxicity. Electrodeposition of Zn and Zn–Ni alloys from ionic liquids has gained significant attention in aerospace and automotive sectors owing to the different environments they provide for electrodeposition. This paper reviews the progress in deposition of zinc and zinc–nickel alloys in non-aqueous systems, especially ionic liquids. In addition, the challenges and technological developments associated with the Zn and Zn–Ni deposition on different substrates and the factors that need to be considered while electroplating at an industrial scale are discussed.

Keywords: ionic liquids; deep eutectic solvents; corrosion resistant coatings; aerospace; electrodeposition; zinc and zinc alloy; metallization; electroplating

1. Introduction

The metallization of a surface is of great technological importance. Several techniques have been developed and used industrially to produce protective coatings. One such technique is ‘electroplating’, also known as metal electrodeposition when a metal is electroplated. Some of the benefits of such coatings include a smooth finish while providing corrosion resistance as well as a lower cost compared with some other types of coatings. The electrodeposition of corrosion-resistant coatings is an important manufacturing process, particularly in the automotive and aerospace sectors, to name a few. Corrosion and wear resistance are traditional areas that still receive significant attention. Intensive research efforts continue towards finding and developing electroplating solutions on new lightweight alloy composites for aerospace applications.

Cadmium (Cd) coatings have been used as a sacrificial protection layer for steel components and parts in many industrial applications, including the aerospace sector, owing to its position in the galvanic series when compared with steel. However, its carcinogenic and toxic nature is a cause of concern and its use is being restricted as per the Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH) regulations and under the Restriction of Hazardous Substances-2 (RoHS 2: Directive 2011/65/EU) [1]. Zinc (Zn) and Zinc–nickel (Zn–Ni) alloys are considered to be more environmentally friendly and as having the potential to replace Cd coatings, and offer excellent corrosion resistance against the protection of ferrous substrates such as fasteners, automobile bodies, and aerospace parts, owing to the position of zinc in the galvanic series and its sacrificial protection to steel [2]. While the major demand for the Zn and Zn–Ni alloy deposits comes from the automotive

sector [3], Zn–Ni alloy deposits are considered to be a potential alternative to Cd plating in the aerospace sector. The use of Zn–Ni alloy coatings in aerospace and defence applications is increasing at a fast rate and their use presents major challenges to the surface coatings industries, by requiring a completely different approach to that used for coating metals. Few automotive and aerospace companies define their own specifications for the Zn and Zn–Ni alloy deposits, keep them for their internal purposes, while few publish them. Nevertheless, the overall objective is to employ Zn-alloy deposits as a replacement to Cd coatings for sacrificial protection of steel against corrosion.

Electrodeposition of Zn and Zn–alloys (containing Ni) is generally carried out from aqueous cyanide acid baths, alkaline cyanide-free baths, and acid chloride baths [4], which are toxic and corrosive. Despite their attractive properties such as high solubility to metal salts, high conductivity, and low viscosity, industrial zinc platings suffer from common problems such as hydrogen embrittlement and low coulombic efficiency [5]. In addition, the spent process water must be treated before recycling and reuse, which require the addition of chemical agents and will contribute to the recycling costs. Furthermore, certain complexing agents that are added to improve the Zn and Zn–Ni deposit properties are subjected to anodic oxidation, and will result in the formation of breakdown products during the electrolysis of Zn–Ni aqueous plating solution, which may pose environmental hazards. Moreover, it reduces the electrolyte lifetime (bath life) and requires frequent disposal followed by fresh preparation of the solution, and increases the production costs. In such a context, one of the major issues in the electroplating sector lies in compliance with legislation such as REACH in the European Union and similar regulations in other countries, which seek to limit the use of hazardous complexing agents and metal precursors in aqueous electrolytes. Though electroplating using aqueous baths remains a key industrial route for coating production, the limitations stated above prevent the technology from being applied to the deposition of certain metals such as Zn and Zn–Ni alloys. Further, hydrogen evolution reaction (HER) also influences the physical and structural properties of zinc electrodeposits owing to its effect on the nucleation and on the electrocrystallisation of zinc [6]. In addition to the metallic zinc deposition process and HER, zinc oxide deposition also competes owing to the induced precipitation, which increases the interfacial pH [7]. The formation of ZnO films is reported to be interesting in optical, photovoltaic, photocatalytic, and optoelectronics applications and displayed great interest in corrosion protection when deposited on different substrates. However, the formation of ZnO is by indirect electrochemical deposition and is significantly affected by the simultaneous hydrogen evolution, as well as the competition between the process of formation of zinc oxide and the formation of hydroxides or mixed salts. Nevertheless, the technological demand in industries such as automotive and aerospace fastener components for higher quality and longer lasting finishes with improved corrosion resistance has driven the development of efficient electrolytes for zinc and zinc alloy electrodeposition. Owing to the disadvantages associated with Zn/ZnO electrodeposition from aqueous medium, deposition in non-aqueous systems can be considered as one of the effective ways to design and optimize the existing processes in order to obtain pure and homogeneous electrodeposits. Therefore, the search for alternative electrolytes for zinc electrodeposition is of primary importance. In recent times, electrodeposition of metal from ionic liquids has gained significant attention owing to the fact that ionic liquids provide different environments/electrolytes for electrodeposition, wide electrochemical windows, high thermal stability, good ionic conductivity, and better mass transport. In addition, ionic liquids (ILs) can eliminate the mechanical stability issues that arise from metals produced in the presence of hydrogen evolution.

Ionic liquids (ILs) consist of an organic cation and an anion (organic or inorganic); both serve as solvents and supporting electrolytes, thereby making them an attractive alternative to toxic solvents or aqueous solutions in the electroplating industry. Figure 1 shows the schematic arrangement of an IL representing a large, bulky asymmetric cationic component and a relatively small symmetric anion [8]. The highly asymmetric structure of the cation makes it difficult to stack with the anions close to each other, and reduces the lattice energy, thus effectively prohibiting IL's crystallization and lowering its melting point. ILs distinguish themselves from traditional molecular liquids in terms of their mass transport and charge transport.

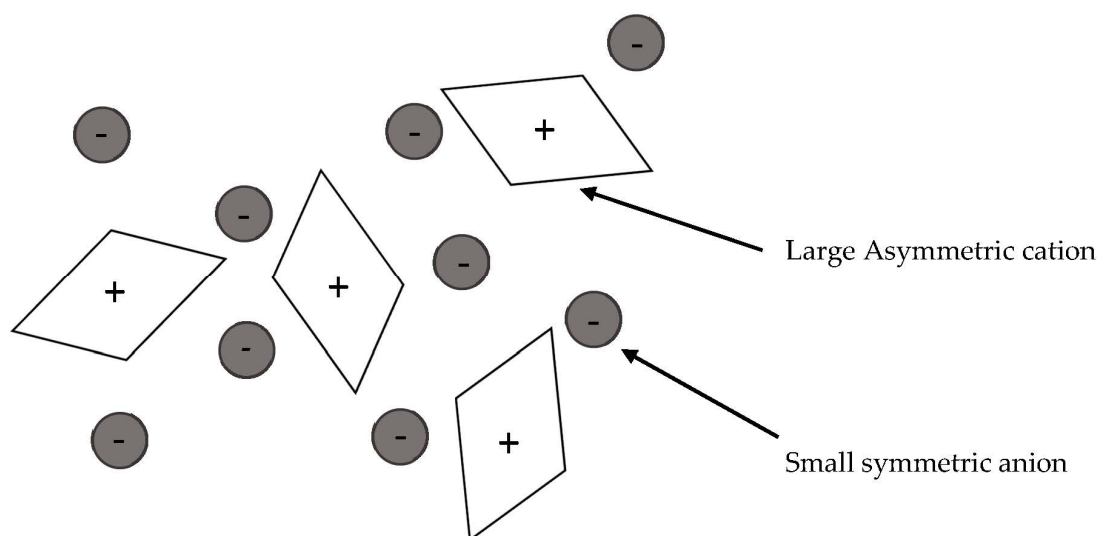


Figure 1. Schematic showing the structure of an ionic liquid.

In general, five types of ILs have been employed in the electrodeposition of zinc and zinc-based alloys and is mentioned in Table 1. These ILs are differentiated in terms of their preparation, mechanism and limitations. A detailed discussion on the ILs and their preparations can be found in the literature [9–11]. Reviews by Tome et al. [12] and Marcus et al. [13] provide an overview on the deep eutectic solvents and their practical applications. Deep eutectic solvents (DESs) are systems composed of a simple eutectic mixture of Lewis or Bronsted acids and bases and contain a variety of anions, with cations being the hydrogen bond donors. On the contrary, ILs are systems with one type of discrete anion and cation. The main advantage of ILs refers to its ability to tailor metal redox potentials and control deposit morphology. The simplest ionic liquids consist of a single cation and a single anion, whereas more complex systems are formed by combining several cations and/or anions, or complex anions, obtained in equilibrium processes. The physicochemical properties of these systems are a function of cation and anion structure and composition. On the contrary, the hydrogen donor (such as urea, carboxylic acids, polyols) and hydrogen acceptor (Lewis or Bronsted acids and bases) are associated via hydrogen bonding in DESs, and do not include purification step in their synthesis unlike ILs. In addition, DESs exhibit reasonable solubility for a wide range of metal salts and oxides and show good tolerance to water and air. Though the potential windows of DESs are wider than aqueous solutions, they are lesser than some ILs. DESs and ILs also vary significantly based on the complexing of the anion, which has a significant influence on the formation of eutectic-based liquid by decreasing the freezing point and delocalization of the charge. While aqueous-based technology is well established, advanced, and used for the production of commercial Zn and Zn–Ni coatings, ILs have attracted much interest as promising electrolyte candidates for metal electrodeposition owing to their remarkable characteristics, especially eliminating the hydrogen evolution during electroplating.

Table 1. Types of ionic liquids (ILs) employed for the deposition of zinc and zinc-based alloys [9].

Type #	Name	Preparation Method
Type I	Halometallate	Mixing an organic chloride with a metal halide such as Cl^- (ZnCl_2)
Type II	Air and water stable	Generally composed of organic cations and discrete anions such as $[\text{BF}_4]^-$ $[\text{PF}_6]^-$
Type III	Deep eutectic solvents	Simple eutectic mixtures of organic halides with hydrogen bond donors (HBDs) such as urea and ethylene glycol (EG)
Type IV	ILs with metal containing cations	Mixing an ionic liquid with cationic metal complex
Type V	Protic ILs	Mixing a bronsted acid to a bronsted base (formed through the transfer of proton)

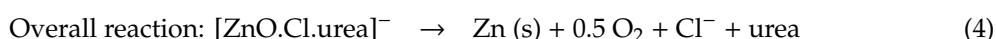
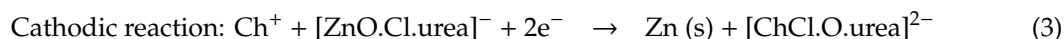
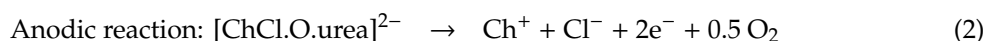
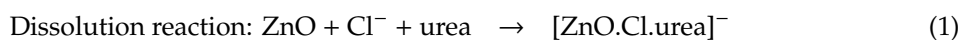
Several reviews on the electrodeposition of metal and metal-alloys in ionic liquids have been published in the last 10 years [14–16]. Most reviews discuss progress in the development of ionic liquids and the type of metals that one can deposit in ionic liquids, along with their compositions. There are few reviews that report progress in ILs in the field of electrodeposition of light metals, rare metals, and noble metals [17,18]. Abbott et al. [19,20] published a series of articles that discussed the properties of ILs and their possible industrial applications in electroplating, highlighting their significance and that of other applications such as electro-polishing. However, no review focuses exclusively on the Zn and Zn–Ni deposition in ILs and DESs. In addition, general reviews on metal electrodeposition published so far focused on only limited works of Zn and Zn–Ni alloys’ deposition in ILs and does not cover the latest developments. Moreover, the reports highlighting certain key areas such as the application of ILs as additives and industrial challenges associated in dealing with ILs for the deposition of Zn and Zn–Ni alloys are scarce. The aim of this review article is to give an overview on the progress of zinc and zinc nickel alloy-based electrodeposition from ILs. It also focuses on electroplating and highlights the aspects that may have to be considered for industrial-scale applications.

2. Zinc Deposition in Ionic Liquids

Few investigations on zinc electrodeposition in the past decade have been carried out in traditional ILs, and demonstrated the possibility to obtain high purity films. Li et al. [18] investigated the electrochemical potential windows and thermal stability of 33 ILs and 23 DESs. The study comprised of five traditional cations, namely, imidazolium, pyridinium, pyrrolidinium, piperidinium, and ammonium, and 13 types of anions. In addition, electrochemical potential windows of choline with different halides such as chloride (Cl^-), bromide (Br^-), and iodide (I^-) were also studied in combination with methyl urea as DESs. Among the selected combinations, deep eutectic solvents composed of choline chloride (ChCl) and methyl urea resulted in the largest potential window with good stability. Besides, ChCl can be synthesized via a one-pot, solvent-less process, making the process scale up simple. Furthermore, ChCl-based ILs are considered closest to commercialisation in the metal finishing industry. The presence of a high concentration of OH groups in ChCl-based ILs favors the metal ion adsorption, even in the presence of significant amount of moisture, and does not affect the electrodeposition of metals such as Zn. Abbott et al. [21] studied the deposition of Zn in ChCl/ ZnCl_2 system (1:2 molar ratio) and observed the formation of clear homogeneous colourless liquid on mixing the constituent components at room temperature. Hull cell results displayed a smooth thick grey/white deposit at a current density of 0.29–0.47 mA cm^{-2} , while a thinner whiter deposit in the range between 0.21 mA cm^{-2} and 0.29 mA cm^{-2} and a non-homogeneous deposit was observed, when deposited at current densities below 0.21 mA cm^{-2} . The cathodic current efficiency (CCE) with respect to metal (Zn) deposition represents the quantity of the metal (Zn) deposited at the cathode under normal electroplating conditions and was reported to be >99%. The Zn deposits obtained on mild steel were non-porous, indicating that the Zn deposit could act as a barrier and mitigate corrosion. However, the potential of the systems needs to be controlled as chlorine evolution reaction (CER) becomes a

problem at higher potentials, such as 2V, owing to the oxidation of chlorozincate complexes at the anode. Electrodeposition of Zn and Zn–Ni alloys from ILs based on eutectic mixtures of ChCl such as ethylene glycol (EG) urea have gained significant interest in the past decade.

These liquid systems consist of large choline cation, which has an unsymmetrical structure and a complex anion formed between Cl^- ion and a hydrogen bond donor (urea, EG). Moreover, they represent a different physical environment in terms of relative viscosity (328 cp for ChCl/2urea vs. 20 cp for ChCl/2EG) and co-ordination ability [22]. Abbott and Ryder group [23,24] and Pereira group [25] studied on the electrodeposition of Zn from ILs using ChCl-based combinations such as urea, EG, and ChCl-based DESs. Zn deposited from ChCl/2urea displayed a rice-grain like morphology, while the ChCl/2EG-based liquid resulted in the formation of very thin platelet like structures with the planar face perpendicular to the electrode surface. Nucleation is a process that determines how often a random arrangement of incoming atoms will spontaneously order themselves into a crystal, whereas growth is how quickly these nucleated regions spread outwards. The two different systems displayed a contrasting behaviour in terms of the nucleation and growth rates. Nucleation in the ChCl/2urea-based liquid is fast, but bulk growth is slow, whereas nucleation in the ChCl/2EG-based liquid is slow, but bulk growth is relatively fast. Generally, ionic liquids are more viscous than the molecular ones owing to stronger Van der Waals forces between cations, and influence the rate of mass transportation of the metal ion species, metal speciation, and interfacial structure. Cyclic voltammogram (CV) results from the works reported by Abbott et al. [22] showed that the magnitude of currents in ChCl/2urea is smaller than in ChCl/2EG during Zn deposition. However, it is worth noting that the difference in magnitude of the currents is a consequence of the high viscosity of the ChCl/2urea system, which affects the mass transport of species, alters the deposition characteristics, and displays different morphology, indicative of a different reduction mechanism and deposition rates. Polzler and Whitehead et al. [26,27] also investigated the zinc electrodeposition from a mixture comprising 1:2 molar ratio of ChCl/ethylene glycol (EG) on a glassy carbon (GC) substrate and compared the voltammetric response of zinc with a choline-free electrolyte containing only the ZnCl_2 salt and EG or sodium ethoxide (EtONa). They demonstrated the role of ChCl and observed an unusual cyclic voltammetry response, suggesting that choline ions blocked the surface of the electrode during the forward cathodic potential sweep and that zinc is deposited during the backward scan. However, the morphology of the obtained Zn deposit from the two liquids, (i) ChCl/2urea and (ii) ChCl/2EG, reported by Abbot group [21,22], appeared to be different, indicative of surface blocking on the electrode owing to the specific adsorption of chloride species on certain crystal faces. The possible reactions at the electrode for the Zn deposition on copper (Cu) substrate employing the ChCl/urea mixture as proposed by Yang et al. [28] are as follows:



Viera et al. [29] investigated it further by extending the mechanistic studies on the electrodeposition of zinc from a ChCl/EG deep eutectic solvent containing the Lewis base and zinc precursor (ZnCl_2). The results confirmed that adsorption of choline and EG species shall induce the blockage of active sites on the glassy carbon electrodes at low potentials, which gradually desorb at potentials $> -0.4 \text{ V}$ (vs. Zn/Zn^{2+}). It is worth noting that these ILs were formulated at a temperature of 70°C , and the Zn deposition from ILs containing zinc chloride (ZnCl_2) was carried out at lower temperatures (40°C). These conditions signify the technical and commercial viability of the zinc deposition process using ILs and do not require initial drying of the metal salt (ZnCl_2) before the process. In addition, liquid chlorozincates are easier to make and handle as they are less susceptible

to hydrolysis, which makes the synthesis and process scale-up simpler. While ChCl-based ILs have been favoured, imidazolium-based cations are also gaining significant attention owing to their superior fluidity and conductivity and, of these, 1-butyl-3-methylimidazolium is the most preferred thanks to its high conductivity. There are few reports highlighting the feasibility and use of other ILs such as 1-butyl-3-methylimidazolium chloride ([BMIm]Cl), 1-butyl-1-methylpyrrolidinium chloride ([BMP]Cl) and bis((trifluoromethyl)sulfonyl)imide anion ([TFSI][−])-based owing to their lower viscosities and melting points. Hsiu et al. [30] electrodeposited Zn particles in ZnCl₂/[EMIm][Cl] IL with different acidity by adding different percentage of ZnCl₂. Scanning electron microscopy (SEM) images confirmed that the morphology of Zn deposits could be controlled by adjusting the deposition temperature and potential. However, the results from Nieszporek et al. [31] displayed a very inhomogeneous morphology of the coatings when ([BMIm]Cl) baths were used for the deposition of Zn on steel substrate. In addition, the results showed that the type of bath used ([ZnCl₂]/[BMIm]Cl), current density applied, and deposition temperature had an impact on the structure and corrosion behavior of the Zn deposit. Wang et al. [32] demonstrated successful deposition of Zn on copper in bis((trifluoromethyl)sulfonyl)imide anion ([TFSI][−])-based ILs employing 1-n-butyl-1-methylpyrrolidinium[BMP] as the cation. The Zn(II) species were introduced by either the anodic dissolution of Zn or the addition of Zn(TFSI)₂ or ZnCl₂, respectively. ZnCl₂ exhibited good solubility in [BMP][TFSI] owing to the excellent interaction of the Cl[−] and TFSI[−] anions, which resulted in the formation of (i) soluble TFSI- co-ordinated Zn(II) species and (ii) partially Cl[−] co-ordinated Zn(II) species corresponding to the formation of two redox couples of Zn(II) species in ZnCl₂ solution. However, Zn deposited using Zn(TFSI)₂ and [BMP][TFSI] displayed higher cathodic current efficiencies than from ZnCl₂ and [BMP][TFSI]-based IL. The poorer efficiency in the latter was attributed to the fact that the liberated Cl[−] anions formed a complicated non-reducible complex by co-ordinating with the one of the redox couples of Zn(II) species in ZnCl₂, that is, partially Cl[−] coordinated Zn(II) species.

3. Zinc-Nickel Alloy Deposition in Ionic Liquids

Alloying of zinc with metals such as nickel improves mechanical properties like hardness and wear resistance, and provides more corrosion protection than pure zinc deposits [33–35]. Zn–Ni alloys coatings can not only be used for traditional corrosion mitigation, but also for other applications such as electrocatalysis. Zn–Ni alloy electrodeposits exhibit different phases as a function of their alloy composition and are assigned based on their distinct reduction potentials from cyclic voltammetric data. Zn–Ni deposits with less than 10 wt % Ni content are a mixture of γ and η -phases, while alloys of 10–17 wt % Ni content consist of γ -phase Ni in the Zn–Ni alloy composition. Ni contents greater than 17 wt % in the Zn–Ni alloy are categorized as a mixture of γ and α -phases. Commercially attractive bright Zn–Ni deposits developed are usually obtained with a nickel content of 12–15 wt % and exhibit γ -phase Zn–Ni alloy. These are mostly electrodeposited from alkaline baths as they are formulated very close to the conventional alkaline non-cyanide Zn bath and differ in terms of addition of Ni generally in small amounts. Zn–Ni alloy coatings, when deposited at low current densities, result in the formation of complex structure with a flat and bright surface, which corresponds to the γ -phase and contain Ni in the range 12 to 16 wt %. γ -phase Zn–Ni alloys behave like a monometallic deposit with higher hydrogen overpotential than pure zinc, are anodic to steel, and are considered to be a possible substitute to cadmium. In addition, these alloys offer an excellent hardness in the range 260–400 HV and corrosion resistance with a good degree of micro-cracking [36,37]. To obtain homogeneous γ -phase Zn–Ni alloy coatings, organic amines are often added to the aqueous electrolyte solution to stabilize nickel. However, cyanide is formed owing to the anodic oxidation of amines during electrolysis of alkaline Zn–Ni baths, indicative of electrolyte breakdown products formation, and poses environmental challenges. As per the reports by Sonntag et al. [38], the average cyanide formation rate is 7 mg/Ah to 10 mg/Ah. With cyanide generation on one hand and addition of Ni source to maintain the concentration on the other hand, this shall not only make the process difficult, but also increases the operation cost. Unlike the deposition of zinc, the deposition of Zn alloys is more

difficult owing to the differences in redox potentials of the alloying elements in aqueous electrolytes. Additionally, Zn–Ni alloy coatings deposited in aqueous electrolytes resulted in anomalous deposition, with preferential deposition of the less noble zinc owing to the pH rise at the surface of the metal substrate (generally ferrous). Considering the limitations associated with aqueous-based electrolytes, employing ILs in Zn–Ni electrodeposition shall make the reduction of either Ni(II) ions or Zn(II) ions difficult, thereby influencing alloy composition and morphology. Before deciding which type of ionic liquid is most suitable for the deposition of a given metal, it is important to consider the reduction potential of the metal and the potential window of the liquid. This is not always trivial as reduction potentials are significantly affected by the coordination of the anion to the metal. Electrodeposition of Zn–Ni alloys were performed in ILs including DESs such as traditional chlorozincate-based ILs [39,40] and ChCl-based DESs [41,42], owing to their tailoring properties. One of the key advantages of employing ILs for the metal alloy deposition such as Zn–Ni centers around its ability to tailor the redox potentials through metal speciation. Tailoring of redox potentials through metal speciation in these ILs allows for the co-deposition of metals that generally have a large difference in redox potentials and resolve the problems of bath instability and formation of anomalous deposits. Andrew et al. [43] studied the electrodeposition of Zn–Ni alloy on copper substrates from DESs/Reline (ChCl/urea = 1:2) and Ethaline (ChCl/EG = 1:2). Though smooth Zn–Ni electrodeposits were achieved, the reactions at the counter electrode (anode) were undetermined and require further investigation. In addition, they also encountered issues associated with the solubility of metal salts (ZnCl_2), metal ions (Zn(II)), and composition control. The conductivity and purity of the deposit were reported to be lower, thereby affecting the efficiency of the process, and had a significant impact/influence on the morphology of the deposit and deposition rate. Moreover, Zn–Ni coatings are prone to sacrificial dissolution of the zinc in the zinc-nickel coating, which hinders its commercial potential in the electroplating sector. Furthermore, electrodeposition of binary Zn–Ni alloys produced from ILs resulted in the formation of Ni rich alloys, known as anomalous deposit, and displayed more positive corrosion potential than that of ferrous substrates, making the Zn–Ni alloy deposit cathodic to steel, such that they cannot be used for sacrificial protection. Moreover, the deposit obtained using the additive-free ChCl/EG-based ionic liquid did not cover the entire surface of the electrode and resulted in the formation of small crystallites without a defined shape. The hygroscopic nature of ChCl-based ILs calls for a long drying procedure, thereby affecting the overall economy of the process. Addition of water to DESs (such as ChCl/urea/EG) for the deposition of Zn–Ni is considered to be one of the effective ways to control the Ni content while favoring the Zn deposition. The addition of water to these systems, in general, does not change the potential window, owing to the fact that the systems reported in literature (i) are less susceptible to moisture, (ii) shift the reduction potential of zinc(II), and (iii) favor the Zn deposition and suppress the growth of nickel. Li et al. [44] studied the deposition of Zn–Ni coatings from the reline- $x\text{H}_2\text{O}$ system (ChCl/urea = 1:2; $x = 0, 1, 3, 5$, and 7 wt %). The CV results showed the system was stable in the electrochemical window between -1.12 V and 1.25 V (vs. Ag/AgCl) for $x \leq 5$ wt %. The stable electrochemical window of the reline- $x\text{H}_2\text{O}$ systems was attributed to the hydrogen bonding between the water molecules and urea, which can suppress the hydrogen evolution reaction to some extent, while increasing the conductivity up to 5 wt % water content in the system. When the water content is increased to 7 wt %, the electrochemical window of the reline-7 H_2O system decreases and becomes unstable, indicating water electrolysis. SEM results displayed a change in morphology from irregular clusters with holes and cracks with no water content to a uniform and compact surface with fine spherical like clusters when the reline (ChCl/urea = 1:2) contained 5 wt % water. Furthermore, X-ray diffraction (XRD) results showed that Zn–Ni alloys deposited from reline (ChCl/urea = 1:2) exhibited a change in phase with the increase in water content. At 0, 3, and 5 wt % water, α -phase Zn–Ni (an Ni rich phase), a mixture of α and γ -phase Zn–Ni, and a single “ γ ” (Ni: 12 to 16%) phase Zn–Ni were observed, respectively. The best corrosion protection was observed when Zn–Ni was deposited from reline-5 H_2O system (ChCl/urea = 1:2 containing 5 wt % water).

Another suitable way to solve the problem of overcoming the anomalous co-deposition of Zn–Ni alloys is to design ILs with metal complexes as part of their structures [14]. Development of ILs with metal containing cations can facilitate the charge balancing anions owing to their easy accessibility to the electrode surface, reducing the polarization and improving the energy efficiency of the process [45]. Besides, grain size and predominant grain orientation of the metal can be controlled by varying the deposition temperature. Steichen et al. [46] studied the electrodeposition of zinc from homoleptic and heteroleptic zinc(II)-containing liquid metal salts with *N*-alkylimidazole (AlkIm) ligands and bis(trifluoromethylsulfonyl)imide (TF_2N^-) anions. Zn–Ni deposits were achieved with metal-based ILs such as [1-*n*-butyl-1-methylpyrrolidinium] bis((trifluoromethyl)sulfonyl)imide [TFSI][BMP]. Employing such ILs and applying the advance plating techniques such as electromagnetic, compositionally modulated multilayer, and pulse plating may considerably enhance the deposition rates of zinc and zinc–alloy with desired thickness and alloy composition, while avoiding the water chemistry and associated defects [47]. However, high current densities ($>-200 \text{ mA cm}^{-2}$) are required to achieve the zinc deposit. The results of Zn–Ni alloy deposition from Yang et al. [40] yielded poor solubilities and the poor co-ordination ability of the [TFSI][BMP], which displayed a poor deposit, coverage, and efficiency. Therefore, the choice of suitable coordinating ligands and charge-balancing anions will be a key challenge in determining the mass transport and the complexity of electrodeposition.

4. Influence of Additives

Few authors have addressed this problem by employing additives in the electrodeposition of zinc and zinc-based alloys from ILs. Additives function as complexing agents, brightening agents by complexing the metal ions and decreasing their reduction potential, by specific adsorption of an organic species on the electrode surface, blocking nucleation and hindering growth.

4.1. Zinc

Additives also function as levellers and brighteners when added to the electrodeposition baths. As a levelling agent, the additive molecules are adsorbed on the high points of the substrate surface (most active sites), and hinder the deposition of metal ions while favoring the metal deposition on low points. Such a deposit exhibits uniform thickness with a good coverage and throwing power. Brightness is related to the smoothness of a surface, which can reflect visible light. As a brightener, additive molecules influence the size of the metal deposited and result in the formation of crystals that have a size smaller than 400 nm. Such deposits produce a reflective surface under visible light conditions, indicating a good degree of brightness. In addition, they also play an important role in tailoring the crystal orientation. Al-Esary [48] studied the effect of additives—nicotinic acid, boric acid, and *p*-benzoquinone—on the deposition of Zn from ethaline ($\text{ChCl}/\text{EG} = 1:2$), and achieved a mirror-like finish on copper substrate with nicotinic acid as the additive. Boric acid and *p*-benzoquinone improved the brightness of the Zn deposit, demonstrating that they can be employed as brighteners. However, these additives resulted in a slight decrease in the conductivity of the ethaline electrolyte. Koyama et al. [49] studied the effects of dihydric alcohols—ethylene glycol, 1,3-propanediol, 1,2-butanediol, and 1,3-butanediol—on the electrodeposition of Zn from 1-ethyl-3-methylimidazoliumbromide/ZnBr, demonstrating that the addition of each of these species enhanced the cathodic current efficiency, obtaining a smooth Zn deposit in all cases. Ethylene glycol was reported to be the superior to other three alcohols in terms of brightness and smoothness of the deposit; cathodic current efficiency when the deposition of Zn is performed within the applied current density range between 50 and 250 A/m^2 . Moreover, the addition of the alcohols $>50 \text{ mol } \%$ concentration resulted in a grey deposit with the formation of dendritic deposits at the edges. Abbott group [50] studied the electrodeposition of zinc from ChCl-based DESs, ChCl/urea and ChCl/EG, employing a series of polar additives including ethylene diamine, acetonitrile, and ammonia. They found that the additives formed a complex with the chloride ions, evidencing the complexing nature of the additive. However, the reports suggested that the additives did not affect the speciation of the metal complex, but shifted the onset in reduction potential as shown in Table 2

and improved the brightness of the deposit. The addition of ethylene diamine and ammonia had a significant brightening effect, probably owing to their ability to inhibit the adsorption of chloride at the electrode surface. Ibrahim et al. [51] demonstrated the effect of acetonitrile and ethylene diamine on the deposit morphology and grain size of zinc coatings electrodeposited from ChCl/urea. They showed that the additives influenced the nature of the zinc deposit from ionic liquid by modifying the morphologies and grain sizes. Pereira et al. [52] reported on the influence of the tartrate ion on the electrodeposition of zinc from the ChCl/EG mixture, reporting that tartaric acid modified the nucleation mechanism of zinc deposition and the morphology of the resultant deposit. The same group extended the work further and studied the influence of organic additives—acetamide, dimethylacetamide, and dimethyl sulfoxide (DMSO) on Zn electrodeposition from choline chloride/ethylene glycol mixture. The addition of acetamide to the ionic liquid displayed an irregular deposit, whereas a uniform deposit was obtained in the presence of dimethylacetamide, and the addition of DMSO did not display a major change in the morphology of the deposit. On comparing the polarization data, Zn deposit with DMSO exhibited the best corrosion resistance. The authors evidenced the fact owing to the compact morphology obtained with the addition of DMSO, which displayed a porosity-free deposit, contributing to the corrosion resistance [53].

Table 2. The onset in reduction potential for the Zn deposition in deep eutectic solvents using different additives [50].

System	Additive	Onset Reduction Potential (V vs. Ag wire)	Difference in Potential (mV vs. Ag wire)
ChCl/urea (1:2 molar ratio)	Nil	−1.080	—
	Acetonitrile	−1.080	0
	Ethylene diamine	−1.120	−40 ¹
	Ammonia	−1.020	60
ChCl/EG (1:2 molar ratio)	Nil	−1.080	—
	Acetonitrile	−1.080	0
	Ethylene diamine	−1.034	46
	Ammonia	−0.991	92

¹ Negative values indicate an increase in shift in reduction potential.

4.2. Zinc-Nickel

Additives play an important role in the Zn–Ni electroplating bath in improving the physical and mechanical properties of the coating such as brightness, roughness, thickness, and hardness, and making the Zn–Ni alloy deposits suitable for corrosion mitigation applications [54]. Additives, when introduced into the electroplating bath, improve the operating performance in terms of cathodic current efficiency, throwing power. Moreover, they control the Zn/Ni alloy ratio, grain size, and crystal orientation, and improve the morphology of the coatings. Thus, with proper selection of additives during Zn–Ni electrodeposition, it is possible to tailor the composition and morphology by selective reduction of either Ni(II) ions or Zn(II) ions. Fashu et al. [55] studied the influence of ethylene diamine tetra acetic acid (EDTA) and ammonium chloride (NH₄Cl) additives on electrodeposition behavior of Zn–Ni alloys from ChCl-based ionic liquid and investigated the composition, morphology, and corrosion performance. The authors found that the addition of ammonium chloride (NH₄Cl) to the ChCl-based ionic liquid refined the grain size of the electrodeposited Zn–Ni films, reduced the Zn content, and increased the cathodic current efficiency of the Zn–Ni deposits and corrosion resistance. In addition, increasing the EDTA concentration resulted in the Zn content of Zn–Ni film, reduced the grain size of the deposits. However, the conductivities and current efficiency of the Zn–Ni ionic liquid electrolytes decrease with the increase in EDTA concentration. Amines are often added as additives owing to their ability to improve the surface coverage of the deposit. Pereira et al. [56] described the effect of adding ethylamine and ethylenediamine to the ChCl/EG eutectic-based ionic liquid on the electrochemical profile of Zn–Ni and deposit morphology. The surface coverage was shown to

be significantly improved after the addition of amines to the plating bath containing the ionic liquid system. The results showed that Zn–Ni alloy obtained with ethylenediamine when added as an additive has the higher corrosion resistance, owing to better grain refinement increase of corrosion potential. Al-Esary [48] studied the effect of additives—boric acid and sodium bromide—on the Zn–Ni deposit in ChCl/2EG, demonstrating that boric acid worked as a brightening agent in refining the crystal size in the Zn–Ni deposit, while sodium bromide contributed towards increasing the conductivity and cohesion of the Zn–Ni deposit. However, the Ni content of the Zn–Ni deposited from the ChCl/2EG-based IL containing the additives reported an increase up to 71.5%, and the alloy became electrochemically more noble and less sacrificial to the steel substrate.

4.3. Ionic Liquids as Additives

Another aspect of Zn and Zn–Ni alloy electrodeposition is that ILs themselves can be used as additives during plating from aqueous electrolytes as a grain refiner, to improve the properties of the deposit, as mentioned previously [57]. ILs as an additive can facilitate charge transfer to the metal ions by forming a cationic complex with the metal ions. Besides, adsorption of ILs on the surface resulted in a smoother and bright deposit, owing to the good charge transfer reactions at the electrodes. Studies showed that the nature of the deposit in terms of grain size and morphology can be altered by employing ILs as suitable additives [58]. Though additives have been proven to enhance the desirable properties of the deposit, the detailed role they play in the electrodeposition of zinc and zinc nickel alloys needs further attention. Deposition using ILs and DESs such as ChCl/EG/urea resulted in the formation of electrolytic breakdown products such as 2-methyl-1,3-dioxolane and chlorinated products, which included chloromethane, dichloromethane, and chloroform in small quantities [59,60]. Further, the challenges with some ILs, such as toxicity, production complexity, and high cost in the process for use, hinders their application in the electrodeposition of zinc and zinc alloys. These need to be addressed. In addition, the high viscosity of ILs can alter the mass transportation of species and present significant issues, resulting in poor throwing power and non-uniformity of coating thickness.

5. Substrate Effect

In recent years, research has focused on the development of lightweight metals and their alloys in applications such as aerospace. The wide spread use of lightweight metals such as magnesium, aluminium, and their alloys have been gaining significant attention owing to their lightweight, density, and so on. Additional properties that contribute to the lightweight metal alloys' versatility in the automotive, electronic, and aerospace industries include a high thermal conductivity, high dimensional stability, good electromagnetic shielding characteristics, high damping characteristics, good machinability, and easy recyclability. These properties make magnesium and aluminium alloys of particular interest to the automotive and aerospace industries, where the weight reduction provides a simple means to achieve higher fuel efficiencies without sacrificing structural strength.

Despite their widespread use and valuable properties, these metals are reactive and corrode aggressively in a humid atmosphere and corrosive environment, such as marine, and in an aqueous environment containing anions such as chloride (Cl^-), fluoride (F^-), bromide (Br^-), and sulphates (SO_4^{2-}). Alloying with metals such as manganese (Mn) and certain rare earth elements improves their corrosion resistance. However, these alloys are known to be susceptible to galvanic corrosion owing to the segregation of the constituents on one hand and the presence of a humid atmospheric or aqueous environment on the other. The possibility of galvanic corrosion arises when dissimilar metals are in electrical and electrolytic (salt solution, acids or alkalis) contact. The more active metal (lower electrode potential) is likely to undergo corrosion. Galvanic corrosion is influenced greatly by the difference of electrode potentials, ratio between the areas of anode and cathode, and electrical conductivity of the electrolyte. While techniques such as dissimilar material joining (DMJ) have been gaining significant attention owing to their multi-functional advantages, riveting (involving hole drilling) is considered to be the widely used technology in the automotive sector. However, the risks

and costs associated with the hole making operations (drilling, stamping, and so on) are mostly from the galvanic corrosion problems [61]. Moreover, anions such as Cl^- , Br^- , I^- , and SO_4^{2-} promote local and generalized corrosion, and result in severe pitting in the metal losing its mechanical stability. To overcome these challenges, one of the most effective ways to prevent the substrate from corrosion is to provide a uniform, pore free metallic coating, which not only acts as a corrosion resistant coating in harsh environment, but also prevents it from physical damage with good adhesion [62]. However, there are certain challenges associated with the plating of Zn and Zn–Ni on substrates that are reactive in nature. For example, the extreme reactivity of magnesium shall inhibit good adhesion of the Zn and Zn–Ni deposit and result in peeling of the coating. Another challenge in the plating of such substrates is that the quality of the coating is affected by the formation of intermetallic species at the grain boundaries and the creation of non-uniform surface potential across the substrate. Therefore, the development of non-aqueous based systems for plating of such substrates shall not only eliminate the aggressive reactions observed in the case of acidic solutions, but also improve the quality of the Zn and Zn–Ni coatings, and improve the corrosion resistance of the components used for aerospace and automotive applications.

Electrodeposition of Zn and Zn–Ni alloys on these substrates from ILs can be employed to protect the substrates from corrosion and hydrogen embrittlement (due to hydrogen generation in case of aqueous systems). Bakkar et al. [63] studied the electrodeposition of Zn onto pure Mg substrate and Mg-alloys, AZ31 and AZ91, using two different types of ChCl-based ILs. One type of IL is formed by mixing choline chloride (ChCl) with different hydrogen bond donors: urea, EG, malonic acid (mal), and glycerol (Gl), with appropriate molar ratios. The other type is formed by mixing ChCl with a metal halide, ZnCl_2 . They investigated the corrosion behavior and reported the corrosion resistance (in terms of corrosion currents), as shown in Table 3. On the basis of the works reported by Bakkar et al. [63], from Table 3, the corrosion currents (I_{corr}) for the Zn deposition on ChCl/urea and ChCl/Gl ILs were observed to be 0.48 and 0.49 mA cm^{-2} , respectively.

Table 3. The electrochemical parameters obtained from the polarization of Zn deposition in different ionic liquids on different substrates [63].

System	Substrate	Temperature, °C	OCP (mV vs. Pt)	E_{corr} (mV vs. Pt)	I_{corr} ($\mu\text{A cm}^{-2}$)
ChCl/ ZnCl_2	Mg	60	−1253	−1207	3.86
ChCl/ ZnCl_2	Mg	25	−1863	−1857	3711.17
ChCl. ZnCl_2	Low carbon steel	25	−664	−651	109.42
ChCl/urea	Mg	60	−1531	−1446	0.48
ChCl/EG	Mg	60	−1489	−1347	12.72
ChCl/Gl	Mg	60	−1594	−1557	0.49
ChCl/Mal	Mg	60	−1962	−1940	31.58

OCP: Open circuit potential; Gl: glycerol; Mal: malonic acid.

However, Zn deposited using ChCl/Gl IL suffered from pitting of the magnesium substrate and also displayed few microcracks. These cracks are reported to be eliminated by changing the mode of deposition from constant current to pulse current. The authors concluded that an increase in the nucleation rate of the electrodeposited atoms resulted in the formation of smaller grains, producing a shinier, smoother deposit with a lower number of cracks. In addition to the choice of ionic liquid, the temperature and water content of the ionic liquid plays a major role in influencing the interaction with substrates. However, the presence of water content alone in the ChCl/Gl did not guarantee the pitting of pure Mg substrate. Table 4 shows the works on the Zn and Zn–Ni carried out on different commercial substrates. Deng et al. [64] investigated the electrochemical reduction of Zn(II)/Zn on Mg alloy substrates in N-butyl-N-methyl-pyrrolidinium dicyanamide ([BMP][DCA])-based IL by performing constant voltage deposition in the range −2.3 V to −2.5 V (vs. Fc/Fc^+). A low melting point water stable IL with good metal (Zn) solubility is formed by mixing dicyanamide ([DCA]) and 1-butyl-1-methylpyrrolidinium [BMP]. The authors reported the formation of complex ions between Zn(II) and DCA anions. The high solubility of ZnCl_2 in the BMP-DCA-based IL was attributed to the formation of complex ions between Zn(II) and DCA anions. In addition, ([BMP][DCA]) IL is reported

to have a wider cathodic potential window than 1-ethyl-3-methylimidazolium ([EMIm][DCA])-based IL. The results suggested that $[\text{Zn}(\text{DCA})_3]^-$ complex anion was formed through the reaction of Zn(II) with DCA^- anions, which later was reduced to Zn metal through a single-step electron transfer process. Current transient results confirmed that the electrodeposition of Zn involved three-dimensional instantaneous nucleation under diffusion control. SEM and adhesion test data results confirmed that a compact and well adherent Zn coating can be deposited on the Mg alloy in the ionic liquid when deposited in the potentials up to -2.4 V. The corrosion behavior of deposited Zn coatings, produced at -2.3 V and -2.4 V, was shown to be better in comparison with the bare Mg substrate. The lower protective performance of the Zn deposited at -2.5 V was attributed to its high porosity and surface area owing to its spongy structure. A large pore size would allow a rapid mass transport of species, permitting the chloride species to reach the Mg substrate and corrode the surface.

Table 4. The Zn deposition in different ionic liquids on different substrates.

Ionic Liquid	Substrate	Zn/Zn-Ni	Reference
HEAP/ZnCl ₂	ITO	Zn	[6]
ChCl/EG	Steel (AISI 304)	Zn	[25]
[BMIMCl]/ZnCl ₂	Carbon steel sheet (S235JR)	Zn	[31]
ChCl/urea	Cu	Zn-Ni	[40]
ChCl/EG	Cu	Zn-Ni	[43]
ChCl/urea	Carbon steel	Zn-Ni	[44]
ChCl/urea	Steel	Zn	[51]
ChCl/ZnCl ₂	Mg	Zn	[63]
ChCl/ZnCl ₂	Mg-alloy (AZ91, WE43, QE22, MgGd5Sc1, MgY4Sc1)	Zn	[63]
ChCl/ZnCl ₂	Low carbon steel	Zn	[63]
ChCl/urea	Mg	Zn	[63]
ChCl/EG	Mg	Zn	[63]
ChCl/GI	Mg	Zn	[63]
ChCl/Mal	Mg	Zn	[63]
[BMP-DCA]/ZnCl ₂	Mg	Zn	[64]
ChCl/EG	Ti/TiO ₂	Zn	[65]
ChCl/EG	Alumina	Zn	[66]
ChCl/Lac	Low carbon steel	Zn	[67]
[BPyI]/ZnCl ₂	Cu	Zn	[68]

Lac: lactic acid; [BMP-DCA]: N-butyl-N-methyl-pyrrolidinium dicyanamide; HEAP: 2-hydroxyethyl ammonium propionate; [BMIMCl]: 1-butyl-3-methylimidazolium chloride; [BPyI]: 1-butylpyrrolidine.

This behaviour can be attributed to the differences in the adherence of ionic liquids cations to the substrate, which affects the deposition characteristics [69]. Though significant works on the Zn deposition on certain light metals, such as Mg-based, in non-aqueous environments has been studied, a complete characterization of the behavior of the substrate still requires detailed research. Factors such as these play a significant role in further development of ILs for the deposition of Zn and Zn-Ni on the Mg- and Al-based alloys, and newly developed lightweight metal alloys as substrates such as Al-Ti and Al-Li and must not be overlooked.

6. Recent Developments

In general, cation plays an important role in controlling the physical properties of the salt and anion on the stability and chemical reactivity. While the cationic structure and size control the mass transport of metal ions to the electrode surface, anions will influence the co-ordination geometry around the metal ion, reduction potential, reduction current, and nucleation. In addition, anions will also affect the conductivity and viscosity of the ILs. The other important role that the cation probably plays in electrodeposition is in controlling the Helmholtz double layer thickness and structure. This area is practically unstudied for the zinc and zinc alloy deposition, although few reports have shown that the cation appears to control the morphology of zinc deposited from various triflamide-based ILs.

A vast number of ILs (estimated to be more than 10^{18}) [70] have been developed over the past 20 years, which is indicative of the possible future market. Further, it is also evident that new classes

of ILs will be developed in the coming years. The choice of ionic liquid electrolyte for depositing Zn and Zn–Ni alloys depends on the reduction potential of the metals and the potential window of the liquid. However, it is worth noting that reduction potentials are significantly affected by the co-ordination of the anion to the Zn metal and its alloys. Alternative precursor salts to halides (chlorides, bromides, fluorides), with high solubility in ionic liquids, must be considered in order to have an inert environment with good conductivity (10 mS cm^{-1}). Panzeri group [71] demonstrated the possibility of obtaining a potentially high quality deposit by reducing the concentration of chloride in the ionic liquid-based plating system. Though the release of chlorine gas was controlled to an extent, they failed to maintain the conductivity. Attempts were made by the introduction of acetate precursor salts in organic solutions as the supporting electrolyte for the electrodeposition of zinc while eliminating the chloride source. Rivas et al. [6] studied the electrodeposition of zinc from chloride, acetate, and propionate-based ILs, and compared the results with coatings obtained using aqueous media. The results displayed a good efficiency and selectivity when Zn propionate was used as a zinc source in the 2-hydroxyethyl ammonium propionate (2-HEAP) ionic liquid-based system, while maintaining a smooth and homogeneous deposit. However, the conductivity and long-term stability of the ionic liquid-based system were not studied. Panzeri et al. [72] developed a chloride-free ionic liquid electrolyte using ethylene glycol as the main supporting electrolyte and zinc acetate as the precursor salt and sodium acetate to increase conductivity. However, the anodic secondary reactions resulted in the formation of acetate-based byproducts. Though the ability of the ILs to electrodeposit zinc and zinc alloys and capability to engineer the redox chemistry are well recognized, the control of metal nucleation characteristics lacks significant research.

Therefore, choosing the right combination of ionic liquid as a supporting electrolyte and additive that can tune the properties of the zinc/zinc nickel alloy deposit remains a primary challenge. In addition, systematic investigations on the electrochemical potential window to characterize the electrochemical stability and tune the zinc/zinc alloy deposit properties need a detailed study. Furthermore, the electrodeposition of zinc and zinc nickel alloys employing ionic liquids as supporting electrolytes on different types of conductive substrates such as high strength steel, aluminium, and aluminium alloys [66] and transparent conductive oxides like indium tin oxide [6] is expected to show great interest for applications in aerospace, corrosion protection, batteries, and photocatalysis. Most of the reports suggest that ILs have the potential to deliver more sustainable plating systems owing to their ability to tailor redox potentials and achieve desired alloy formation with good deposit properties. In addition, the quality of metal and metal-alloy deposits depends on the pretreatment/cleaning of the substrate before electroplating. Pretreatment of substrate involves the surface cleaning of substrate by degreasing in a solvent or a surfactant-based solution, followed by an aqueous pickle, rinse, and anodic etching to remove the oxide film, prior to deposition. It is worth noting that metal substrates such as aluminium (Al) and magnesium (Mg), having large negative electrode potentials, require larger anodic pulses for a longer period to remove the adherent oxide. In such a context, ILs can be considered as a potential alternative to remove the oxide/hydroxide layer of the substrates before deposition in ILs. The substrates pretreated using ILs will differ from aqueous pretreatments, thereby eliminating the need for drying before deposition and overcoming the problem of oxide/hydroxide layer formation, with reactive, rapidly oxidizing metals. Moreover, careful control of IL droplets (also known as droplet elimination) after deposition from the surface is very important when plating in ILs, because droplets act as weak points for the deposited layers and result in peeling off from the substrate [73]. Therefore, the surface preparation before Zn and Zn–Ni alloy plating and droplet elimination after the plating process are considered to be the key issues that require significant attention for obtaining a deposit with good adhesion in the case of fasteners, joints, bolts, and so on. In addition, recycling, regeneration, and reuse of ILs from plating solutions and rinse waters remains challenging [74].

7. Industrial Scope

If ILs are to be employed for electrodeposition on a larger (industrial) scale, the effect of impurities either emanating as a byproduct from the synthesis of ILs or traces of water in the form of drag-out needs to be considered. Adopting the ionic liquid-based system on an industrial scale for electroplating applications requires suitable recycling and disposal methods [75,76]. Though the non-volatile nature of the ILs makes them attractive for electroplating applications, there are certain issues associated with them when employed at industrial scale. In addition, the high viscosity of ILs affects the mass transportation of the species, which leads to the low mobility and diffusion coefficient of metal ions. Therefore, the design and preparation of ILs with the desired physical and chemical properties such as viscosity, stability, conductivity, and composition require a significant effort. Furthermore, ionic liquids cannot be easily purified by conventional methods such as distillation. An additional issue that might arise during the scale up is the heat capacity of the ionic liquids. On the basis of the work reported by Waliszewski et al. [77], the heat capacity values of imidazolium and pyridinium salts were in the range of 300 to 600 J K⁻¹mol⁻¹, indicating that the ILs might actually have to be cooled rather than heated. Another disadvantage with the use of some ionic liquids is that they may suffer from ohmic heating, owing to their low electrical conductivity during electroplating. Research on ILs the field of electroplating technology has expanded significantly over the past decade. Once the technical performance of an ionic liquid is fully demonstrated, it becomes obvious that, at a certain point, the price determines the final commercial success of a product as it decides the economic feasibility of the IL-based system or process. At that point, a good marketing strategy is to explain that the higher costs of using ILs also bring added value. Any available cost analysis for a given plating system is usually based upon academic research, because of the trade secrets and commercial sensitivity involved in the proprietary electrolytes developed by industries and commercial organisations. Thus, the cost discussions on Zn and Zn–Ni alloys are based upon the information available in the literature on non-commercial electrolytes used by various science and engineering research laboratories. It is, however, worth noting that most of the academic work is primarily initiated after conducting a survey of literature and discussions with commercial electroplaters. Figure 2 shows the cost comparison of ionic liquid-based systems against aqueous electrolytes considering an industrial scale of 100 L make up. The cost is calculated considering the quantity of individual constituent components required for the IL-based system from the references [6,43,50,72,78] and the value of each constituent is calculated based on the Sigma-Aldrich and Merck pricing. From Figure 2, ILs seem uneconomical compared with traditional aqueous and organic solvents owing to their high cost, which greatly prohibited their applicability on a large scale. However, it is worth noting that recycling the drag out solution (process solution transferring into subsequent rinse water tanks) shall enhance the life of the ionic liquid-based plating solution, saving cost while eliminating the environmental impact of the process due to the drag out (reducing the source of pollutants). The plating solution and the rinse water can be recycled many times without affecting the quality of the coatings formed, as long as the contamination level is closely monitored. After performing Zn and Zn–Ni alloy plating using ionic liquid-based systems, a film of the bath solution will remain on the parts, the rack, or barrel and remain in cavities and gaps owing to their high viscosities [79]. Hence, corresponding measures should be taken to tackle the problems mentioned above and a key objective of future research should focus on not only reducing the cost of the ILs, but also minimizing the practical problems associated with the process. The scope of ionic liquids in the electroplating process of Zn/Zn–Ni alloys for aerospace applications depends on its impact on the environment.

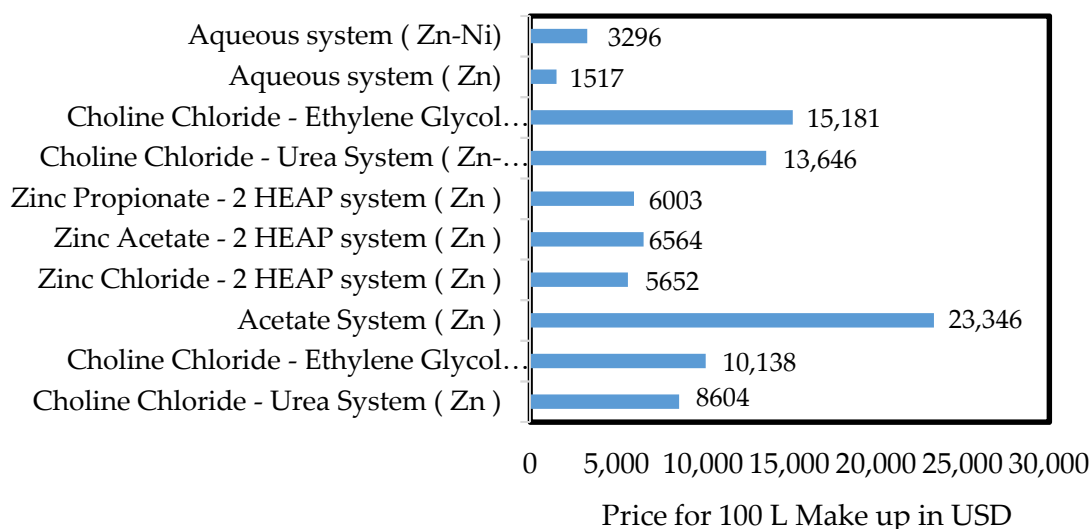


Figure 2. Plot showing the cost comparison of the ionic liquid based systems against the aqueous systems considering the initial make up of 100 L solution. HEAP: 2- hydroxyethyl ammonium propionate.

The fact that harsh, environmentally unfriendly chemicals in deposition baths may be replaced by recyclable ionic liquid electrolytes and contribute to the current efficiencies might be a selling point for ILs. While the ILs are expected to progressively become more inexpensive and available, significant research in the electroplating of Zn and Zn–Ni systems will help to explore the mechanism and rules underpinning the electrodeposition process. On one hand, ILs have been gaining popular attention in the field of electroplating and attracting industries majorly in the aerospace and automotive sectors. On the other hand, the stability of most ILs developed so far under practical plating conditions such as varying current densities and temperatures is still unknown. In addition, most deposition studies performed so far are carried out in laboratory conditions and data in practical plating systems are scarce. One of the main issues associated with large-scale electroplating using ILs is to achieve a reproducible surface finish with desired throwing power (ratio of deposit thickness at high current density to thickness at lower density ~ 1.0). The life of the Zn and Zn–Ni alloy coatings deposited from ionic liquid based system is a key factor that needs significant consideration in the aerospace sector. Testing protocols may need further development to assess the coating quality and life in laboratory that mimic real service conditions.

Understanding the factors related to the mass transportation of the species and complexation owing to the metal speciation are expected to help in the design of more efficient ionic liquid systems and development of methods for monitoring the properties of ionic liquid plating baths. Performing the evaluation, validation studies on the deposition of zinc and zinc alloys shall enable the IL-based system to match the most practical plating systems. Besides, developing halide-free ILs as electrolytes for the electrodeposition of zinc and zinc-based alloys on a larger scale will also address the environmental issues prevailing in the electroplating industry and favor the automotive sector, while deposition on lightweight metal alloy structures such as Al, Al-alloy, Mg, and Mg-alloy shall drive the aerospace industry towards a sustainable technology. Issues associated with the use of ILs include the REACH approval costs associated with the development of new compounds and their listing under the European rules: end-of-life vehicles (ELV), waste electrical and electronic equipment (WEEE), and restriction of hazardous substances (RoHS), and finding technical solutions to lower the costs on one hand. On the other hand, transferring the technology from academia to the industry and translating it into products with commercial value will boost the possibility of ILs entering more markets in the near future.

8. Summary and Outlook

ILs have gained significant attention in the past decade and are expected to enter the commercial market as a possible candidates to replace the existing aqueous technology for the deposition of Zn and Zn–Ni alloys. This review highlighted the progress in the development in the electrodeposition of Zn and Zn–Ni alloys covering a wide range of electrolytes, from traditional chlorozincate-based ionic liquids to acetate and propionate-based ones. In addition, the review also focused on the ILs employed so far for corrosion-resistant coating applications in the electroplating sector. Much of the work covered in this review is based on the Zn and Zn–Ni alloy electrodeposition from choline chloride-based ILs such as ChCl/urea/ethylene glycol/malonic acid/glycerol on different substrates (and their characterization). Studies on the protic ILs and other IL alternatives to ChCl-based ones for the deposition of Zn and Zn–Ni alloys are scarce, and these needs to be explored further. Furthermore, the influence of the chain length of ionic liquid cation on the quality of the deposit; deposit characteristics such as grain size, nucleation, and growth mechanism; Zn–Ni alloy formation; and corrosion performance of the newly developed ILs needs detailed study. While other systems such as acetate- and propionate-based ones have been gaining significant attention as an alternative to chloride-based systems, the regulating effects of parameters such as the concentration of metal salts, additives, and water content on the electrodeposition process in such ILs, in relation to mass transport, speciation, and interfacial structure, need detailed study. Many of their properties need to be understood sufficiently to exploit them in industrial applications. Nevertheless, many challenges remain. In addition, studies on the development of ionic liquids (ILs) involving simple and lineal cations and anions to improve the electrodeposition of zinc are scarce. The development of halide-free ionic liquids as electrolytes for the electrodeposition of Zn and Zn–Ni alloys is likely to address some challenges in the electroplating industry, such as environmental toxicity owing to the release of chlorine gas and formation of chlorinated compounds, and support the automotive and aerospace sectors in becoming more environmentally friendly.

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