



Electrochemical synthesis, characterization and some properties of a polymer derived from thioflavin S

Nada F. Atta *

Department of Chemistry, College of Science, University of Cairo, 12613 Giza, Egypt

Received 11 December 2004; received in revised form 30 April 2005; accepted 27 May 2005

Available online 14 July 2005

Abstract

Polymeric films derived from thioflavin S were electrosynthesized on mild steel and silver electrodes in sulfuric acid and lithium perchlorate-containing aqueous solutions. The introduction of thioflavin S in an acidic solution protected the surface of steel from corrosion. The electrochemical behavior of the steel coated with a layer of poly(thioflavin) was examined by electrochemical impedance spectroscopy. The films exhibited a capacitive behavior and were semi-conductive in nature. Infra red reflectance measurements of the polymer films at the steel surface showed that the polymer structure retained the aromatic structure of the benzene and thiazole rings with the distinction of a nitrogen quinone vibrational band. Surface morphology of the polymer film was examined with scanning electron microscopy. The films are yellow, compact and dense when electrochemically formed onto steel surfaces when compared to a blue rather porous when formed onto silver electrode. The mechanism of electropolymerization of thioflavin is given and found similar to that of aniline with the possibility of metal chelation with the sulfur and/or nitrogen in the thiazole ring.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Thioflavin S; Electropolymerization; Conducting polymers; Corrosion inhibition; Electrochemical impedance spectroscopy

1. Introduction

Electrochemically synthesized polymers such as 3- and 3,4-substituted poly(pyrroles) and poly(thiophenes) and their derivatives have been investigated extensively and are used currently in a wide variety of applications including microelectronics, electrode materials, sensors and optoelectronics [1]. Poly(aniline) and its derivatives have been also important for many technological applications [2]. Conducting polymers were used successfully for chemical analysis [3] and as sensing materials for chemical sensors [4]. Among the most recent applica-

tion of these materials is their use in the corrosion protection of metals in aqueous environments [5]. The replacement of these polymeric materials for chromium(VI)-containing coatings in corrosion control for iron alloys will have a desirable impact on environmental and health protection. Several conducting polymeric systems were used successfully for this purpose [6,7].

Thioflavin is a thiazole-based structure and is widely used to demonstrate neurofibrillary tangles and senile plaques known as amyloids in Alzheimer's diseased brain tissue sections [8]. Thioflavin S is also known as prumiline or direct yellow [9], and has the suggested structure given in Fig. 1. The structure shows two important features for the compound, the first is the presence of two thiazole moieties and the second has

* Tel.: +20 2 567 6561; fax: +20 2 572 7556.

E-mail address: nada_fahl@yahoo.com

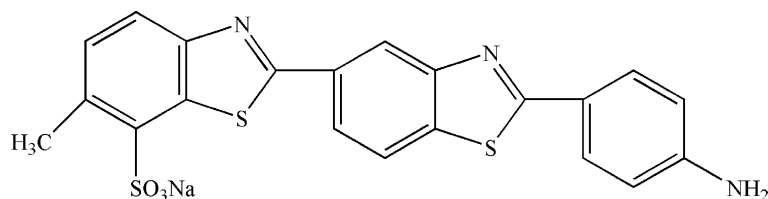


Fig. 1. Structure of thioflavin S.

an aniline derivative structure. On the other hand, thiazole derivatives are known to inhibit the corrosion of mild steel in hydrochloric acid solutions [10]. However, to the best of our knowledge, the literature did not cite any work that shows the possible polymer formation of thioazole derivatives. The electropolymerization of thioflavin S and its possible application as an inhibitor for mild steel in acidic medium were not yet described in the literature.

In this work, the electropolymerization of thioflavin S onto mild steel type 1010 and silver substrate is presented. The polymer film structure was examined by surface reflectance infrared spectroscopy and the surface morphology of the film at the steel substrate was determined by scanning electron microscopy. The corrosion protection ability of the poly(thioflavin S) film for mild steel in sulfuric acid solutions was evaluated using polarization and electrochemical impedance spectroscopy (EIS) techniques.

2. Experimental

2.1. Chemicals and materials

Thioflavin S and all other chemicals used in this study were purchased from Aldrich Chem. Co. (Saint Louis, USA). Chemicals were used as received without further purification. Silver wire (1.0 mm diameter, 99.9% pure) was purchased from Alfa Aesar (Ward Hill, USA). Mild steel substrates with the following chemical composition (in wt.%): 0.05 C, 0.6 Mn, 0.36 P, 0.03 S and Fe (balance) were supplied by Alcoa Steels (Pittsburgh, USA). The steel specimens were machined into cylindrical form, 2.0 cm long and 1.2 cm in diameter. They were inserted in Pyrex[®] glass tubing and sealed with a Varian high vacuum Torr Seal[®] to ensure that only a flat surface with controlled surface area is in contact with the electrolytic synthesis or test solutions. Electrochemical polymerization and corrosion tests were carried out in a three-electrode one-compartment glass cell. The working electrodes were mild steel disc or plates or silver wire. All the potentials in electrochemical polymerization, polarization and the EIS measurements were recorded with reference to a saturated Ag/AgCl

electrode. The auxiliary electrode was a 2 cm × 2 cm platinum sheet or 10 cm (length) × 1.5 mm (diameter) platinum wire. Working electrodes were mechanically polished using metallurgical papers of different grades, followed by thorough rinsing with distilled water.

2.2. Instrumentation and methods

An EG & G potentiostat/galvanostat model 371A (Oak Ridge, USA) was used for the polymer film formation. A Gamry PC3/750 potentiostat/galvanostat/ZRA system (Wilmington, USA) was used for polarization and EIS measurements. This system was interfaced to a personal computer to control the experiments and the data were analyzed using Gamry CMS-300 framework/analysis software.

The electrochemical synthesis of the conducting polymer film was carried out from a solution consisting of 0.02 M thioflavin S, 1.0 M H₂SO₄ or 0.05 M thioflavin S and 0.5 M LiClO₄ dissolved in de-ionized water. The polymer films were electrochemically deposited at the steel surface using a linear polarization signal with the following characteristics: $E_i = -1.0$ V, $E_f = +1.0$ V with a scan rate 1.0 mV s⁻¹. Prior to electrochemical deposition of the polymer film, the steel electrode was “activated” by holding its potential for 1 min at -1.2 V. Polarization experimental conditions are as indicated in the following sections. The polymer films were deposited onto silver substrate using cyclic voltammetry (CV) technique with the potential limits as follows: $E_i = -1.0$ V, $E_h = +1.5$ V, $E_f = -1.0$ V with a scan rate = 50 mV s⁻¹.

The polarization and EIS measurements on surface films formed of thioflavin S at steel surface were conducted in a 1.0 M H₂SO₄. The data analysis software applied non-linear least squares fitting (NLLS) with Levenberg–Marquardt algorithm [11]. The measurements were performed under potentiostatic control at different applied potentials. The working electrode was conditioned prior to performing the impedance measurement to ensure current stabilization. Thus, the working electrode was held at the same constant potential used for the EIS experiment for 10 min. The constant applied potential was decided from the polarization experiment recorded for the film in 1.0 M H₂SO₄. All impedance measurements were recorded

between 10 mHz and 5.0 kHz with ac amplitude of 10 mV. Except for temperature effect studies, all experiments were performed at room temperature ($20\text{ }^{\circ}\text{C} \pm 0.2$).

2.3. Surface characterization

The surface morphology of the polymer film was characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray analyzer (EDAX) [Philips model XL 30]. The structure of the organic film on the steel substrate was examined using surface reflectance Fourier transform-infrared spectroscopy (FT-IR) (Nicolet Magna-IR spectrometer, Nic-Plan IR microscope and a Spectra Tech stage controller). Polymer films were electrochemically generated at flat steel or silver wire samples, dried and immediately measured.

3. Results and discussion

3.1. Electrochemical deposition of thioflavin S at steel substrates

The electrochemical formation of poly(thioflavin S) was achieved using a linear sweep controlled potential signal between -1.0 V and 1.0 V , scan rate was 1.0 mV s^{-1} . The potential-current diagram is given in Fig. 2. The results of Fig. 2 indicate an increase of current at the onset of potential ramp between -1.0 V and -0.70 V . This region is indicative of a gas evolution namely hydrogen as expected in sulfuric acid used and as expected for steel surfaces [12]. A slight increase in current follows between the potential limits of -0.70 V and -0.3 V . The hydrogen evolution rate decreases and oxide formation is concurrent with the polymer film deposition. A broad current peak is then observed that is characteristic for the steel passivation and the surface starts to display a yellowish-

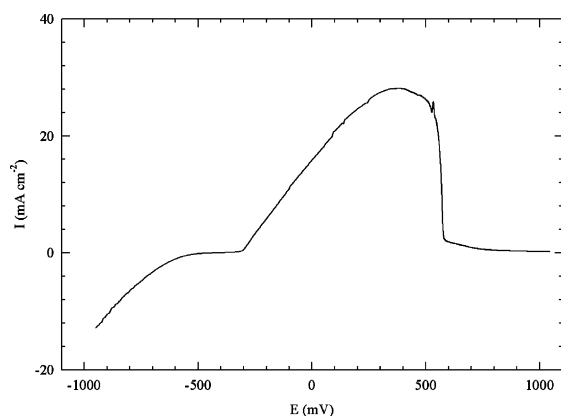


Fig. 2. Linear sweep voltammetry of mild steel in presence of thioflavin in 1.0 M sulfuric acid, scan rate 1.0 mV s^{-1} .

green polymer deposit. The peak current at $+0.4\text{ V}$ is indicative of maximum deposition rate of the polymer film and the completion of passivity imparted to the surface of steel. At a potential value of $\approx +0.55\text{ V}$ the current decreases and no indication was observed for a trans-passive region for the oxide/polymer layer at the steel surface. The resulting polymer is a thick dense film that covers homogeneously the exposed surface of the steel electrode.

3.2. Poly(thioflavin S) films as inhibitors for the corrosion of mild steel in H_2SO_4

Table 1 shows the polarization data of inhibited steel in $1.0\text{ M H}_2\text{SO}_4$ at different temperatures. The amount of thioflavin used in these solutions, was $2.1 \times 10^{-4}\text{ M}$. Anodic (β_a) and cathodic (β_c) Tafel slopes were reported in the literature to be in the range 60–79, 134–146 for β_a and β_c , respectively [13]. The different values found in this study for the poly(thioflavin S) used suggest that the primary mechanisms for inhibition in this study differ from those reported earlier. The corrosion rate can be calculated using the Stern–Geary equation [14]:

$$I\text{ (mA)} = \frac{\left[\frac{\beta_a \times \beta_c}{2.3(\beta_a + \beta_c)} \right]}{R_p} \quad (1)$$

R_p is the polarization resistance that is calculated from the linear polarization scan. The corrosion rate can also be calculated by extrapolating the Tafel lines of the potentiodynamic scans to the “rest” potential. It was found that the corrosion rate calculated from the potentiodynamic, Tafel and polarization resistance experiments followed comparable trends. The rate of corrosion increases with temperature as indicated by the increase in current values given in Table 1. Since the corrosion rate is directly related to corrosion current, the inhibition efficiency ($I\%$) at different temperatures for poly(thioflavin S) can be calculated from the following relation:

$$I\% = \frac{i_a - i_c}{i_a} \times 100 \quad (2)$$

where i_a and i_c are the corrosion rates in uninhibited and inhibited solutions, respectively. On the other hand, the

Table 1
Electrochemical parameters for mild steel in presence of thioflavin in $1.0\text{ M H}_2\text{SO}_4$

T ($^{\circ}\text{C}$)	$-E$ (mV)	β_c (mV decade $^{-1}$)	β_a (mV decade $^{-1}$)	I_{corr} (10^{-5} A cm^{-2})
30	434	88.2	57.2	9.7
35	425	89.8	82.2	26.5
40	423	90.1	77.2	38.8
45	417	80.5	82.8	69.5
50	414	74.2	73.2	70.2

degree of coverage θ at constant applied potential is given by [13]:

$$\theta = \frac{1 - i_c}{i_a} \quad (3)$$

The inhibition efficiencies calculated from linear polarization are equal to the values obtained by potentiodynamic method. These types of comparison between the inhibitor efficiencies evaluated by the two methods have also been reported earlier in the literature [15]. The efficiency of inhibition decreases with increase in temperature and varies between 96% and 61% between the temperature ranges of 30–50 °C. The corresponding corrosion rates are 2.25, 6.17, 9.03, 16.18, and 16.35 MPY at 30, 35, 40, 45, and 50 °C, respectively.

3.3. Electrochemical impedance spectroscopy studies

This section of the current work is concerned with the characterization of the resulting polymer film and its protection mechanism on steel substrate. The EIS measurements were carried out at a potential value of 0.20 V at which the polymer film is deposited and a passive layer has been also formed. Fig. 3a shows the Bode plots for “bare” stainless steel surface in absence (a) and presence of different concentrations of thioflavin, $\approx 2.0 \times 10^{-5}$ (b), 3.0×10^{-5} (c), 8.5×10^{-5} (d), 1.5×10^{-4} (e) M. In the treatment of data, an equivalent circuit similar to that published by Ren and Pickup [16] was used. The data shown in Fig. 3a show that a dramatic change in conductivity is observed with increase in the amount of thioflavin added. Thus, the polymer capacitance is affected by the redox process at its interface and its conductivity is a function of its bulk resistance. Moreover, a diffusion parameter was also used in the modeling that corresponds to the diffusion phenomena through the film. Therefore, we assume a film deposition of poly(thioflavin S) that thickens with the amount of monomer in solution and a passive oxide film formation. At high frequency region of the data of Fig. 3a the impedance values are related to polymer film parameters. The observed increase in the value of impedance is in agreement with the suggestion of increase in film thickness. The lower frequency domain describes the electrochemical corrosion reactions at the metal substrate. Fig. 3b shows the EIS diagram represented as a “Nyquist” plot recorded after 5 min of immersion of a polymer-coated mild steel specimen in 1.0 M sulfuric acid. The polymer film was formed with different thickness using the same electrolytic solution composition as described in the experimental section. The number of repetitive scans used was 1(a), 3(b), 5(c) and 7(d) cycles. The applied dc potential used was +0.20 V during the EIS measurements. It could be noticed that the obtained diagrams do not represent perfect semicircles, generally attributed to the frequency dispersion. They present

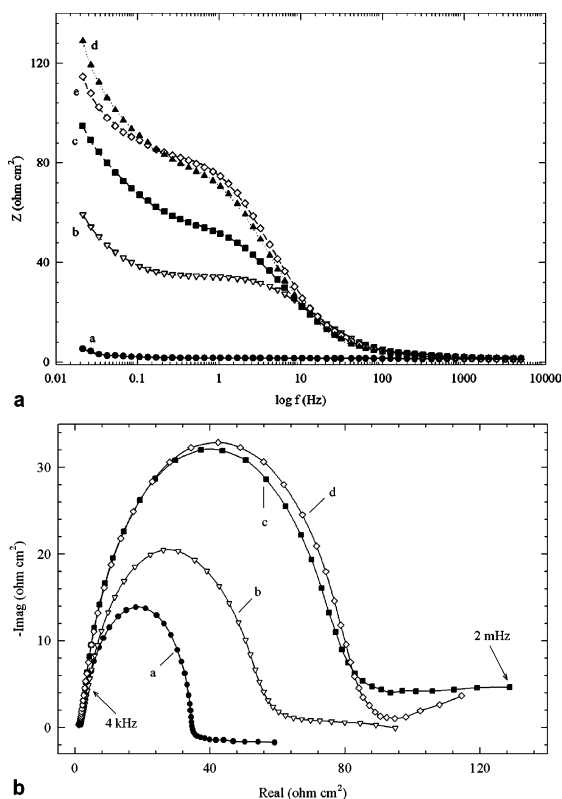


Fig. 3. (a) Bode plot of mild steel in absence (a), and presence of 2.0×10^{-5} (b), 3.0×10^{-5} (c), 8.5×10^{-5} (d), 1.5×10^{-4} (e) M thioflavin and 1.0 M sulfuric acid. (b) Nyquist plot of poly(thioflavin) films on mild steel formed with different number of cyclic voltammetry, 1(a), 3(b), 5(c) and 7(d) cycles in 1.0 M H_2SO_4 .

only one capacitive loop that increases in diameter when the film thickness increases. This is indicative for increase in film protection at the surface of substrate. It would be expected that as the polymer layer that protects the surface of steel is thickened, the charge transfer resistance related to the exchange of charge between the substrate and the electrolytic medium should increase [17]. It is important to notice that the behavior of the steel-poly(thioflavin) shows a capacitive behavior that increases as the film thickness increases. Moreover, at an applied potential of +0.2 V there is a transition of the film from a non-conductive to a semi-conductive state. When the polymer film is relatively thicker (i.e. for films formed with more than five cycles), the charge transfer resistance increases and the oxide film formed due to electrochemical corrosion reaction starts to compete for the total charge transfer. The diffusion behavior is not observed at low frequency domains of the impedance spectrum. This could be explained in term of polymer doping with anionic species that do not allow further ionic exchange within the film matrix.

If f_{\max} is the value of the frequency at the maximum imaginary part of the loop, R_{ct} is the transfer resistance without the inhibitor, C_{dl} is the double layer capacitance, and R'_{ct} is the transfer resistance in presence of the polymer coating at the diameter of the loop. The previous parameters are related by

$$I\% = \left(\frac{1 - R_{ct}}{R'_{ct}} \right) \times 100 \quad (4)$$

$$C_{dl} = \frac{1}{2} \times \pi \times f_{\max} \times R_t \quad (5)$$

The values obtained from the equivalent circuit for the steel-polymer electrode are given in Table 2. These results show an improvement in inhibition behavior of steel in presence of organic compound.

The previous data prove the following observations:

- The value of transfer resistance increases in presence of the inhibitor that in turn increases the efficiency of protection for mild steel in the corroding medium.
- A polymer film is formed at the steel surface that inhibits its corrosion in the acidic medium.
- The system consists of steel/polymer/electrolyte interfaces. Since the impedance diagram obtained has a semicircle appearance, it could be concluded that a charge transfer process mainly controls the electrochemical process at the polymer/electrolyte interface.
- The polymer layer has semi-conducting and capacitive properties that increase with thickening of the polymer film.

3.4. Structure and surface characterization

Fourier-transform IR with reflectance microscopy of thioflavin S and poly(thioflavin S) is shown in Fig. 4. The data represent the IR spectra of a thioflavin S KBr-pellet (cf. Fig. 4a) compared to an as-grown film at mild steel (cf. Fig. 4b) obtained by direct reflectance from the surface. The assignment of the IR peaks is as follows [18]:

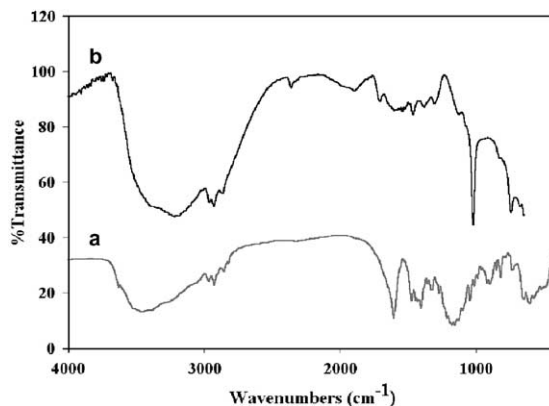


Fig. 4. Infra red spectrum of KBr-pellet (a) and as-grown film on mild steel surface (b).

- At 1400–1620 cm^{-1} several bands appear associated to the aromatic carbon–carbon stretching vibrations.
- In the region 2800–3000 cm^{-1} the bands appearing could be attributed to the aromatic C–H stretching vibrations.
- A broad band appeared at 3200 cm^{-1} that is obviously attributed to the N–H stretching.
- The sharp band appearing at around 1050 cm^{-1} could also be attributed to the vibration of nitrogen quinone. A similar strong band appeared at 1140 cm^{-1} for some poly(aniline) base was suggested earlier [19].

Therefore, from the IR we can conclude that the polymeric film formed on mild steel surfaces maintains the aromatic character and contains nitrogen quinone similar to that present in the fully oxidized form of poly(aniline) known as pernigraniline.

In order to obtain information about the surface morphology of the polymeric films grown on mild steel surfaces, SEM technique has been used. Fig. 5 shows the SEM microphotograph of bare mild steel surface (a) and that coated with the polymeric film (b). As it can be observed, the morphology of this film appears to be scaly. This morphology is different compared to that obtained for other polymeric films at platinum surfaces [20].

Table 2

Parameters obtained from equivalent circuit for mild steel covered by poly(thioflavin) formed with different thickness in 1.0 M H_2SO_4

Cycles ^a	R_s ($\Omega \text{ cm}^2$)	C_{dl} (10^3 F cm^{-2})	R_{ct} ($\Omega \text{ cm}^2$)	C_c (10^3 F cm^{-2})	Z_W ($n = 0.5$) ($10^3 \Omega \text{ cm}^2$)	Q (10^3 F cm^{-2})	n
1	8.50	0.84	38.3	98.1	10.2	44	0.9
3	12.5	0.22	221	231	11.5	72	0.7
5	7.10	0.07	645	535	12.3	81	0.8
7	10.8	0.04	692	591	12.1	78	0.8

Q is a constant phase element, n represents the capacitance behavior, Z_W is the Warburg element, and other elements are as indicated in the text.

^a Number of cycles for polymer film formation.

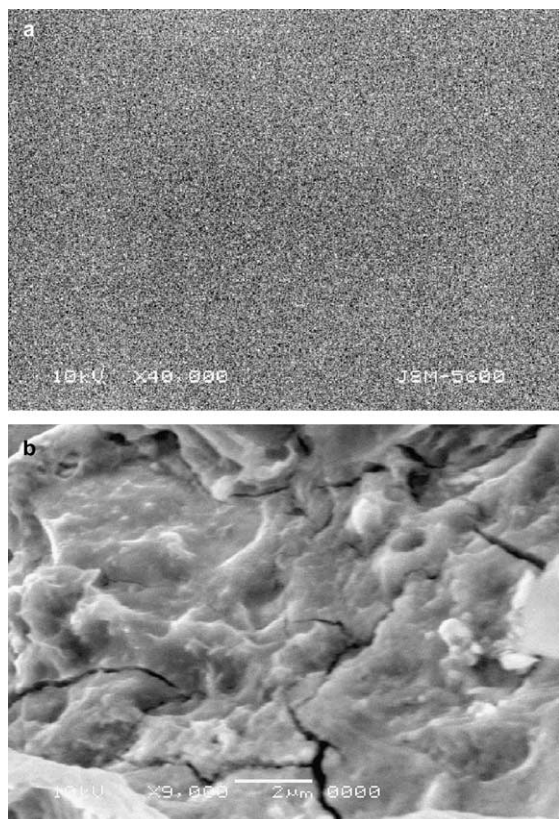


Fig. 5. SEM pictures of bare mild steel (a) and poly(thioflavin) on mild steel (b).

A polymer with similar surface morphology was also obtained at graphite surface. It is shown in Fig. 5b surface cracks exist for the polymer film. Those defects could result in ineffective barrier for protection for the underlying substrate. However, those cracks were not identified for thin films formed under similar conditions.

3.5. Electropolymerization of thioflavin S onto silver substrates

The electrochemical polymerization of thioflavin S at silver electrode was achieved by cycling the potential repeatedly between -0.2 V and $+1.0$ V in a solution containing 0.02 M thioflavin S and 1.0 M H_2SO_4 in water. The cyclic voltammogram is shown in Fig. 6. The CV is characterized by the appearance of a pre-oxidation peak at ≈ 0.45 V followed by a well-defined oxidation peak at $+0.60$ V. We should expect a concurrent oxidation of silver at this potential. The increase in the peak current values for successive cycles indicates the film thickening. This was ascertained by the appearance of a reduction peak at $+0.22$ V followed by a rather broad peak at $+0.10$ V. Moreover, both current-peaks increase with number of cycle. The above results indicate that the

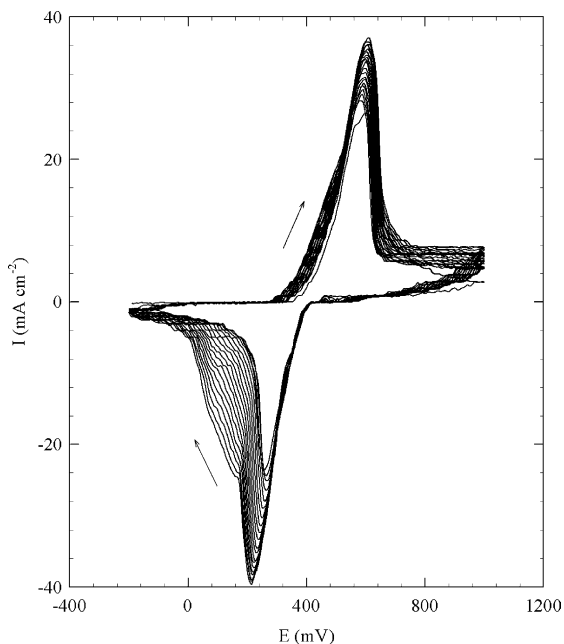


Fig. 6. Repeated cyclic voltammograms for the electropolymerization of poly(thioflavin) over silver. Scan rate 100 $mV s^{-1}$.

polymer film resulting from the thioflavin S possesses an appreciable extent in conduction that allows successive deposition as manifested in current increase. The morphology of the resulting film is given in Fig. 7. The resulting polymer formed at silver substrate has similar yellow color compared to that formed at steel surface. However, careful inspection of Fig. 7 shows that the polymer formed at silver substrate has relatively porous and less dense structure when compared to that formed at the steel surface. It was cited in the literature that five-membered thiazole heterocycle serve as iron(II) ligands [21]. On the other hand, a membrane containing thiazole polyether derivatives exhibited high selectivity toward silver(I) ion that indicates the possible complexation of silver ion with the thiazole ring [22]. In this respect the

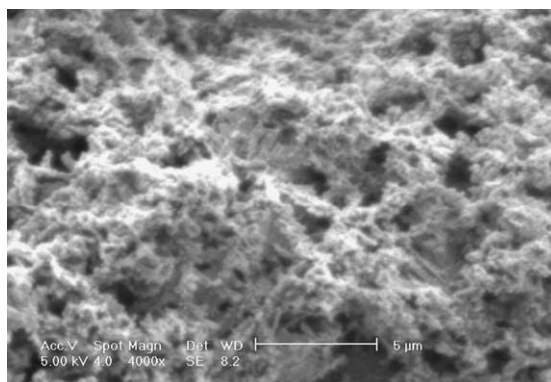


Fig. 7. SEM picture of poly(thioflavin S) on silver electrode.

mechanism of polymerization given in Fig. 8 can be justified for the formation of the poly(thioflavin S) on steel or silver electrodes. Thus, the first step is the formation of a complex between the oxide film formed at the surface of substrate that is rich in Fe(II) in case of steel and Ag(I) in case of silver. The shown mechanism steps follow the proposed sequence as mentioned in the literature [23]. “M” represents the metal ion formed at the surface of substrate upon oxidation. Similarly, the rate determining step for the polymer formation is the elimination of electron and proton for the formation of dimer. This step is followed by the oxidation of the dimer and the formation of a quinoid diimine structure. The third step is the formation of a dimer-cation that is

accompanied by loss of hydrogen. The polymer is formed with the general formula given in Fig. 8 ($1 - y$ measures the function of oxidized units). As could be noticed from the cyclic voltammetry as the progression in the number of cycles increases the onset of polymerization shifts to a lower oxidation potential value. It is important to notice that the dimer formed in the first step and followed with trimer, etc. results in the formation of a conjugated structure with an extended π -orbital system. It was noticed that the type of electrolyte affected the color of the resulting polymer, thus a blue colored film was formed at the surface of silver when using lithium perchlorate. This indicates that the type of dopant affects the chromic characteristics of the film

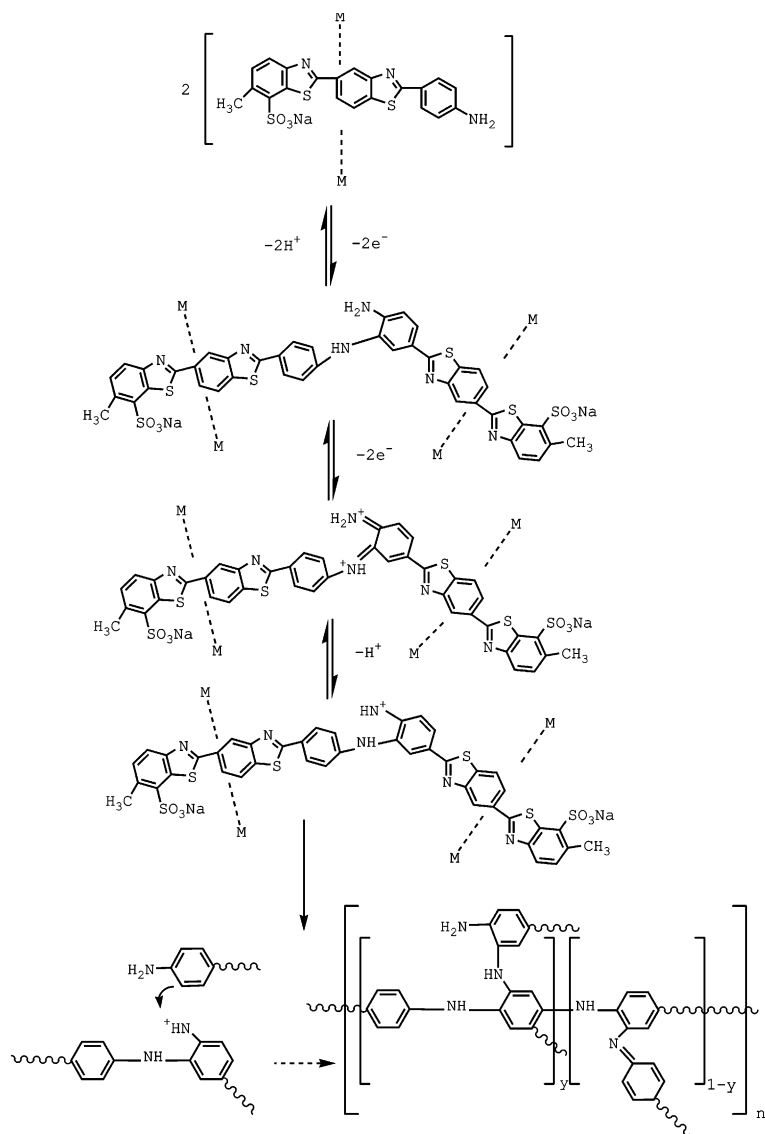


Fig. 8. Proposed mechanism for the electropolymerization of thioflavin.

as was indicated earlier in the literature for aniline-like structured polymers [24].

4. Conclusion

The electro-oxidation of thioflavin S in acid medium on mild steel surfaces resulted in the formation of a passivating polymeric film. This passive film hindered further thioflavin S oxidation and partially inhibited the mild steel corrosion. The surface reflectance IR spectrum of the polymeric film showed characteristic band of aromatic C–H stretching vibration and aromatic C=C stretching vibration. These bands suggested that the polymeric film maintained the aromatic character. The band associated with N–H stretching vibration did not decrease appreciably in intensity. Moreover, the electrochemical polymerization mechanism of thioflavin S proceeds in a similar way to that proposed for aniline. A sharp quinoid nitrogen vibration band appeared indicating full oxidation of the resulting polymer. This is the first report that thioflavin S could be used efficiently as an inhibitor for mild steel in acidic solutions. EIS data suggest that the film has a capacitive nature and the charge transfer resistance increases with film thickness. It was possible to form the film on a silver electrode. The morphology of this film has a more porous like structure when compared to a rather compact film on the steel surface.

Acknowledgements

The author would like to thank the partial financial support provided by the Division of Research of the University of Cairo (Egypt) through grant from “Young Researcher Program” and the National Science Foundation (USA).

References

- [1] Guernion NJL, Hayes W. 3- and 3,4-substituted pyrroles and thiophenes and their corresponding polymers—A review. *Curr Org Chem* 2004;8(7):637–51.
- [2] Negi YS, Adhyapak PV. Development in polyaniline conducting polymers. *J Macromol Sci Polym Rev C* 2002;C42(1):35–53.
- [3] Trojanowicz M. Application of conducting polymers in chemical analysis. *Microchim Acta* 2003;143(2–3):75–91.
- [4] Nicolas-Debarnot D, Poncin-Epaillard F. Polyaniline as a new sensitive layer for gas sensors. *Anal Chim Acta* 2002;475(1–2):1–15.
- [5] Dominis AJ, Spinks GM, Wallace GG. Comparison of polyaniline primers prepared with different dopants for corrosion protection of steel. *Prog Org Coat* 2003;48(1):43–9.
- [6] Tallman DE, Spinks G, Dominis A, Wallace GG. Electroactive conducting polymers for corrosion control—Part 1 General introduction and a review of non-ferrous metals. *J Solid State Electrochem* 2002;6(2):73–84.
- [7] Spinks GM, Dominis AJ, Wallace GG, Tallman DE. Electroactive conducting polymers for corrosion control—Part 2. Ferrous metals. *J Solid State Electrochem* 2002;6(2):85–100.
- [8] Kowa H, Sakakura T, Matsuura Y, Wakabayashi T, Mann DMA, Duff K, et al. Mostly separate distributions of CLAC- versus A beta 40- or thioflavin S-reactivities in senile plaques reveal two distinct subpopulations of beta-amyloid deposits. *Am J Pathol* 2004;165(10):273–81.
- [9] Aldrich handbook of fine chemicals and laboratory equipments, Aldrich Chemical Co., Saint Louis; 2004. p. 1583.
- [10] Quraishi MA, Ahmad S, Venkatachari G. Corrosion inhibition of mild steel in boiling hydrochloric acid by some thiazole derivatives. *Bull Electrochem* 2002;18(9):399–402.
- [11] MacDonald JR. Impedance spectroscopy emphasizing solid materials and systems. New York: Wiley Interscience; 1987.
- [12] Veloz MA, Gonzalez I. Electrochemical study of carbon steel corrosion in buffered acetic acid solutions with chlorides and H₂S. *Electrochim Acta* 2002;48(2):135–44.
- [13] Abd El-Maksoud SAA. The effect of hexadecyl pyridinium bromide and hexadecyl trimethyl ammonium bromide on the behavior of iron and copper in acidic solutions. *J Electroanal Chem* 2004;565(2):321–8.
- [14] Stern M, Geary AL. Electrochemical polarization. A theoretical analysis of the shape of polarization curves. *J Electrochem Soc* 1957;104:56–63.
- [15] Hermas AA, Morad MS, Wahdan MH. Effect of PhTPbBr on the electrochemical and corrosion behaviour of 304 stainless steel in H₂SO₄ solution. *J Appl Electrochem* 2004;34(1):95–102.
- [16] Ren X, Pickup PG. An impedance study of electron transport and electron transfer in composite polypyrrole + polystyrene sulphonate films. *J Electroanal Chem* 1997;420(1–2):251–7.
- [17] Kraljić M, Mandić Z, Duić Lj. Inhibition of steel corrosion by polyaniline coatings. *Corros Sci* 2003;45:181–9.
- [18] Socrates G. Infrared characteristic group frequencies. New York: John Wiley & Sons; 1994.
- [19] Palaniappan S, Shekhar RC. Synthesis of 7-hydroxy-4-methyl coumarin using polyaniline supported acid catalyst. *J Mol Catal A Chemical* 2004;209(1):117–24.
- [20] Shinde V, Chaudhari S, Patil PP, Sainkar SR. Electrochemical polymerization of 2,5-dimethylaniline on low carbon steel. *Mater Chem Phys* 2003;82(3):622–30.
- [21] Gehring AM, DeMoll E, Fetherston JD, Mori I, Mayhew GF, Blattner FR, et al. Iron acquisition in plague: modular logic in enzymatic biogenesis of yersiniabactin by *Yersinia pestis*. *Chem Biol* 1998;5(10):573–86.
- [22] Choi JH, Koh YK, Kwon IC, Kim HS, Park HJ, Kim SJ, et al. Synthesis and potentiometric properties of polyethers containing thiazole and oxazole derivatives. *Bull Korean Chem Soc* 1999;20(5):581–6.
- [23] Bejan D, Duca A. Voltammetry of aniline with different electrodes and electrolytes. *Croat Chem Acta* 1998;71(3):745–56.
- [24] Dhawan SK, Ram MK, Malhotra BD, Chandra S. Novel electrochromism phenomenon observed in polyaniline films. *Synth Met* 1995;75(2):119–22.