Article

Hybrid Zinc-Based Multilayer Systems with Improved Protective Ability against Localized Corrosion Incorporating Polymer-Modified ZnO or CuO Particles

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Abstract: Localized corrosion and biofouling cause very serious problems in the marine industries, often related to financial losses and environmental accidents. Aiming to minimize the abovementioned, two types of hybrid Zn-based protective coatings have been composed. They consist of a very thin underlayer of polymer-modified ZnO or CuO nanoparticles and toplayer of galvanic zinc with a thickness of ~14 µm. In order to stabilize the suspensions of CuO or ZnO, respectively, a cationic polyelectrolyte polyethylenimine (PEI) is used. The polymer-modified nanoparticles are electrodeposited on the steel (cathode) surface at very low cathodic current density and following pH values: 1/CuO at pH 9.0, aiming to minimize the effect of aggregation in the suspension and dissolution of the CuO nanoparticles; 2/ZnO at pH 7.5 due to the dissolution of ZnO. Thereafter, ordinary zinc coating is electrodeposited on the CuO or ZnO coated low-carbon steel substrate from a zinc electrolyte at pH 4.5–5.0. The two-step approach described herein can be used for the preparation of hybrid coatings where preservation of particles functionality is required. The distribution of the nanoparticles on the steel surface and morphology of the hybrid coatings are studied by scanning electron microscopy. The thickness of the coatings is evaluated by a straight optical microscope and cross-sections. The protective properties of both systems are investigated in a model corrosive medium of 5% NaCl solution by application of potentiodynamic polarization (PDP) curves, open circuit potential (OCP), cyclic voltammetry (CVA), and polarization resistance (Rp) measurements. The results obtained allow us to conclude that both hybrid coatings with embedded polymer-modified CuO or ZnO nanoparticles ensure enhanced corrosion resistance and protective ability compared to the ordinary zinc.

Keywords: hybrid coatings; corrosion; CuO and ZnO nanoparticles; polymeric modification

1. Introduction

Corrosion of metals, and, in particular, low-carbon steel, is a global problem that causes major economic, social, and environmental damage [1]. This phenomenon proceeds by different mechanisms and is of different types, some of which can be classified as very dangerous—local corrosion and biofouling. Local corrosion occurs in most cases practically imperceptible to the naked eye, penetrating deep inside the structure or equipment, while the damage is sudden and often with catastrophic consequences. Although corrosion protection is a subject of investigation by many research teams and laboratories, so far, no reliable methodology has been developed to prevent this event.

One of the most commonly used metals for corrosion protection of steel is zinc, as well as some zinc alloys thereof. Zinc coatings and alloys are known mainly as “sacrificial type” because zinc dissolves before iron during the corrosion attack and is more corrosion-resistant at atmospheric conditions. The reason for this is the appearing surface layer of low soluble corrosion products (mainly oxides and hydroxides), the latter hindering the penetration of the aggressive environment deeply inside.

One way to achieve better corrosion resistance is through the application of metallic or organic coatings [2], the latter acting as a barrier to aggressive agents. According to the scientific literature, the incorporation of selected nano- or micro-sized particles (silicates, oxides of various metals, carbon particles, etc.) improves the anticorrosion, “self-healing”, and mechanical indicators of the coatings [3–6]. The higher protective ability of steel substrates from localized corrosion can be obtained, for example, by application of polyaniline-based composite coatings [7] or by deposition/electrodeposition of a modified ZnO nanoparticles layer on their surface [8–14].

For example, polarization curves of ZnO-alginate coated steel show a lower corrosion current compared to the bare steel. It seems that electrophoretic deposition of colloidal particles is a fast and efficient method for obtaining uniform coatings on metallic surfaces [12,15,16]. By altering the applied potential, deposition time, and composition of the suspension, it is possible to control the thickness and microstructure of the deposited coatings. Both aqueous and non-aqueous ZnO suspensions can be used for the preparation of coatings on metal surfaces. It is known that ZnO combines the surface properties of an oxide with a pH-dependent charge density due to proton adsorption–desorption on ZnOH sites [17]. In addition, the pH value of the point of zero charge of these nanoparticles is at pH 9.4–9.6, i.e., they are positively charged below this pH and negatively charged above it [18,19]. The pH value of the solution strongly influences the particle size in the abovementioned pH regions where dissolution and aggregation (pH 6.5 and 9.4) occur [18].

It follows that one method to prepare stable ZnO suspension is to adjust the pH to regions with high electrostatic repulsion between the particles. Lowering the pH below 6.5 was found to increase the particles’ charge, but the ZnO dissolved rapidly under acidic conditions. Another method for stabilization of particles suspension is surface modification using polyelectrolytes, which can control electrostatic (and steric) forces between particles.

Biofouling is another great problem, especially for marine structures, leading to increased fuel consumption of ships, as well as to microbiologically induced corrosion degradation. In order to minimize this process, the substrate can be treated with selected biocides [20–22]. It is expected that this action will lead to long-term protection against biocorrosion due to the controllable release of the biocide. To the best of our knowledge, copper-based coatings can be used as antifouling ones due to their toxicity to marine microorganisms [23–26]. According to [27], in the marine environment, the antifouling action of the copper-based coatings is realized through the release of cuprous and copper ions, the latter reacting with chlorine ones. It is also demonstrated that CuO nanoparticles may dissociate into Cu^{2+} , and higher concentrations of these ions significantly affect the growth of aquatic microorganisms [28]. Some investigators claim that the dissolution of CuO nanoparticles depends on several factors such as particle size, shape and surface charge, and characteristics of the media (pH, ionic strength, dissolved organic matter) [29,30].

Keeping in mind the investigations of [30–32], one possible method to prepare a stable suspension (suitable for subsequent electrodeposition) of CuO nanoparticles is to adjust the pH to regions with high electrostatic repulsion between the latter. At acidic conditions, CuO nanoparticles are highly charged and stable. At the isoelectric point, they have practically no charge, and the repulsive forces between them weaken, which leads to unstable suspension. After the isoelectric point, the repulsive forces become stronger again, decreasing aggregation. Additionally, for suspension stabilization, surface modification of the particles with polyelectrolytes can be applied to control the electrostatic and steric forces.

According to [33], electrophoretic deposition seems to be an attractive technique offering a high deposition rate and obtaining relatively thick films. In addition, the control of the colloidal behavior of the nanoparticles plays a key role in preparing stable suspensions suitable for electrophoretic deposition. The general peculiarity is that the particles need to obtain a significant surface charge density in order to be well dispersed in the suspension.

The main idea of the present investigations is to show the processes of polymer modification of ZnO and CuO nanoparticles and their incorporation in a protective hybrid

coating system as an underlayer followed by electrodeposition of ordinary Zn as a toplayer (in a two-step procedure). It is expected that the presence of ZnO or CuO nanoparticles will create an additional barrier between the zinc coating and the steel substrate, thus blocking (slowing down) the penetration of the corrosion medium deep inside and ensuring passive corrosion protection against localized corrosion and/or biofouling. The protective characteristics of the newly obtained systems are evaluated in a model corrosive medium by the application of potentiodynamic polarization (PDP) curves, open circuit potential (OCP), cyclic voltammetry (CVA), and polarization resistance (R_p) measurements. In addition, a comparative conclusion about the protective characteristics concerning both hybrid coating systems and ordinary zinc in that model medium is completed.

2. Materials and Methods

2.1. Materials and Preparation of Stable ZnO Suspension

Commercially available ZnO nanoparticles (Sigma-Aldrich, Darmstadt, Germany, <100 nm particle size) are applied. Poly(ethyleneimine) (PEI, $M_w = 25$ kDa) was also purchased from Sigma-Aldrich. This polyelectrolyte is selected aiming to improve the stability of ZnO suspension against aggregation and later to promote the nanoparticles' cathodic deposition on steel substrate by electrophoresis. PEI is charged in neutral and acidic solutions due to protonation of $-N-$, $-NH-$, or $-NH_2$ groups.

Stable ZnO suspension is prepared and evaluated according to [34]—0.1 g/L ZnO nanopowder is added to a 0.1 g/L PEI aqueous solution. Thereafter, the so-obtained suspension is ultrasonicated for 10 min with the aim of improving the dispersion of ZnO nanoparticles. The pH value of the suspension at the beginning is ~ 10 , but thereafter, this parameter decreases up to ~ 7.5 during the suspension dilution with water in order to achieve a concentration of 4×10^{-2} g/L.

2.2. Materials and Preparation of Stable CuO Suspension

Commercially available CuO nanopowder (from Sigma-Aldrich, <50 nm) is used for the investigations. The stock suspension of CuO nanoparticles of concentration 1 g/L is prepared by sonication in ice for 15 min while the working concentration is set to 4×10^{-2} g/L in order to ensure better quality for the follow-up experiments. The CuO nanopowder (1 g/L) is added to a PEI aqueous solution (1 g/L), and the suspension is ultrasonicated for 15 min to improve the CuO dispersion. The initial pH value of the suspension is ~ 11 , but it decreases rapidly after dilution with water, reaching ~ 7.5 .

2.3. Characterization of ZnO and CuO Nanoparticles

Both types of nanoparticles are characterized in terms of their stability and particle size. A Dynamic Light Scattering (DLS) particle sizer (Zetasizer Nano ZS, Malvern, Malvern Instruments Ltd., Worcestershire, UK) is used to measure their hydrodynamic diameter. A He-Ne laser is applied as a light source, and the intensity of the scattered light is measured by a detector at 173° . The intensity size distribution and the z-average diameter are obtained from the autocorrelation function. The electrophoretic mobilities U_e of the nanoparticles are measured with a Mark 2 apparatus (Rank Brothers, Cambridge, UK) using a flat cell at room temperature. Their electrokinetic zeta potential ζ is calculated from the electrophoretic mobility by applying Smoluchowski equation $\zeta = 4\pi\eta U_e / \epsilon$, where ϵ is the electric permittivity and η is the viscosity of the medium. Scanning Electron Microscopy (INCA Energy 350 unit, Oxford Instruments, Oxford, UK) is used for evaluation of the surface morphology of the samples obtained [34]. Cross-sections of both hybrid coatings are investigated with straight optical microscope Zeiss Axioscope 5 (ZEISS, Jena, Germany)—magnification $\times 100$.

2.4. Electrodeposition of Hybrid Coatings Containing ZnO

The proposed hybrid coatings are obtained on low-carbon steel samples with working area of 6 cm² (sizes 3 cm × 1 cm × 0.1 cm) and prepared by two-step electrodeposition in the following way:

- (1) First step is to electrodeposit a layer of PEI coated ZnO nanoparticles on low-carbon steel sample at pH 7.5 (to minimize the ZnO solubility effects) at a cathodic current (direct current—DC) density of 0.02 A/dm² and application of non-soluble anodes. The duration of this step is 10 min. As already discussed, the role of PEI is to provide large electrostatic repulsive forces between the positively charged ZnO nanoparticles stabilizing in such a way that the ZnO suspension is promoting their further electrodeposition on the cathode.
- (2) Second step is to electrodeposit zinc coating (thickness ~14 µm) on the obtained ZnO nanoparticles layer from slightly acidic zinc electrolyte (pH 4.5–5.0) at a cathodic current (direct current—DC) density of 2 A/dm² by using soluble zinc anodes. The duration of this step is 20 min.

The electrolyte for obtaining ordinary zinc coating consists of 150 g/L ZnSO₄·7H₂O, 30 g/L NH₄Cl, and 30 g/L H₃BO₃.

2.5. Electrodeposition of Hybrid Coatings Containing CuO

The procedure is identical to the previous one—first, a layer of PEI coated CuO nanoparticles are electrodeposited on steel substrate at pH 9.0 (to minimize the CuO solubility and aggregation effects) at a cathodic current (direct current—DC) density of 0.02 A/dm² and application of non-soluble anodes. Second step is the electrodeposition of zinc (thickness ~14 µm) from the same electrolyte and the same conditions. The duration of the first and second steps is the same—10 min for Step 1 and 20 min for Step 2.

2.6. Corrosion Characterization

The characterization of the newly obtained hybrid coatings compared to the ordinary zinc in terms of the protective properties and corrosion behavior is realized by applying the following electrochemical methods—potentiodynamic (PDP) polarization, polarization resistance (Rp), open circuit potential (OCP), and cyclic voltammetry (CVA).

The protective ability of the galvanic and other coating types can be evaluated by application of the polarization resistance (Rp) method. The value of this parameter is known to be inversely proportional compared to the value of the corrosion current, which follows from the frequently used equation of Stern and Gerry concerning the electrochemical polarization. The measurements are realized in tri-electrode electrochemical glass cell with a volume of 300 mL (working electrode is the coating; reference electrode is Saturated Calomel Electrode; counter electrode is a platinum wire) with a scan rate of 1 mV/s. According to the abovementioned equation, higher Rp values are an indicator for better protective ability and lower corrosion rate as well. The corrosion resistance (as well as the protective ability) of the coatings are estimated with “Corrovit” device (Producer “Tacussel”, Villeurbanne, France). The standard deviation of the experimental results obtained is in the range of about 10%.

Potentiodynamic polarization (PDP) investigations are generally used for accelerated characterization of the corrosion behavior of the coatings at conditions of external polarization. The same tri-electrode electrochemical cell, reference electrode, and counter electrode described above are used for these investigations. Potential range is between −1.2 and 0.4 V, and scan rate is 1 mV·s^{−1}. VersaStat 4 unit (Princeton Applied Research, Oak Ridge, TN, USA) is the electrochemical workstation used. The testing of the samples is realized after preliminary temporizing during 15 min period in the model medium. The potentiodynamic scan initially starts from the cathodic area (−100 mV negative from the corrosion potential). Thereafter, the polarization passes through the corrosion potential zone, reaching the anodic area where the dissolution process occurs. The standard deviation of the experimental results obtained is in the range of about 10%.

PDP curves are stopped after visual appearance of the steel substrate is checked by “naked eye”. The OCP and the R_p measurements are carried out for a prolonged interval of 25 days. CVA tests are carried out in the potential interval between -1.9 and 0.2 V with a scan rate of 10 mV/s. More information about the principles and features of the methods used are described elsewhere [34,35].

2.7. Corrosive Medium

Electrochemical corrosion tests are performed at ambient temperature in a model corrosive medium of 5% NaCl solution with pH value of ~ 6.7 .

2.8. Reproducibility

The results from the investigations are based on average of 5 samples per type and per stage for initial and follow-up measurements.

3. Results and Discussion

3.1. Characterization of ZnO Nanoparticles Dispersion

The dispersion of ZnO nanoparticles in water leads to a self-adjusting pH of 7.5 and a zeta potential of 25 mV. This is below 30 mV, which is accepted as the minimum zeta-potential for electrostatically stabilized suspensions. However, the adsorption of PEI increases the zeta-potential value of the polymer-covered ZnO nanoparticles to about 50 mV, which is high enough to provide stabilization of the suspension. The pH of the suspension remains stable for 72 h after its dilution to a concentration of 4×10^{-2} g/L (pH 7.5). More information concerning the characterization of ZnO nanoparticles is presented elsewhere [34].

3.2. Characterization of CuO Nanoparticles

The stabilization of the CuO nanoparticles with PEI is conducted at pH 9.5, aiming at minimizing the undesirable effects. The zeta potential of the CuO nanoparticles increases after the addition of PEI. The particles exhibit a positive charge: the zeta potential increases from +50 mV for bare CuO nanoparticles at acidic conditions up to +58 mV in the presence of PEI, slightly decreasing at pH 7.0–9.5 and more strongly at pH 11.0. The zeta potential of CuO nanoparticles at the isoelectric point (pH 9.5) is high enough after the adsorption of PEI to minimize the aggregation in the suspension. According to zeta potential measurements, CuO nanoparticles have a positive charge at pH values below the isoelectric point, and the PEI chains are positively charged as well [32]. The latter authors found the best stabilization conditions at pH 3 and pH 9. At pH 3, fully protonated amine groups $[-(\text{NH}_3)^+]$ of the PEI repel each other, while the un-protonated amine groups form weak dative bonds with the Cu^{2+} ions on the surface. At pH 9, stronger dative bonds are formed between the Cu^{2+} ions on the surface and the unprotonated amine groups. At both pH values, the mechanism of stabilization was characterized as electro-steric repulsion [32].

The main conclusion from the above experiments is that the nanoparticles in both suspensions are stabilized against aggregation (zeta-potential of the particles increase to about 50 mV due to the polyelectrolyte adsorption), which is of importance for obtaining layers containing well-dispersed oxide particles of low solubility at pH of the suspensions close to their isoelectric points.

3.3. Surface Morphology and Cross-Sections

Figure 1 shows typical Scanning Electron Microscopy (SEM) micrographs of layers prepared by electrodeposition of A/. ZnO nanoparticles covered with PEI on steel surface; B/. ZnO nanoparticles covered with PEI, followed by electrodeposition of ordinary zinc coating at pH 4.5–5.0. The microstructure of the coatings shows a nearly homogeneous distribution of the particles [34].

Figure 1. SEM micrographs of hybrid ZnO-containing coatings: (A) ZnO nanoparticles before electrodeposition of ordinary zinc; (B) final coating after zinc electrodeposition.

It is obvious that a small number of microscopic pores also appear on the surface, probably caused by water electrolysis during deposition of the ZnO nanoparticles, according to [14]. In addition, it seems that some of the ZnO nanoparticles appear on the surface of the final coating, most likely as a result of their detachment from the steel substrate and the displacement during the zinc electrodeposition.

Figure 2 presents SEM micrographs of CuO nanoparticles coated with PEI after deposition on steel substrate from a suspension with a concentration of 4×10^{-2} g/L at pH 9.0 (Figure 2A). It seems that most of the electrodeposited particles have a size close to that of the primer dry CuO nanoparticles (less than 50 nm). The surface morphology of the hybrid zinc coating with incorporated CuO nanoparticles is demonstrated in Figure 2B. Both micrographs show the formation of uniform zinc coatings on the steel substrate consisting of needle-like formations, most likely with metallic character (zinc compounds).

Figure 2. SEM micrographs of hybrid CuO-containing coatings: (A) CuO nanoparticles before electrodeposition of ordinary zinc; (B) final coating after zinc electrodeposition.

The cross-sections of both hybrid coatings are demonstrated in Figure 3. It is obvious that the thickness of the coatings is about 14 μm . The coatings are randomly thick through their length, and the border with the steel substrate is easily visible. A very thin layer most likely consisting of ZnO or CuO nanoparticles can be observed in that area.

Figure 3. Cross-sections of hybrid ZnO/Zn (A) and CuO/Zn (B) hybrid coatings.

These investigations confirm, in general, the presence of the ZnO and CuO nanoparticles underlayer and the toplayer of ordinary zinc. The estimation mark (shown in white in the lower-right corner of the cross-section) is 10 μm .

3.4. Polarization Resistance Measurements

The experimental results obtained after polarization resistance measurements for a 25 days period of time are presented in Figure 4. It is obvious that both hybrid coatings ZnO/Zn and CuO/Zn demonstrate higher R_p values, reaching $\sim 1240 \Omega \cdot \text{cm}^2$ for ZnO/Zn and $1120 \Omega \cdot \text{cm}^2$ for CuO/Zn at the end of the test. The R_p values of the ordinary zinc vary during the investigating period, reaching about $820 \Omega \cdot \text{cm}^2$ on the twenty-fifth day. It can also be registered that the curve of CuO/Zn shows an ever-increasing trend in contrast to the other samples. Finally, it can be summarized from these results that the newly developed hybrid coatings demonstrate better protective properties against the steel substrate compared to the ordinary zinc in a model medium containing Cl^- ions as corrosion activators.

According to some previous investigations, the reason for such behavior of the hybrid coatings in a neutral corrosive medium is the appearance of a protective layer of zinc corrosion products [35,36]. In the case of hybrid systems, this layer is most likely mixed with the nanoparticles, especially after a prolonged time interval. This will lead to an additional physical barrier effect hindering the penetration of the corrosive agents (Cl^- ions) deep inside, demonstrating an additional protective function. This influence will be supported by the presence of some PEI amounts in the affected area, leading to a slowdown of the corrosion rate. The effect of PEI as a corrosion inhibitor in a NaCl aqueous solution

has earlier been attributed to electrostatic interactions between PEI and the metal substrate, evidenced by X-ray photoelectron measurements [37].

Figure 4. Polarization resistance (R_p) measurements of ordinary Zn and of both hybrid coatings in the model corrosive medium of 5% NaCl.

3.5. Open Circuit Potential

The experimental data from the OCP measurements during the test period for the investigated samples are presented in Figure 5. It can be registered that all the potentials are shifted in the positive direction from about -1.08 V at the beginning of the measurement up to about -1.03 V for Zn and hybrid ZnO/Zn and about -1 V for CuO/Zn at the end. This observation can be explained by the fact that after 25 days, the corrosion process is penetrated deep inside the hybrid coating, most likely reaching the underlayer. In the case of CuO/Zn, the potential is more positive as a result of the appearance of some CuO.

Figure 5. Open circuit potential (OCP) measurements of ordinary Zn and both hybrid coatings in the model corrosive medium of 5% NaCl.

3.6. Polarization Resistance Measurements

Figure 6 demonstrates the potentiodynamic polarization curves of the investigated coatings (as received). It can be seen that both hybrids have lower corrosion current densities compared to the ordinary zinc in that medium, and their corrosion potentials are shifted in the negative direction. This confirms their sacrificial nature, i.e., they will dissolve first in the case of corrosion attack, thus protecting the steel substrate to a higher degree. However, it must be noted that all three coating types are of “sacrificial type” and

will protect (but with different efficiencies, the latter being greater for the hybrids) the steel substrate since the corrosion potential of the latter is about -0.7 V in that medium.

Figure 6. Potentiodynamic polarization measurements of ordinary Zn and both hybrid coatings in the model corrosive medium of 5% NaCl.

The most important electrochemical parameters obtained from this investigation are presented in Table 1.

Table 1. Some important electrochemical parameters obtained from the potentiodynamic polarization measurements (the presented values refer to a representative curve selected from investigations performed with a group of samples of a given species).

Sample/Parameter	$I_{\text{corr}}, \text{A} \cdot \text{cm}^{-2}$	$E_{\text{corr}}, \text{V}$	$I_{\text{pass}}, \text{A} \cdot \text{cm}^{-2}$
CuO/Zn	1.02×10^{-5}	-1.094	6.3×10^{-4}
ZnO/Zn	9.9×10^{-6}	-1.104	1.3×10^{-4}
Zn	1.8×10^{-5}	-1.065	–

Aiming to obtain additional information about the corrosion behavior of all samples, the latter are the objects of potentiodynamic polarization investigations after 25 days of immersion in the model medium. The results are shown in Figure 7. It is obvious that the corrosion potential of the hybrid ZnO/Zn is placed more negatively compared to the corrosion potential of the ordinary zinc. Contrary to this, the corrosion potential of CuO/Zn is shifted strongly in the positive direction, becoming more noble. The most likely reason for this seems to be the appearance of CuO as a result of the corrosion process. In addition, it can be registered that the passivation area does not exist anymore for all the samples investigated. A possible reason for this result seems to be the partial dissolution of the systems, leading to appearing of some corrosion products with barrier properties but also to thinning of the protective layer in depth, and probably partial access of the corrosive agents to the substrate.

Figure 7. Potentiodynamic polarization measurements of ZnO/Zn, CuO/Zn, and ordinary Zn after 25 days' immersion in the model corrosive medium of 5% NaCl.

The electrochemical parameters are shown in Table 2.

Table 2. Some important electrochemical parameters obtained from the potentiodynamic polarization measurements after 25 days' immersion in the model corrosive medium (the presented values refer to a representative curve selected from investigations performed with a group of samples of a given species).

Sample/Parameter	$I_{\text{corr}}, \text{A} \cdot \text{cm}^{-2}$	$E_{\text{corr}}, \text{V}$
CuO/Zn	1.2×10^{-5}	−0.612
ZnO/Zn	1.3×10^{-5}	−1.053
Zn	1.4×10^{-5}	−1.024

3.7. Cyclic Voltammetry

The experiments realized via this method are reported in Figure 8. They are carried out in the starting electrolytes (suspensions) for the electrodeposition of ZnO or CuO nanoparticles, respectively. It is obvious that the electrodeposition process of ZnO or CuO nanoparticle layers (which occurs at low current density) leads to a lower cathodic current rate— 1.5×10^{-4} A for ZnO and 5.1×10^{-4} A for CuO, respectively. Both nanoparticle layers are electrodeposited with overvoltage compared to ordinary zinc (their deposition begins at more negative potentials); see the inset in Figure 8A.

Figure 8. Cont.

Figure 8. Cyclic voltammetry measurements of ZnO/Zn, CuO/Zn, and ordinary Zn: (A) Inset – cathodic process; (B) Inset – anodic process

The anodic branches of both CVA curves confirm the presence of thin layers (ZnO or CuO, respectively), which are dissolved during the anodic polarization—Figure 8B (inset).

4. Conclusions

The presented investigations demonstrate the possibility for stabilization of ZnO and CuO nanoparticles in their suspensions against aggregation (as mentioned above, the zeta-potential of the particles increase to about 50 mV due to polyelectrolyte adsorption). The main idea was to realize a formation of positively charged, PEI-covered nanoparticles, which would be suitable for further electrophoretic deposition at appropriate pH values on the cathode (low-carbon steel substrate) as an underlayer.

Thereafter, an ordinary zinc coating is electrodeposited from a zinc sulfate electrolyte. The obtained hybrid coatings show general homogeneous surface morphology. The results confirm the ZnO or CuO incorporation in the hybrid coating, mainly near the interface between the steel and zinc coating.

The investigation of the corrosion resistance and electrochemical behavior of the obtained coatings with the same thickness as the ordinary zinc one shows better corrosion resistance and protective ability during a prolonged time interval as well as at conditions of external anodic polarization. Both hybrid coatings were found to improve the anticorrosion behavior of steel in a neutral model corrosion medium (5% NaCl) compared with ordinary zinc coating.

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