

Solid State Conductivity of Optimized Polypyrrole Coatings on Iron Obtained from Aqueous Sodium Salicylate Solution Determined by Impedance Spectroscopy

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In this work the optimization procedure for corrosion resistance, surface analysis and electrical properties of PPy-Fe electrodes have been examined. Polypyrrole (PPy) film was electrochemically synthesized in a one step process from an aqueous solution of sodium salicylate and pyrrole with certain concentrations, different parameters and type of polymerization process. The PPy-Fe electrodes were analyzed using scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS). The adhesion of PPy was tested by applying ASTM sellotape test which proved that PPy coatings are strongly adherent to the iron surface. Potentiodynamic polarization in 0.1M NaCl showed improvement of corrosion protection properties of coated PPy-Fe sample compared to the bare iron. The degree of improvement depends on the concentration of sodium salicylate and pyrrole, deposition time, deposition techniques and its parameters, and on the pH of solution. Impedance spectroscopy (IS) measurements showed different impedance behavior and conductivity of PPy depending on the current density at which the polymer was synthesized.

Keywords: Polypyrrole, iron, sodium salicylate, conductivity, impedance spectroscopy

1. INTRODUCTION

In recent years, conducting polymers have attracted attention of many researchers and engineers of different fields of science [1,2]. Because of their conjugated double bond they possess electronic properties similar to metals [2]. One especially promising of those polymers is Polypyrrole (PPy) [1]. Because of its excellent properties such as high biocompatibility [3], good adhesion to

substrate [2], excellent electrical and mechanical and thermal properties [1], it has been widely studied and it is a promising material for many commercial applications [1]. PPy can be used as electrode material for energy storage devices [2], electrochemical batteries [2] and solid electrolytic capacitors [1], electrocatalyst and biosensor, photoluminescent and electroluminescent materials [2], gas sensor, wires, microactuators, electrochromic windows and displays [1], “artificial muscles” [2], and anticorrosive coatings [2].

Conducting polymers as protection for corrosion of metals have been extensively studied in recent years; especially polypyrrole films as corrosion protection of iron/steel [4, 5, 6, 7, 8, 9]. PPy coatings were applied utilizing different methods, e.g. anodisation or cyclic voltammetry, in different electrolytes, and the corrosion properties were investigated. Previous research on the corrosion protective properties of PPy films is listed in table 1.

Table 1. Corrosion properties of PPy films obtained from literature.

Measurement technique	Solution for corrosion measurement	Result	Ref.
Potentiodynamic polarization	HCl	Corrosion protection of iron became better with synthesized galvanostatically PPy film; PPy coatings increased E_{corr} and decreased i_{corr}	[5]
Linear polarization Impedance spectroscopy Weight loss	NaCl	PPy synthesized in saccharinate electrolytic solution provides corrosion protection of iron.	[4]
Potentiodynamic polarization Impedance spectroscopy		PPy film doped with inhibitor anions such as molybdate provides corrosion protection of mild steel.	[6]
Open circuit potentials Impedance spectroscopy		PPy coatings synthesized in potassium tetraoxalate provide corrosion protection of iron and protection time increases exponentially with increasing synthesis charge.	[7]
Impedance spectroscopy	H ₂ SO ₄	PPy coating cannot provide anodic protection of mild steel electrode in 0.1 M H ₂ SO ₄ . After short immersion time, PPy coatings in contact with this electrolyte became undoped	[8] [9]

The conducted research suggests that PPy is a promising coating for corrosion protection of iron. In order to determine the conductivity of PPy films, different types of measurement techniques have been applied [10, 11, 12, 13, 14, 15]. Mao and Pickup [10] determined the electric conductivity of PPy and poly-MPMP⁺ on platinum using rotating disk voltammetry. The in situ conductivities of PPy were observed to increase exponentially with increasing potential as it is oxidized. Hence, their



determination of conductivity was based on an empirical expression of conductivity of polymer as a function of the applied potential. The investigation of PPy conductivity has been also studied by using four-points method [11, 12, 13]. Based on this type of technique the influence of surfactants [11], doping level [12] of PPy and the temperature [11, 12, 13] on the conductivity of PPy films was determined. The model which was used to describe the conduction process was based on a conduction model developed for amorphous silicon by Mott and Davis [12, 13]. The results suggested that this model provides good qualitative behavior of the conductivity, however, it does not provide a good description of the transport properties in PPy coatings [13]. Also two-probe resistivity measurement system was used to determine conductivity of polypyrrole (PPy) and polypyrrole-graphene oxide (PPy-GO) composites [14]. In situ conductance measurements during electropolymerization have been carried out by Kankare and Kupila [15]. They developed a mathematical model which is based on theories of conformal mapping and elliptic integrals and predicts that conductance is linearly related to the conductivity and approximately to the logarithm of the thickness of the polymer layer. Using a specially designed Pt double-band electrode, the PPy was electrochemically deposited. During electropolymerization, the conductance was simultaneously recorded. Examples of obtained conductivity values of PPy films (prepared using different electrochemical conditions) are presented in table 2.

In this work a one-step electropolymerization process of pyrrole on iron from sodium salicylate aqueous solution was studied. The PPy coating was optimized with respect to its corrosion protection properties. The choice of the sodium salicylate as electrolyte in coatings process can be considered as an additional improvement. Sodium salicylate belongs to non-steroidal, anti-inflammatory agents which reduce pain and fever. Compared to equal doses of ASPIRIN, sodium salicylate is less effective, however it produces the same adverse reactions as ASPIRIN [26]. Thus, the salicylate molecules incorporated in the PPy layer during the coating process could act as a drug, which could be released during incorporation of the implant in human body, in possible biomedical applications of the PPy-coated Fe [27].

Table 2. Conductivity determination of PPy films obtained from literature.

Synthesis of PPy film		σ [S·cm ⁻¹]	Type of measurement technique	Ref.
Polymerization type	Solution			
Galvanostatic electropolymerization	0.1 M Py 0.1 M TEAP acetonitril	10^{-8} - $5 \cdot 10^{-6}$	Rotating disk voltammetry	[10]
	0.05 M Py 0.0125 sodium dodecylsulfate	9.7 – 12.9	Conductance measurement	[15]

Chemical	0.05 M Py + aq. solution: anionic surfactant, anhydrous ferric sulfate as oxidant	0.049	Four - Point	[11]
	0.2 M Py 1M HCl aq. 0.25 M ammonium peroxydisulfate	0.180	Two - Probe	[14]
	0.02 M Py 0.06 M FeCl ₃ aq.	0.0024	Impedance spectroscopy	[16]

Also electrical properties of PPy/Fe electrodes prepared from sodium salicylate solution such as impedance behavior, resistance, conductance and conductivity were studied. The determination of conductivity was based on a mathematical model developed by Kankare and Kupila [15]. To calculate the conductance of deposited polymer, Kupila and Kankare used an ac conductometer [15]. In this work conductance has been obtained from impedance measurements. Since the double-band electrode was made of Fe, the conductivity reflects PPy-Fe interaction and polymer layer close to the Fe electrode, which could be different from the polymer surface layer due to gradient in layer porosity or oxidation state. This approach has not been carried out for PPy coated iron before.

2. EXPERIMENTAL

The materials that were used in the work are: iron ($\geq 99.5\%$) (Chempur Feinchemikalien und Forschungsbedarf GmbH), pyrrole monomer ($\geq 98\%$), sodium salicylate ($\geq 99.5\%$), salicylic acid, sodium hydroxide ($\geq 98\%$), formic acid ($\geq 98\%$) and sodium chloride ($\geq 99.5\%$) (all Sigma-Aldrich).

The iron electrodes were mechanically polished with abrasive papers: 220, 500, 1200 – grade respectively and immersed in ethanol for approx. 3 minutes in ultrasonic bath. Afterwards, the samples were rinsed with ethanol and dried. After the experiments, the samples were rinsed with distilled water and dried in N₂ stream. The Fe double – band electrode was mechanically polished with abrasive papers: 500 and 1200 – grade and rinsed with acetone before each experimental.

Different setup configurations were used depending on the type of measurements. The coating and corrosion experiments were performed in a one-compartment cell with three electrode system controlled by PGU 1A-OEM-MI (JPS). The working electrode was a rectangular Fe sheet (20 mm x 20 mm) with exposed area of 176.71 mm² in polymerization experiments or 78.54 mm² in corrosion measurements. An Ag/AgCl electrode in 3M KCl solution was used as reference electrode and a Pt sheet (10mm x 10 mm) as counter electrode. To prevent an additional input of chloride ions, a second Haber-Luggin capillary filled with the corrosive medium was applied to the reference. All the

experiments were performed in a Faraday cage. The measurements (potentiodynamic polarization) were conducted in 0.1 M NaCl aqueous solution at potentials from -300 mV (rel. OCP) to 1 V with scan rate $3 \text{ mV} \cdot \text{s}^{-1}$. The limit of current density was $10 \text{ mA} \cdot \text{cm}^{-2}$. Each experiment has been performed three times and the averages of these are presented.

Impedance and conductivity measurements were carried out in a 2-electrode system controlled by IM6ex (ZAHNER Elektrik). All experiments were performed in air and Faraday cage at frequency range 30 Hz – 10k Hz with amplitude of 20 mV. For these measurements special double-band electrode was prepared based on description provided by Kupila and Kankare [15] (see figure 1). The electrode consists of two Fe sheets separated with a gap of $80 \mu\text{m}$. To each sheet a lead was attached. The assembly was cast with epoxy resin.

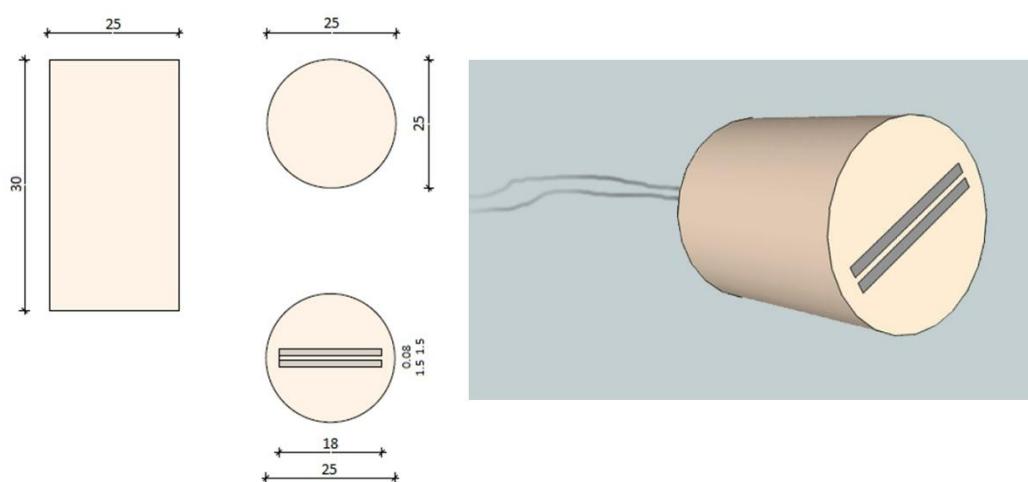


Figure 1. Fe double-band electrode for conductivity measurements (dimensions in mm)

Scanning electron microscopy (SEM) picture was obtained on a HITACHI S-4800 instrument with 1.5k magnification. X-ray photoelectron spectroscopy (XPS) analysis was carried out with a PHI 5600 ESCA System spectrometer. Adhesion measurements were based on the standard sellotape test - ASTM Test Method D 3359 (ISO 2409).

3. RESULTS AND DISCUSSION

3.1. Optimization procedure of PPy electrodes for corrosion resistance

Optimization procedure has been carried out in order to determine the optimum condition of synthesis of PPy coatings for corrosion protection of iron. Initially polypyrrole was galvanostatically ($2.5 \text{ mA} \cdot \text{cm}^{-2}$) synthesized in 0.1M sodium salicylate and 0.1 M Py aqueous solution (pH = 9.5) for 10 minutes. Following included a change of experimental conditions to optimize the corrosion resistance of iron. The changes include: concentration of electrolyte, concentration of monomer, deposition time,

deposition parameters, such as: current density (galvanostatic mode) and potential (potentiostatic mode) and also pH of the electrolyte. In every step, the corrosion properties of the synthesized PPy film on Fe were checked. The optimization procedure and its results are summarized in table 3.

Hence, optimization procedure includes the 5 steps which consist of two measurements: electrochemical deposition (fig. 2a) and electrochemical polarization curves (fig. 2b). The deposition process of PPy on iron from sodium salicylate aqueous solution is characterized in two stages. In the first stage the formation of passive interphase layer occurs and is seen on the $E(t)$ graph (fig. 2a) as a peak which corresponds to a sudden increase of potential. After reaching the maximal potential, the polymerization of Pyrrole is induced resulting in a decrease of potential. The second stage corresponds to the steady state growth of polypyrrole and can be seen as constant potential over time in figure 2a.

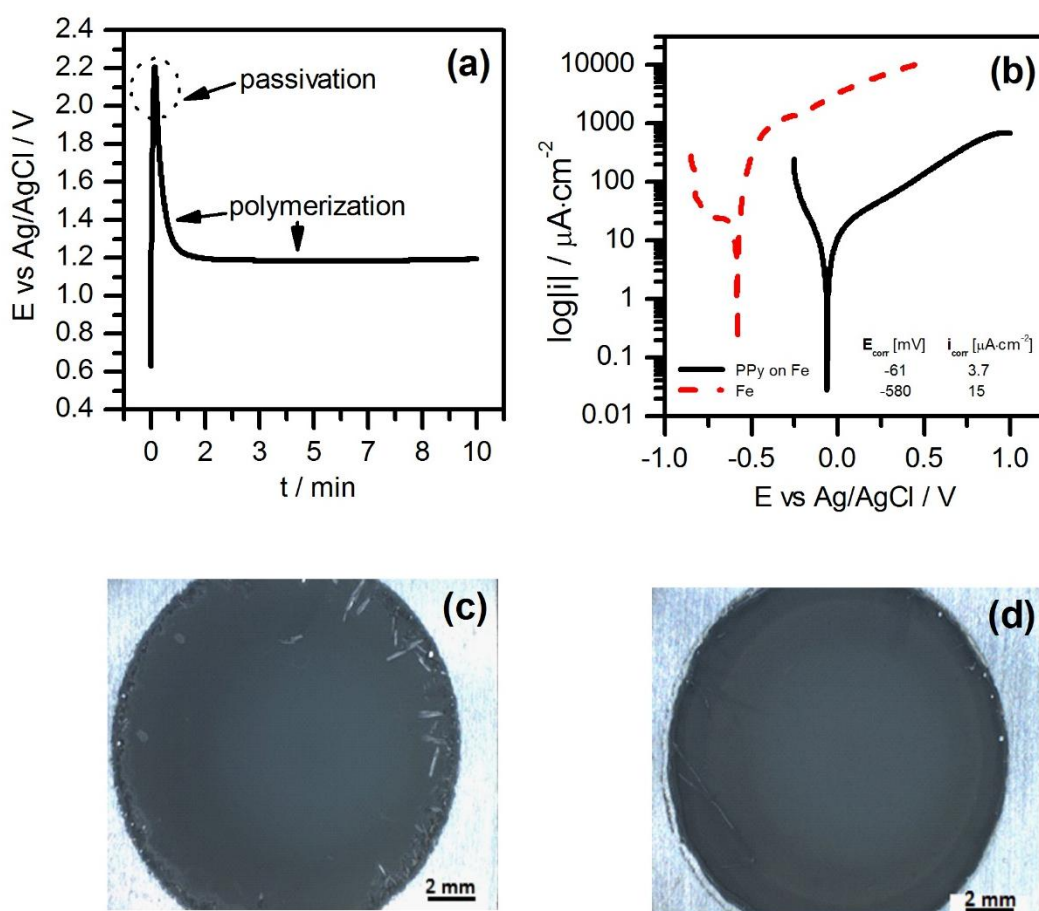


Figure 2. a) Representative anodisation graph for galvanostatic electropolymerization of Py on Fe electrode in sodium salicylate solution, b) representative Tafel-plot for PPy/Fe electrodes in 0.1M NaCl. Polymer obtained galvanostatically during 20 min at $2.5 \text{ mA} \cdot \text{cm}^{-2}$ in 0.1M sodium salicylate solution (pH=9.5) and 0.1M pyrrole, c) PPy sample before corrosion measurement, d) PPy sample after corrosion measurement

This general electrode position behavior of PPy has already been reported by other authors [8, 22, 23]. However, sometimes different deposition behavior was observed depending on the applied

deposition parameter in each optimization step. The experiments showed that by increasing the sodium salicylate concentration, a blocking layer was formed on the iron surface and the potential increased linearly within the first minute. Polypyrrole formation was observed but the corrosion properties were not improved as much as for 0.1M sodium salicylate solution. With increasing pyrrole concentration the passivation peak was lowered as well as the steady state potential. This corresponds to the better deposition efficiency. Nevertheless, for 0.5M and 1M pyrrole concentration the layers detached during cleaning the samples after the coating process. When the solution is altered to an acidic pH of 4 the deposition not only consists of two stages. A third stage occurs before the passivation corresponding to the dissolution of iron. Due to this dissolution the formed polypyrrole layer showed less protective behavior than layers formed in a solution with higher pH-values.

Table 3. Optimization procedure of PPy electrodes for corrosion resistance of Fe – highlighted are the best corrosion properties obtained for each optimization step.

Optimization parameters		Corrosion parameters		Remarks	
		E_{corr} [mV]	i_{corr} [$\mu\text{A}\cdot\text{cm}^{-2}$]		
Concentration of sodium salicylate	0.1 M	-102	8	For 0.5 and 1M formation of a strongly passivating iron-salicylate blocking layer	
	0.5 M	-186	96		
	1 M	-190	12		
Concentration of Py	0.1 M	-102	8	with increasing Py concentration the formed PPy layer became thicker, more unstable and detached from the surface	
	0.5 M	-139	12		
	1 M	-462	12		
Deposition time	10 min.	-102	8	for coating time longer than 20 minutes the PPy growth becomes unstable	
	20 min.	-61	3.7		
	30 min.	-41	4.4		
	60 min.	-41	4.5		
Deposition techniques	Galvanostatic	$1 \text{ mA}\cdot\text{cm}^{-2}$	-78	6	PPy synthesized at $5 \text{ mA}\cdot\text{cm}^{-2}$ is probably overoxidized; potentials of 0.6 and 0.8 V are not sufficient to synthesized appropriate thick protecting PPy layer;
		$2.5 \text{ mA}\cdot\text{cm}^{-2}$	-61	3.7	
		$5 \text{ mA}\cdot\text{cm}^{-2}$	-186	4.4	
	Potentiostatic	0.6 V	-416	8.3	
		0.8 V	-377	23	
		1 V	-75	5.2	
		1.2 V	-60	5.1	
pH	4	-357	11	Basic solution provides better corrosion protection of iron – in acidic solution additionally dissolution of iron occurs	
	6	-169	5.6		
	7	-273	5.8		
	8	-40	3.6		
	9.5	-61	3.7		

Optimization procedure helped to determine the optimum condition for synthesis of PPy coatings from sodium salicylate aqueous solution to increase the corrosion protection of iron. PPy coatings synthesized galvanostatically ($2.5 \text{ mA}\cdot\text{cm}^{-2}$) for 20 minutes from aqueous solution of 0.1 M

sodium salicylate and 0.1 M pyrrole (pH=9) showed the best corrosion protection of iron. Figure 2 shows the coated surface prepared in optimized condition before (c) and after (d) corrosion measurement in 0.1 M NaCl. The corrosion measurement did not change or damage the polypyrrole layer.

Hence, in this work a one-step electropolymerization process of pyrrole on iron from sodium salicylate aqueous solution was synthesized successfully. The deposition process depends on the pH of the electrolyte, and its general behavior is similar to that obtained by other authors [8, 22, 23] in presence of other solutions.

Also, the optimization of PPy coatings with respect to its corrosion protection properties has been done. It was observed that PPy coatings increase the corrosion potential and decrease the corrosion currents densities, thus slow down the corrosion process of iron. The appearance of the sample before and after corrosion measurements in 0.1M NaCl is shown (Fig. 2cd). No influence of the corrosion test to an iron sample coated with PPy from sodium salicylate aqueous solution could be noticed. Also the PPy film after corrosion measurements has still remained homogenous and adherent to the Fe surface. This underlines the superb stability of the coating. This property is also important, especially for implants which experience mechanical or abrasive forces during the implantation or implant that are incorporated in human body for longer times.

3.2. Surface analysis with SEM, XPS and adhesion test

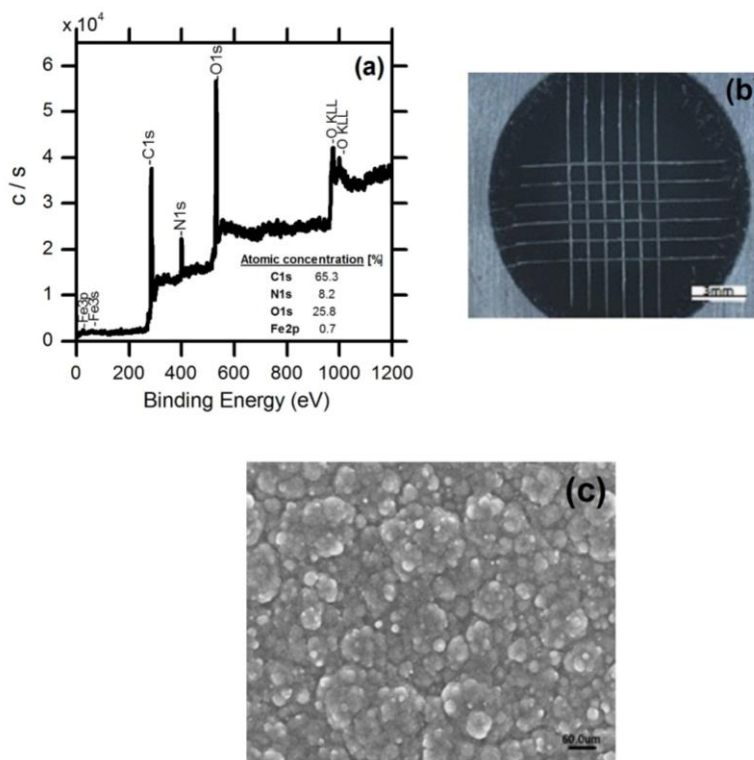


Figure 3. a) XPS spectra, b) Microscope pictures after adhesion measurements, c) SEM micrograph, of PPy film obtained galvanostatically ($2.5 \text{ mA} \cdot \text{cm}^{-2}$) during 20 min. on iron in 0.1 M Py + 0.1 M sodium salicylate aqueous solution (pH = 9)

Several analysis techniques were used to characterize the PPy coatings: SEM, XPS, and adhesion measurements. For these analyses, PPy films were synthesized galvanostatically ($2.5 \text{ mA}\cdot\text{cm}^{-2}$) on Fe for 20 minutes in 0.1 M Py and 0.1 M sodium salicylate aqueous solution ($\text{pH} = 9$). PPy coatings obtained in this condition are homogenous and their surfaces are characterized by a cauliflower-like structure constituted by spherical grains with magnitude of a few micrometers (Fig. 3c). This type of surface structure was already reported by several other authors [4, 5, 17, 18, 19, 20, 21] and corresponds to polypyrrole coatings formed on different base surfaces. The XPS spectrum demonstrate that surface consists mainly of C (65.3%), O (25.8%) and N (8.2%), as shown in figure 3a. The presence of these atoms proved the successful deposition of PPy on Fe surface. The small amount of Fe (0.7%) indicates presence of a thick PPy coating. The XPS results are similar to others [24, 25], thus provide strong evidence of the presence of a successfully applied PPy coating. Adhesion measurement was based on a standard ASTM D33359-09 norm. The PPy-Fe sample after adhesion measurement is presented in figure 3b. No detachment of PPy coatings from Fe surface after adhesion measurements is noticeable (0-5% of removed area). Based on a classification chart of standard ASTM sellotape test, the adherence is estimated to be a class 5A/5B. Hence, the PPy coatings prepared galvanostatically ($2.5 \text{ mA}\cdot\text{cm}^{-2}$) for 20 minutes in 0.1 M Py and 0.1 M sodium salicylate aqueous solution ($\text{pH} = 9$) are strongly adherent to the iron surface.

3.3. Electrical properties of PPy-Fe electrodes

Impedance spectroscopy has been performed in order to determine conductivity of PPy film deposited onto Fe double-band electrode. PPy film was galvanostatically prepared in 0.1 M pyrrole and 0.1 M sodium salicylate aqueous solution at $1 \text{ mA}\cdot\text{cm}^{-2}$, $2.5 \text{ mA}\cdot\text{cm}^{-2}$ or $4 \text{ mA}\cdot\text{cm}^{-2}$ with different deposition times. The determination of conductivity was based on a mathematical model for the conductance of a growing polymer layer on a double-band electrode developed by Kankare and Kupila [15]. This model predicts that conductance is linearly related to the conductivity and approximately to the logarithmic of the thickness of the polymer layer. It is important that the approximation of the conductance curve includes only its linear section to get the information about the conductance value of deposited polymer [15]. In this work conductance values have been obtained from impedance measurements, which were carried out after each deposition experiment. Impedance spectroscopy measurements were performed until the constant or increasing behavior of impedance modulus was achieved. A similar impedance behavior was observed for the PPy sample prepared at 1 and $2.5 \text{ mA}\cdot\text{cm}^{-2}$ (Fig. 4 a, b). The graphs show that if the applied current density was higher, a faster growth of PPy occurred between Fe electrodes. The moment at which two Fe electrodes become connected is seen as rapid decrease of modulus of impedance value. The time after which the connection of Fe double-band electrodes was obtained for 1 and $2.5 \text{ mA}\cdot\text{cm}^{-2}$ was respectively 50 min and 5 min. However, the time after the constant or increase behavior of impedance modulus was obtained equaled 15 h 45 min for $1 \text{ mA}\cdot\text{cm}^{-2}$ and 5 h 37 min for $2.5 \text{ mA}\cdot\text{cm}^{-2}$. In order to clarify the significant “jump” in the impedance value for a specific electropolymerization experiment the process of polymer growth should be described. The schematic and microscope pictures of Fe double-band electrode before and

during electropolymerization process at 1 and 2.5 mA·cm⁻² are presented in figure 5ab. In the early stages of the electropolymerization process, PPy is deposited on the iron electrodes and grows in the both longitudinal and transverse directions (II). Then the capacitance behavior of |Z| on impedance spectrum is observed. After some time of deposition, the polymer layer becomes thicker which results in the connection of PPy films synthesized at each of Fe electrode (III). Connection of these two polymers layers is seen during IS measurements as sudden drop of impedance value and resistivity behavior of |Z| is observed.

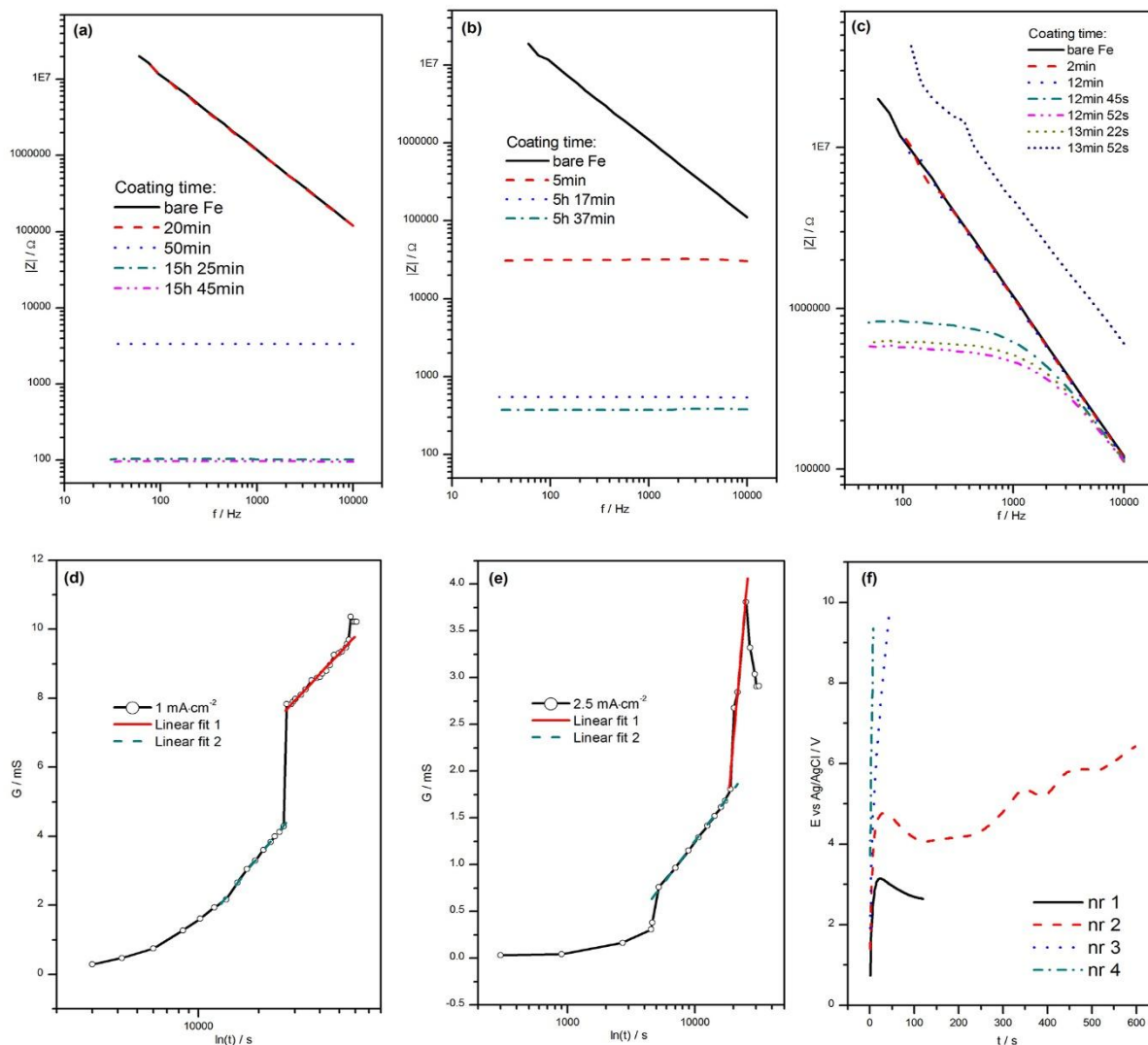


Figure 4. Impedance spectrum of Fe and PPy-Fe double-band electrodes with PPy galvanostatically synthesized at 1 mA·cm⁻² (a) 2.5 mA·cm⁻² (b) and (c) 4 mA·cm⁻², Conductance – time curve for PPy-Fe double – band electrode prepared at (d) 1 mA·cm⁻² and (e) 2.5 mA·cm⁻², Potential-time curves (f) for galvanostatic electropolymerization of Py on Fe double-band electrode at 4 mA·cm⁻² during 2 min. (nr 1), 10 min. (nr 2), 45 s (nr 3) and 7.5 s (nr 4)

Different impedance behavior has been observed for PPy-Fe electrode prepared galvanostatically at 4 mA·cm⁻² (Fig. 4c). After 12 minutes of polymerization process, modulus of

impedance of PPy-Fe electrode start to decrease and its capacitance-resistance behavior is observed up to 13 minutes and 22 second of deposition time. After this time, impedance of that prepared PPy-Fe electrode rapidly increase to the value higher than pure Fe and capacitance behavior of $|Z|$ is observed again. This atypical impedance behavior can be explained based on potential-time curves obtained during deposition process (Fig. 4f). It is observed that during 7 minute of polymerization, deposition process was stable and homogenous PPy film was obtained. However, after this time, unstable growth of polymer occurred. Each next deposition steps (nr 3, 4) exhibited very fast increase of potential and allowed only for a short polymerization time (45 s, 7 s). Fast increase of potential can be due to formation of PPy-sodium salicylate blocking layer with different oxidation state and thus structure of PPy film. These all result in an unstable growth of polymer onto Fe double-band electrode which can be seen in figure 5c. Based on impedance measurements for polymerization time at which the polymer connection between Fe electrodes occurred, the resistance of PPy film was determined at the frequency of about 600 Hz. This allowed calculations of conductance values which were determined as an inverse of resistance. The conductance – time curves for deposition current densities of $1 \text{ mA}\cdot\text{cm}^{-2}$ and $2.5 \text{ mA}\cdot\text{cm}^{-2}$ have been shown in figure 4de. Based on the slope of $G(\ln(t))$ curves and mathematical model [15], the conductivity of PPy film has been determined (see formula 1).

$$G = \frac{\sigma l}{\pi} \left(\ln \frac{8fj}{\pi a} + \ln t \right); \quad G = A + B \cdot \ln t; \quad B = \frac{\sigma l}{\pi} \rightarrow \sigma = \frac{B\pi}{l} \quad (1)$$

G – conductance [S]; σ – conductivity [$\text{S}\cdot\text{cm}^{-1}$]; l – length of the band electrode [cm]; a – half the length of a gap between electrodes [cm]; t – time of galvanostatic electropolymerization [s]; A, B – approximation parameters; f – “volume yield” of polymer [$\text{cm}^3\cdot\text{C}^{-1}$]

For each polarization current densities two areas of linear variation of $G(\ln(t))$ were observed (fig. 4de). Thus two linear approximations were done. Table 4 presents the conductivity values obtained for PPy synthesized at 1 and $2.5 \text{ mA}\cdot\text{cm}^{-2}$.

Table 4. Conductivity values of PPy film synthesized at 1 and $2.5 \text{ mA}\cdot\text{cm}^{-2}$.

		Linear fitting	
		1	2
σ [$\text{mS}\cdot\text{cm}^{-1}$]	$i_{\text{deposition}} = 1$ [$\text{mA}\cdot\text{cm}^{-2}$]	10.9	12.7
	$i_{\text{deposition}} = 2.5$ [$\text{mA}\cdot\text{cm}^{-2}$]	27.29	5.9

The conductivity values obtained for PPy prepared at $1 \text{ mA}\cdot\text{cm}^{-2}$ from two different linear approximations are similar. Thus, the rapid change of conductance occurs probably due to the change or destruction in structure of deposited PPy film which could have occurred between deposition and impedance experiments. The conductivity values obtained for PPy prepared at $2.5 \text{ mA}\cdot\text{cm}^{-2}$ from two different linear approximations are different (Tab. 4). However, differences here can be due to changes in structure and in oxidation state of polymer film during deposition process and is seen as a sudden increase of conductance values and change of the slope in the $G(\ln(t))$ plot (Fig. 4e). It was observed

that with the increasing deposition time and thus thickness of PPy film, the conductivity was higher. Hence, depending on oxidation state different conductivity properties of PPy can be obtained. Changes in the oxidation state of the polymer can be due to it having achieved its critical thickness, or due to solution in which the deposition process was carried out. Hence, depending on deposition parameters and solutions in which deposition process takes place, different structure and conductivity of PPy film can be obtained.

Conductance graphs obtained for PPy-Fe sample prepared at 1 and 2.5 mA·cm⁻² are similar to that obtained by other authors [15]. Also the conductivity value obtained for PPy was mostly similar to that obtained by others (see in table 2). Only in one case [15] conductivity was much higher. The reason of that can be due to different electrolytes which were used during coating process. Thus, probably depending on the electrolyte, a different degree of doping of polypyrrole film with electrolyte molecules is obtained, resulting in different conductivity values.

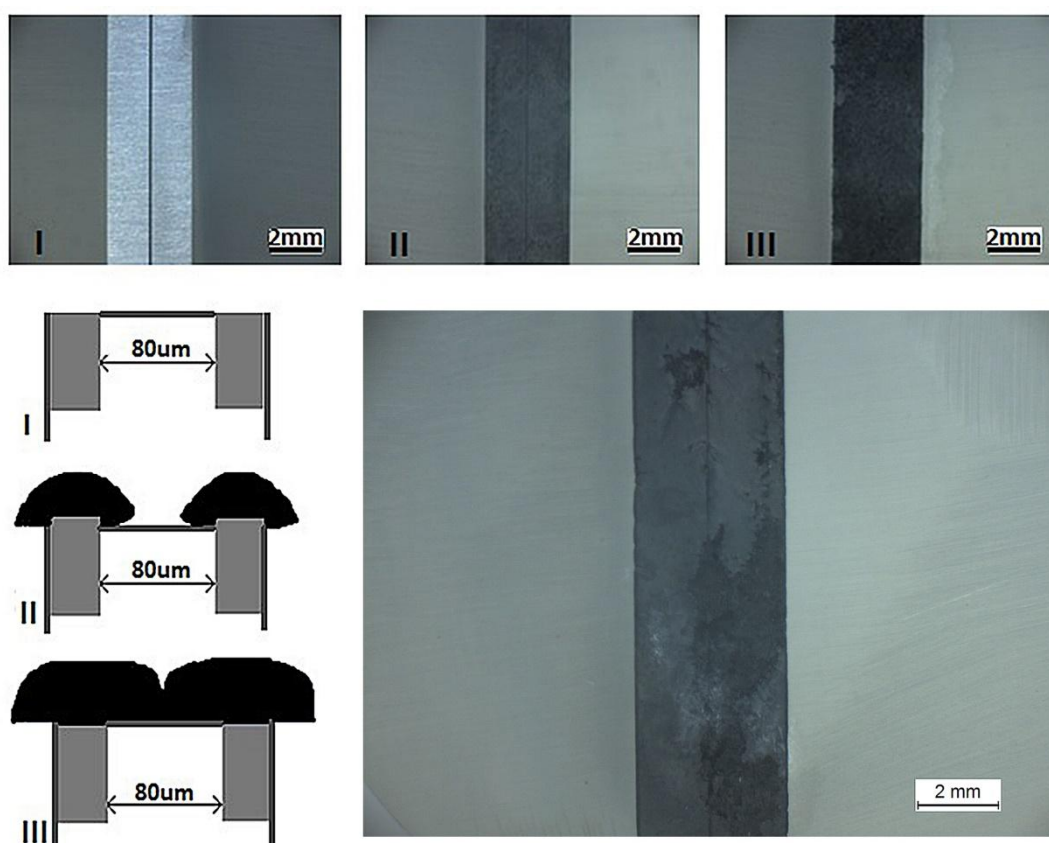


Figure 5. Microscopic (a) and schematic (b) picture of Fe double-band (I) and PPy-Fe electrode (II,III) before and during polymerization process; (c) microscopic picture of PPy-Fe sample during deposition at 4 mA·cm⁻²

Because of the long deposition time (compared to other studies [15]) after which the constant or decrease of conductance was achieved (15 h 45 min for 1 mA·cm⁻² and 5 h 37 min for 2.5 mA·cm⁻²), different behavior of PPy coatings synthesized from sodium salicylate could be observed. PPy

coatings prepared at $1 \text{ mA}\cdot\text{cm}^{-2}$ exhibited approximately constant conductivity value during all deposition process. Thus, deposition process of that sample was stable and homogenous polymer film was obtained. However, PPy coatings prepared at $2.5 \text{ mA}\cdot\text{cm}^{-2}$ exhibited two different conductivity values which is probably due to changing in oxidation state of polymer. Thus, because of the long deposition time, different state and thus different deposition and conductivity behavior of PPy is observed. Therefore, PPy coatings with a range of thickness, oxidation states, structure and conductivity can be achieved.

To the best of our knowledge, the solid state conductivity of PPy on Fe was studied here the first time. The impedance spectroscopy was performed in air, thus no direct and additional influence of the electrolyte is affecting these measurements. Also the approach allows determination of the conductivity of deposited polymer without any damage of the surface, which is impossible using methods such as two- or four-probes [11, 14].

4. CONCLUSION

Polypyrrole (PPy) deposition on iron in an aqueous sodium salicylate solution was studied. The coating parameters were optimized and the best corrosion protection achieved by galvanostatically applying $2.5 \text{ mA}\cdot\text{cm}^{-2}$ in a 0.1 M sodium salicylate solution containing 0.1 M pyrrole with a pH of 9.5 for 20 minutes to iron. The results also showed that the coating applied under optimized conditions is not damaged by corrosion measurements carried out by potentiodynamic polarization in 0.1 M NaCl. The deposited polypyrrole layer has a cauliflower-like structure, and the XPS results showed the presence of nitrogen on the surface comparable to literature, demonstrating the successful deposition of PPy layer on Fe. ASTM D33359-09 standard showed that the polypyrrole layer exhibited a very good adhesion to the substrate.

Impedance spectroscopy measurements have been done to determine the conductivity of PPy film deposited galvanostatically (at 1, 2.5 and $4 \text{ mA}\cdot\text{cm}^{-2}$) onto Fe double-band electrode. The conductivity of the PPy-Fe electrodes depends on the deposition current density. PPy films synthesized in 0.1 M sodium salicylate at $1 \text{ mA}\cdot\text{cm}^{-2}$ exhibit slightly higher conductivity ($3.59 \text{ mS}\cdot\text{cm}^{-1}$) compared to PPy films prepared also in 0.1 M sodium salicylate but at $2.5 \text{ mA}\cdot\text{cm}^{-2}$ ($1.32 \text{ mS}\cdot\text{cm}^{-1}$). The conductivity of PPy synthesized at $4 \text{ mA}\cdot\text{cm}^{-2}$ couldn't be determined due to unstable deposition process. In this study the corrosion behavior of the PPy coated iron was tested in 0.1M NaCl solution. In view of biomedical applications (e.g., biodegradable Fe-base implants), corrosion tests should be carried out in simulated body fluid or cell culture medium at body temperature in future work. Further investigations should also include cell adhesion and proliferation on the coated surface. Another factor that will be investigated is the long term corrosion behavior of PPy iron coated samples.

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References

1. L. Wang, X. Li and Y. Yang, *React. Funct. Polym.*, 47 (2001) 125
2. T. V. Vernitskaya and O. N. Efimov, *Russ. Chem. Rev.*, 66 (1997) 443
3. P. M. George, A. W. Lyckman and D. A. LaVan, *Biomaterials*, 26 (2005) 3511
4. J. I. Martins, M. Bazzouai, T. C. Reis, E. A. Bazzouai and L. Martins, *Synthetic Met.*, 129 (2002) 221
5. M. Bazzouai, J. I. Martins, T. C. Reis, E. A. Bazzouai, M. C. Nunes and L. Martins, *Thin Solid Films*, 485 (2005) 155
6. L. M. Duc and V. Q. Trung, *INTECH*, 7 (2013) 143
7. H. Nguyen Thi Le and B. Garcia, *Electrochim. Acta*, 46 (2001) 4259
8. N. V. Krstajić and B. N. Grgur, *Electrochim. Acta*, 42 (1997) 1685
9. B. N. Grgur and N. V. Krstajić, *Prog. Org. Coat.*, 33 (1998) 1
10. H. Mao and P. G. Pickup, *J. Am. Chem. Soc.*, 112 (1990) 1776
11. J. Stejskal, M. Omastova, S. Fedorova, J. Prokes and M. Trchova, *Polymer*, 44 (2003) 1353
12. A. Kaynak, *Turk. J. Chem.*, 22 (1998) 81
13. J. P. Travers, P. Audebert and G. Bidan, *Mol. Cryst. Liq. Cryst.*, 118 (1985) 149
14. P. Manivel, S. Kanagaraj, A. Balamurugan, N. Ponpandian, D. Mangalaraj and C. Viswanathan, *J. Appl. Polym. Sci.*, 131 (2014) 40642
15. J. Kankare and E. L. Kupila, *J. Electroanal. Chem.*, 322 (1992) 167
16. T. K. Vishnuvardhan, V. R. Kulkarni, C. Basavaraja and S. C. Raghavendra, *B. Mater. Sci.*, 29 (2006) 77
17. M. Bazzouai, L. Martins, E. A. Bazzouai and J. I. Martins, *Electrochim. Acta*, 47 (2002) 2953
18. F. Beck, R. Michaelis, F. Schloten and B. Zinger, *Electrochim. Acta*, 39 (1994) 229
19. T. Darmanin, W. Taffin de Givenchy and F. Guittard, *Macromolecules*, 43 (2010) 9365
20. M. Bazzouai, J. I. Martins, S. C. Costa, E. A. Bazzouai, T. C. Reis and L. Martins, *Electrochim. Acta*, 51 (2006) 4516
21. I. L. Lehr and S. B. Saidman, *Corros. Sci.*, 49 (2007) 2210
22. J. O. Iroh and W. Su, *J. Appl. Polym. Sci.*, 71 (1999) 2075
23. W. Su and J. O. Iroh, *Electrochim. Acta*, 44 (1999) 4655
24. F. Singer, D. Ruckle, M. S. Killian, M. C. Turhan and S. Virtanen, *Int. J. Electrochem. Sci.*, 8 (2013) 11924
25. M. C. Turhan, M. Weiser, M. S. Killian, B. Leitner and S. Virtanen, *Synthetic Metals*, 161 (2011) 360
26. <http://pubchem.ncbi.nlm.nih.gov>, 03-06-2014, 9:30
27. M. Moravej and D. Mantovani, *Int. J. Mol. Sci.*, 12 (2011) 4250

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