

Polypyrrole coatings for corrosion protection of stainless steel

Electrochemical synthesis of PPy films with different thicknesses, using stainless steel electrode (18% Cr, 10% Ni) as a substrate ($A=1.27\text{ cm}^2$), was performed at constant current (5 mA) under controlled polymerization time from a solution of 0.5M H_2SO_4 containing 0.1M Py ($E = 0.95 \div 1.05\text{ V/SHE}$). The electrochemical characteristics of the synthesized PPy-films on stainless steel electrode were determined using cyclic voltammetry in the potential range from 0.95 to -0.6 V/SHE, and sweep rate of 10 mVs^{-1} in 0.5M H_2SO_4 solution, while their anticorrosion features were studied by polarization current-potential measurements in 0.5, 1.0 and 1.5M solutions of H_2SO_4 , and electrochemical impedance spectroscopy (EIS) performed in the solution of 1M H_2SO_4 , in the frequency range from 100 kHz to 10 mHz at a corrosion potential of -0.1 V/SHE (a.c. signal of 5 mV). The parameters of the $R(QR)$ equivalent electric circuit (EEC) for the best fit of the experimentally obtained data, where: R_1 is the ohmic resistance of the electrolyte; the element Q (with n), represents the double layer capacitance C_{dl} at the polymer/solution interface; the element R_2 is the charge transfer resistance, were obtained using the software developed by Boukamp.

Key words: polypyrrole (PPy), stainless steel, corrosion protection, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), electrical equivalent circuits (EEC)

1. INTRODUCTION

Intrinsically conductive polymers, e.g. polyaniline, polypyrrole, polythiophene and their derivatives [1], ensure a big number of applications, such as adhesives, antistatic films, actuators [2], lithium batteries [3], sensors [4], drug delivery [5], and also offer corrosion protection of metal surfaces [6, 7].

A number of different corrosion protection mechanisms involving intrinsically conductive polymers were proposed [8]: barrier protection, anodic and cathodic protection and corrosion inhibitors. Anodic protection enables formation of passive oxide layers on the metal surface that changes the electrode potential in the passive region, which is used for easier deposition of ICPs during electrochemical polymerization. Actually it was shown that both, anodic and cathodic protection exists at the same time, meaning concurrent oxidation and reduction of conducting polymers on metal surfaces [8].

Polypyrrole (PPy) offers some advantages over other conducting polymers: very simple electrochemical synthesis on metal substrates, using both, potentiostatic or galvanostatic methods, the great conductivity of the film in wide pH range, high thermal stability of the film (150 °C in the air), as well as very

good mechanical properties. The excellent electronic conductivity of PPy (1 Scm^{-2}) enables the electrochemical synthesis of this coating with an excellent corrosion protection capabilities [9].

During the deposition of PPy on a mild steel electrode from aqueous oxalic acid solutions using constant currents, the induction period was noticed as a result of the active dissolution of the iron at negative potentials [10]. As a result of the precipitation of Fe (II)-oxalate the potential shifts to the positive values between 400 and 600 mV/SCE when PPy is electrodeposited. Analyses of anticorrosion protection of PPy films with different thicknesses coated on mild steel substrate, in the 0.1 M H_2SO_4 solutions indicated that PPy coating in the contact with electrolyte are rapidly dedoped, driven by the anodic dissolution of iron through the pores of the coating. But, the polymer film is not completely reduced which could be result of the difficulties in the diffusion of the counter ions through the pores of the PPy film. It was shown [10] that as the time spent, the film is reduced to a higher degree which lowers the film conductivity and the corrosion rate of the iron.

The possibility for application of PPy films doped with hexacyanoferrates, $\text{Fe}(\text{CN})_6^{3-/4-}$, to be used in protection of stainless steel against pitting corrosion in strong acid solutions containing chlorine salts, was also shown [11]. The negatively charged multilayer dense polymer films were successful in the blocking approach of chlorides to the surface of the passivated steel, providing in that way protection from the pitting corrosion. Namely, the development of the iron hexacyanoferrate film offers the stabilization of

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the iron and chromium passive layers created on stainless steel surfaces.

In this study, the electrochemical synthesis of PPy films with different thicknesses, using stainless steel electrode as a substrate ($A=1.27 \text{ cm}^2$), was performed at constant current of 5 mA at controlled polymerization time from a solution of 0.5M H_2SO_4 containing 0.1M Py. The characteristic of the synthesized PPy-films and their protection capabilities were studied by cyclic voltammetry, polarization current-potential measurements, as well as electrochemical impedance spectroscopy (EIS).

2. EXPERIMENTAL

High grade chemicals: pyrrole (Py) (Merck), and H_2SO_4 (Merck) were used as received.

Electrochemical synthesis of PPy films were carried out in the three electrode cell containing 0.1 M Py and 0.5 M H_2SO_4 . During the process of electrochemical synthesis the solutions were agitated with purified nitrogen ($\sim 120 \text{ bubbles min}^{-1}$). Polymerization was performed with constant current, 5 mA (3.94 mAcm^{-2}), $E = 0.95 \div 1.05 \text{ V/SHE}$. The quantity of the deposited PPy were regulated by anodic (polymerization) charge of $0.36 \text{ Ccm}^{-2}\mu\text{m}^{-1}$ (2.38 Cmg^{-1}).

A glass cell with three electrode system, consisting of working, auxiliary and referent electrode was used during the synthesis and characterization of the polymer and composite films. A stainless steel (18% Cr, 10% Ni) electrode with surface area, $A = 1.27 \text{ cm}^2$, was used as working electrode, platinum foil ($\sim 20 \text{ cm}^2$) as an auxiliary electrode and saturated calomel electrode as referent electrode. All potentials were referred to the standard hydrogen electrode (SHE).

The working electrode, stainless steel, was first mechanically polished with fine emery cloths and polishing alumina of $1 \mu\text{m}$, after what it was treated in ultrasonic bath for removal of the polishing traces.

The electrochemical characteristics of the electrodeposited PPy films on stainless steel electrodes were studied by cyclic voltammetry in the potential window from 0.95 to -0.6 V/SHE , and sweep rate of 10 mVs^{-1} in 0.5M H_2SO_4 solution. The corrosion behavior of stainless steel covered by PPy-films were determined by polarization current-potential measurements in 0.5, 1.0 and 1.5M solutions of H_2SO_4 , and electrochemical impedance spectroscopy (EIS) performed in the solution of 1M H_2SO_4 , in the frequency range from 100 kHz to 10 mHz at a corrosion potential of -0.1 V/SHE (a.c. signal of 5 mV). Electrical equivalent circuits (EEC) for the best fit of the experimentally obtained data were obtained using software developed by Bernard A. Boukamp [12].

3. RESULTS AND DISCUSSION

Electrodeposition of PPy coatings on stainless steel electrodes were performed from the solutions of 0.5M H_2SO_4 containing 0.1M Py, applying a constant current of 5mA. The data for the electrochemical synthesis of the films with different thicknesses are given in the Table 1.

Table 1 – Electrode position conditions for PPy films with different thicknesses on stainless steel electrode ($A = 1.27 \text{ cm}^2$), applying constant current of 5mA

$m_{\text{PPy}} \text{ (mg)}$	$\tau \text{ (s)}$	$Q_{\text{pol}} \text{ (mC)}$	$Q_{\text{pol}} \text{ (mCcm}^{-2}\text{)}$
0.1	48	240	189
0.25	120	600	472.44
1	480	2400	1889.76
2	960	4800	3779.53

The quantity of the PPy films (0.1, 0.25, 1.0, and 2.0 mg) for the constant current (5 mA), i.e. current density (3.94 mAcm^{-2}), was controlled by the time for the electrochemical treatment.

The synthesized PPy films were characterized potentiodynamically by the method of cyclic voltammetry in the potential range from 1.1 to -0.4 V/SHE in the solution of 0.5M H_2SO_4 (Figs. 1 and 2).

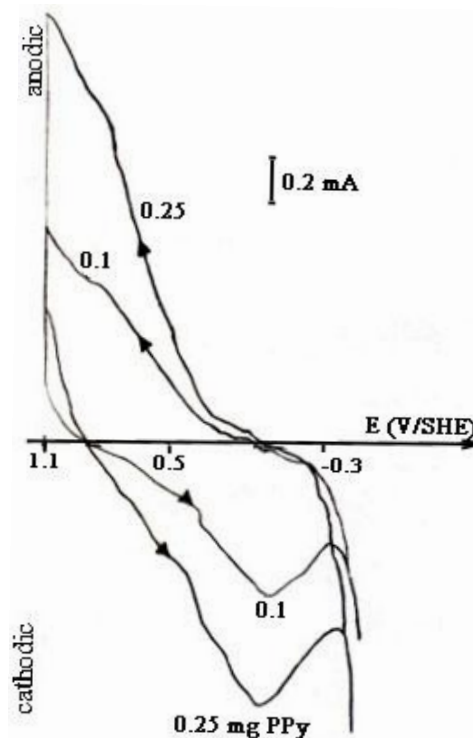


Figure 1- Voltammograms for PPy films (0.1 and 0.25 mg) deposited on stainless steel electrode (1.27 cm^2) in the solution of 0.5M H_2SO_4

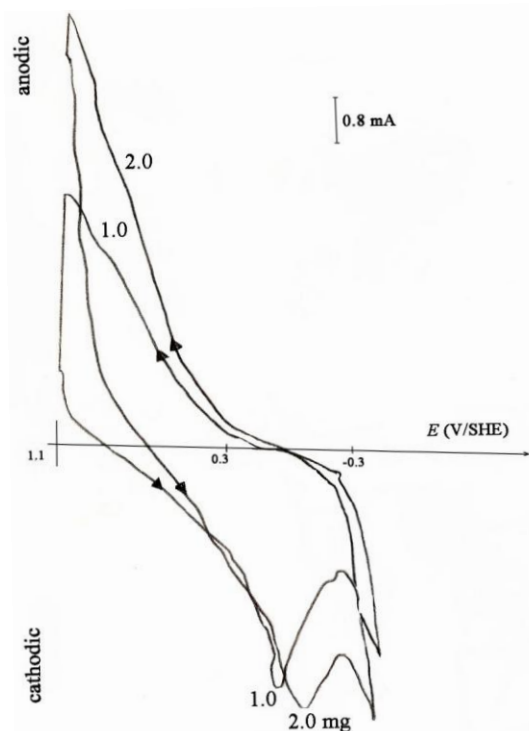


Figure 2 - Voltammograms for PPy films (1.0 and 2.0 mg) deposited on stainless steel electrode (1.27 cm^2) in the solution of $0.5 \text{ M H}_2\text{SO}_4$

The values of the redox capacitance, q_{red} , calculated by the integration of the area under the anodic, i.e. cathodic part of the j/E dependences are presented in the Table 2.

Table 2 - Electrochemical properties of PPy films with different thicknesses

m_{PPy} (mg)	m (mg cm^{-2})	δ (μm)	q_{red} (mCcm^{-2})
0.1	0.079	0.52	35.6
0.25	0.197	1.30	80.3
1	0.787	5.20	220.5
2	1.575	10.40	277.2

q_{red} values increases as the quantity of PPy deposited increases, and takes values from ~ 36.0 to 277 mCcm^{-2} , for 0.1 and 2.0 mg PPy, respectively. Except the capacitive behavior of polymer films, q_{red} includes Faradaic processes of oxidation and reduction of the films (cathodic and anodic maximums on the voltammograms), as well [13]. Voltammograms on Figs. 1 and 2 clearly indicate the reversible redox behavior of the PPy films.

The corrosion rate of bare stainless steel, as well as, that covered with PPy-films, in the solution of H_2SO_4 (0.5, 1.0, and 1.5 M), was determined using the polarization current – potential dependences, Tables 3-5.

Table 3 - Data obtained from the polarization current-potential dependences in a solution of $0.5 \text{ M H}_2\text{SO}_4$

m_{PPy} (mg)	b_c^* (mV/dec)	b_a^{**} (mV/dec)	$j_{\text{corr.}} \cdot 10^6$ (Acm^{-2})	$v_{\text{corr.}}$ (mm/year)
without film (0)	140	700	16.6	0.193
0.1	160	450	11.0	0.1277
0.25	170	390	10.0	0.1161
1	180	315	8.9	0.103
2	195	265	7.9	0.092

*Tafel slope for the cathodic reaction

** Tafel slope for the anodic reaction

Table 4 - Data obtained from the polarization current-potential dependences in a solution of $1.0 \text{ M H}_2\text{SO}_4$.

m_{PPy} (mg)	b_c (mV/dec)	b_a (mV/dec)	$j_{\text{corr.}} \cdot 10^6$ (A/cm^2)	$v_{\text{corr.}}$ (mm/year)
without film (0)	155	740	12.0	0.139
0.1	120	420	10.0	0.1161
0.25	165	380	8.7	0.101
1	170	275	7.9	0.092
2	180	240	6.9	0.08

Table 5 - Data obtained from the polarization current-potential dependences in a solution of $1.5 \text{ M H}_2\text{SO}_4$.

m_{PPy} (mg)	b_c (mV/dec)	b_a (mV/dec)	$j_{\text{corr.}} \cdot 10^6$ (A/cm^2)	$v_{\text{corr.}}$ (mm/year)
without film (0)	125	620	7.6	0.088
0.1	140	400	5.5	0.064
0.25	160	380	4.68	0.054
1	175	345	4.36	0.0506
2	130	310	3.98	0.046

As it can be seen from the data in Tables 3-5, for the bare stainless steel in the acid solutions, the values of the cathodic Tafel slope, b_c , takes low values, while in presence of PPy films it increases. This data that the protection coefficients increase as the thickness (the quantity) of PPy films grow up.

This influence of the organic molecules on the kinetics of hydrogen reaction can be mainly explained by the adsorption polymer layer on the metal surface which partly or completely inhibits the hydrogen reaction, i.e., to a large degree hinders the process of transport of mass (in this case H^+ ions) and charge (electrons) [14].

The electrochemical impedance spectroscopy (EIS) measurements of stainless steel electrode coated

with PPy films with different thicknesses (quantity) were carried out in the solution of 1M H₂SO₄, at a corrosion potential (-0.1 V/SHE), in the frequency range from 10 mHz to 100 kHz, applying the *ac* signal of 10 mV. Log Z-log *f* and ϕ -log *f* (Bode) plots

for PPy films (0.1 and 1.0 mg) deposited on stainless steel electrode, treated in the acid solution (1M H₂SO₄), at different time, are presented in the Figs. 3 and 4.

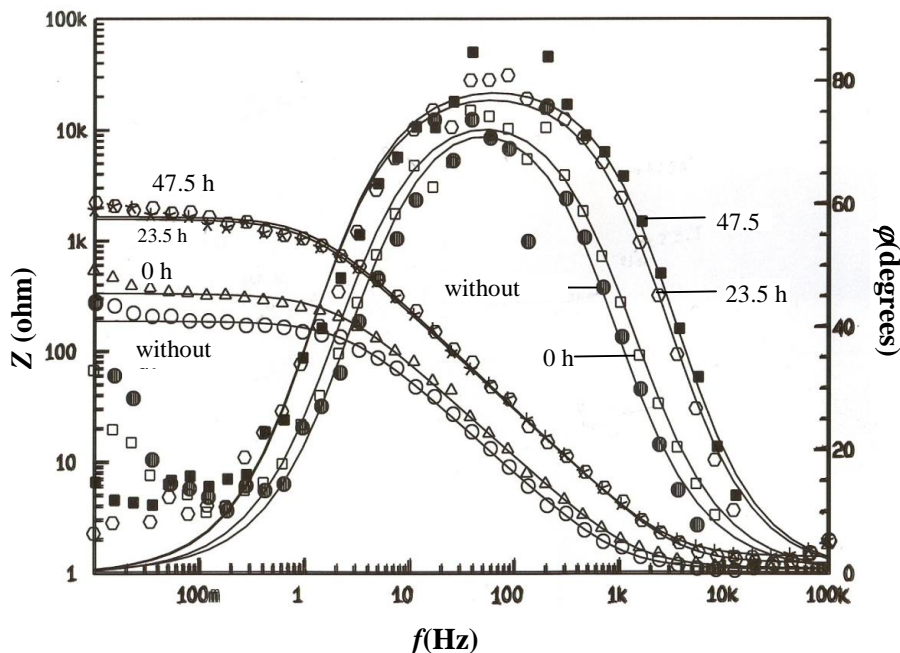


Figure 3 - Log Z-log *f* and ϕ -log *f* (Bode) plots for the system stainless steel without polymer film, and covered with 0.1 mg PPy film, treated in 1M H₂SO₄, at a corrosion potential (-0.1 V/SHE), and different time: 0; 23.5; and 47.5 h. Symbols represent the experimentally obtained data, and the line (—) theoretical (fitted) curves for the R(QR) EEC

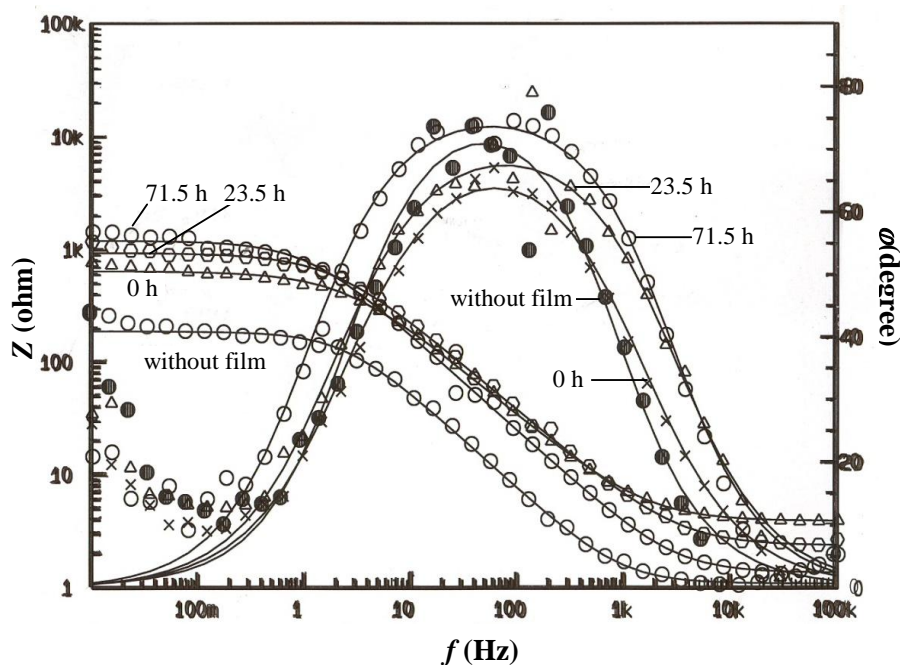
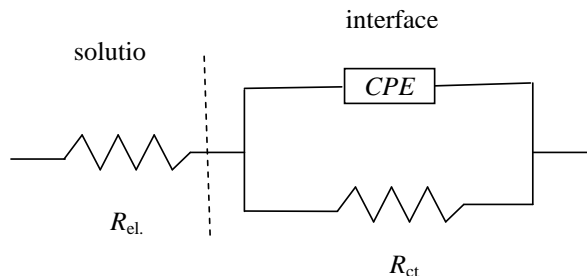


Figure 4 - Log Z-log *f* and ϕ -log *f* (Bode) plots for the system stainless steel without polymer film, and covered with 1.0 mg PPy film, treated in 1M H₂SO₄, at corrosion potential (-0.1 V/SHE), and different time: 0, 23.5, and 71.5 h. Symbols represent the experimentally obtained data, and the line (—) theoretical (fitted) curves for the R(QR) EEC

According to the basic shape, Bode plots designate that the impedance behavior of the system stainless steel plate / 1M H₂SO₄ without or in the presence of PPy, coated on its surface, can be presented by the electrical equivalent circuit (EEC) given below:



where:

R_{el} – represents the ohmic resistance of the electrolyte between the working and the auxiliary electrode.

CPE – signifies so called constant phase element, i.e., a non-ideal capacitor, characterized by the element Q (with the exponential coefficient n), and denotes the double layer capacitance (C_{dl}) ($C_{dl} = Q^{1/n}$),

characterizing the processes at the polymer / solution interface.

R_{ct} – designates the polarization resistance which for the corrosive systems is in the direct relationship with the corrosion current density by the equation:

$$j_{corr.} = \frac{RT}{zF} \cdot \frac{1}{R_{ct}}$$

For the linear $\log Z - \log f$ dependences with a given slope, the impedance can be presented by the equation:

$$Z = 1 / Q (j\omega)^n$$

The value of the coefficient n represents the slope of the linear $\partial(\log Z) / \partial(\log f)$ dependences varies between 0.8 and 0.95, characteristic for a non-ideal capacitor.

Experimentally obtained values were fitted using the software Boukamp [12], Figs. 3 and 4 (the lines). The best fitting data, Tables 6 and 7, were gained applying the simple R(QR) EEC.

Table 6 - Basic parameters for R(QR) EEC for the best fit of the experimentally obtained data for the system stainless steel without polymer film, and covered with 0.1 mg PPy, 1M H₂SO₄; $E = -0.1$ V/SHE.

t (h)	$R_{el}(\Omega)$	$R_{ct}(\Omega)$	$C_{dl}(F)$	$j_{corr.} \cdot 10^6 (Acm^{-2})$
without film (0 mg PPy) measured immediately	1.054	183.74	$4.581 \cdot 10^{-4}$	54
0.1mgPPy measured immediately	1.124	338.9	$3.169 \cdot 10^{-4}$	29
after 23.5 h	1.44	1599.7	$1.03 \cdot 10^{-4}$	6.2
after 47.5 h	1.26	1678.6	$9.84 \cdot 10^{-5}$	5.9
after 71.5 h	1.25	1844.5	$1.015 \cdot 10^{-4}$	5.4

Table 7 - Basic parameters for R(QR) EEC for the best fit of the experimentally obtained data for the system stainless steel without polymer film, and covered with 1.0 mg PPy, 1M H₂SO₄; $E = -0.1$ V/SHE

t (h)	$R_{el}(\Omega)$	$R_{ct}(\Omega)$	$C_{dl}(F)$	$j_{corr.} \cdot 10^6 (Acm^{-2})$
without film (0 mg PPy) measured immediately	1.054	183.74	$4.581 \cdot 10^{-4}$	54
1.0 mgPPy measured immediately	3.87	644	$1.752 \cdot 10^{-4}$	15.4
after 23.5 h	2.397	952.3	$1.43 \cdot 10^{-4}$	10.4
after 47.5 h	1.397	1456.2	$1.616 \cdot 10^{-4}$	6.8
after 71.5 h	1.39	1221	$1.597 \cdot 10^{-4}$	8.1

The results evaluated for the set up bare stainless steel, and/or coated with PPy, (0.1 and 1.0 mg) / 1M H₂SO₄, Tables 6 and 7, completely characterize these systems, direct the following conclusions:

- As the thickness of PPy films, and the treatment time in the acid solution increases, Q , i.e. C_{dl} , takes lower values.

- Significantly enlarged R_{ct} , and at the same time declined j_{corr} values in the presence of the polymer film in respect to the plain metal surface (without film) indicate an inhibition of the corrosion process of metal surface.

CONCLUSIONS

Based on the achieved results it can be concluded:

- Electrodeposited PPy films in quantities of 0.1 – 2.0 mg (thicknesses from 0.52 to 10.4 μm) on a stainless steel substrate ($A = 1.27 \text{ cm}^2$) from 0.5M H_2SO_4 solution containing 0.1M Py, applying a constant current (5 mA) and a potential ranged between 0.95 and 1.05 V/SHE), shows reversible redox behavior.

- Significantly increased values of the redox capacitance, q_{red} , from $\sim 36 \text{ mCcm}^{-2}$ to $\sim 277 \text{ mCcm}^{-2}$ could be noticed with the PPy quantity from 0.1 to 2.0 mg (i.e. thickness from 0.52 to 10.4 μm).

- Reduction of the corrosion current, j_{corr} , as well as corrosion rate, v_{corr} , was also confirmed with the quantity growth of PPy deposited on stainless steel electrode.

- The impedance behavior of PPy films at the corrosion potential of stainless steel, $E = -0.1 \text{ V/SHE}$, can be presented by the simple R(QR) – EEC.

- Electrochemical and impedance measurements of PPy films deposited on stainless steel electrode indicate fairly efficient anticorrosion protection and chemical stability in solutions of 1M H_2SO_4 .

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IZVOD

KOROZIONA ZAŠTITA NERĐAJUĆEG ČELIKA POLIPIROLNIM PREVLAKAMA

Elektroprovodljivi PPy-filmovi različite debljine su elektrohemijski sintetizovani konstantnom anodnom strujom (5 mA; $E = 0.95 \div 1.05 \text{ V/ZVE}$) na elektrodi od nerđajućeg čelika (18% Cr, 10% Ni; $A = 1.27 \text{ cm}^2$) iz rastvora 0.5 M H_2SO_4 koji sadrži 0.1 M Py. Elektrohemijske i koroziono zaštitne karakteristike sintetizovanih PPy-filmova bili su određivani pomoću ciklične voltametrije, polarizacijskih struja-potencijal zavisnosti, kao i elektrohemijom impedansnom spektroskopijom, u vodenim rastvorima sulfurne kiseline. Koristeći softver Boukamp dobijeni su parametri R(QR)-ekvivalentnog električnog kola (EEK), za najbolje fitovanje eksperimentalno dobijenih podataka.

Ključne reči: polipirol (PPy), nerđajući čelik, ciklična voltametrija (CV), elektrohemijom impedansna spektroskopija (EIS), ekvivalentno električno kolo (EEK)

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