COMPARATIVE RESEARCH REGARDING CORROSION PROTECTIVE EFFECT OF DIFFERENT SANDWICH TYPE NANOSTRUCTURES OBTAINED FROM PORPHYRINS AND PSEUDO-BINARY OXIDES BY CHANGING THE DEPOSITION ORDER

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Abstract

Macrocyclic compounds like porphyrins form very stable metallic complexes which show a great potential as corrosion-inhibiting agents. Free porphyrins and metalloporphyrins can be adsorbed on metal surfaces creating protective layers against corrosion. Furthermore, porphyrins can even form coordinative bonds with the base metal during the formation of the adsorbed layer. Recent studies proved that pseudo-binary oxides of zinc containing niobium and tantalum exhibit excellent corrosion resistance in many different environments. These experimental results focused on obtaining thin films based on porphyrins/pseudo-binary oxides and pseudo-binary oxides/porphyrins. The pseudo-binary oxide nanomaterials ($Zn_3Ta_2O_8$ and $Zn_3Nb_2O_8$) were synthesized by solid-state method. The novel mixed substituted A_3B porphyrins, each containing one pyridyl group, have been obtained by multicomponent Adler-Longo synthesis. The topography of thin films was thoroughly characterized by AFM microscopic techniques. The corrosion protection exhibited by these nanostructures after deposition on carbon steel was comparatively assessed in 0.1 mole/L H_2SO_4 media. Different electrochemical techniques, such as: open circuit potential measurement and potentiodynamic polarization technique with Tafel representation were used. The performed tests reveal that corrosion protection is fairly good, with the best results indicating that the electrode covered with $Zn_3Ta_2O_8$/5-pyridyl-10,15,20-tris(3,4-dimethoxy-phenyl)porphyrin offers the highest inhibition efficiency: 95,91%.

Keywords: thin films, corrosion, porphyrins, pseudo-binary oxides, AFM.

1. INTRODUCTION

Steel is a type of widely used engineering material for many industries and is found in manufacturing, construction, defence, transportation, medicine, and other applications [1]. However, steel is affected by corrosion leading to high degree and with blunt economical implications: every year, billions of dollars are spent on capital replacement and control methods [2].

Heterocyclic organic compounds, have been proved to be corrosion inhibitors for carbon steel in various aggressive environments [3,4]. Porphyrin derivatives are capable of developing supramolecular structures, forming oriented self- assembles and strong bonds with metal surfaces. The unoccupied d orbital of iron, can accept π electrons from the porphyrin conjugated system, leading to the formation of an adherent adsorptive film [5].

In recent years, corrosion of steel was investigated in aggressive aqueous media and the effect of porphyrins as corrosion inhibitors was put into evidence [6-11]. Attempts to improve the corrosion stability of zinc coatings have been based on the use of alloys containing more noble metals or on the addition of surface inhibitors [12].

Our preliminary studies showed that substitution of zinc oxide with niobium and tantalate, to produce pseudo-binary oxides, exhibit improved corrosion resistance in neutral medium.

The present paper describes a comparative study of the corrosion inhibition properties in 0.1 mole/L H_2SO_4 media, exhibited by bilayer depositions on carbon steel electrodes, based on different combinations of the following compounds: $Zn_3Ta_2O_8$, $Zn_3Nb_2O_8$, 5-(4-pyridyl)-10,15,20-tris(phenoxy-phenyl) porphyrin and 5-(4-pyridyl)-10,15,20-tris(3,4-dimethoxy-phenyl) porphyrin.

2. EXPERIMENTAL

Novel mixed substituted A_3B porphyrins: 5-(4-pyridyl)-10,15,20-tris(phenoxy-phenyl) porphyrin (PyTFen) and 5-(4-pyridyl)-10,15,20-tris(3,4-dimethoxy-phenyl)porphyrin (PyTDMeO), have been synthesis by multicomponent Adler-Longo method [13-15]. The porphyrin adlayers were obtained using the drop-casting method. PyTFen and PyTDMeO were dissolved in tetrahydrofuran (10^{-4} mole/L) and volumes of 20μL from this solution were applied as drops on the sample surfaces. After solvent evaporation thin films of PyTFen or PyTDMeO have been obtained.

Powder samples of $Zn_3Ta_2O_8$ and $Zn_3Nb_2O_8$ pseudo-binary oxides were obtained by solid-state method. The starting materials for the synthesis were: tantalum (V) oxide - Ta_2O_5 (99.99 %, Merck), niobium (V) oxide - Nb_2O_5 (99.99 %, Merck) and zinc oxide – ZnO (99.99 %, Merck). Each mixture of oxides was milled and afterwards heated at 1200 ºC for 3 h soaking time. The heating and cooling rate of the heated furnace was set at a rate of 5 ºC/min. The samples were dissolved under aggressive conditions in a HF mixture for 2 hours, at 200ºC and subsequently diluted with a controlled volume of double distilled water. These solutions were used to form adlayers on carbon steel surfaces (5 minutes immersion), before or after porphyrin deposition.

The bilayer morphologies were investigated by atomic force microscopy – AFM (Model Nanosurf® EasyScan 2 Advanced Research), using the non-contact mode cantilever (scan size of 2 μm x 2 μm). The corrosion behaviour was studied using a Voltalab potentiostat Model PGZ 402. A single compartment three-electrode cell was employed along with a platinum wire as the counter electrode and saturated calomel electrode (SCE) as reference electrode. Bare (OL) and coated carbon steel substrates were used as working electrodes. The composition of the carbon steel was (wt.%): C: 0.12 ÷ 0.18, Si: 0.10 ÷ 0.35, Mn: 0.70 ÷ 1.10, P: 0.03, S: 0.07 ÷ 0.13 and Fe: 98.21 ÷ 98.98. All potentials reported in this article were referenced to the standard hydrogen electrode (SHE). The electrolyte solution was 0.1 mole/L H_2SO_4. Before each experiment the electrode surface was mechanically polished to a mirror-like surface using emery paper of different grades, rinsed with double distilled water and degreased with ethanol.

The potentiodynamic polarization curves, recorded after 30 minutes immersion in corrosion solution, were analyzed using VoltaMaster 4, v.7.09 software. This software performed the Tafel fitting and calculated the values of the corrosion potential (E_{corr}), corrosion current density (i_{corr}) and corrosion rate (v_{corr}).

3. RESULTS AND DISCUSSION

3.1 Morphological characterization

Figure 1 shows AFM images recorded for various bilayers based on combinations of pseudo-binary oxides and porphyrins. The surface roughness - the average roughness (S_a) and the mean square root roughness (S_q) – were calculated from AFM data, according to [16].

The chosen measured area (5.139 pm^2) for the roughness values of the bilayers were: S_a= 21 nm and S_q= 27 nm for $Zn_3Ta_2O_8$/PyTFen; S_a= 6.3 nm and S_q= 8.7 nm for $Zn_3Ta_2O_8$/PyTDMeO; S_a= 15 nm and S_q= 20 nm for $Zn_3Nb_2O_8$/PyTFen; S_a= 10 nm and S_q= 13 nm for $Zn_3Nb_2O_8$/PyTDMeO; S_a= 32 nm and S_q= 40 nm for PyTFen/$Zn_3Ta_2O_8$; S_a= 34 nm and S_q= 43 nm for PyTFen/$Zn_3Nb_2O_8$; S_a= 19 nm and S_q= 25 nm for PyTDMeO/ $Zn_3Ta_2O_8$ S_a= 29 nm and S_q= 37 nm for PyTDMeO/ $Zn_3Nb_2O_8$, respectively.

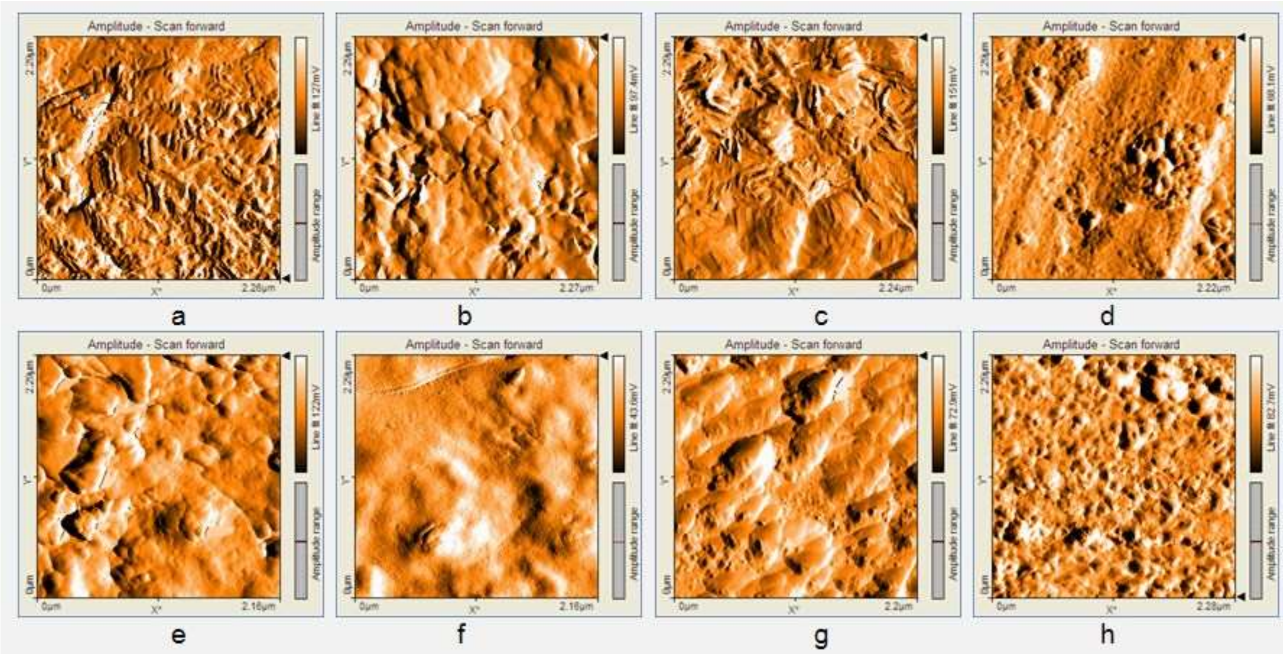

Fig. 1. 2D AFM surface images of a) $Zn_3Ta_2O_8$/PyTFen; (b) $Zn_3Ta_2O_8$/PyTDMeO; (c) $Zn_3Nb_2O_8$/PyTFen; (d) $Zn_3Nb_2O_8$/PyTDMeO; (e) PyTFen/$Zn_3Ta_2O_8$; (f) PyTFen/$Zn_3Nb_2O_8$; (g) PyTDMeO/ $Zn_3Ta_2O_8$ and (h) PyTDMeO/ $Zn_3Nb_2O_8$ bilayers deposited on carbon steel surfaces

These results show that the carbon steel surface, modified with $Zn_3Ta_2O_8$ / PyTDMeO bilayer showed the smallest values for both S_a and S_q, indicating uniform and continuous deposition, which are the main requirements for a material to protect a surface.

3.2 Corrosion protection evaluation

The corrosion protection property of the obtained bilayers was monitored in 0.1 mole/L H_2SO_4 aqueous solutions, by measuring the open circuit potential (OCP) for 30 minutes and recording polarization curves with Tafel representation.

Figure 2 shows the open circuit potential plotted against time for various carbon steel electrodes modified with all possible binary combinations formed from an oxide and a porphyrin ($Zn_3Ta_2O_8$, $Zn_3Nb_2O_8$, PyTFen and PyTDMeO). It can be observed that the bilayers move the electrode OCP values, toward more negative directions, by comparison with the bare electrode. The OCP values of the film modified electrodes were relatively negative immediately after they were immersed in solution and afterward a constant potential was observed. The potentiodynamic polarization measurements were performed by sweeping the potential between − 1.3 and 0.2 V, in 0.1 mole/L H_2SO_4 electrolyte solution, at a scan rate v = 1 mV/s.

The corrosion inhibition efficiency IE(%) was calculated on the basis of equation (1) [17]:

$$IE\% = \left(1 - \frac{i_{corr}}{i^0_{corr}}\right) \times 100 \qquad (1)$$

where, i^0_{corr} and i_{corr} are the corrosion current densities in the absence and presence of bilayers.

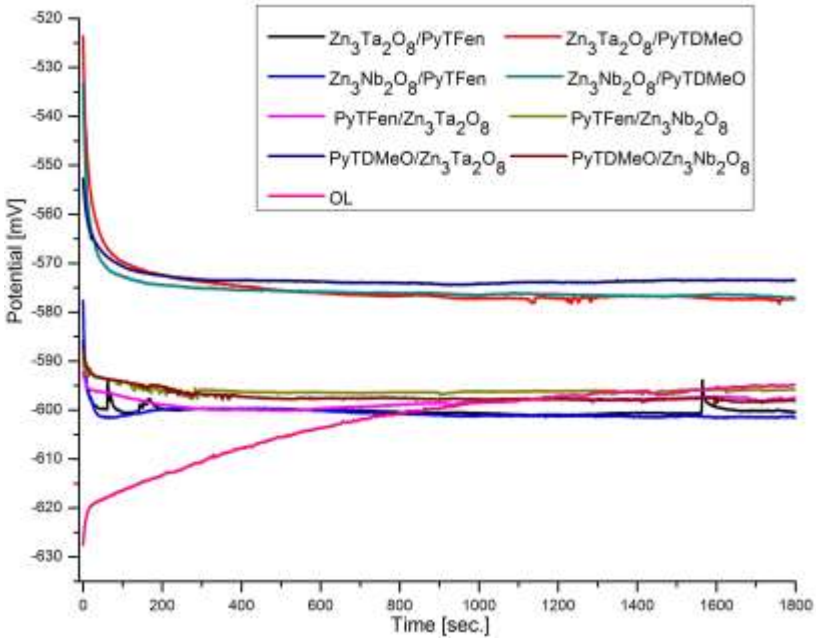

Fig. 2. Evolution of OCP with time, in 0.1 mole/L H_2SO_4 electrolyte solution, recorded for bare and bilayer modified carbon steel electrodes: $Zn_3Ta_2O_8$/PyTFen; $Zn_3Ta_2O_8$/PyTDMeO; $Zn_3Nb_2O_8$/PyTFen; $Zn_3Nb_2O_8$/PyTDMeO; PyTFen/$Zn_3Ta_2O_8$; PyTFen/$Zn_3Nb_2O_8$; PyTDMeO/$Zn_3Ta_2O_8$ and PyTDMeO/$Zn_3Nb_2O_8$

The slopes were determined in the Tafel region of the anodic and cathodic curves for segments of about 50 mV, before and after the corrosion potential. The current density corresponds to the rate of electrochemical reactions associated with corrosion processes taking place on OL surface, during polarization in 0.1 mole/l H_2SO_4 media.

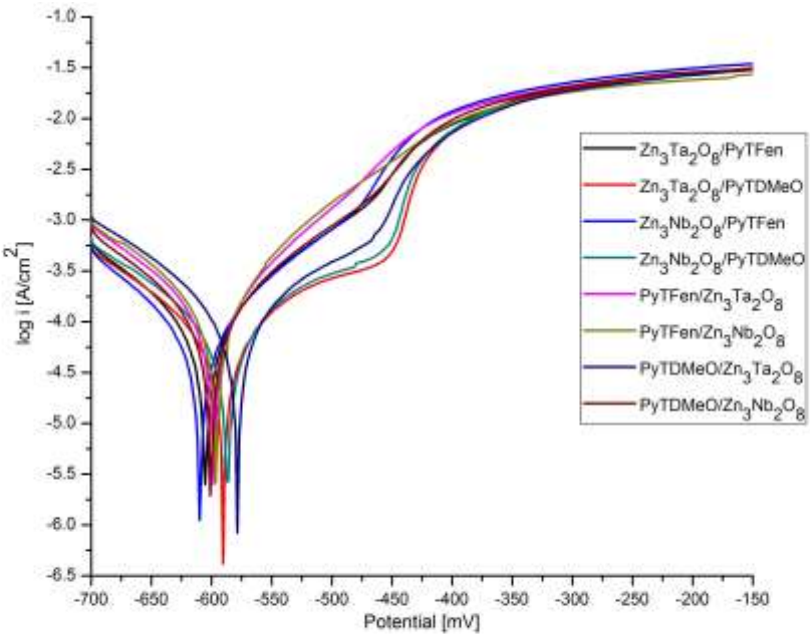

Fig. 3. Tafel representation of polarisation curves recorded in 0.1 mole/L H_2SO_4 for the bilayer modified carbon steel electrodes, *v* = 1 mV/s.

Table 3. Tafel parameters derived from potentiodynamic curves of carbon steel electrodes, unmodified and modified with bilayers based on porphyrins and pseudo-binary oxides, after 30 minutes immersion in 0.1 mole/L H_2SO_4.

Electrode	E_{corr} [mV]	i_{corr} [mA/cm²]	v_{cor} [mm/Y]	IE [%]
Bare (OL)	-592.0	1.5707	18.25	0
$Zn_3Ta_2O_8$ / PyTFen	-606.5	0.1141	1.325	92.73
$Zn_3Ta_2O_8$ / PyTDMeO	-591.8	0.0642	0.746	95.91
$Zn_3Nb_2O_8$ / PyTFen	-611.1	0.0901	1.047	94.26
$Zn_3Nb_2O_8$ / PyTDMeO	-588.3	0.0822	0.956	94.76
PyTFen / $Zn_3Ta_2O_8$	-600.0	0.1354	1.573	91.37
PyTFen / $Zn_3Nb_2O_8$	-597.4	0.1742	2.025	88.90
PyTDMeO / $Zn_3Ta_2O_8$	-580.0	0.1244	1.446	92.07
PyTDMeO / $Zn_3Nb_2O_8$	-602.1	0.1306	1.518	91.68

The performed tests reveal that the corrosion protection is fairly good for all studied bilayers. The deposition order of the various compounds influenced the inhibition efficiency as follows: when the porphyrin derivative formed the top layer, a better efficiency was observed than when this layer was obtained using pseudo-binary oxides.

The best results were recorded for the electrode modified with $Zn_3Ta_2O_8$ / PyTDMeO bilayer, where a corrosion inhibition efficiency of 95,91% was calculated.

4. CONCLUSIONS

Two pseudo-binary oxides - $Zn_3Ta_2O_8$ and $Zn_3Nb_2O_8$ - and two novel mixed substituted A_3B porphyrins - PyTFen and PyTDMeO - were deposited as bilayers in different order on the surface of carbon steel electrodes.

The electrochemical parameters of the Tafel curves illustrate a good corrosion protection in the presence of all combinations deposited on carbon steel surfaces.

The best results were recorded for the $Zn_3Ta_2O_8$ / PyTDMeO modified electrode, with a corrosion inhibition efficiency of 95.91%. Based on AFM results, the surface of carbon steel modified with this bilayer showed the smallest values for both S_a and S_q, indicating a very good correlation between rugosity and corrosion protection. This uniform and continuous deposition satisfy the main requirement for a material to protect a surface.

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