

# Development of Electrodeposited Zn/nano-TiO<sub>2</sub> Composite Coatings with Enhanced Corrosion Performance

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**Abstract.** Pure zinc coatings have been found ineffective when are used in aggressive environments such as those which contain chlorides or industrial pollutants [1]. In this paper, Zn/nano-TiO<sub>2</sub> composite coatings with various contents of TiO<sub>2</sub> nanoparticles (diameter size of 10 nm) were prepared on low-carbon steel by electro-codeposition technique. The deposition was carried out at different cathodic potentials ranging from -1600 mV to -2100 mV for different deposition times between 5-15 min. Pure Zn coatings were also produced under the same experimental conditions for comparison. Present work aims to investigate the effects of selected electrodeposition parameters (cathodic potential, TiO<sub>2</sub> nanoparticle concentration in the plating bath and electrodeposition time) on the corrosion behavior of electrodeposited Zn/nano-TiO<sub>2</sub> composite obtained. The corrosion experiments were performed in natural seawater, using electrochemical methods such as open circuit potential, potentiodynamic polarization and linear polarization resistance. The results showed that the inclusion of TiO<sub>2</sub> nanoparticles into zinc matrix lead to an improved corrosion resistance comparatively with pure zinc coatings obtained under similar conditions.

## 1. Introduction

The composite layers obtained by the process of codeposition the various dispersed phases with the metals in the process of electro-crystallization. There are still little information due to the limited conditions of production and the properties of the heterogeneous surfaces obtained [1-3]. A method of manufacturing these composite layers, which began to be investigated in 1962, is based on electrolysis of the dispersed phase suspension in a metallic plating bath [4].

Pure and composite zinc coatings have been and are widely used since ancient times, as the most advantageous methods of protection against the corrosion of ferrous and other materials [1-3].

Electrodeposition is one of the most common methods in the industry as the electrochemical coating method, presenting some advantages, requiring simple apparatus, requiring no expensive reagents, and last but not least, it shows great efficacy in the sense that it can be produced a large quantity, high quality and a variety of applicability of the resulting products. The development of these electrodeposition processes has led to a substantial increase in empirical information not only on electrodeposition processes in electrolyte suspensions, but also on the conditions required to obtain a satisfactory composition of composite layer with controlled composition [5-9].



Electrodeposition of composite layers offers the possibility of obtaining new materials by incorporating different dispersion particles into the metal matrix during the electro reduction of the metal in the electrolysis process of its salts.

One of the additives studied and most often used in the electrodeposition process is gelatin, since it reduces the adsorption of hydrogen ions used as an additive along with the basic chloride and, of course, increases cathodic efficiency [10].

A significant current and future interest is to use ceramic nanoparticles in the electrodeposition process in order to obtain nanocomposite materials as layers on top of other materials [11,12]. These types of ceramic particles can be:  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$ , which have a better corrosion resistance than pure zinc. In this case, where particulate matter is used in the electrolyte solution, the process of agglomerating the ceramic particles could occur and therefore a stirring method is needed [1-13].

The method of preparing composite coatings is the most important but least controllable variable that leads and explains sometimes contradictory data about the heterogeneous properties of composite layers [1-10]. This problem of particle formation and sedimentation can be solved by introducing some additive into the electrolyte solution [14,15]. The purpose of the paper is to improve the surface in the sense of lowering the roughness of the electro-codeposited layer and to increase the mechanical properties, especially the hardness. In practice, solutions containing between 150-300 g / L  $\text{ZnSO}_4 \times 7\text{H}_2\text{O}$ , i.e. about 1-2 equivalents-gram, are usually used. Solutions with high concentration of zinc sulphate at medium current density give macrocrystalline deposits. Other salts, in addition to the zinc sulphate electrolyte, are usually alkali metal or alkaline earth metal sulphates or chlorides, salts soluble in the environment, for example:  $\text{Na}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{Al}_2\text{SO}_4$ , and so on. Sulphates and chlorides of alkaline metals are introduced into the zinc electrolyte in particular to increase electrical conductivity, because the solutions of zinc sulphate and sulphates of bivalent metals (cadmium, nickel, copper, etc.) do not have good electrical conductivity [10-16].

Addition of sodium sulfate between 10 g / L and 100 g / L in  $\text{ZnSO}_4$  solution has almost no influence on cathodic polarization. In turn, the electrical conductivity of the solution greatly increases, which has a favorable influence on the dispersion capacity of the electrolyte. Electrolysis of zinc in acidic solutions, the value of anodic and cathodic polarization also depends on the nature of the anions to which the zinc or other cations introduced into the solution are bound. Zinc matrix composites are typically obtained from sulphate solutions, but sometimes alkaline electrolytes with cyanide and non-cyanide alkali electrolytes can be used. Particles that can be codeposited in the zinc matrix are: silicon carbide, silicon oxide, aluminum oxide, titanium dioxide, cerium oxide, vanadium oxide, graphite. [17,18,19].

Our research work aims to investigate the effects of selected electrodeposition parameters (cathodic potential,  $\text{TiO}_2$  nanoparticle concentration in the plating bath and electrodeposition time) on the corrosion behaviour of electrodeposited Zn/nano- $\text{TiO}_2$  composite obtained. The corrosion experiments were performed in natural seawater, using electrochemical methods such as open circuit potential, potentiodynamic polarization and linear polarization resistance. The results showed that the inclusion of  $\text{TiO}_2$  nanoparticles into zinc matrix lead to an improved corrosion resistance comparatively with pure zinc coatings obtained under similar conditions.

## 2. Experimental set-up

### 2.1. Preparation of nanocomposite layers and kinetic studies

Experiments to obtain Zn / $\text{TiO}_2$  nanocomposite coatings in zinc matrix, with nanoparticles of titanium oxide ( $\text{TiO}_2$ ), having a mean diameter of 10 nm, were performed at room temperature in an electrolyte with the composition specified in Table 1.

The electrodeposition experiments were performed in a three electrode electrochemical cell, where the cathode (the support of the layers) was made of carbon steel of dimensions 25 mm x 25 mm x 0.5 mm. The anode made from the zinc bar positioned at a distance of 30 mm from the cathode, having the same size with the cathode to maintain the zinc ions content constantly in the electrolyte solution.

A reference electrode (Ag / AgCl with saturated KCl solution having - E = -199 mV vs. the normal NHE hydrogen electrode) was used. All three electrodes are positioned vertically and parallel to each other. In this configuration, the particles are held in suspension in solution by means of a magnetic stirrer. A potentiostat type VoltaLab PGZ 100 connected to a computer was used for electrochemical measurements.

**Table 1.** Composition and parameters of Zn plating bath.

Compound	Concentration, g / L
ZnSO <sub>4</sub> ·7H <sub>2</sub> O	200 g/L
Na <sub>2</sub> SO <sub>4</sub>	15 g/L
ZnCl <sub>2</sub>	35 g/L
TiO <sub>2</sub> Nanoparticles	5, 10, 20 g/L
pH	4,85
Temperature	25°C
Cathodic potentials	-1600, -1900, -2100 mV vs. Ag/AgCl
Electrodeposition time	5, 10, 15 min.
Magnetic stirring	300 rpm

For the electro-codeposition kinetics study, a VoltaLab PGZ 100 potentiostat connected to a computer was used. In this step a circular zinc plate representing the anode (pure Zn) and the copper substrate in cylindrical form representing the cathode were used. The same reference electrode was used for kinetics studies. In this configuration, the TiO<sub>2</sub> nanoparticles are also kept suspended in the solution by means of a magnetic stirrer.

The following layers were obtained:

Pure Zinc defined layers as: Zn / nano TiO<sub>2</sub> (0 g / L);

Composite layers with a concentration of 5 g / L TiO<sub>2</sub> nanoparticles in the defined solution as: Zn / nano TiO<sub>2</sub> (5 g / L);

Composite layers with a concentration of 10 g / L TiO<sub>2</sub> nanoparticles in the defined solution as: Zn / nano TiO<sub>2</sub> (10 g / L);

Composite layers with a concentration of 20 g / L TiO<sub>2</sub> nanoparticles in the defined solution as: Zn / nano TiO<sub>2</sub> (20 g / L).

## 2.2. Corrosion study of obtained layers

The electrochemical cell used in the electrochemical corrosion tests was also a three electrode one. The cell contains a reference electrode (Ag / AgCl with saturated KCl solution having - E = -199 mV vs. normal NHE hydrogen electrode), a Pt-Rh network representing the counter electrode and pure Zn or Nanocomposite layers representing the cathode. All three electrodes are positioned vertically and parallel to each other. The corrosion experiments were carried out in sea water, taken from the Romanian seaside area, namely Mangalia. This solution has a pH = 7.95, salinity = 11.9‰, conductivity = 19.8 mS, and the volume of solution used in the corrosion tests was 210 mL.

## 3. Results and discussion

### 3.1. The effect of TiO<sub>2</sub> nanoparticles on electrochemical measurements during electrodeposition

The electro-codeposition mechanism is considered to occur in the following steps [1]:

- At the time of introduction into the electrolyte, a layer of adsorbed ionic species is formed at the surface of the particles forming the diffuse double electric layer around each particle.

- The particles are conveyed by stirring and under the influence of electric current, they will spread to the surface of the cathode.

- When the adsorbed ionic species on the particles are reduced, the particles are embedded in the electrodeposited cathodic layer.

These ionic species cannot directly pass through a charge transfer stage, so that the first step in depositing a metal must be its chemical transformation into an electroactive specie. This stage takes place during the diffusion transport of the ionic species to the surface of the electrode which takes place inside the hydrodynamic limit layer or in some cases in the double layer [1].

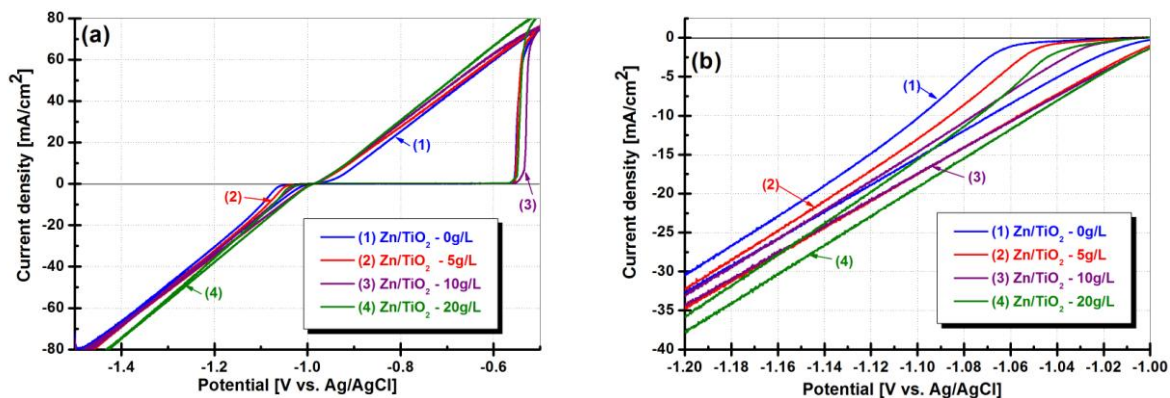
Cyclic voltammetry is one of the most widely used electrochemical methods of investigation, providing information about the electroactive species involved in electrochemical processes (intermediates, products) about the coupling of chemical steps with electrochemical steps, about electro sorption phenomena, as well as kinetic data on the studied processes [2,3].

In this method of investigation, the controlled parameter is the electrode potential that varies over time, and the measured parameter is the current flowing through the electrode.

Using the potentiostat, a controlled potential is applied to the working electrode and the current flowing is measured against a reference electrode. In voltammetry, the two electrodes between which the current flows are: the working electrode and the auxiliary electrode (this electrode must have a surface much larger than the working electrode, which makes it not polarized) [2].

For the cyclic voltammetric study of electro-codeposition process, a voltage starting from a potential of -100 mV (Ag / AgCl) electrode potential was applied to the circuit terminals, reaching the value of -500 mV (vs Ag / AgCl) and then Returned to the potential value of -1500 mV (vs Ag / AgCl). The required potential variation was made for a scanning rate of 1 mV / sec.

Figure 1 (a) and (b) shows the cyclic voltammetry curves plotted at a cathodic potential with and without dispersion of TiO<sub>2</sub> nanoparticles, following the variation of the current density with the reduction potential of the metal.



**Figure 1.** Comparative cyclic voltammetric diagrams performed for electrodeposition of: (1)-Zn/TiO<sub>2</sub> (0 g/L), (2)-Zn/TiO<sub>2</sub> (5 g/L), (3)-Zn/TiO<sub>2</sub> (10 g/L), (4)-Zn/TiO<sub>2</sub> (20 g/L), (a) corresponding to all scanned potential domain and (b) zoom in the cathodic potential range.

According to figure 1 (a) - (b), the presence of TiO<sub>2</sub> nanoparticles in the solution has different effects. Compared to the pure zinc diagram, the TiO<sub>2</sub> nanoparticle curves at a concentration of 5 g / L, 10 g / L and 20 g / L in the zinc plating electrolyte show a shift to more positive potentials.

Considering a constant value of the -1.4 V (vs Ag / AgCl) as cathodic potential in figure 1 (a), it is noted that the current density reveals the lowest value for the pure Zn layer, the corresponding value being of -66.34 mA / cm<sup>2</sup> (t = 100 sec). For the Zn / nano-TiO<sub>2</sub> layer (5 g / L), the current density value increases to -68.68 mA / cm<sup>2</sup> (t = 100 sec) and increases even more for the Zn / nano-TiO<sub>2</sub> layer (20 g/L), the current density value reaching -74.86 mA / cm<sup>2</sup> (t = 100 sec).

The presented results confirm the activation of the Zn electroreduction process in the presence of  $\text{TiO}_2$  dispersed nanoparticles. This behavior demonstrates that one of the intermediate steps of particle codeposition is the adsorption of metal ions on their surface and their migration to the surface of the cathode, the effect of which is the activation of the entire zinc electro-crystallization process. Other authors concluded also that the addition of dispersed nanoparticles moves the nickel reduction curves to more positive potentials. The change in the reduction potential is attributed to the increase in the active surface due to cathodic adsorbed nanoparticles and a possible increase in ionic transport through nanoparticles with adsorbed ionic layers.

### 3.2. The dependence of the thickness of the practical layer obtained versus the codeposition time

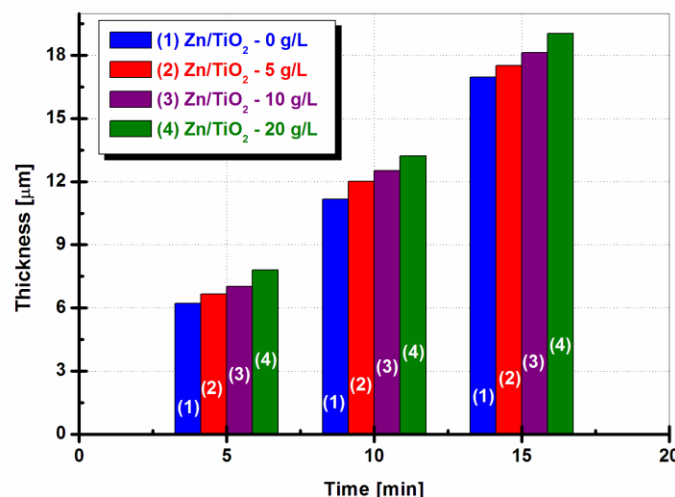
Following electrodeposition, a first examination was visual, and the conclusion drawn from the examination is that at elevated cathodic potential between -1600 mV and -2100 mV, the layer is uniformly deposited having a bright silver color.

Determination of the (practical) thickness of the obtained layers was performed by weighing the samples before and after deposition using the electronic balance of the KERN type, and applying the following formulas:

$$G = \frac{m_d}{S} \text{ and } \Delta G = \frac{G}{\rho_{\text{Zn}}}$$

Where:  $G$  - layer thickness ( $\text{g} / \text{cm}^2$ );  
 $m_d$  - mass deposited at cathode (g);  
 $S$  - active area ( $\text{cm}^2$ );  
 $\Delta G$  - layer thickness ( $\mu\text{m}$ );  
 $\rho_{\text{Zn}}$  - zinc density ( $\text{g} / \text{cm}^3$ ).

The investigations made on these samples confirm that at higher electrodeposition times, the deposited layer or electro-codeposited is more consistent in terms of the practical thickness obtained. The variation of the comparative values of the practical thicknesses corresponding to the layers deposited at the cathodic potential  $E = -1600\text{mV}$  depending on the time of the electrodeposition process (5 min, 10 min, 15 min) is shown in figure 2.



**Figure 2.** Layer thicknesses of electrodeposited layers obtained at cathodic potential of  $E = -1600\text{mV}$ , vs. time of electrodeposition (5 min, 10 min, 15 min): (1) - Pure Zn pur; (2) - Zn/nano-TiO<sub>2</sub> (5 g/L), (3) - Zn/nano-TiO<sub>2</sub> (10 g/L and (4) - Zn/nano-TiO<sub>2</sub> (20 g/L).



From figure 2 it can be noticed that the thickness of all Zn / nano-TiO<sub>2</sub> nanocomposites, with all the concentration of TiO<sub>2</sub> added in the electrolyte, is higher than the thickness of pure zinc layers, considering the same electrodeposition parameters (cathodic potential and time). From figure 2 it can also be noticed that the increase of the concentration of dispersed TiO<sub>2</sub> dispersed phase (5 g / L, 10 g / L and 20 g / L) in the electrolyte also increases the thickness of Zn / nano-TiO<sub>2</sub> nanocomposites.

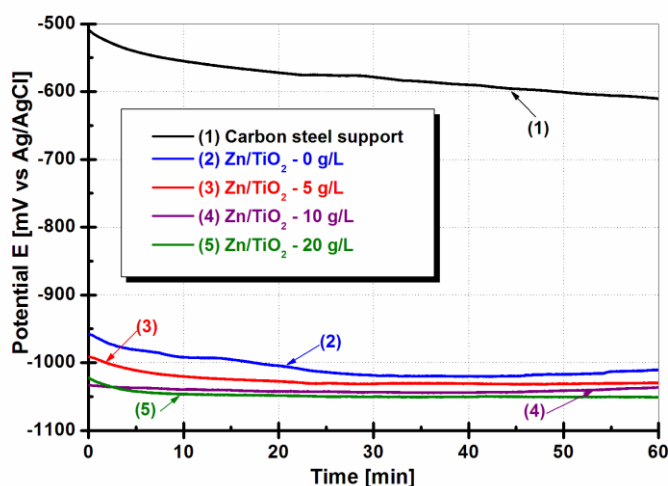
Thus, at the cathodic potential of  $E = -1600\text{mV}$  and the time of 5 minute, the thickness of pure Zn layer has a value of  $6.2097\text{ }\mu\text{m}$ . With the addition of the first TiO<sub>2</sub> concentration (5 g / L), the layer reaches a thickness value equal to  $6.6484\text{ }\mu\text{m}$  and increasing even further to  $7.0196\text{ }\mu\text{m}$  (at TiO<sub>2</sub> concentrations of 10 g / L) and  $7.7958\text{ }\mu\text{m}$  (for TiO<sub>2</sub> concentrations of 20 g / L).

### 3.3. Evaluation of the corrosion resistance for obtained nanocomposite layers

The evolution of open circuit electrode potential (OCP) during time of immersion in corrosive environment is an electrochemical, corrosion test method, indicating the electrochemical oxidation tendency of a material in a corrosive environment. After a period of immersion it stabilizes around a steady state value. This potential may vary over time as changes occur at the surface of the electrode (oxidation, passive layer formation or immunity). The open circuit potential is used as a corrosion behaviour criterion.

Passivation is an electrochemical and / or chemical process which consists in lowering the corrosion rate to very low values due to the qualitative modification of the metal interface / corrosive agent. This change may be due to the formation of a poorly soluble oxide or salt film or a chemisorbed, adherent oxygen layer lacking discontinuities acting as a kinetic barrier and preventing oxidation and solvation of the formed ions. In the state of passivity, metals are virtually immune to corrosion and, from an electrochemical point of view, behave like noble metals.

Figure 3 shows the time variation of the open circuit electrode potential for the uncoated support material (1), the pure Zn layers (2), Zn / TiO<sub>2</sub> nanocomposites - 5 g / L (3), Zn / TiO<sub>2</sub> - 10 g / L (4) and Zn / TiO<sub>2</sub> - 20 g / L (5), obtained at the imposed cathode potential of  $E = -2100\text{mV}$  and the electrodeposition time of 15 minutes.



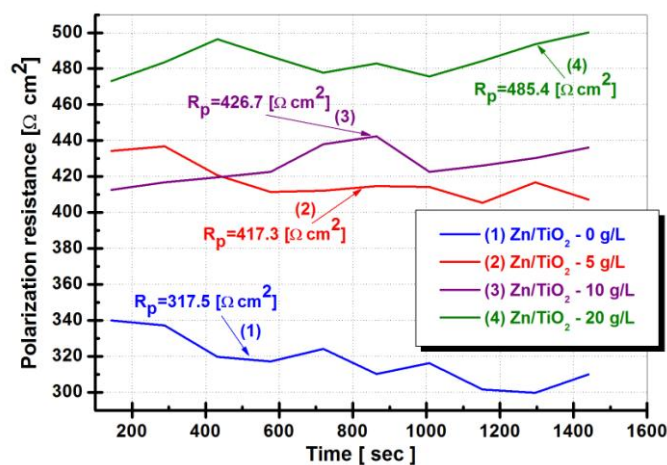
**Figure 3.** Time variation of the open circuit electrode potential corresponding to: (1) - the uncoated support material; (2) - Pure Zn layer; (3) - Zn / TiO<sub>2</sub> nanocomposite (5 g / L); (4) - Zn / TiO<sub>2</sub> nanocomposite (10 g / L); and (5) - Zn / TiO<sub>2</sub> nanocomposite (20 g / L), obtained at the imposed cathodic potential of  $E = -2100\text{ mV}$  vs. Ag/AgCl and the electrodeposition time of 15 minutes.

It can be seen from figure 3 that the uncovered support material does not reach the passivation state, its potential decreasing continuously during the immersion time and the end of the first monitoring period. The time evolution of the free potential of pure Zn and Zn / TiO<sub>2</sub> nanocomposites reveals an almost instantaneous passive state since immersion. These observations confirm the beneficial contribution of the studied Zn / TiO<sub>2</sub> coatings deposited on carbon steel, from the point of view of corrosion immunity. These Zn / TiO<sub>2</sub> nanocomposite coatings act as a kinetic barrier and prevent oxidation and solvation of the formed corrosion products.

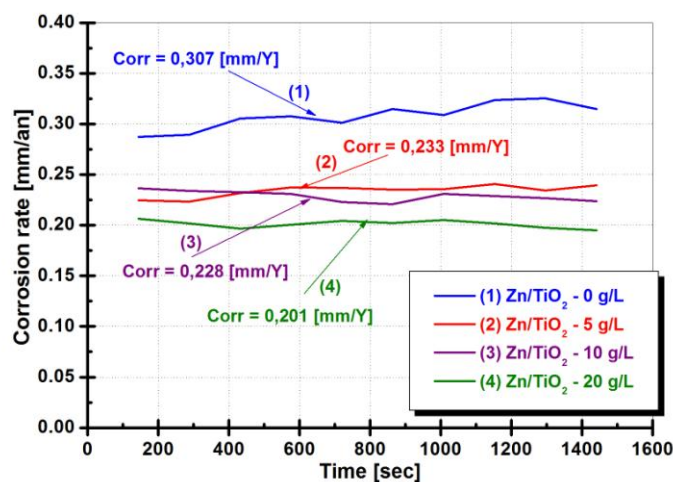
From figure 3 it can also be noticed that with the increase of the concentration of  $\text{TiO}_2$  nanoparticles in the electrolyte, the potential is more electronegative. This behavior can be attributed to the ceramic nanoparticles embedded in the zinc matrix.

Linear polarization is an electrochemical corrosion monitoring technique, being the only method to determine corrosion rate directly in the real time. Response time and data quality of this technique make this method clearly superior to all other forms of corrosion monitoring.

Figure 4 shows the polarization resistance obtained by several linear polarization around open circuit potential with a small perturbation of  $\pm 40$  mV. The diagrams correspond to pure Zn layers and Zn /  $\text{TiO}_2$  nanocomposites obtained with 5 g / L to 20 g / L of dispersed  $\text{TiO}_2$  nanoparticles. All the electrodeposited layers were obtained at the imposed cathodic potential of  $E = -2100\text{mV}$  and the time of the electrodeposition process equal to 15 minutes.



**Figure 4.** Polarization resistance corresponding to electrodeposited layers: (1) - Pure Zn; (2) - Zn/ $\text{TiO}_2$  - 5 g/L; (3) - Zn/ $\text{TiO}_2$  (10 g/L) (3); (4) - Zn/ $\text{TiO}_2$  (20 g/L), obtained at an imposed cathodic potential of  $E = -2100\text{mV}$  and electrodeposition time of 15 minutes.



**Figure 5.** The corrosion rate expressed as penetration rate of : (1) - Pure Zn; (2) - Zn/ $\text{TiO}_2$  - 5 g/L; (3) - Zn/ $\text{TiO}_2$  (10 g/L) (3); (4) - Zn/ $\text{TiO}_2$  (20 g/L), obtained at an imposed cathodic potential of  $E = -2100\text{mV}$  and electrodeposition time of 15 minutes.

It should be noted that the polarization resistance is directly proportional to corrosion resistance, better if the polarization resistance is high then the studied material exhibits increased corrosion resistance. From figure 4, it can be clearly seen that the smallest polarization resistance belongs to the pure Zn layer, while that corresponding to Zn /  $\text{TiO}_2$  nanocomposite layers increases with increasing the dispersed phase concentration added to the electrolyte. Linear polarization measurements have demonstrated that the incorporation of  $\text{TiO}_2$  nanoparticles into the zinc matrix leads to improved

polarization resistance and therefore to the improved corrosion resistance in tested corrosive environment.

Figure 5 shows the corrosion rate obtained by linear polarization, corresponding to tested electrodeposited layers, expressed as penetration rate.

From figure 5, it can be clearly seen that the highest corrosion rate belongs to the pure Zn layer, whereas that corresponding to Zn / TiO<sub>2</sub> nanocomposite layers decreases with the increasing of the dispersed phase concentration added to the electrolyte.

Linear polarization measurements have once again demonstrated that the incorporation of TiO<sub>2</sub> nanoparticles into the zinc metallic matrix leads to improved corrosion resistance.

#### 4. Conclusions

The paper aimed to obtain nanocomposite coatings by electrochemical method with dispersed phase of nanometric TiO<sub>2</sub> particles (10 nm) in zinc matrix with the application of improving the anti-corrosion properties. The properties of the Zn / TiO<sub>2</sub> nanocomposite layers obtained are compared with the pure zinc layers obtained at the same time and cathodic potential parameters.

Following the analysis of the experimental results of this research paper led to the following conclusions:

The important factors that influence the quality of nanocomposite layers are: electrolyte composition, electrolysis conditions (cathodic potential, deposition time, temperature, stirring mode).

The nano dispersed TiO<sub>2</sub> particles in the zinc plating solution are contributing to the electrolysis process, which is confirmed by their effect on the the cyclic voltammetry at the cathodic potential traced in the electrolyte

Both in the case of pure zinc layers and nanocomposite layers, the thickness of the layer increases with the increase of the required cathodic potential. For nanocomposite coatings, layer thickness is slightly higher comparatively with that of pure zinc at the same deposition time, thus confirming the inclusion of TiO<sub>2</sub> nanoparticles in the zinc matrix.

The thickness of the electrodeposited layers increases with the increase of the electrodeposition time, a higher increase is observed in the thickness of the nanocomposite layers compared to the thickness of the pure zinc layers obtained at the same imposed cathodic potential.

The comparative study of corrosion resistance shows an improvement by including TiO<sub>2</sub> nanoparticles in the zinc matrix. Thus, the polarization resistance,  $R_p$ , increases from 317  $\Omega \cdot \text{cm}^2$  for pure zinc layers to 485  $\Omega \cdot \text{cm}^2$  for Zn / nano-TiO<sub>2</sub> nanocomposites (20 g / L).

The corrosion rate, expressed as penetration rate, decreases from 0.307 mm / year for pure zinc layers to 0.201 mm / year for Zn / nano-TiO<sub>2</sub> nanocomposite layers.

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