# Condensed Matter and Interphases

**Review**

# Zinc-nickel alloy coatings: electrodeposition kinetics, corrosion, and selective dissolution. A review

**D. V. Burliaev, O. A. Kozaderov✉, P. Volovitch²**

*¹Voronezh State University,
1 Universitetskaya pl., Voronezh 394018, Russian Federation*

*²PSL University, CNRS-Chimie ParisTech, Institut de Recherche de Chimie Paris,
11 rue Pierre et Marie Curie, Paris, France*

**Abstract**

A review of the literature is devoted to the patterns of the electrodeposition of zinc-nickel alloys including the kinetics of cathodic reduction of zinc, nickel, and zinc-nickel alloys in ammonium chloride, sulphate, and glycinate deposition electrolytes. We studied the data on the effectiveness of the corrosion resistance of zinc-nickel coatings and summarised the principal patterns of selective dissolution of the Zn-Ni alloys. The role of the addition of glycine to an ammonium chloride deposition electrolyte was determined in the modification of the morphological and anticorrosive properties of the coatings.

**Keywords:** electrodeposition, kinetics, zinc-nickel coatings, ammonium chloride electrolyte, glycine, current efficiency, corrosion, selective dissolution, voltammetry, chronoamperometry

## 1. Introduction

Zinc-nickel coatings considerably exceed pure zinc coatings in terms of their anticorrosive properties and also possess excellent physical properties [1], and, as a result, they are widely used in the aviation [2, 3], aerospace [4], and automotive industries [1–5]. Zinc-based coatings with a Ni content of 10–18 at. % show the best mechanical characteristics and protective properties in relation to steel [6–11], as they mainly consist of a zinc-enriched γ-phase which has high corrosion resistance, hardness, and strength [1–14]. The principal method of synthesis of Zn–Ni coatings is the cathodic electrodeposition [15–24], therefore it is very important to study the kinetic patterns of the electrochemical synthesis of these coatings as well as the specific features of the formation of their anticorrosive properties and the increase of electrocatalytic activity.

## 2. Zinc-nickel alloys: general description and production

The analysis of the phase diagram of the Zn–Ni system [6] is indicative of the complex nature of the interaction between the components which is typical for Zn – transition metal systems. The γ phase, which forms the basis of most corrosion-resistant Zn–Ni coatings, corresponds to the homogeneity region of 74–85 at. % Zn. It crystallises from the alloy at 881 °C and can be described by different formulas, for example, $NiZn_3$, $Ni_2Zn_{11}$, $Ni_3Zn_{10}$, $Ni_4Zn_{22}$, or $Ni_5Zn_{21}$ [7, 8]. The mechanical strength of the alloy reaches its maximum and stabilises with a

✉ Oleg A. Kozaderov, e-mail: ok@chem.vsu.ru

nickel content of more than 20 at. %, which also improves the thermal stability of the alloys [9, 10]. Anticorrosive and mechanical properties of zinc-nickel alloy coatings depend heavily on the phase composition. Homogeneous coatings consisting of γ-phase of the $Ni_2Zn_{11}$ (or $Ni_5Zn_{21}$) composition and corresponding to the nickel content of 10–18 % (wt) are most corrosion-resistant [2, 4, 11, 12].

Electrodeposition is the main method for the production of zinc-nickel alloy coatings [1–15]. A specific feature of this process for Zn-Ni systems is that it follows the mechanism of anomalous codeposition when a more electronegative component (zinc) is deposited first despite the presence of nickel, which is a more electropositive component. The mechanism of this process has been studied well in chloride and sulphate solutions [16–18]. Anomalous codeposition can be explained by the hydroxide suppression mechanism. As it happens, a secondary process of hydrogen evolution takes place at the same time with the electrodeposition based on the reaction:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-,$$
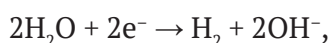
during which the medium is alkalised. The increased pH of the electrolyte solution contributes to the formation of the adsorptive zinc hydroxide $Zn(OH)_{2\,(ads)}$. Therefore, metal zinc is reduced at the cathode from the adsorbed hydroxide film blocking the transportation of nickel to the surface of the electrode. As a result, the reduction of nickel and hydrogen is suppressed [19, 20]. Along with the hydroxide suppression mechanism, a hypothesis of underpotential deposition of zinc is also suggested as an explanation of the anomalous codeposition [20, 21].

The quality of the synthesised Zn–Ni coating greatly depends on a number of factors: the composition and pH of the deposition electrolyte, the hydrodynamic regime, current density or electrode potential of the deposition, the temperature, and the material used as a substrate for the deposition [21, 22]. A variation in the factors leads to changes not only in the chemical and phase compositions of the coatings, but also in current efficiency, morphology, and visual and anticorrosive characteristics [21–24]. For instance, when studying the influence of the substrate material on the process of electrodeposition of zinc-nickel alloys, it was shown that a coating

deposited on a copper substrate has a more homogeneous chemical composition as compared to the coating deposited on a steel substrate. The nature of the substrate can also influence the phase composition of the coatings and its mechanical properties [23].

Zinc-nickel alloy coatings are deposited from electrolytes of various compositions, including oxalate [25], citrate [26], sulphate [27], chloride [28], sulphate-chloride [29], ethylenediamine [30], ammine, and ammonia-chloride [29, 31] solutions. Currently, cyanide, sulphamate, and pyrophosphate electrolytes are less popular due to ecological reasons as well as their low performance and high cost [29].

Deposition electrolytes often contain different additives that significantly influence the properties of the synthesised alloys. Complexation additives are widely used that ensure a more compact morphology of the coatings, their fineness, smoothness, and typical gloss. Among them are sodium acetate in weakly alkaline electrolytes [32], amines and 5,5′-dimethyl hydantoin [24] in strongly alkaline (pH = 9-10) electrolytes [24], saccharin (pH = 13–14) [33], polyethylene glycol, coumarin, piperonal, and vanillin (pH = 14) [34], gelatine in acid electrolytes [35], boric acid, glycerol, mannitol, sorbitol (pH = 1–3) [36, 37], and many others.

It was shown, based on the example of an alkaline solution of the electrolyte with the addition of 5,5′-dimethyl hydantoin, that the increased content of nickel in an electrolyte solution increases its atomic fraction in the coating. However, at the same time, the current efficiency of the electrodeposition of the alloy significantly decreases. It probably occurs due to the acceleration of a side process, e.g. hydrogen evolution. An increasing of cathodic current density also has a similar influence. The influence of temperature is ambiguous. Indeed, the dependence of nickel content in the coating on the temperature has an extreme character, as an increase in temperature contributed to the rise of the current efficiency of the target process. It was assumed that it was generated by cathodic depolarisation and the increase in overpotential of the hydrogen evolution. Most likely an increased stirring rate of the electrolyte accelerates the diffusion-controlled formation of

zinc hydroxide, thus increasing the rate of zinc deposition and, as a result, reducing the nickel content in the coating. This, in its turn, increases the current efficiency due to the reduction of the contribution of the hydrogen evolution reaction to the overall rate of the cathodic process [24, 31, 38, 40–42].

The above-mentioned factors can considerably influence the morphology of the deposited coatings. For example, an increased content of nickel in the electrolyte leads to a rougher and more inhomogeneous surface [24].

An advantage of acid electrolytes is the slightly greater content of nickel in the deposited alloy, which improves the anticorrosive characteristics of the coatings. On the other hand, the coatings synthesised from alkaline electrolytes can have a more compact morphology of the surface due to the slower electrodeposition and reduced rate of the side process of hydrogen evolution. However, in most cases acid electrolytes are more available and environmentally-friendly [43]. Among acid solutions, an ammonium chloride deposition electrolyte is the most optimal from the point of view of its environmental safety, cheap and available components, easy production, ability to use at room temperature, and chemical and phase compositions of the synthesised Zn-Ni coatings. Polyligand ammonia-chloride-glycinate solutions with pH < 7 are promising electrolytes for the deposition of alloys of the Zn–Ni system [4, 11, 14]. The addition of an aminoacetic acid improves the morphology of the coatings, reducing the rate of the hydrogen evolution reaction, thus increasing the current efficiency of the electrodeposition.

### 1.1. Kinetics of cathodic deposition of zinc, nickel, and zinc-nickel alloys
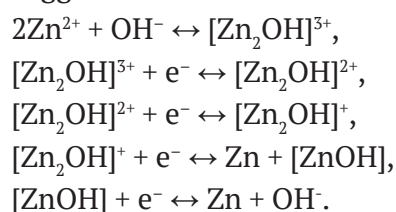
According to multiple studies, the kinetics of the cathodic reduction of zinc depends heavily on the electrolyte composition. Indeed, as for simple electrolytes (sulphate, chloride, and cyanide) without any additives, the process of electrodeposition is mainly determined by concentration polarisation, while adsorption processes become more important when organic substances are added to the electrolyte [44, 45].

In [46] it is shown that the limiting stage of the process changes over time in an ammonium chloride electrolyte. The analysis of deposition
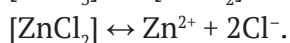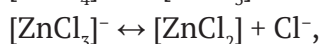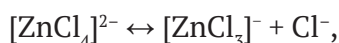
in the Cottrel coordinates criterion for diffusion control $i–t^{-1/2}$, shows that at the beginning the curves are not extrapolated to the origin of the coordinates. This is most likely indicative of a certain kinetic stage at the interphase boundary, for instance, a heterogeneous chemical reaction. This reaction may be due to the adsorption of discharging hydrated zinc or zinc hydroxide ions. The likelihood of this process increases with the time of electrodeposition as the pH of the near-electrode layer rises.

With an increase in the duration of the process, the dependence $i–t^{-1/2}$ is extrapolated to the origin of the coordinates, which is indicative of the establishment of the diffusion control over the process of zinc electroreduction. At the same time, the calculated value of the diffusion coefficient shows that the process of diffusion mass transfer of discharging particles probably occurs in the solid phase, particularly in the film which forms on the electrode surface from the adsorbed and discharging particles. The reaction order for zinc is close to one with a potential of −1.05 V and equals 1.5 with a potential of −1.1 V. This indicates the accelerated electroreduction of zinc with the shift of the deposition potential towards the negative region. Over time, a new heterogeneous process takes place – crystallisation with the formation of two-dimensional nuclei. It is proved by the linearization of chronoamperograms in the criteria coordinates $\lg (i/t) – t^2$ [46].

According to [47], electrochemical stages in the cathodic process of zinc deposition with pH > 2 were preceded by a quick chemical reaction of the formation of a binuclear zinc hydroxocomplex. Therefore, the following mechanism for the electrochemical process was suggested:

$2Zn^{2+} + OH^- \leftrightarrow [Zn_2OH]^{3+}$,

$[Zn_2OH]^{3+} + e^- \leftrightarrow [Zn_2OH]^{2+}$,

$[Zn_2OH]^{2+} + e^- \leftrightarrow [Zn_2OH]^+$,

$[Zn_2OH]^+ + e^- \leftrightarrow Zn + [ZnOH]$,

$[ZnOH] + e^- \leftrightarrow Zn + OH^-$.

At the same time, the reduction of zinc in chloride electrolytes is preceded by the dissociation reaction of an instable complex $[ZnCl_4]^{2-}$:

$[ZnCl_4]^{2-} \leftrightarrow [ZnCl_3]^- + Cl^-$,

$[ZnCl_3]^- \leftrightarrow [ZnCl_2] + Cl^-$,

$[ZnCl_2] \leftrightarrow Zn^{2+} + 2Cl^-$.

The discharge of zinc ions in this case occurs from the hydrated ions [47,48]:

$Zn(H_2O)_x^{2+} + 2e^- \leftrightarrow Zn + xH_2O$.
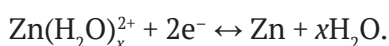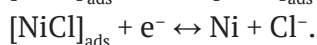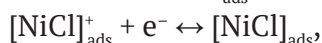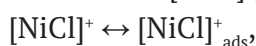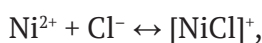
Nucleation during the electrodeposition of zinc from sulphate solutions occurs instantly with pH ~ 2. When the pH of the solution increases up to 4, continuous nucleation begins prevailing over instantaneous nucleation. Presumably, this is related to the acceleration of the formation of the adsorbed particle $ZnOH_{(ads)}$ which blocks the active deposition centres on the substrate surface [49].

It was established [50] that 3D zinc nucleation is typical for the chloride electrolyte. Nucleation occurs continuously with low concentrations of $ZnCl_2$ (from 0.01 to 0.1 M) and instantly when the salt concentration increases up to 0.6 M. Zinc is mainly found in the complex form $[ZnCl_4]^{2-}$.

During the electrodeposition of nickel, the reaction of hydrogen evolution contributes more to the overall rate of the cathodic process as compared to zinc [51]. According to the distribution diagram [52], nickel is mainly in the form of $[NiCl]^+$ in chloride electrolytes, therefore, the presumable mechanism of the cathodic nickel deposition can be presented in the following way [51, 52]:

$Ni^{2+} + Cl^- \leftrightarrow [NiCl]^+$,

$[NiCl]^+ \leftrightarrow [NiCl]^+_{ads}$,

$[NiCl]^+_{ads} + e^- \leftrightarrow [NiCl]_{ads}$,

$[NiCl]_{ads} + e^- \leftrightarrow Ni + Cl^-$.

In this case, under conditions of a small overpotential, the penultimate charge transfer reaction is presumably considered to be limiting, while the diffusion of nickel ions towards the electrode surface becomes the limiting stage in case of a further shift of the deposition potential towards the negative region [51, 52].

Linear sweep voltammetry is widely used to establish the principal patterns of electrodeposition for the film alloys of the zinc-nickel system. The analysis of the dependence of the cathode current density at the peak of a voltammogram on the square root of the scan rate proves that the stage of diffusion mass transfer is at least one of the limiting stages [50, 53–60]. The maximum peak potential on cathodic voltammograms shifts with the increase of the scan rate and linearly depends on the scan rate logarithm. Therefore, the charge transfer stage irreversibly continues.

Peak current ($i_p$) also rises with the increase of the potential scan rate in proportion to $V^{1/2}$ in the presence of amino acids in the deposition electrolyte [62–64], which is typical for reversible processes controlled both by diffusion and the charge transfer stage. At the same time, the values of the Semerano $X_C$ criterion for the solutions with glycine, alanine, and serine are 0.35, 0.35, and 0.38 respectively, which is indicative of the irreversibility of the process of reduction of nickel ions in these solutions [62, 65]. The control of the process by the charge transfer stage is proved by the shift of the peak potential in the studied electrolytes towards negative values with the increase of the potential scan rate and its linear dependence on lg $V$. It is interesting that the $i_p – V^{1/2}$ dependencies are not extrapolated to zero, which indicates the contribution of the side reaction of hydrogen evolution to the process of nickel deposition [62]. Linear dependence $i_p$ from the square root of the rotation rate of the disc electrode $w^{1/2}$ in the studied solutions in the range of values of $w$ from 2 to 17 rps is indicative of the presence of diffusion limitations. With the rotation rates of the disk electrode $w = 17 \div 25$ rps, current is essentially independent of the rotation rate of the electrode, which shows that the process already occurs in the kinetic mode [62, 65]. The values of the concentration criterion Semerano $X_C < 1$, in their turn, indicate the presence of adsorption complications in the process. Thus, based on the above-mentioned analysis we can assume that the process of the reduction of nickel ions from the solutions with glycine, alanine, and serine is irreversible and occurs in the mixed kinetics mode complicated by adsorption [62]. Similar patterns are also valid for succinate and asparaginate nickelling electrolytes [66].
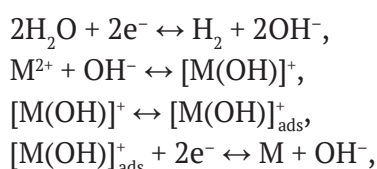
The nucleation mechanism during the deposition of a zinc-nickel alloy is studied using chronoamperometry. Thus, the analysis of chronoamperograms of the electrodeposition of Zn-Ni alloy from an acid sulphate deposition electrolyte without additives showed that nucleation occurs in a

continuous mode of activation of potential nucleation centres [67]. The addition of an aminoacetic acid to a sulphate nickelling solution accelerates the cathodic electrodeposition of nickel [68], and in this case, the nucleation stage proceeds according to the mechanism of instantaneous nucleation [69]. As for an acid sulphate nickel plating electrolyte with the addition of boric acid, saccharin, and coumarin [70], electrodeposition proceeds in mixed diffusion-kinetic mode, and the activation of potential 3D nucleation centres also occurs instantly.

To take into account the contribution of the hydrogen evolution reaction to the total value of cathode current in [69], authors used an approach which allows obtaining partial curves of nickel deposition and hydrogen evolution using non-linear approximation [53]. It was established that the contribution of the hydrogen reaction to the total rate of the cathodic process increased from 2 % with a potential of –1.23 V to 18 % with a potential of –1.43 V (SCE), which naturally reduces the current efficiency of nickel electrodeposition [69].

In an acid chloride deposition electrolyte containing the product of condensation of vanillin and hexamine (VH) crystallisation is controlled by diffusion: cathodic current reaches its maximum ($I_{max}$) at $t = t_{max}$, then a smooth decrease of current was observed. To determine the kinetics of the process, the obtained current transients were plotted in the coordinates $(I/I_{max})^2 - (t/t_{max})$ and compared to the theoretical curves calculated using the Scharifker-Hills model for instantaneous and continuous 3D nucleation [53].

According to the commonly acknowledged method of electrode deposition of iron sub-group metals [71, 72], the cathodic process in such systems occurs in the following way:

$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$,

$M^{2+} + OH^- \leftrightarrow [M(OH)]^+$,

$[M(OH)]^+ \leftrightarrow [M(OH)]^+_{ads}$,

$[M(OH)]^+_{ads} + 2e^- \leftrightarrow M + OH^-$,

where M = Fe, Co, Ni. Obviously, the electrodeposition mechanism greatly depends on the stability of the $[M(OH)]^+_{ads}$ and $[M(OH)]^+$ particles. As for the zinc-nickel system, the $[Ni(OH)]^+$ complex has greater thermodynamic stability than $[Zn(OH)]^+$ [71]. The $[Ni(OH)]^+$ concentration near

the cathodes remains approximately constant, although the cathode process is complicated by the parallel hydrogen evolution, therefore the currents on the theoretical curves must have higher values. Nevertheless, if the activation of 3D nucleation centres proceeds instantly in the absence of the VH additive along the entire length of the curve, then in the presence of the additive (but only with more positive deposition potentials) the initial sections of the curves correspond more to the mechanism of continuous nucleation. However, with greater periods of time there are almost no differences between the two solutions.

A similar kinetic situation is observed in acid sulphate electrolytes for the deposition of alloys of the zinc-nickel system with and without the addition of the condensation product of vanillin and serine (VS). The adding of an organic additive results in a change in the mechanism of 3D nucleation from instant to continuous, and it occurs in the entire range of deposition potentials [73].

In [74] it was established that instantaneous 3D nucleation is also typical for chloride-citrate electrolytes for the deposition of Zn-Ni alloys regardless of the deposition potential, temperature, or pH of the solution. However, if the solution is enriched with nickel ($[Ni^{2+}]/[Zn^{2+}] = 4$), the nucleation mechanism is characterised by the continuous activation of nucleation centres. The effect is accounted for by the fact that citrate ions block some part of the active centres of the cathode surface, which are available for the reduction of $Ni^{2+}$ ions, and at the same time inhibit the hydrogen evolution [74,75].

*1.2. The corrosion resistance of zinc-nickel alloys*

Zn-Ni coatings with a composition of 10-18 at. % Ni ensure optimal corrosion protection as compared to cadmium and its alloys as well as pure zinc [76–78]. In [9, 78, 79] it was established that the phase composition considerably influences the corrosion resistance of coatings in addition to the chemical composition and surface morphology. The γ-phase of $Ni_5Zn_{21}$ has the greatest corrosion resistance, and the enrichment of the surface layer with nickel has an additional influence on the corrosion process. This layer probably stabilises zinc hydroxide $Zn(OH)_2$ on the surface of the alloy as the main product of corrosion, which prevents further alloy dissolution, providing a barrier effect that is more effective than that of zinc oxide ZnO

[9, 79]. The high corrosion resistance of these coatings correlates to the homogeneous surface morphology. Indeed, the presence of cracks, grooves, and structural inhomogeneities has a negative effect on the corrosion resistance of the alloys [9].

Electrochemical corrosion of a zinc-nickel alloy coating in aqueous chloride solutions can proceed in accordance with the following mechanism [80]:

• Anodic dissolution of zinc:

$Zn \rightarrow Zn^{2+} + 2e^-$,

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$

and/or:

$Zn^{2+} + 2Cl^- \rightarrow ZnCl_2$.
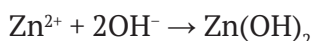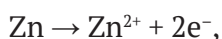
The formation of other products of zinc and, less likely, nickel oxidation is also possible [79]. As for the initial stage of the dissolution of Zn-Ni coatings in chloride solutions, the main products are simonkolleite $Zn_5(OH)_8Cl_2 \cdot H_2O$, zinc oxide ZnO and hydrozincite $Zn_5(CO_3)_2(OH)_6$ [81].

• Cathodic process, reduction of molecular oxygen present in the electrolyte solution:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$.
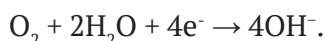
In addition, the corrosion process is often complicated by the phase transformation

$\gamma (Ni_5Zn_{21}) \rightarrow \beta (NiZn) \rightarrow \alpha (Ni)$,
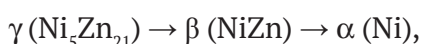
resulting from a gradual change in the chemical composition of the alloy during the dissolution in accordance with the phase diagram of the Zn-Ni system [82].

Corrosion of the Zn-Ni alloy often leads to significant morphological changes in the surface of the alloy coating: a large number of cracks are formed on its surface during the dissolution. The process occurs mainly selectively, as dezincification of the surface is observed, and the surface is also covered with sparingly soluble products of the corrosion process [82].

The analysis of the transients of the corrosion potential of zinc-nickel coatings with various compositions, as compared to similar data obtained with iron and zinc, showed that Zn-Ni-coatings with a nickel content less than 18 at. % remain sacrificial in relation to the protected metal and are characterised by a higher corrosion potential as compared to pure zinc [17,

83]. If the corrosion potential of zinc remains relatively constant, practically not changing over time, the corrosion potential of any Zn-Ni coating gradually increases and stabilises. Primarily, this can be related to the partial dezincification of the surface of zinc-nickel alloys, which leads to the increased surface concentration of a more electropositive component, nickel. The increased concentration of nickel in the coatings during its dezincification leads to a shift in the corrosion potential towards the positive region. A similar dependence is also usually observed for the corrosion rate $i_{corr}$: the increased concentration of nickel in the alloy contributes to a decrease in the value $i_{corr}$ [84–87].

The introduction of the complexing agent $NH_4Cl$ into the chloride deposition electrolyte significantly reduces the current density of the corrosion in case of the dissolution of the zinc-nickel coating [88]. This may be related to an improvement in the morphology of the coatings due to the complexation of metal ions, a decrease in their deposition rates, and the formation of fine-crystalline dense coatings.

In [89] authors studied the influence of the temperature (from 25 to 70 °C) on the electrodeposition and effectiveness of corrosion resistance of zinc-nickel coatings synthesised from an ammonia-chloride electrolyte, and it showed that the best morphology and the lowest corrosion current density is typical for the coating obtained at 25 °C.

Fine-grained nanocrystalline zinc-nickel coatings with an increased corrosion resistance can also be obtained by deposition from an alkaline electrolyte with the addition of 2,2-bipyridine and 5,5′-dimethylhydantoin [90].

### 1.3. Selective dissolution of zinc-nickel alloys

Under specific conditions, selective dissolution is typical for the electrodeposited zinc-nickel alloys, that is the oxidation of the electronegative component, zinc, with further enrichment of the surface layer with an electropositive component, nickel, which is usually accompanied by the development of the surface [91-93].

A region of low currents which is practically independent of potential is observed on the anodic polarisation curves obtained on zinc and zinc-nickel coatings in sulphate, chloride, and carbonate solutions. A sharp increase in the

current density is observed when reaching the critical potential of the selective dissolution of the alloy $E_{cr}$. Determination of the composition of the solution after selective dissolution allows determining the selectivity factor (SF) characterising the process:

$$SF = \frac{n_{Zn}^{2+} \cdot n_{Ni}}{n_{Ni}^{2+} \cdot n_{Zn}} .$$

Here $n_{Ni}^{2+}$ and $n_{Zn}^{2+}$ are the total amount of nickel and zinc in the solution after selective dissolution, while $n_{Ni}$ and $n_{Zn}$ are the total amount of nickel and zinc in the alloy. The highest selectivity factor is observed in the alloy $(NH_4)_2SO_4$ (SF = 74.3÷77.1), and the lowest in the alloy $NaHCO_3$ (SF = 3.54÷5.24), while the NaCl solution is characterised by an intermediate value SF = 19.1÷31.2 [92].

A study of the selective dissolution of the alloys of the Zn-Ni system in a chloride solution, particularly at increased temperatures, conducted in [94], showed that the anodic process has three stages. Active dissolution of the alloy begins at a potential of ≈ -1.2 V (SCE) and is accompanied by the formation of a layer of corrosion products, mainly zincates, on the alloy surface:

$$Zn + 4OH^- = [Zn(OH)_4]^{2-} + 2e^-.$$

The dissolution of the alloy slows down in a potential region that is more positive than –0.9 V (SCE), and zinc oxide ZnO and zinc hydroxide $Zn(OH)_2$, as well as, less likely, $NiCl_2$ and/or $NiClOH_{(ads)}$ are formed. Thus, a porous passivating layer, which includes a number of different corrosion products, is formed on the surface of the alloy. According to previous studies [12, 94, 95], the presence of nickel stabilises the $Zn(OH)_2$ layer on the surface which can inhibit the adsorption of $Cl^-$ more effectively as compared to ZnO. As a result, the likelihood of pitting decreases, which significantly increases the corrosion resistance of the coating in chloride environments [94].

Surface chemical and morphological modifications of electrodeposited and chromium(III)-passivated monophasic zinc-nickel coatings induced by selective dissolution and corrosion in chloride solutions are demonstrated in [96]. The passivated samples showed slower anodic dissolution, less significant de-alloying, smaller surface dezincification and lower coating cracking.

The selective dissolution (SD) of Zn-Ni alloys is used to obtain nanoporous nickel, which is a catalyst for various reactions, for example, oxidation of CO or methanol or a reduction of hydrogen or oxygen [97–100]. Thus, in [97], using selective dissolution of a heterophase zinc-nickel alloy consisting of NiZn and $NiZn_3$, they obtained finely dispersed nickel with the size of particles in the surface phase being 40–60 nm in a 2 M solution of NaOH.

In addition to the selective dissolution of zinc-nickel alloys, mostly in alkali solutions [101], other methods are also used to synthesise nanoporous nickel, for example, cathodic treatment of the nickel surface in a saturated solution $ZnCl_2$ – NaCl [102]; selective dissolution of pyrometallurgical alloys of the $Ni_{30}Mn_{70}$ type in an ammonium sulphate solution [103]; SD of the alloys similar to $Mg_{90-x}Ni_xY_{10}$ (x = 10, 15, 20, 25 at. %) in citric acid [104], SD of the alloys of the Cu-Ni system in acid solutions [105], the SD of the alloys of the Ni-Al system alkaline solutions [98], etc.

According to previous studies [104, 106], the SD of binary alloys (including the zinc-nickel system) has 4 stages:

1. Quick dissolution of a more electronegative component.

2. Regrouping of the atoms of more electropositive components into clusters.

3. Fusion and growth of neighbouring clusters of the electropositive component with the formation of ligaments between clusters.

4. Enlargement of ligaments between clusters.

The cyclic voltammogram of a smooth nickel electrode and zinc-nickel alloy after alkaline treatment (practically nanoporous nickel) shows the presence of anodic peaks at 0.38 V for a smooth nickel surface and at 0.49 V for a nanoporous nickel surface [107]. In this case, the average values of the current density on the dezincified surface are significantly greater than the corresponding values for smooth nickel. It is related to a change in morphology, and, therefore, a more developed surface of nanoporous nickel can be successfully used in sorption, catalysis, and electrocatalysis processes [107,108].

Anodic oxidation of methanol in an alkaline solution with nanoporous nickel proceeds almost 12 times faster than with smooth nickel. This indicates the significant effectiveness of the use

of nanoporous nickel in the process of methanol oxidation, for example, in fuel cells based on this process.

Cathodic processes in an alkaline solution on nanoporous nickel obtained by the selective dissolution of Zn-Ni alloys are also more effective as compared to smooth nickel. Thus, nanoporous nickel has greater electrocatalytic activity in the hydrogen evolution reaction [108], which can be used in the industry to intensify the process of hydrogen production [107–111].

## 2. Conclusions

Zinc-nickel alloy coatings with a nickel content of 18 at. % have optimal corrosion resistance and mechanical characteristics among binary zinc-based alloys, which makes them a promising material for the corrosion protection of various types of steel. The γ-phase, which can be described by different formulas ($NiZn_3$, $Ni_2Zn_{11}$, $Ni_3Zn_{10}$, $Ni_4Zn_{22}$, $Ni_5Zn_{21}$), forms the basis of most corrosion-resistant zinc-nickel alloys. In addition to the corrosion protection of various types of steel, zinc-nickel alloys can be used as the initial material for the electrochemical synthesis of porous (as well as nanoporous) nickel, which is a promising electrocatalyst for various processes, using the method of the selective dissolution. The key feature of the synthesis of alloys of the Zn-Ni system is the anomalous nature of codeposition of components, during which the prevailing reduction of a more electronegative component, zinc, occurs at the cathode. Electrodeposition of zinc-nickel alloys is conducted from various acid and alkaline electrolytes. The use of additives allows regulating certain properties of the coatings, such as chemical and/or phase composition, morphology, and anticorrosive characteristics. Aminoacetic acid (glycine) is a promising organic additive to acid (chloride, ammonia, and sulphate) electrolytes for the deposition of alloys of the Zn-Ni system. At the same time, according to previous studies, the influence of the addition of glycine is not clear as the current efficiency of the target process of the deposition of alloys can either increase or decrease depending on the composition of the solution and other conditions. Also, there are practically no data on the influence of glycine on the kinetics of zinc and nickel reduction and the mechanism of their nucleation. Therefore, it is important to conduct studies aimed at the establishment of the kinetics of electrodeposition of zinc-nickel alloy coatings, assessment of the effectiveness of their corrosion resistance, as well as study the patterns of selective dissolution of alloys in order to obtain nanoporous nickel electrocatalysts.

## Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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## Information about the authors

*Oleg A. Kozaderov*, DSc in Chemistry, Head of the Department of Physical Chemistry, Faculty of Chemistry, Voronezh State University, Voronezh, Russian Federation; e-mail: ok@chem.vsu.ru. ORCID iD: https://orcid.org/0000-0002-0249-9517.

*Dmitrii V. Burliaev*, postgraduate student, Department of Physical Chemistry, Faculty of Chemistry, Voronezh State University, Voronezh, Russian Federation; e-mail: dimn0@yandex.ru. ORCID iD: https://orcid.org/0000-0003-3826-686X.

*Polina Volovitch*, Professor, PSL University, CNRS-Chimie ParisTech, Institut de Recherche de Chimie Paris, Paris, France; e-mail: polina.volovitch@chimieparistech.psl.eu. ORCID iD: https://orcid.org/0000-0001-5729-9830

All authors have read and approved the final manuscript.