

Application of Stabilized Polyaniline Microparticles for Better Protective Ability of Zinc Coatings

N. Boshkova, K. Kamburova, N. Tabakova, N. Boshkov, Ts. Radeva

Abstract—Coatings based on polyaniline (PANI) can improve the resistance of steel against corrosion. In this work, the preparation of stable suspensions of colloidal PANI-SiO₂ particles, suitable for obtaining of composite anticorrosive coating on steel, is described. Electrokinetic data as a function of pH are presented, showing that the zeta potentials of the PANI-SiO₂ particles are governed primarily by the charged groups at the silica oxide surface. Electrosteric stabilization of the PANI-SiO₂ particles' suspension against aggregation is realized at pH>5.5 (EB form of PANI) by adsorption of positively charged polyelectrolyte molecules onto negatively charged PANI-SiO₂ particles. The PANI-SiO₂ particles are incorporated by electrodeposition into the metal matrix of zinc in order to obtain composite (hybrid) coatings. The latter are aimed to ensure sacrificial protection of steel mainly in aggressive media leading to local corrosion damages. The surface morphology of the composite zinc coatings is investigated with SEM. The influence of PANI-SiO₂ particles on the cathodic and anodic processes occurring in the starting electrolyte for obtaining of the coatings is followed with cyclic voltammetry. The electrochemical and corrosion behavior is evaluated with potentiodynamic polarization curves and polarization resistance measurements. The beneficial effect of the stabilized PANI-SiO₂ particles for the increased protective ability of the composites is commented and discussed.

Keywords—Corrosion, polyaniline particles, zinc, protective ability.

I. INTRODUCTION

THE process of the corrosion degradation of the steel is a great economical problem which could lead also to ecological and social (human) losses. It is well known that steel constructions like bridges, tanks, ships, armature etc. are widely used in the world – for example in the industry and civil engineering.

One common method to preserve steel against corrosion is the application of different types of protective coatings, including composite ones being with good adhesion and able to create strong physical barrier between the metal/alloy surface and the surrounding corrosive media.

PANI is a conducting polymer that can exist in different forms, depending on the degree of protonation or extent of oxidation of its chains. It is widely studied as an additive to

the conventional organic coatings used for protection of metallic substrates against corrosion. Two forms of PANI are most extensively studied in anticorrosive coatings: the conducting emeraldine salt (ES) and non-conducting emeraldine base (EB). The ability to intercept electrons at the metal surface and to transport them is typically attributed to ES, while the success of EB as anticorrosive additive in the coating is attributed to its ability to oxidize and reduce in a reversible way [1]. This electrochemical mechanism is most probably combined with barrier effect against corrosion species [2].

At present, it remains unknown whether the conductive or non-conductive forms of PANI provide better corrosion protection for metals. The findings of Holness et al. [3] convincingly demonstrate that the ES induces a significant oxide layer growth on a steel surface, which is an indication for enhanced corrosion underneath the ES. However, no enhanced corrosion has been found for the case of ES on zinc, where the formation of an insulating and very protective interfacial layer was proposed. Comparing ES and EB coatings, Spinks et al. [4] concluded that the EB provided better protection against corrosion for steel substrates. Many studies indicate that coatings based on EB are equally capable of maintaining the potential of the steel substrate within the passive region. For the case of EB on zinc, an isolating layer has also been found to appear as in the case of ES on zinc [5].

II. MATERIALS AND METHODS

A. Preparation of PANI Particles

Preparation of colloidal suspension of PANI particles is one way to increase their active surface area. In the present work, the preparation of stable suspensions of colloidal PANI-SiO₂ particles (in the EB form), suitable for incorporation into the metal matrix of a zinc coating by electrodeposition on a steel surface, is described. Incorporation of individual particles is expected to provide a more homogeneous distribution into the zinc coating matrix.

PANI-SiO₂ colloids are prepared in water using dispersion oxidative polymerization of aniline hydrochloride in the presence of fine silica particles and ammonium peroxydisulfate according to the procedure described in the literature [6]. When the mixture is thermostated to – 4 °C, stable suspension of approximately spherical particles is obtained.

B. Electrodeposition Process

Zinc and composite coatings with embedded PANI-SiO₂ particles are electrodeposited from a slightly acidic sulfate electrolyte (pH about 4.5-5.0) containing ZnSO₄·7H₂O – 150

N. Boshkova, K. Kamburova, and Ts. Radeva are with the Institute of Physical Chemistry, Bulgarian Academy of Sciences (IPC-BAS), Sofia 1113, Acad. G. Bonchev, bl. 11, Bulgaria (e-mail: nelly.boshkova@ipc.bas.bg, kamelia@ipc.bas.bg, radeva@ipc.bas.bg).

N. Tabakova is with the Institute of Organic Chemistry, BAS (e-mail: tabakova@orgchm.bas.bg).

N. Boshkov is with the IPC-BAS, Sofia 1113, Acad. G. Bonchev, bl. 11, Bulgaria (corresponding author, phone: 0035929792521, e-mail: NBoshkov@ipc.bas.bg).

g/L, $(\text{NH}_4)_2\text{SO}_4 - 30 \text{ g/L}$, $\text{H}_3\text{BO}_3 - 30 \text{ g/L}$ and wetting agent AZI (concentration 50 mL/L). The electrodeposition process is carried out in a glass cell with volume of 300 mL at room temperature, current density value of 2 A/dm^2 and application of metallurgical zinc anodes.

The concentration of the added PANI-SiO₂ particles in the zinc sulfate solution for obtaining of the composite coating is 10^{-1} g/L .

Both coating types (ordinary Zn and composite one) are electrodeposited on low carbon steel samples with sizes $20 \times 10 \times 1 \text{ mm}$. The thickness of the coatings is calculated to be about 10-12 μm .

C. Methods for Characterization of the Coatings

- Scanning Electron Microscopy

The size of the particles obtained after polymerization of aniline in the presence of fine SiO₂ particles as well as the surface morphology of the composite coatings is examined by Scanning Electron Microscopy using a JEOL JSM 6390 electron microscope (Japan).

- Cyclic Voltammetry (CVA)

The investigations are carried out aiming to characterize the cathodic and anodic processes occurring in the starting electrolyte in the presence or absence of PANI-SiO₂ particles. The cyclic voltammetry measurements are carried out in a three-electrode glass cell with 250 mL volume by using of VersaStat 4 (PAR) unit at a scan rate of 10 mV/s. Saturated calomel electrode (SCE) is applied as a reference electrode and platinum plate is the counter electrode. Working electrode is a Pt-rod with area of 0.164 cm^2 .

- Potentiodynamic Polarization Curves (PDP)

Potentiodynamic polarization curves are performed for evaluation of the electrochemical behavior of the coatings at conditions of external polarization in model corrosion medium using a VersaStat 4 (PAR) unit.

The investigations are carried out in a three-electrode electrochemical cell of 250 mL volume at a scan rate of 1 mV/s. Counter-electrode is platinum wire and saturated calomel electrode is used as a reference electrode. Prior to initiating the experiment, the coating samples (working electrode) are kept in the test medium at open circuit potential (OCP) conditions during 10 minutes in order to stabilize the potential value.

- Polarization Resistance (Rp)

Polarization resistance (Rp) measurements are realized by using of "Corrovit" unit applying the same electrolytic test cell and according to Stern-Geary equation - higher Rp value (in ohm.cm^2) corresponds to higher corrosion resistance and to lower corrosion rate, respectively.

- Corrosion Medium and Reproducibility

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

The results are in average of three samples per type, i.e. for

each measurement three replicates of ordinary Zn and composite Zn coatings are used.

III. RESULTS AND DISCUSSION

Fig. 1 presents the dependence of the electrophoretic mobility of the PANI-SiO₂ colloidal particles on pH for aqueous suspension with concentration 10^{-1} g/L after 1 min sonication. The initial pH of the suspension is 2.2 and it is enhanced to pH 8.0 by addition of NaOH.

It can be seen that the particle charge changes from positive to negative with increasing of pH, most probably due to the ionization of the silanol groups on the particle surface. The suspension shows isoelectric point at pH 5.0-5.5, accompanied with visible aggregation as a result of the full charge neutralization at these pH values. In the range of pH 5.5 – 8.0, the aqueous suspension is stabilized against aggregation due to the increased repulsion between the negatively charges on the particles surface. In this pH regime, the suspension changes its color from dark green (pH < 5.5) to blue, indicating transformation of ES of PANI to EB. Since the incorporation of the PANI-SiO₂ particles into the ordinary zinc coating is performed at pH 4.5 - 5.0, where the suspension is not stable, we covered the particles by a layer of positively charged polyelectrolyte poly(diallyldimethyl-ammonium chloride) (PDADMAC) to stabilize the suspension against aggregation and to make the PANI-SiO₂ particles suitable for electrophoretic deposition on steel (cathode) surface.

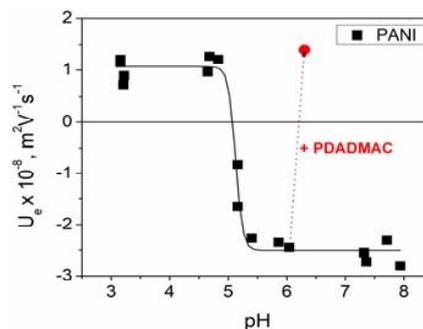


Fig. 1 pH dependence of electrophoretic mobility of PANI-SiO₂ particles in 10^{-1} g/L aqueous suspension. Particles become positively charged after addition of PDADMAC with concentration 10^{-1} g/L

The adsorption of PDADMAC is carried out at pH 6.3 from aqueous solution of the polymer with a concentration 10^{-1} g/L . This concentration is high enough to recharge the particles surface from negative to positive (electrophoretic mobility becomes $+1.4 \times 10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$) and to keep the suspension stabilized against aggregation. It is important to note that the color of the suspension remains blue, i.e. the electrostatic adsorption of the positively charged PDADMAC has no influence on the EB form of PANI. When the pH value of the suspension containing PDADMAC covered PANI-SiO₂ particles is decreased from pH 6.3 to pH 5.0, the suspension remains visible stable, keeping its blue color.

- Scanning Electron Microscopy Characterization

The typical size of the PANI-SiO₂ particles after polymerization of aniline is determined by electron microscopy to be in the range 300-400 nm (Fig. 2).

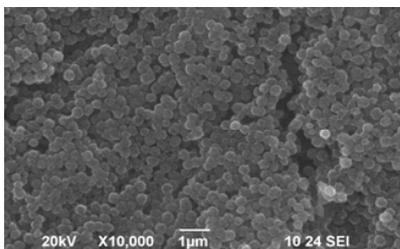


Fig. 2 SEM micrographs of PANI-SiO₂ particles obtained after polymerization of aniline

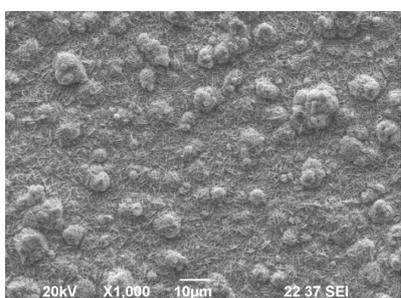


Fig. 3 Surface morphology of composite zinc coating with incorporated PANI-SiO₂ particles

The surface morphology of the composite zinc coatings with embedded PANI-SiO₂ particles is demonstrated in Fig. 3. It can be suggested that, after adding to the zinc electrolyte solution, some agglomeration between the particles occurs since their size become several times larger after incorporation into the composite coating compared to the size in the starting PANI-SiO₂ suspension.

More precise observation of the surface shows that the greater part of the composite coating is covered by needle-like formations, most probably with metallic character. This could be a result from changes in the orientation of the zinc coating during the electrodeposition process as a result of the presence of the PANI-SiO₂ particles.

- Cyclic Voltammetry

Cyclic voltammetric curves are presented in Fig. 4. The presence of PANI-SiO₂ particles in the zinc sulfate electrolyte affects strongly the cathodic process showing a depolarization effect: deposition of the composite coating begins earlier (with about 150-200 mV in positive direction) compared to the ordinary zinc one.

However, after the beginning of the deposition of the composite coating, the cathodic rate slows down: at potential value of -1.4 V it is about 5 times lower than that of the ordinary zinc coating. The reason for this could be the presence of the PANI-SiO₂ particles, which cover the greater part of the cathode surface due to their greater sizes thus

hindering to a certain degree the deposition of the zinc ions.

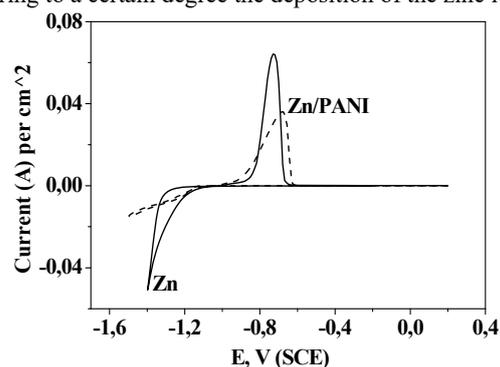


Fig. 4 CVA curves of pure zinc coating (solid line) and composite coating (dashed line)

- Potentiodynamic Polarization Curves

The results obtained for both coating types are presented in Fig. 5. It is seen that marked differences appear between the polarization curves of the investigated coatings. The corrosion potential of the ordinary zinc coating is placed at more positive potential values compared to the composite one. The anodic branch of the zinc coating is steeper which means that the dissolution process is more intensive in that potential area. The length of the curve of the composite coating is longer than that of the ordinary zinc coating, i.e. the composite coating lasts longer at conditions of external anodic polarization.

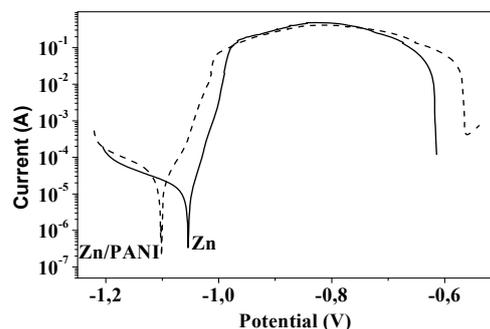


Fig. 5 PDP curves of pure zinc coating (solid line) and composite coating (dashed line)

- Polarization Resistance

The results obtained for both coatings after 15 days exposure in the model corrosion medium are demonstrated in Fig. 6.

The presented data clearly show that the polarization resistance of both coatings is almost equal at the beginning of the test (first day). The most probable reason is that, during this period, the corrosion processes are still at their initial stage and the surface consists predominantly of zinc.

After a definite period of time, the corrosion activators (chlorine ions) penetrate deeply inside the coatings leading to appearance of corrosion products. In general, the latter have barrier properties and protect the substrate to a certain degree. In the composite coating, PANI-SiO₂ particles that present in the metal matrix will slow down the penetration rate of the

corrosion medium. In this case, a mixed layer of zinc corrosion products and PANI-SiO₂ particles seems to appear, protecting the steel substrate to a greater degree. In addition, it is well known that PANI can be used as an inhibitor and its presence in the mixed layer will increase the protective characteristics of the composite coating.

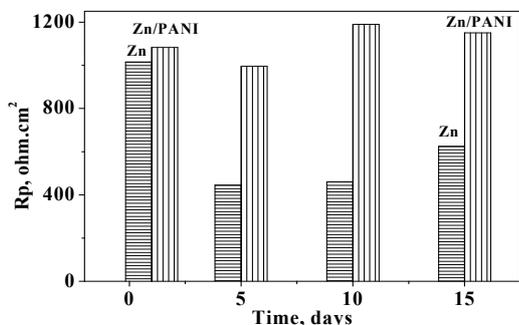


Fig. 6 Rp measurements of pure zinc and composite coatings

IV. CONCLUSIONS

Stabilized suspension of negatively charged PANI-SiO₂ particles (EB at pH 6.3) is prepared by saturated adsorption of positively charged polyelectrolyte in aqueous solution.

The incorporation of thus prepared particles into an ordinary zinc coating strongly affects the cathodic deposition process, causing a depolarization effect with about 150-200 mV in the positive direction compared to the ordinary zinc coating.

The composite zinc coating lasts longer at conditions of external anodic polarization compared to the ordinary zinc sample.

Prolonged corrosion investigations in the model medium of 5% NaCl solution demonstrate better corrosion resistance and protective ability of the composite zinc coating in the presence of chlorine ions as corrosion activators.

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REFERENCES

- [1] E. Armelin, C. Aleman, J. I. Iribarren, Anticorrosion performances of epoxy coatings modified with polyaniline: A comparison between the emeraldine base and salt forms, *Prog. Org. Coat.* 65 (2009) 88-93.
- [2] Y. Zhang, Y. Shao, X. Liu, C. Shi, Y. Wang, G. Meng, X. Zeng, Y. Yang, A study on corrosion protection of different polyaniline coatings

for mild steel, *Prog. Org. Coat.* 111 (2017) 240-247.

- [3] R. J. Holness, G. Williams, D. A. Worsley, H. N. McMurray, Polyaniline inhibition of corrosion-driven organic coating cathodic delamination on iron, *J. Electrochem Soc.* 152 (2005) B73-B81.
- [4] G. M. Spinks, A. Dominis, G. G. Wallace, Comparison of emeraldine salt, emeraldine base, and epoxy coatings for corrosion protection of steel during immersion in a saline solution, *Corrosion* 59 (2003) 22-31.
- [5] Y. Luo, A. Vimalanandan, X. Wang, M. Rohwerder, Study of the buried interface between zinc and emeraldine base coating, *Electrochimica Acta* 161 (2015) 10-16.
- [6] J. Stejskal, P. Kratochvil, S. P. Armes, S. F. Lascelles, A. Riede, M. Helmstedt, J. Prokes, I. Krivka, Polyaniline dispersions. 6. Stabilization by colloidal silica particles, *Macromolecules* 29 (1996) 6814-6819.