



MONOLAYER AND BILAYER CONDUCTING POLYMER COATINGS FOR CORROSION PROTECTION OF COPPER IN 0.5 M H₂SO₄ SOLUTIONS

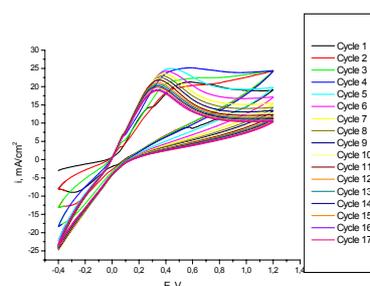
Florina BRÂNZOI,^{a,*} Viorel BRÂNZOI^b and Zoia PAHOM^b

^a“Ilie Murgulescu” Institute of Physical Chemistry, 202 Splaiul Independenței, 060021 Bucharest, Roumania

^bDepartment of Applied Physical Chemistry and Electrochemistry, University Politehnica of Bucharest, 132 Calea Grivitei, 010737 Bucharest, Roumania, e-mail: iv_branzoi@chim.upb.ro

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In this study, monolayer poly (N, N' dimethylaniline) (PNDMA), polyaniline (PANI), and bilayer PNDMA/PANI, PANI/PNDMA coatings have been electropolymerized on copper by potentiodynamic and galvanostatic synthesis techniques from aqueous solutions 0.1 M N,N' dimethylaniline, 0.1M aniline, 0.05 M sodium dodecyl sulphate (SDS) and 0.3 M oxalic acid. In order to include dodecylsulphate ions as dopant in the N, N' dimethylaniline, SDS was also added to the polymerization solution of N, N' dimethylaniline. Characterization of monolayer and bilayer polymer coatings was carried out by cyclic voltammetry, Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM) techniques. Corrosion behaviour of PNDMA-SDS/PANI coated copper was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques in 0.5M H₂SO₄ solutions. The results of the corrosion tests showed that PNDMA-SDS/PANI coatings ensure good corrosion protection of copper in aggressive media. Bilayer coatings revealed better corrosion inhibition efficiencies than monolayer coatings.



INTRODUCTION

Conducting polymers have attracted considerable attention in the scientific and technological fields in recent years due to their electrical, thermal, environmental, optical, chemical, and biological properties, the ease of their preparation and their broad applicability.¹⁻⁶ Conducting polymer coatings as polyaniline (PANI) and polypyrrole (PPY) on copper electrode can be obtained electrochemically and these coatings provide important protective properties against corrosion.⁷⁻¹⁶ Recently, conducting polymers have received considerable interest as corrosion protective coatings for oxidizable metals. The electrochemical polymerization is a simple, relatively inexpensive and most convenient route for synthesizing of novel conducting polymers on metallic surfaces. Several studies have been carried

out and reported on the protective behaviour of conducting and insulating forms of polymers on different metallic surfaces.^{8-9, 17-21} Copper is widely used as reactive metal in electrical and electronic devices. Aluminum is quickly replaced by copper as interconnect material and is the best choice for integrates circuits, particularly microprocessors, because of its low resistivity and its improved electromigration performance.²¹⁻²⁶ In this study, two different conducting polymers were investigated, primarily as coatings on copper surface using monolayers of Poly N, N' dimethylaniline (PNDMA) and polyaniline (PANI) and then bilayer coatings of type PNDMA/PANI and PANI/PNDMA which were electrodeposited on copper surface by potentiodynamic and galvanostatic techniques from aqueous synthesis solutions of 0.1M N, N' dimethylaniline, 0.1M aniline, 0.05 M sodium dodecyl sulphate and

* Corresponding author: fbrinzoi@chimfiz.icf.ro

0.3 M oxalic acid. Characterization of monolayer and bilayer polymer coatings was carried out by cyclic voltammetry, Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM) techniques. Corrosion behaviour of PANI/PNDMA-SDS coated copper was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques in 0.5 M H₂SO₄ solutions.

EXPERIMENTAL

PNDMA and PANI were supplied from Fluka, acid oxalic dehydrate (H₂C₂O₄) was received from Merck. In all electrosynthesis experiments, an aqueous solution of the NNDMA (0.1M), SDS (0.05M), PANI (0.1M) and oxalic acid (0.3 M) was prepared by using doubly distilled water. Electrochemical measurements were carried out in an electrolytic cell with a single compartment and three electrodes. As working electrode it was used a copper cylindrical with surface area of 0.5 cm², platinum plate as counter electrode and saturated calomel electrode (SCE) as reference electrode. Before each experiment, the working electrode was polished with a series of emery papers of different grit sizes (320 to 2400). After polishing, the Cu electrode was washed with acetone and doubly distilled water and dried at room temperature. All electrochemical studies were carried out with an automated model VoltaLab 40 potentiostat/galvanostat and Autolab 302N with EIS dynamic controlled by a personal computer. The PNDMA-SDS and PANI coatings were synthesized by the electrochemical polymerization of N, N' dimethylaniline on copper substrates from aqueous oxalic acid solution using cyclic voltammetry. The aqueous solution contains 0.3 M oxalic acid, 0.1M N, N' dimethylaniline, 0.05M sodium dodecyl sulfate (SDS) and 0.1M aniline. Electrosynthesis was performed by scanning the potential between -0.4 and 1.2V at a scan rate of 20mV/s by potentiodynamic technique and galvanostatic methods (monolayer at current densities 5mA/cm² and bilayer at 3mA/cm², the deposition of each layer was allowed for 15 min). After deposition the working electrode was removed from the electrolyte and rinsed with double distilled water and dried in air. The electroactivity of coatings was tested in a monomer-free solution of 0.3 M acid oxalic. The polymer structure was determined using Bruker optics FT-IR spectrometer with ATR in the spectral range 4000-650cm⁻¹. SEM was employed to characterize the surface morphology with JEOL JSM-5500LV SEM. Anti-corrosion control of the coated electrodes was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques in 0.5M H₂SO₄ solutions. Tafel tests were performed by scanning the potential from cathodic to anodic potentials with respect to open circuit potential at a scan rate of 2mV/s. Electrochemical impedance measurements were carried out in the frequency range of 100 kHz to 10 mHz with amplitude 5mV at the open circuit potential of PNDMA-SDS/PANI coated and uncoated electrodes.

RESULTS AND DISCUSSION

Before electropolymerization of PNDMA-SDS, the copper working electrodes was first polarized

in 0.3M aqueous oxalic acid solution by cycling the potential electrode on the range potential of -400mV up to 1200 mV versus SCE at a potential scan rate 20mV/s. Voltammograms recorded at the passivation of copper electrode in oxalic acid medium is shown in Fig. 1. This procedure of copper electrode passivation before electropolymerization process it was reported also, in speciality literature.²⁷⁻²⁸ The recorded voltammograms in aqueous oxalic acid solution during passivation procedure are same as those obtained by other researchers. This passivation mechanism is based on the formation of the insoluble compounds on the surface. These insoluble species consist of copper oxides, insoluble copper oxalates such as Cu(Ox) and Cu(Ox)₂²⁻. These conditions lead to passivation of the electrode by formation of a thin insoluble copper oxalate layer which inhibits metal dissolution without preventing the electropolymerization process. Optimization of the electropolymerization conditions lead to deposition of PNDMA or PANI films that have the best anticorrosion performance.

Analyzing Fig. 1, it can be observed that at the first cycle on the anodic branch appears a high and sharp oxidation peak at the potential 170mV (on the potential range of -50mV up to + 250mV) and with a peak current density of 10.2 mA/cm² which points out that dissolution of Cu began and that the dissolution process is very strong now and also that this process produces Cu²⁺ ions in its vicinity.²⁷⁻³⁰ These ions interact with the oxalate electrolyte to form insoluble copper oxalate.

Fig. 2A shows cyclic voltammogram recorded during synthesis of PNDMA doped with SDS on passive copper electrode between -500 mV and 1200mV with a scan rate of 20mV/s. The first oxidation peak during the first cycle of potential scan is observed starting at around 57-175mV which is associated with the electrodisolution of copper while the second oxidation peak can be attributed to the oxidation of the monomer (NDMA) at about 420mV. The intensity of the oxidation wave of NDMA gradually decreases and oxidation potential shifts to higher potentials with the increase of the cycles number. The appearance of a broad oxidation peak at 592 mV and reduction peak at 128mV occurs at the second reverse potential sweep.³¹⁻³³ The values of each oxidation and reduction peak increase with scan number. This indicates building up an electroactive PNDMA-SDS on the copper electrode, this film can be considered that a first layer on the copper surface first layer.

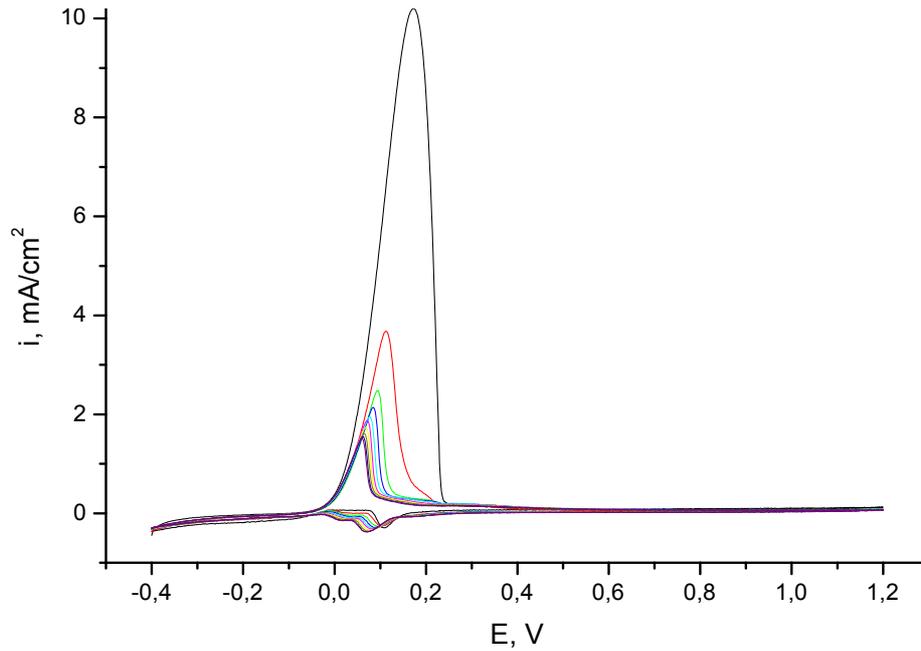
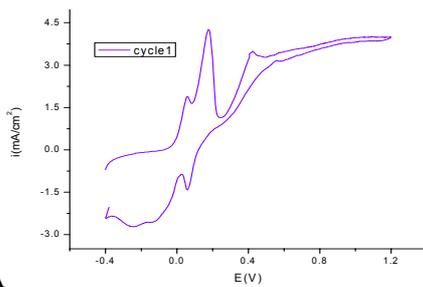
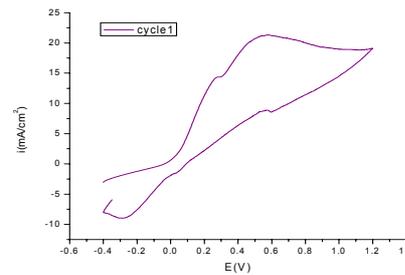


Fig. 1 – Cyclic voltammogram recorded during the polarization of Cu electrode in 0.3M oxalic acid solution at scan rate 30mV/s and on the potential range of -400 to 1200mV.



A



B

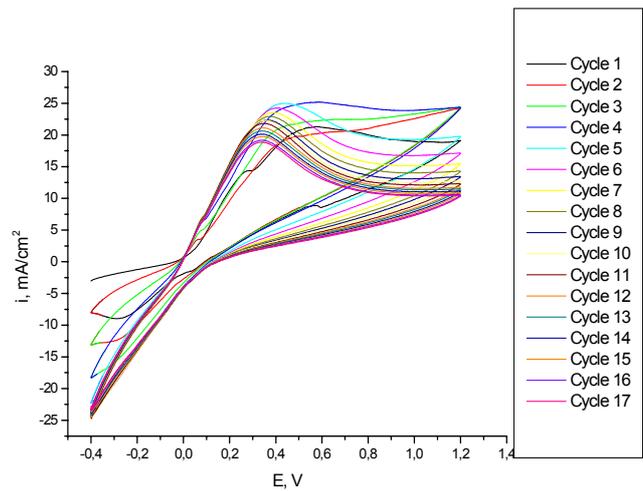
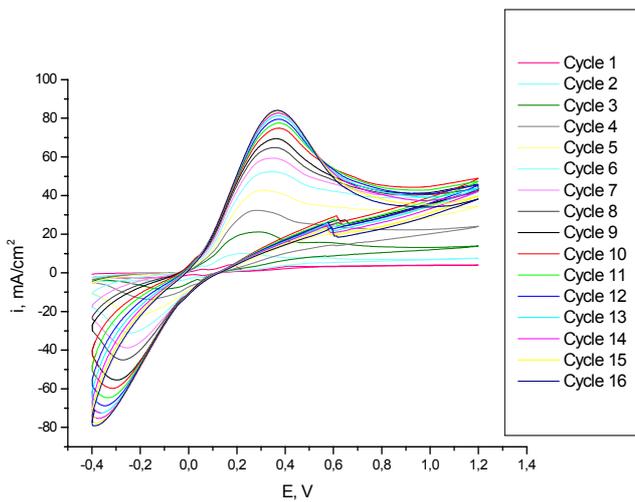


Fig. 2 – Cyclic voltammograms obtained during deposition PNDMA-SDS/PANI on Cu electrode in 0.3 M oxalic acid solution containing 0.1M NDMA + 0.05M SDS- at the potential range between -0.5 and 1.2V vs.SCE at a scan rate of 20 mV/s. A-monolayer PNDMA-SDS/Cu and B –bilayer PANI/PNDMA-SDS/Cu. Inset: first cycle.

Fig. 2B shows cyclic voltammogram recorded during synthesis of PANI on modified electrode type PNDMA-SDS/Cu in 0.3M oxalic acid

solutions, between -500 mV and +1200mV with a scan rate of 20mV/s. In this way on the copper electrode surface was obtained a bilayer which was

noted thus: PANI/PNDMA-SDS/Cu. The positive cycle of these voltammograms is characterized by: an anodic peak at the 512mV which has been attributed to the transformation of PANI from reduced leucoemeraldine (LE) state to the partially oxidized emeraldine (EM) and the conversion of emeraldine to fully oxidized pernigraniline (PF) form. This behaviour can be explained in the following mode: it is well known that polyaniline can exist in three different oxidation states such as leucoemeraldine (fully reduced form), emeraldine (partially oxidized form) and pernigraniline (fully oxidized form). These forms of polyaniline are dependent on the applied potential. The reduction peak at 128 mV is due to the transformation of polyaniline from emeraldine to leucoemeraldine state.³⁴⁻³⁵ Increases in the current of peak shows that the deposition thickness increases with cycles. There are few studies related to the inhibitory effect of bilayer coatings of conductive polymers on copper corrosion in acidic medium.³⁶⁻³⁷ Bilayer coatings were successfully deposited onto the copper coated first with monolayer PNDMA-SDS in this study, in order to study their efficiency as corrosion inhibitors. The visualization of Cu electrode after 17th scan reveals the formation of a green-dark colored coating. The coating is uniform and strongly adherent to the Cu surface.

The coatings were undertaken under galvanostatic conditions as well. Fig. 3 shows the

E-t curves obtained during the formation of PANI/PNDMA-SDS coatings on copper for 3mA/cm² applied constant current densities. As can be seen from Fig. 3, deposition of PANI on the PNDMA-SDS (monolayer) is characterized by a sharp rise up to a maximum positive value, after which the potential remains to a constant value. Regarding the galvanostatic electropolymerization of PANI layer at 3mA/cm² onto the PNDMA-SDS modified electrode, potential immediately reached the value corresponding to the polymerization process.

The current–potential behaviour of PNDMA-SDS/PANI coated copper electrode in 0.3M oxalic acid without monomer is depicted in Fig. 4 on the potential range of -0.2 and +1.2 V vs. SCE at scan rate of 20mV/s. The stability of any conducting polymer in reduced and oxidized states is an important parameter for different applications. The main reason that determines the lifetime of a conducting polymer is a chemical stability of the matrix itself. The stability of PNDMA-SDS/PANI bilayer coating was measured by cyclic voltammetry (over 15 cycles) in electrolytes without monomers (see Fig. 4). The appearance of oxidation and reduction wave after many cycles (up 20) shows the stability of these electroactive films.³⁸⁻⁴⁰ When cycling occurs the current density decreases with each cycle and finally reaches to stable value.

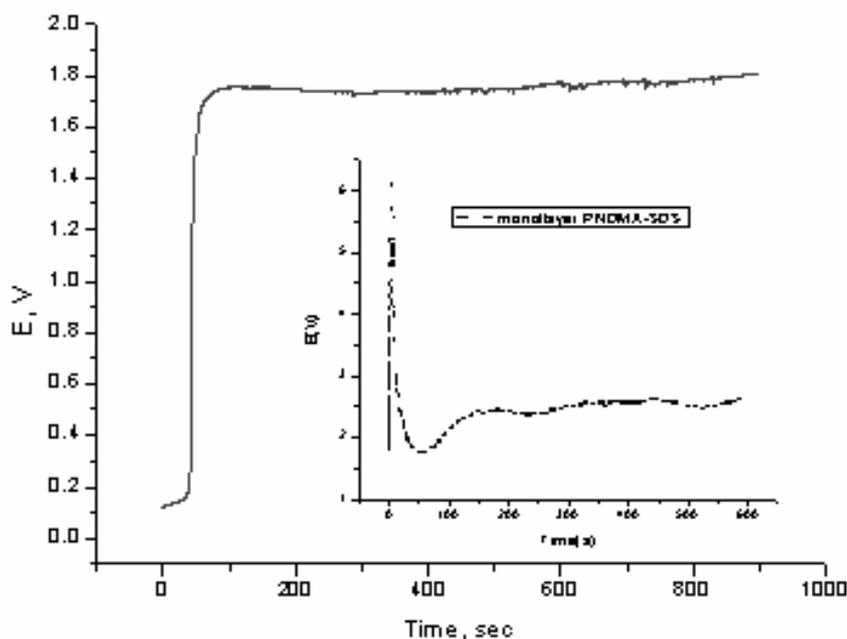


Fig. 3 – Galvanostatic deposition of PANI on the PNDMA-SDS (monolayer) with formation of a bilayer coating at 3mA on the electrode surface where previously was deposited monolayer PNDMA-SDS at 5mA. Inset: monolayer PNDMA-SDS.

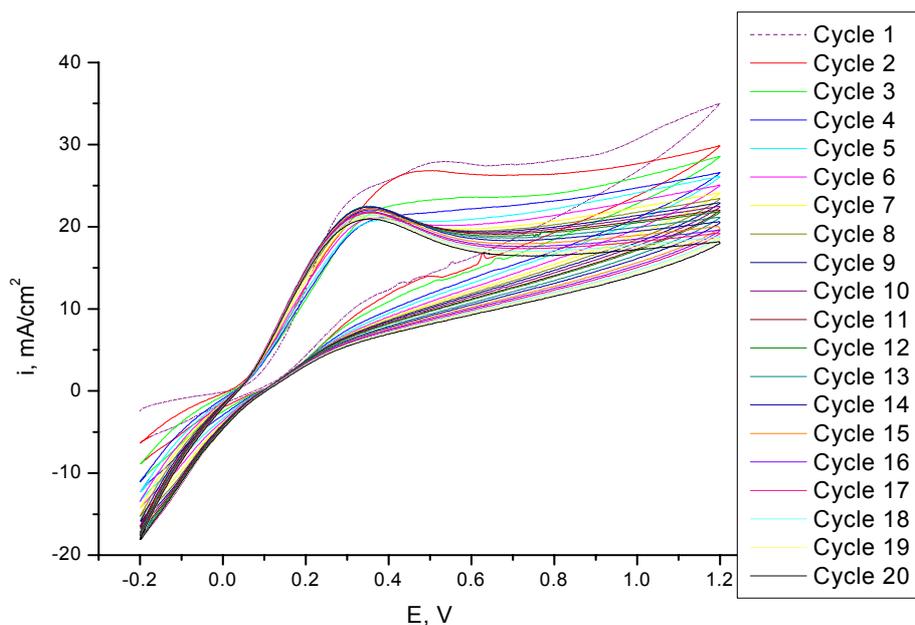


Fig. 4 – Cyclic voltammograms of copper electrode coated with PANI/PNDMA-SDS bilayer in 0.3M oxalic acid solution without monomer in potential range between -0.2 and 1.2 V vs. SCE and scan rate of 20mV/s.

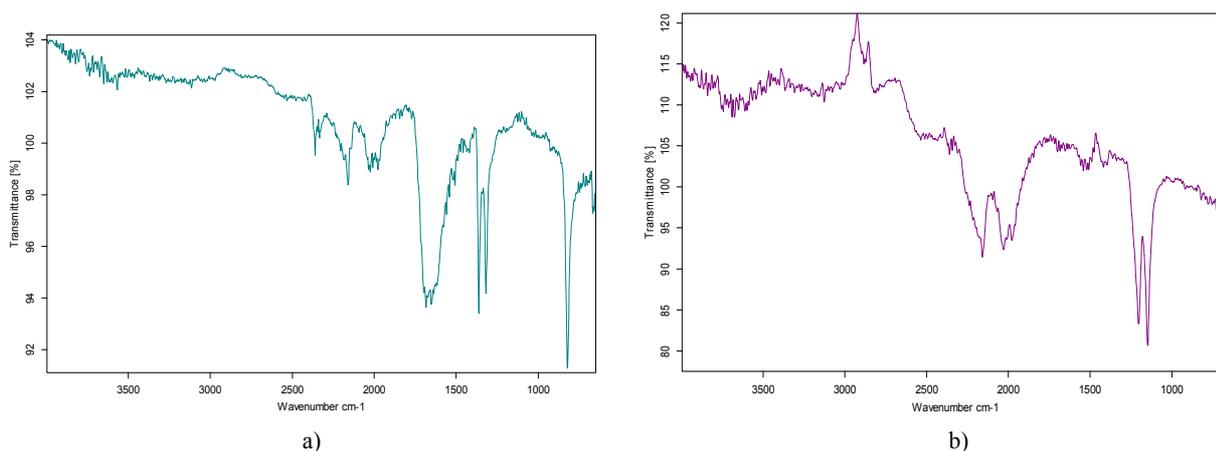


Fig. 5 – FT-IR Spectrum of PNDMA-SDS and PANI/PNDMA-SDS/PANI deposited on Cu electrode under cyclic voltammetric conditions in a potential region between -0.5 and 1.2V vs SCE.

The FT-IR spectra of PNDMA-SDS/Cu and PANI/PNDMA-SDS/Cu coatings are shown in Fig. 5. The characteristic bands in the FT-IR spectrum of PNDMA-SDS (Fig. 5a) coating synthesized on Cu from aqueous oxalic acid medium are assigned as follows: a small band at 3424cm^{-1} due to the characteristic N-H stretching vibration suggests the presence of NH groups in N, N dimethylaniline units, the band at 1652cm^{-1} and 1508cm^{-1} is an indicative of stretching vibration in quinoid rings and benzenoid rings. The bands at about 1363cm^{-1} is assigned to the C-H stretching of CH_3 group, the band appearing near 1316cm^{-1} represents C-N stretching vibration in aromatic amines. The

presence of substituted aromatic rings indicating polymer formation is demonstrated by the band at about 823cm^{-1} . The bands at 900 and 700cm^{-1} are assigned to the in-plane and out-plane C-H of the aromatic rings. The band appearing at $2024\text{--}2365\text{cm}^{-1}$ indicates that the DS^- anion is present with the oxalate anion as dopant in the PNDMA-SDS layer films. The FT-IR spectra of PANI/PNDMA-SDS (bilayer film) coating synthesized on Cu from aqueous oxalic acid medium is shown in Fig. 5b. The main characteristic bands of PANI/PNDMA-SDS are assigned: the peak at 1435cm^{-1} and 1389cm^{-1} is due to the quinoid rings and benzenoid ring. The observation

of the band at 1203 cm^{-1} suggests the presence of the carboxyl groups of the dopants in the polymer film. The bands at 1146 cm^{-1} and 836 cm^{-1} are assigned to the in-plane and out-plane C-H of the aromatic rings. The presence of the N-H stretching band at 3226 cm^{-1} , a band located at 3800 cm^{-1} corresponds to the CuC_2O_4 . The bands at 2351, 2037, 928, 836 and 736 were most probably related to the screening of dopants ions in the polymer matrix.

The SEM images of PANI/PNDMA-SDS coatings deposited on copper are shown in Fig. 6. It clearly reveals that the PANI/PNDMA-SDS coating is a homogeneous and a uniform film. The coating is strongly, adherent to the copper surface. The quality of the coating is so excellent that no crack on the coating is observed. It can be observed from Fig. 6 that the PNDMA-SDS/PANI coating is uniform, on the Cu surface and the quality of the coating is so excellent. No apparent change in the surface morphology of the coating was occurred after the potentiodynamic polarization measurements.

Polarization curves of uncoated and PANI/PNDMA-SDS coated copper in 0.5 M

H_2SO_4 medium are shown in Figs. 7-8. Polymers coated surfaces exhibited significant decrease in anodic and cathodic currents which indicated suppression of the cathodic and anodic reactions. Corrosion potentials (E_{corr}) and corrosion density (i_{corr}) determined by extrapolation of linear portions of the anodic and cathodic Tafel curves of copper electrode coated with polymers at different immersion times and uncoated copper are shown in Table 1.

Further, polarization studies were performed in 0.5M H_2SO_4 environment in order to evaluate the protection abilities of the composite coatings against corrosion. Therefore, polarization behavior of copper electrode was compared to those obtained for PANI/PNDMA-SDS coated copper obtained by electropolymerization and galvanostatic methods. Tafel plots obtained from the polarization tests are shown in Figs. 7-8 and the corresponding kinetic parameters: corrosion current density (i_{corr}), corrosion potential (E_{corr}), Tafel constants, polarization resistance (R_p) and corrosion rates are given in Table 1.

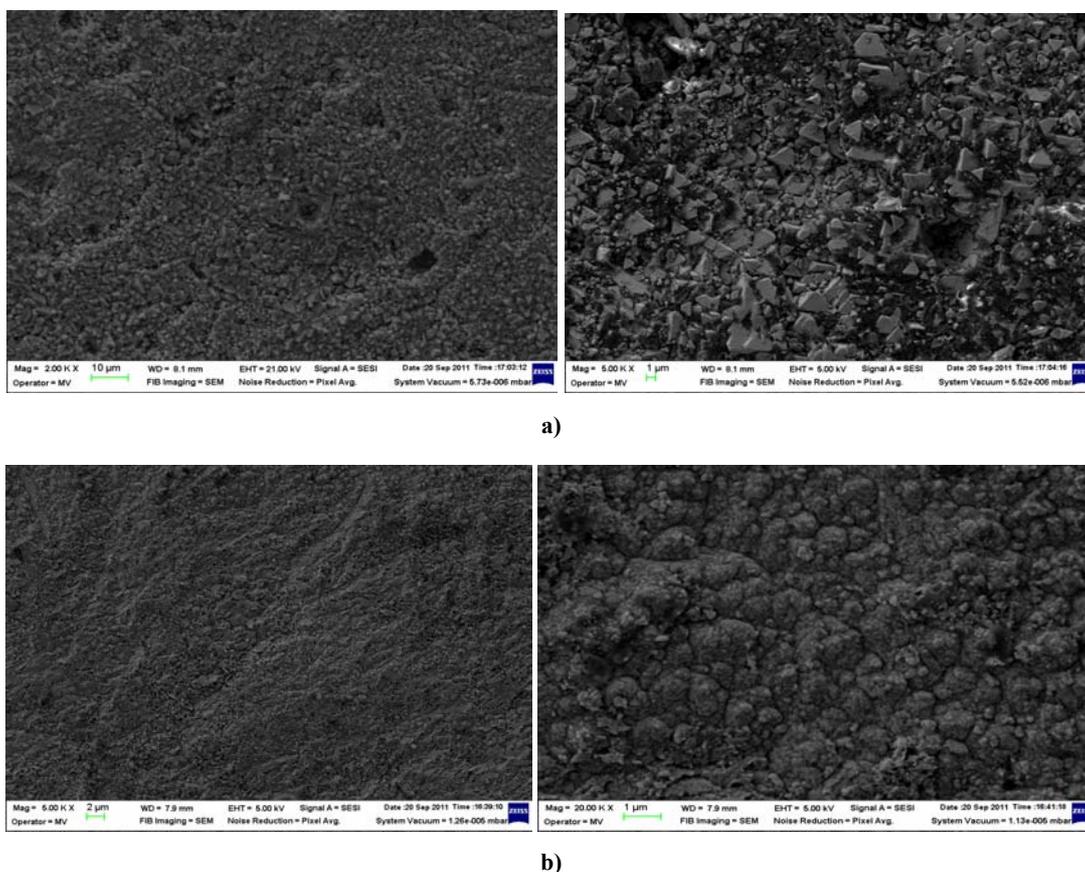


Fig. 6 – SEM images of copper electrode coated with PANI/PNDMA-SDS a) before and b) after immersion in H_2SO_4 .

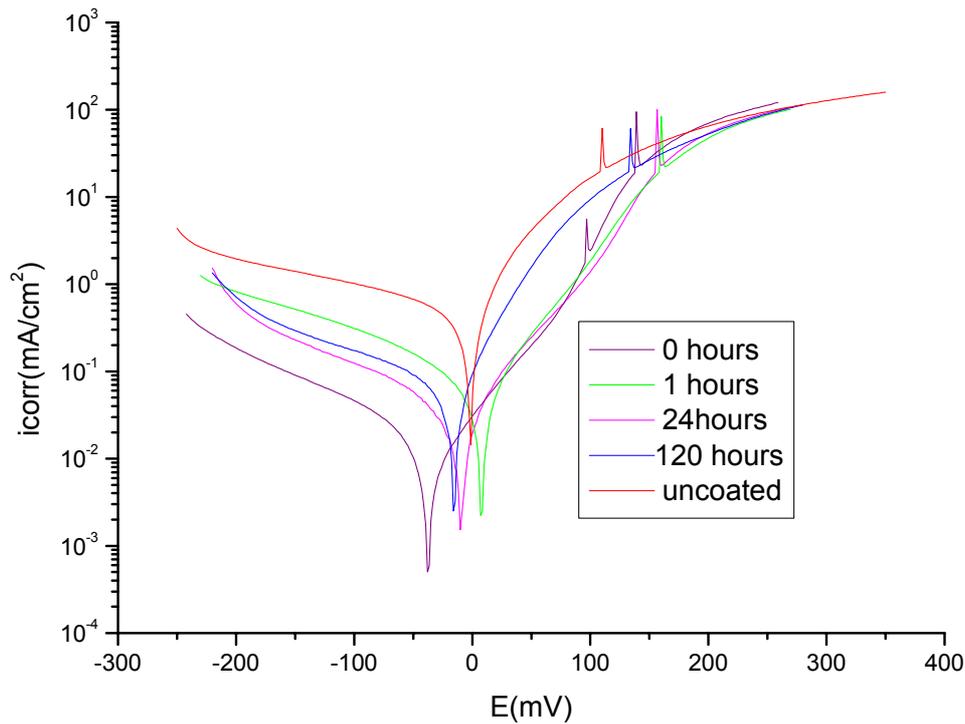


Fig. 7 – Tafel curves recorded in 0.5M H_2SO_4 solution for uncoated and PANI/PNDMA-SDS coated copper electrodes at different immersion times.

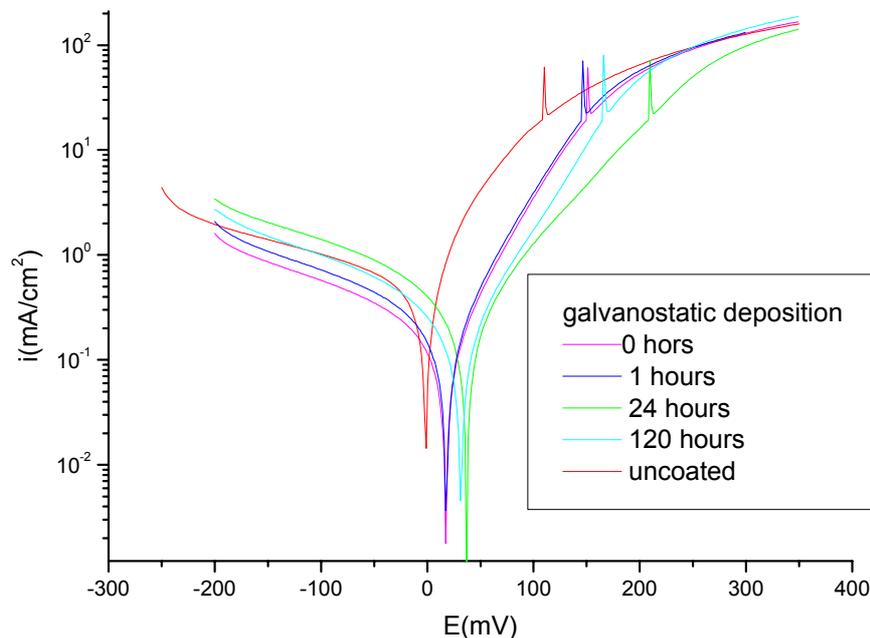


Fig. 8 – Tafel curves recorded in 0.5M H_2SO_4 solution for uncoated and PANI/PNDMA-SDS coated –galvanostatic deposition copper electrodes at different immersion times.

Analysis of the polarization curves from Figs. 7-8 indicates that the kinetic corrosion parameters of uncoated surface of copper electrode and their comparison with the kinetic parameters from coated surface of copper electrode at different immersion times in 0.5M H_2SO_4 solutions. The

corrosion current densities for the PANI/PNDMA-SDS coated copper as a function of immersion time were lower than those for bare copper. Corrosion behavior of PANI/PNDMA-SDS coated copper electrode revealed that the polymer coated electrode had considerably higher corrosion

resistance and slower corrosion rate compared to uncoated copper electrode (uncoated copper). The corrosion rate of PNDMA-SDS/PANI coated copper was found to be ~40 times lower than which was observed for uncoated copper. It was clear that the polymer coatings hindered the attack of the corrosive agent (H_2SO_4) on copper surface.

The corrosion of copper in 0.5 M H_2SO_4 in the absence and presence of composite coatings (PANI/PNDMA-SDS) were investigated by EIS at the open circuit potential condition on the

frequency range between 100 kHz and 40 mHz with an AC wave of ± 10 mV (peak-to-peak) and the impedance data were obtained at a rate of 10 points per decade change in frequency. The Nyquist diagrams (Fig. 9a) show only one semicircle and the diameter of the semicircle decreases once with increasing of immersion time, suggesting that the formed protective film was strengthened by the addition of coatings.

Table 1

Tafel parameters of coated and uncoated surface of copper electrode in 0.5M H_2SO_4 solutions at different immersion times and at 25°C

	Immersion time (h)	E_{corr} (mV)	R_p (Ωcm)	i_{corr} (mA/cm^2)	b_a (mV)	b_c (mV)	E (%)	$P_{mm/year}$
Cu + 0.5 M H_2SO_4	0	-3.1	39	0.54	69	11.6	-	6.36
Cu coated PNMDA-SDS/PANI + 0.5 M H_2SO_4	0	-39	949	0.014	60	123	97	0.16
	1	-10.5	566.4	0.020	60	116	96	0.23
	24	7.4	270	0.043	61	116	93	0.50
	120	-17	254	0.050	45	150	91	0.58
	Galvan 0h	-29	240	0.063	41	125	89	0.74
	Galvan 1h	-28	148	0.08	52	111	85	0.94
	Galvan 24h	36	106	0.11	65	98	79	1.29
	Galvan 120h	15	82	0.13	68	135	76	1.53

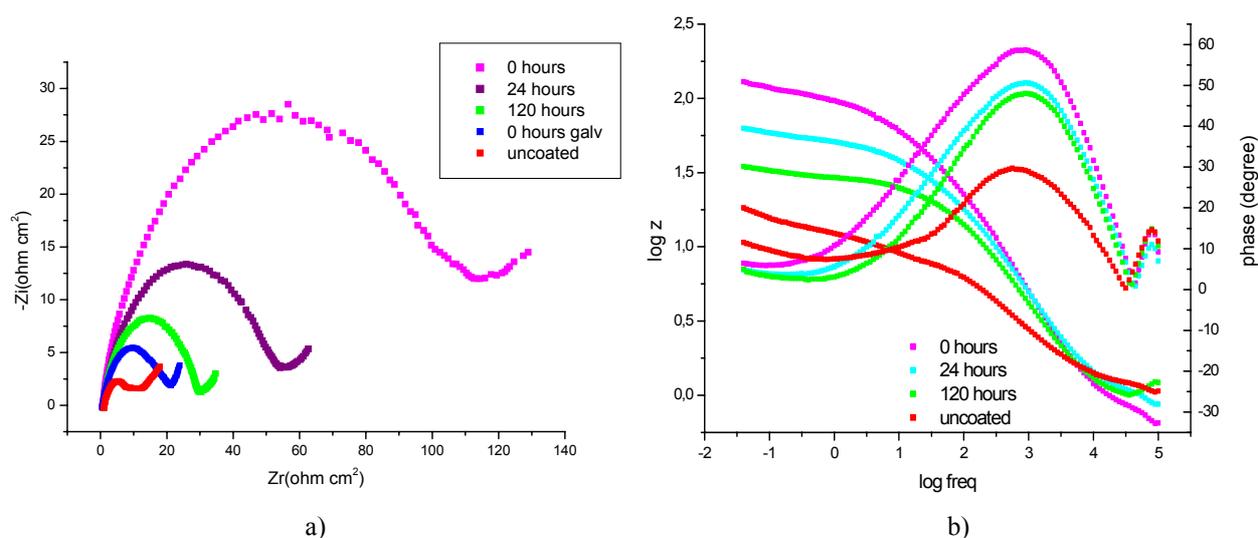


Fig. 9 – EIS spectra a) Nyquist plots and b) Bode plots for uncoated and PANI/PNDMA-SDS-coated copper electrode at different time immersion.

Fig. 9a also indicates that the diameters of the capacitance loops in the presence of coatings (PANI/PNDMA-SDS) are bigger than those in the absence of coatings, suggesting that these coatings has good anticorrosion performance on the copper in 0.5 M H₂SO₄.

The Bode plots are shown in Fig. 9b are in accordance with Nyquist diagrams. It can be observed that in absence of coatings the electrode presents one time constant corresponding to a phase angle of about 25° at medium and low frequencies, this fact indicates an inductive behaviour with low diffusive tendency.⁴¹⁻⁴⁴ On the contrary, in the presence of the coatings, on the curve-phase angle versus log frequency appears a maximum very well defined corresponding to a phase angle of about 65° which means that in this case the electrode has a strong capacitive behaviour, according with the results obtained by electrochemical polarization and in concordance with the Nyquist diagrams. Analyzing the Nyquist diagrams it can be observed that at low and medium frequencies on the diagrams appears short diffusive branch with the very wide capacitive loops from high frequencies range. This fact confirms once again that these polymer coatings assure very good anticorrosion protection.

CONCLUSIONS

We have successfully synthesized uniform and strongly adherent PNDMA-SDS/PANI coatings on Cu by electrochemical polymerization (layer by layer) and galvanostatic deposition of N, N' dimethylaniline, SDS and aniline from oxalic acid solution.

The FT-IR spectroscopic study indicates that the electrochemical polymerization of PNDMA-SDS/PANI has occurred and results into the formation of oxidized form of N, N' dimethylaniline and aniline on the Cu electrode surface.

The SEM image of the PNDMA-SDS/PANI coating deposited on Cu is shown in Fig. 6. It can be observed that the PNDMA-SDS/PANI coating is uniform, is strongly adherent on the Cu surface and the quality of the coating is so excellent.

The corrosion rate of PNDMA-SDS/PANI coated copper is found to be ~40 times lower than that which can be observed for uncoated copper.

The potentiodynamic polarization and EIS studies reveal that the PNDMA-SDS/PANI acts as corrosion protective layer on Cu in 0.5M H₂SO₄ solution.

Bilayer coatings displayed better corrosion inhibition efficiencies than monolayer coatings.

The new complex nanostructured composite obtained from this process is promising and might lead to industrial applications in the protection of the copper substrates against corrosion.

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