



Original scientific paper

## Electrodeposition of zinc-nickel alloys from ethylene glycol-based electrolytes in presence of additives for corrosion protection

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Received: May 19, 2023; Accepted: July 17, 2023; Published: July 27, 2023

### Abstract

*In the present work the electrodeposition of zinc-nickel alloys with 15-20 wt.% nickel from non-aqueous solutions based on ethylene glycol is investigated. Potentiostatic deposition conditions are used, which are found to offer optimal coating quality and superior control over composition. In addition, ammonium chloride is evaluated as additive to partially suppress nickel incorporation into the deposit and to enhance layer quality. Layers composition, surface morphology of the deposits and their anticorrosive properties are investigated. The electrochemical characteristics of the Zn-Ni electrolytes are studied using cyclic voltammetry measurements. From the phase composition point view, X-ray diffraction results confirm that a metastable  $\gamma$  phase is present in the as deposited Zn-Ni alloys with nickel content 16-18 wt.%. Corrosion tests show that the barrier behaviour against corrosion of Zn-Ni films electrodeposited from the  $\text{NH}_4\text{Cl}$  containing bath is superior in comparison to layers plated from an additive-free bath. The use of the additive enlarges the grains and provides a compact surface structure, which upskills the anticorrosive behaviour of the deposit.*

### Keywords

Plating, non-aqueous solvent, ammonium chloride, anticorrosion coating

### Introduction

Zinc has a number of characteristics that make it a well-suited corrosion protective coating for iron and steel products. Zinc excellent corrosion resistance in most environments accounts for its successful use as a protective sacrificial coating on a variety of products and in many exposure conditions [1]. There are different ways to apply zinc coatings on steel-based products such as hot-dip galvanizing, sherardizing, thermal spraying or electroplating and each of them has unique features. Among the protective methods, electrodeposition provides a smooth and hard surface,

good bonding between the deposited layer and metal substrate, easy control of the coating thickness and the possibility to deposit metallic alloys [2].

The latter point is of particular interest, since it is well-established that zinc alloys can provide better protection than pure zinc; therefore, zinc alloys have a great practical importance in the field of coating technology [3,4]. According to the available literature, electrodeposited Zn-Co [5], Zn-Ni [6], and Fe-Zn [6] can improve the corrosion resistance properties in comparison to pure zinc layers. Currently, Zn-Ni alloy coatings have become an important and eco-friendly alternative to toxic cadmium coatings [7,8]. Among the possible film compositions, zinc-rich stoichiometry is one of the most exploited due to the low corrosion potential ( $E_{corr}$ ) of the  $\gamma$ -phase (9-15 wt.% Ni) that makes it an ideal sacrificial layer in case the substrate is exposed to the environment [2].

Generally, aqueous solutions of a simple salt or a complex salt type are preferred in various industrial applications for the electrodeposition of Zn-Ni alloys [9-13]. The major reasons for carrying out electrodeposition in non-aqueous electrolytes (such as conventional organic solvents, ionic liquids and molten salts [14]) are the low vapor pressure and the wide electrochemical window of these media [15,16]. These characteristics make them safe to use for electrodeposition and stable over time. Water content is an important parameter in the case of electrodeposition from non-aqueous solutions, since it considerably influences the electrochemical behaviour of the metallic ions present in the bath, the potential window of the electrolyte and its conductivity/viscosity. In the case of deep eutectic solvents, water contamination can be beneficial or detrimental according to the metal plated [17]. In general, the research on alternative electrolytes is an attractive research topic and new non-aqueous solutions have been developed to apply electroplating processes to metal surfaces [15,16,18,19]. Indeed, non-aqueous electrolytes have been employed to successfully deposit a large variety of Zn-based alloys: Zn-Fe [20], Zn-Mn [21], Zn-Co [22] and Zn-Sn [23]. Water-free solutions have been widely employed also to deposit Zn-Ni [24,25].

One of the aspects of the electrodeposition from non-aqueous electrolytes that has received limited attention in the last years is the use of additives to improve the quality of the deposits. Additives are routinely employed in industrial plating from aqueous solutions to control the morphology of the layers, to prevent pitting or to enhance levelling [26]. However, it is evident that the mechanism of action for additives in ionic liquids is very different to that in aqueous systems. As such, it is probable that additives like brighteners and levellers will be unique to each ionic liquid/metal system studied. In general, looking for additives suitable for electrodeposition in non-aqueous solvents is a matter of major interest in modern electrochemistry. The use of additives has been evaluated, for example, in the case of Ni deposition from choline chloride/ethylene glycol [27,28], for Zn plating from choline chloride/ethylene glycol and choline chloride/urea [29] or for Co deposition from chloride/ethylene glycol [30]. The use of additives has been investigated also for the deposition of alloys. Alesary *et al.* [31], for example, evaluated the effect of some additives on the deposition of Zn-Sn in choline chloride/ethylene glycol. Fashu *et al.* [32], in turn, studied the effect of  $\text{NH}_4\text{Cl}$  and EDTA on the deposition of Zn-Ni in choline chloride/ethylene glycol. In particular, they observed that ammonium chloride influenced the amount of Ni co-deposited. Moreover, the morphology, composition, nucleation, and roughness of the Zn alloy deposits were significantly influenced when the electrodeposition was performed in electrolytes containing this additive.

In the present work, the use of ammonium chloride as additive for the electrodeposition of zinc-nickel alloy on steel substrate has been investigated. The choice of using  $\text{NH}_4\text{Cl}$  was inspired by the interesting results obtained by Fashu *et al.* [32] in the choline chloride/ethylene glycol system. Plating was carried out from a non-aqueous solution for the deposition of Zn-Ni based on the use of

ethylene glycol (EG) as solvent [24]. The electroplating of Zn-Ni alloys was performed using zinc chloride, nickel chloride as metal sources and ammonium chloride as additive to enhance coating quality and uniformity. The effect of  $\text{NH}_4\text{Cl}$  addition was investigated from the electrochemical, morphological and corrosion resistance point of view.

## Experimental

Zinc-nickel alloy was electrochemically deposited on a steel substrate from an organic solution. The bath consisted of anhydrous ethylene glycol (Sigma Aldrich; purity 99.8 %; water content  $\leq 0.003$  %), nickel (II) chloride hexahydrate (Sigma Aldrich; purity  $\geq 98$  %), zinc (II) chloride (Sigma Aldrich; purity  $\geq 98$  %) and ammonium chloride (Sigma Aldrich; purity  $\geq 99.5$  %), which were employed as received. The salts were dissolved in EG according to the following quantities: 0.4 M  $\text{ZnCl}_2$ , 0.05 M  $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$  and 0.6 M  $\text{NH}_4\text{Cl}$ . The resulting electrolytes were used to perform Zn-Ni deposition. Solutions were maintained in temperature (60 °C) by using a thermal jacket during solution preparation, electrochemical characterization and electrodeposition. Annealing at 400 °C for 1h in inert atmosphere ( $\text{N}_2$ ) has been done for some selected samples. A standard three-electrode cell setup, with an AMEL 2550 potentiostat/galvanostat, was employed for the electrochemical characterization. During the cyclic voltammetry (CV), platinum wires were used as working, counter and reference electrodes [33]. Without stirring, a 20  $\text{mV s}^{-1}$  scan rate was applied. In order to perform potentiostatic deposition tests, an AMEL 2550 potentiostat/galvanostat was used. In this case, mild steel plates were used as working electrodes and platinum wires as reference and counter electrodes. Oxides were removed from the steel surface by immersing it in acetone and etching it in a 20 wt.% HCl solution. Cathodic efficiencies in the 60-70 % range were observed for Ni contents ranging from 16 to 18 wt.%. Potentiodynamic polarization tests were done in a 3.5 wt.% NaCl aqueous solution. A 1  $\text{mV s}^{-1}$  scan rate was employed, without stirring. SEM was carried out employing a Zeiss EVO 50 EP setup. XRD was done by a Philips PW1830 ( $K_{\alpha 1\text{Cu}} = 15.4058$  nm) setup. In order to measure the films composition and their thickness by X-rays fluorescence spectroscopy (XRF), a Fischerscope X-ray XAN was employed. Conductivity was measured using an AMEL model 2131 conductivity meter, while viscosity was evaluated using a Haake Viscotester VT5R rotational viscometer. Electrolytes water content was determined *via* Karl Fischer titration with a Metrohm 870 KF Titrino Plus. Repeatability of both deposition experiments and characterization was proofed by repeating the tests at least twice. Atomic force microscopy (AFM) was carried out using a NT-MDT SOLVER PRO (in contact mode). Glow discharge optical emission spectroscopy (GDOES) was performed using a Spectruma GDA 750 analyzer.

## Results and discussion

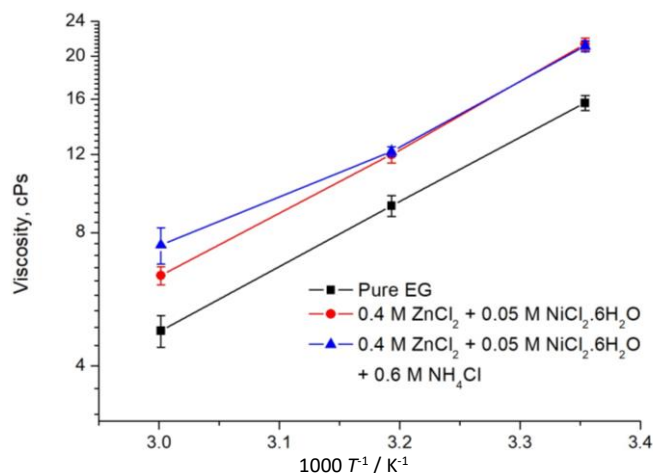
### *Electrolyte water content*

The global amount of moisture present in the electrolyte is an important parameter in the case of electrodeposition from non-aqueous solutions. A relevant percentage of water can considerably influence the electrochemical behaviour of the bath [17] or lead to the co-deposition of a significant level of impurities [34]. The amount of water dissolved in the ammonium chloride free bath has already been determined in our previous work [24]:  $1.42 \pm 0.02$  wt.%. In the present work, however, a relevant amount of ammonium chloride was added to the electrolyte (potentially dragging in more water). For this reason, the amount of water dissolved in the additivated version of the Zn-Ni plating bath based on EG was determined. The Karl-Fischer measurements carried out evidenced a global

water content equal to  $1.63 \pm 0.03$  wt.%. This value is similar to the one observed without  $\text{NH}_4\text{Cl}$ , suggesting a limited impact of its addition on overall water content.

### Electrolytes physical characterization

One of the most important physical properties that must be evaluated, in the case of electrodeposition from non-aqueous electrolytes, is viscosity. Indeed, while aqueous electrolytes are normally characterized by values of viscosity close to that of water ( $\sim 1$  cP), water-free baths can present values significantly higher. These high levels of viscosity can strongly influence the electrodeposition process, limiting ionic mobility. Consequently, viscosity was evaluated for pure EG, for the additive-free solution and for the electrolyte with ammonium chloride as an additive (Figure 1).



**Figure 1.** Viscosity data for pure EG and for the two Zn-Ni electrolytes (with and without  $\text{NH}_4\text{Cl}$ )

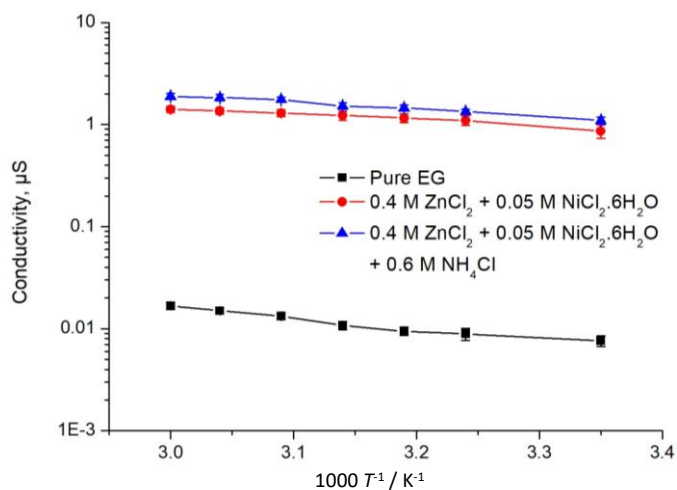
Temperature dependence of viscosity was modelled by Arrhenius law [35], which correlates the viscosity and temperature according to equation 1.

$$\eta_T = \eta_\infty e^{\frac{E_\eta}{RT}} \quad (1)$$

where  $E_\eta$  is the activation energy,  $\eta_\infty$  is the limit viscosity. It appears evident in Figure 1 that salt addition ( $\text{NH}_4\text{Cl}$ ) to pure ethylene glycol increases the viscosity of the solution. Conversely, temperature decreases viscosity due to the increase in ions mobility. Measured viscosities are considerably higher than water, which may constitute a disadvantage for deposition from ethylene glycol-based solutions. High viscosities, indeed, limit the ionic diffusion in the solution [36] and result into lower conductivity [37]. Nevertheless, the viscosity of EG based solutions is significantly lower than most non aqueous based solutions [35] and, in general, compatible with electroplating.

Besides viscosity, also conductivity is a fundamental parameter for an electrolyte intended for electrodeposition. The conductivity of a solution is generally proportional primarily to the concentration and to the type of ions present. Temperature is another important parameter that greatly affects conductivity. Generally, ions mobility in an electrolyte increases proportionally to the temperature [38]. Figure 2 reports the data obtained from the conductivity measurements performed on pure EG, on the additive-free solution and on the  $\text{NH}_4\text{Cl}$  additivated electrolyte.

Pure ethylene glycol is characterized, as expected, by a very low conductivity, due to the absence of dissociated species. The conductivity of pure ethylene glycol strongly increases with the addition of  $\text{ZnCl}_2$  and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ . These two salts readily dissolve and dissociate in ethylene glycol and they yield ions able to efficiently conduct electricity. Moreover, the addition of  $\text{NH}_4\text{Cl}$  further increases the conductivity of the Zn-Ni electrolyte to higher values at different temperatures as shown in Figure 2.

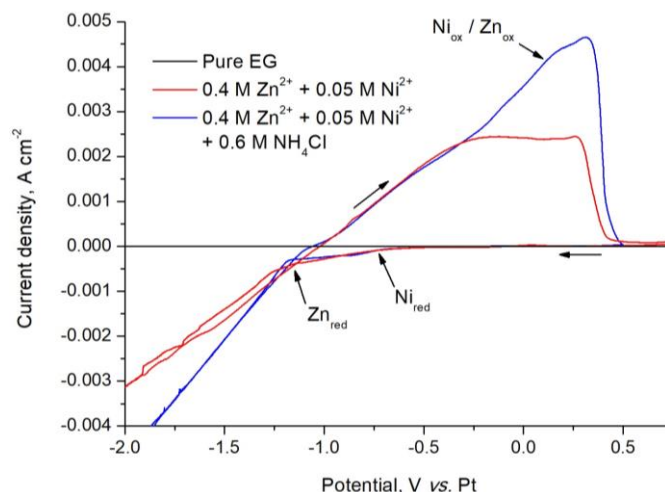


**Figure 2.** Conductivity data for pure EG and for the two Zn-Ni electrolytes (with and without  $\text{NH}_4\text{Cl}$ )

The effect of temperature on conductivity is evident for all the electrolytes, with higher temperatures resulting in higher conductivities. Recorded conductivity values, even though considerably lower than those typical of deep eutectic solvents [35], are compatible with electroplating processes. Deposition was performed at  $60^\circ\text{C}$  exactly to take advantage of the higher ionic mobility, higher conductivity and lower viscosity.

#### Electrochemical characterization

The electrochemical properties of the Zn-Ni plating solutions, both with and without the additive, were studied by cyclic voltammetry (Figure 3). The electrochemical behaviour of pure EG was acquired for comparison.



**Figure 3.** Cyclic voltammetry for pure EG and for the two Zn-Ni electrolytes (with and without  $\text{NH}_4\text{Cl}$ ); scan rate =  $10\text{ mV s}^{-1}$

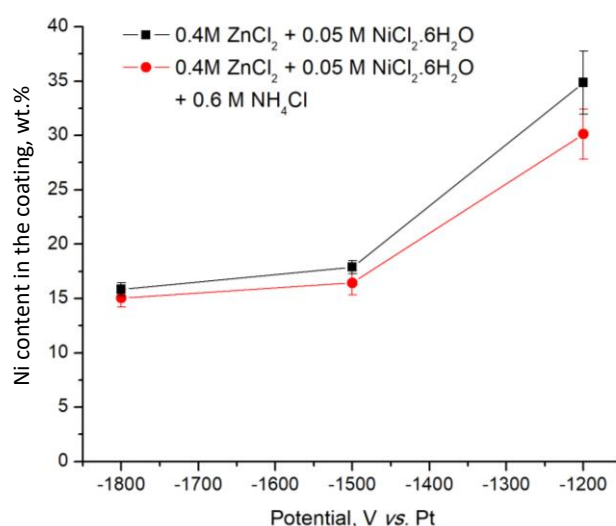
As expectable, the voltammetry of pure EG, due to its very low conductivity, is visible as a flat line. For what concerns the non-additivated Zn-Ni, two clear reduction peaks for the two metals were detected [24]. A neat separation between the reduction potentials of Zn ( $\text{Zn}_{\text{red}}$ ) and Ni ( $\text{Ni}_{\text{red}}$ ) could be clearly observed both with and without the additive. The first was observed around  $-1.25\text{ V vs. Pt}$ , while the latter was observed around  $-0.6\text{ V vs. Pt}$ . The  $\text{Ni}_{\text{red}}$  potential was not substantially changed by the addition of  $\text{NH}_4\text{Cl}$ , while the  $\text{Zn}_{\text{red}}$  potential was slightly shifted towards more positive values ( $-1.2\text{ V vs. P}$ ). In addition, the current density observed at potentials lower than  $\text{Zn}_{\text{red}}$

was considerably increased by the addition of  $\text{NH}_4\text{Cl}$ , suggesting a higher partial current for Zn deposition in presence of the additive. Considering these two effects,  $\text{NH}_4\text{Cl}$  was expected to reduce the concentration of Ni in the deposits. Finally, at negative potentials, a sharp increase in current density was always observed. This could be related with hydrogen evolution at the cathodic side due to the breakdown of the hydration water introduced in the electrolyte with the metallic salts.

Considering the reduction potentials observed, potentials lower than  $-1.2$  V were expected to allow Zn-Ni co-deposition. For this reason, they were considered for subsequent deposition tests. For what concerns the anodic side of the voltammogram, a superimposition of different anodic peaks was observed ( $\text{Ni}_{\text{ox}}/\text{Zn}_{\text{ox}}$ ). These correspond to the dissolution of Zn and Ni from different phases present in the Zn-Ni alloy deposited during the cathodic scan.

#### Potentiostatic deposition tests

Following the electrochemical characterization of the electrolyte, potentiostatic co-deposition tests were carried out (Figure 4).

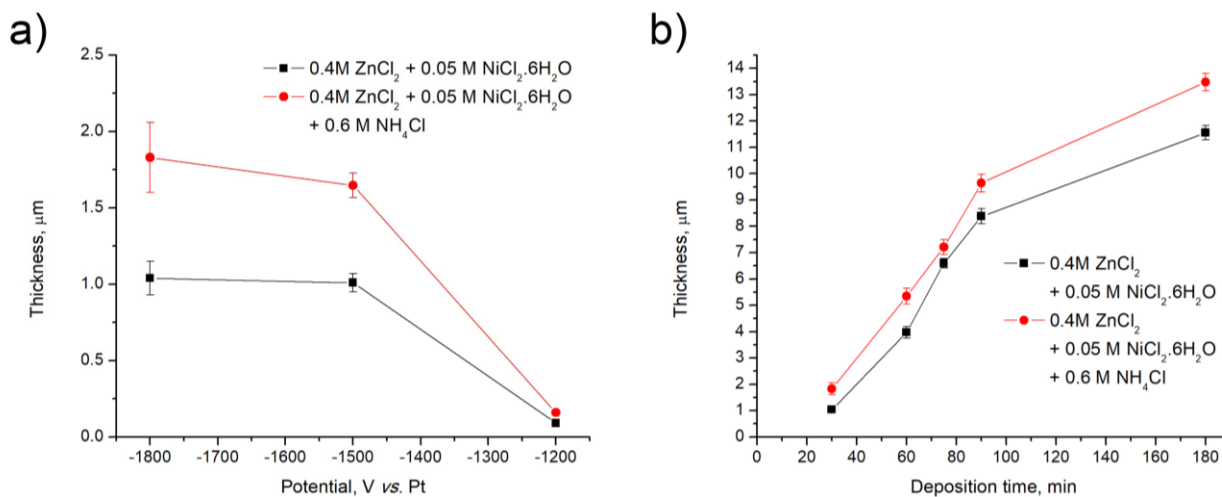


**Figure 4.** Composition vs. potential for the  $\text{NH}_4\text{Cl}$ -free and for the  $\text{NH}_4\text{Cl}$  additivated electrolytes (deposition time = 30 min)

As expectable, decreasing deposition potentials resulted in the co-deposition of lower amounts of Ni [24]. The presence of  $\text{NH}_4\text{Cl}$  induced, in line with the behaviour observed during the voltammetric tests, a decrease in the quantity of co-deposited Ni. At  $-1200$  mV vs. Pt the variation observed was  $-13.57$  wt.%, at  $-1500$  mV vs. Pt it was  $-8.11$  wt.% and at  $-1800$  mV vs. Pt it was  $-5.05$  wt.%.

The thickness of the resulting deposits is generally correlated to their Ni content and, for this reason, it was determined via XRF. Figure 5a shows the result obtained. The alloys characterized by the highest Zn contents were also characterized by the most relevant growth rate. The presence of ammonium chloride in the bath not only decreased Ni codeposition, but also significantly increased the thickness of the coatings. At  $-1200$  mV vs. Pt the increase observed was  $77.78$  %, at  $-1500$  mV vs. Pt it was  $63.07$  % and at  $-1800$  mV vs. Pt it was  $75.96$  %.

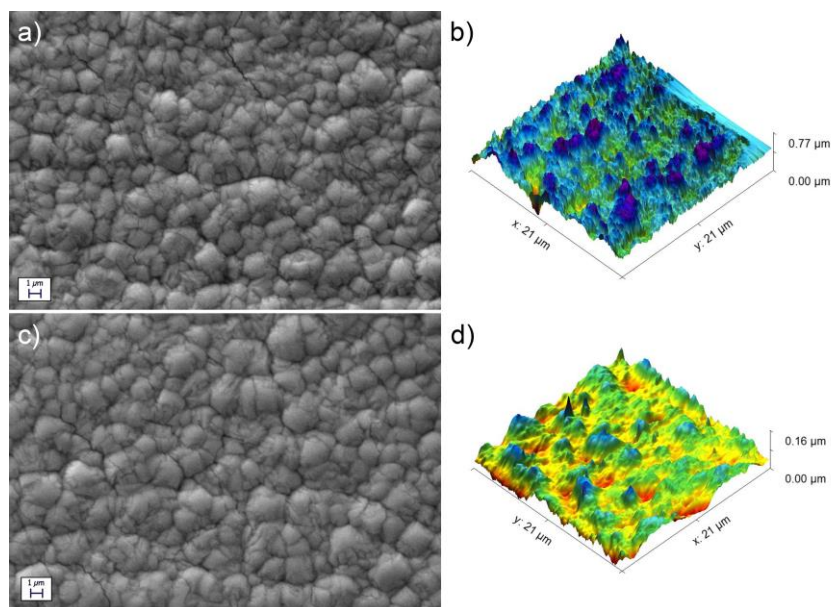
The dependence of thickness on deposition time was evaluated as well (Figure 5b). It is possible to observe a non-linearity in the growth rate at high deposition times and a delayed start (probably as a consequence of an unfavorable nucleation kinetic). By adding ammonium chloride, the deposited layer thickness slightly increased.



**Figure 5.** Thickness vs. potential at a constant deposition time of 30 min (a) and thickness vs. time at a constant deposition potential of -1800 mV vs. Pt (b) for the NH<sub>4</sub>Cl-free and for the NH<sub>4</sub>Cl additivated electrolytes

### Morphological characterization

The morphology of the Zn-Ni layers deposited at -1800 mV vs. Pt was analyzed. Figure 6a depicts the SEM morphology without ammonium chloride, while Figure 6c shows the SEM image of the layer plated with NH<sub>4</sub>Cl. Figures 6b and 6d show the corresponding AFM images. A mild cracking is evident in both cases. The typical nodular morphology of an electrodeposited layer is clearly visible in both cases, but the layer deposited in absence of NH<sub>4</sub>Cl looks more cracked and rougher.



**Figure 6.** SEM (a) and AFM (b) morphology of Zn-Ni layer deposited without NH<sub>4</sub>Cl; SEM (c) and AFM (d) morphology of Zn-Ni layer deposited with NH<sub>4</sub>Cl

Atomic force microscopy (AFM) was performed to observe the topography and roughness characteristic of Zn-Ni coatings both with and without ammonium chloride as shown in Figure 6b and 6d. The sample deposited from the 0.4 M ZnCl<sub>2</sub> + 0.05 M NiCl<sub>2</sub> · 6H<sub>2</sub>O + 0.6 M NH<sub>4</sub>Cl solution allowed smoother Zn-Ni coatings. The surface roughness  $R_a$  was calculated for the sample with additive and it resulted equal to 13.52 nm for the 20×20 μm area shown in Figure 6d. In contrast, the sample deposited from the 0.4 M ZnCl<sub>2</sub> + 0.05 M NiCl<sub>2</sub> · 6H<sub>2</sub>O solution had a rougher surface. The measured surface roughness  $R_a$  resulted equal to 68.39 nm for the 20×20 μm area shown in Figure 6b.

The distribution of the two elements, nickel and zinc, along the thickness of the deposited coatings was evaluated using GDOES (Figure 7). Data obtained are qualitative due to the impossibility to calibrate the etch rate of the plasma in the GDOES system.

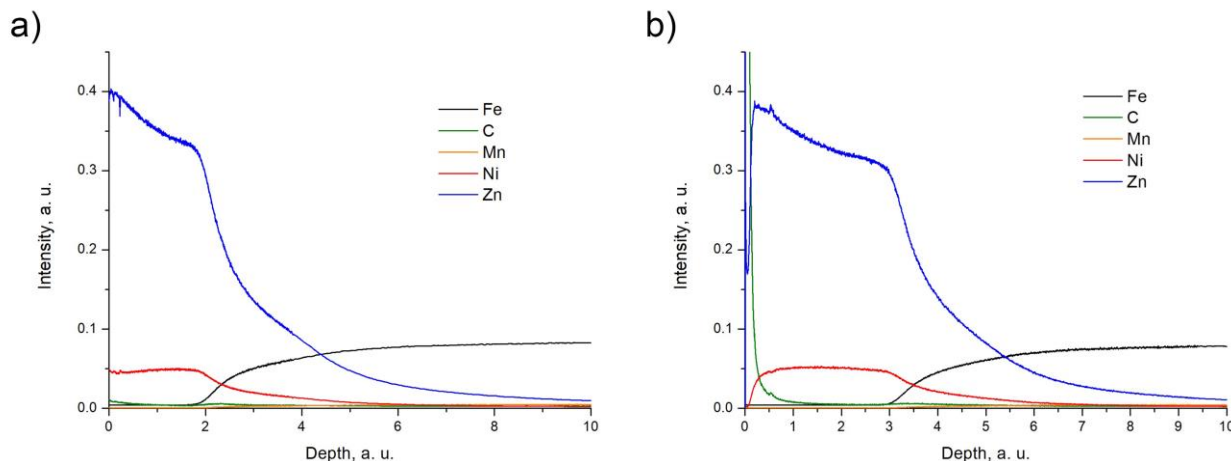


Figure 7. GDOES characterization of two Zn-Ni layers, deposited without (a) and with (b) NH<sub>4</sub>Cl

Despite their qualitative nature, the data obtained are valuable in order to carry out some considerations. According to Figures 7a and 7b, the composition of the layer was found to be not uniform along the thickness. The Ni concentration showed a gradient moving from the surface of the coating (depth 0) to the interface with Fe. Comparing the deposit plated without ammonium chloride (Figure 7a) with the one plated with ammonium chloride (Figure 7b), it can be seen that the latter was more uniform. Indeed, without the additive, Zn content increased by 20.48 % between the interface with Fe and the outer surface. If this value is normalized with respect to the thickness of the layer measured *via* XRF (9.04 microns), the concentration gradient is 2.27 % μm<sup>-1</sup>. With the additive, Zn increased by 22.83 %, but the thickness was higher. By normalizing with respect to the XRF thickness, the value of 1.69 % μm<sup>-1</sup> can be obtained. Meanwhile, in both cases, the level of carbon contamination was found to be negligible.

Phase composition of the deposited layers

The phase composition of the layer plated at -1800 mV vs. Pt was analysed using XRD (Figure 8). Two coatings, annealed at 400 °C and non-annealed, were analysed to compare the effect of annealing.

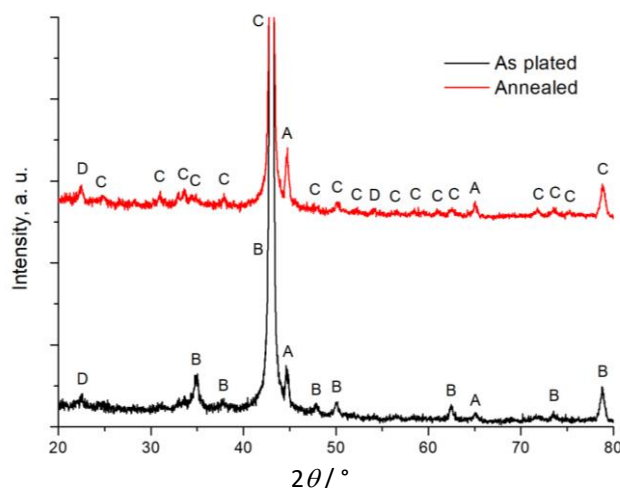


Figure 8. XRD characterization of a Zn-Ni layer deposited with NH<sub>4</sub>Cl before and after annealing at 400 °C for 1 h (A = Fe substrate; B = Zn-Ni peaks before annealing; C = Zn-Ni peaks after annealing; D = secondary phases)



From the X-ray diffractogram registered before annealing (Figure 8), some reflections typical of the cubic  $\gamma$  phase are noticeable (marked as B in the graphs). However, these do not totally correspond to the peaks expected for the fully ordered  $\gamma$  phase. This behaviour is indicative of the fact that the ionic liquid-based electrolyte deposits a metastable  $\gamma$  phase with short range order, which can be obtained only by electrochemical methods.

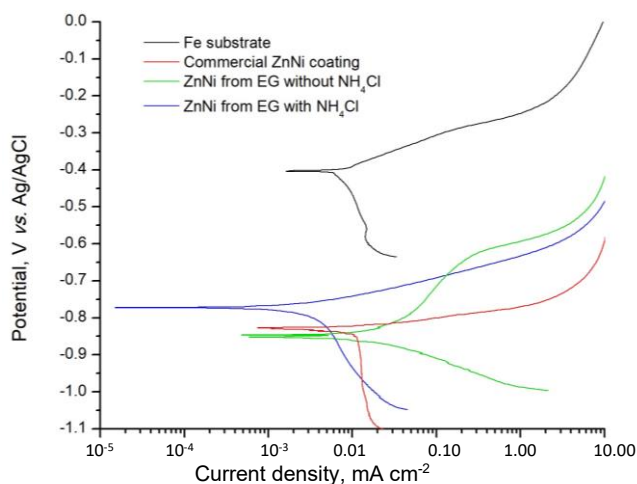
This behaviour has been observed in water based electrolytes [39] and also in the same EG based electrolyte here described in absence of  $\text{NH}_4\text{Cl}$  [24]. In particular, the peak at  $34.95^\circ$  is substantially difficult to explain without taking into consideration the presence of a metastable phase. In addition, some high-intensity reflections expectable for the  $\text{Ni}_5\text{Zn}_{21}$  phase are not present [24,39]. The phase composition obtained in presence of  $\text{NH}_4\text{Cl}$  is therefore similar to the case without additive [24].

The heat treatment process, carried out at  $400^\circ\text{C}$ , significantly altered the phase composition of the alloy. The resulting diffraction features were found to totally match the theoretical spectrum of the stable  $\gamma$  phase. By comparing the X-ray diffraction patterns before and after annealing, the intensity of the  $\gamma$  phase peaks increases. Moreover, the peaks look sharper with respect to the case without additive [24]. This is probably indicative of a larger crystallite size. To support this statement, the mean crystallite size for the layer obtained in presence of  $\text{NH}_4\text{Cl}$  was calculated using the Scherrer equation on two intense peaks (corresponding to the 330/411 and 552/633 reflections). This resulted equal to  $32.36 \pm 2.03$  nm, whereas the non-additivated solution yielded a mean crystallite size equal to  $11.06 \pm 1.84$  nm [24].

### Corrosion performances

The corrosion behaviour of the electrodeposited Zn-Ni coatings was examined for four different as-plated samples (Figure 9). The linear polarization curves of the Zn-Ni alloys were recorded and compared with those obtained for the steel substrate in order to estimate the corrosion protection. In addition, a commercial Zn-Ni layer (electrodeposited from the Glovel 800 bath, an alkaline Zn-Ni formulation by GLOMAX) was analysed for comparison.

The corrosion potential of both commercial and EG-based Zn-Ni alloys is more negative compared to steel ( $-440$  mV) and a little nobler than zinc (which has corrosion potentials not higher than  $-1000$  mV in 3.65 % wt. NaCl solutions [40]) due to their nickel content. During corrosion, Zn dissolves first as sacrificially and leaves a layer enriched with Ni or corrosion products of the two metals [41]. This layer can act as a physical barrier to further corrosion and it shows that Zn-Ni coatings can offer protection for ferrous-based substrates [42].



**Figure 9.** Linear polarization tests for the iron substrate, for a reference commercial Zn-Ni layer and for the two layers plated in presence and in absence of  $\text{NH}_4\text{Cl}$

Table 1 reports the corrosion data measured for the samples represented in Figure 9.

**Table 1.** Corrosion data for the different samples analyzed

Sample	$E_{corr}$ / mV vs. Ag/AgCl	$I_{corr}$ / $\mu\text{A cm}^{-2}$
Fe substrate	- 402	7.5
Commercial Zn-Ni (Glovel 800)	- 826	11.8
Zn-Ni from EG without $\text{NH}_4\text{Cl}$ (0.4 M $\text{ZnCl}_2$ + 0.05 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ )	- 852	27.1
Zn-Ni from EG with $\text{NH}_4\text{Cl}$ (0.4 M $\text{ZnCl}_2$ + 0.05 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ + 0.6 M $\text{NH}_4\text{Cl}$ )	- 772	3.7

EG solutions without additive showed corrosion properties similar to commercial ones. The tests showed that corrosion resistance was slightly improved by the use of  $\text{NH}_4\text{Cl}$ , even if the content of Ni slightly decreased. This effect is probably due to the increased grain size resulting from the deposition of Zn-Ni in presence of  $\text{NH}_4\text{Cl}$ . Moreover, the addition of  $\text{NH}_4\text{Cl}$  resulted in a more positive corrosion potential. Corrosion current density ( $I_{corr}$ ) decreased after the addition of  $\text{NH}_4\text{Cl}$  with respect to non additivated solutions. Thus, Zn-Ni alloys electrodeposited from  $\text{NH}_4\text{Cl}$  presented improved corrosion resistance. In general, Zn-Ni alloys obtained from EG were characterized by corrosion rates lower than pure Zn [40], which makes them suitable for Zn replacement as corrosion protection layers.

## Conclusions

In the present work, Zn-Ni electrodeposition on steel was successfully performed from an ethylene glycol-based bath in presence of ammonium chloride as additive. Cyclic voltammetry, viscosity and conductivity measurements allowed to analyze the characteristics of the EG-based Zn-Ni plating bath with and without addition of ammonium chloride. Cyclic voltammetry clearly evidenced the presence of reductions features for both Ni and Zn. The presence of ammonium chloride shifted the reduction peak of Zn towards more positive values and increased the cathodic currents for Zn plating. These two aspects resulted into an increase in the amount of co-deposited Zn, which was punctually detected by performing potentiostatic deposition tests. The morphology of the resulting layers was studied using SEM and AFM, evidencing a beneficial effect of  $\text{NH}_4\text{Cl}$  on the roughness and on the cracking level of the coatings. Regarding the phase composition of the Zn-Ni layers, X-ray diffraction spectroscopy highlighted the phases and intermetallics in the deposited layers. Evidence of metastable  $\gamma$  phase formation, in analogy with what observed in the existing literature for the additive free bath, was observed. Finally, potentiodynamic polarization tests were carried out to investigate the corrosion behaviour of the deposits. Zinc dissolved first as sacrificial material and the rest of the layer, which was enriched with nickel or corrosion products of the two metals, acted as a physical barrier. This barrier became stronger and more stable with the addition of  $\text{NH}_4\text{Cl}$ . Layers deposited in the presence of  $\text{NH}_4\text{Cl}$  presented the best corrosion properties, probably as a consequence of their comparatively larger grain size. The work carried out demonstrated that Zn-Ni layers with good anticorrosive properties can be obtained from EG based solutions additivated with ammonium chloride. The knowledge acquired thanks to the present experimental work constitutes a significant step towards the industrial implementation of non-aqueous electrolytes for the efficient deposition of corrosion protective Zn-Ni layers.

**Conflict of interest:** The authors declare no conflict of interest.

**Acknowledgements:** The authors wish to thank Prof. Luca Magagnin for providing financial support to the work carried out.

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