



The General Mathematical Model for the Oscillatory Behavior of the Electrochemical Systems with Electropolymerization of Heterocyclic Compounds in Organic Solvents in Passivation Conditions

Volodymyr Tkach*, Vasyl Nechyporuk, Petró Yagodynets

Universidad Nacional de Chernivtsi, 58012, Calle de Kotsyubyns'ky, 2, Chernivtsi, Ucrania

(*) volodya@llanera.com

Recibido: 17/03/2013

Revisado: 02/07/2013

Aceptado: 23/07/2013

Resumen

Se reporta el comportamiento electroquímico del sistema formado por compuestos heterocíclicos, en soluciones de acetonitrilo, electropolimerizados sobre electrodos de hierro y bajo condiciones de pasivación. Se creó un modelo matemático para predecir el mecanismo más probable así como el comportamiento de este sistema (incluyendo la determinación de las posibles causas de las inestabilidades electroquímicas). Empleando este modelo es posible predecir las condiciones bajo las cuales el sistema puede comportarse como un oscilador. En sistemas donde la electropolimerización se realiza en mezclas de acetonitrilo-agua y en presencia de un medio ácido las oscilaciones electroquímicas pueden ser causadas por efectos de los protones presentes en el medio, los cuales están involucrados en la síntesis de la macromolécula (manifestándose en la formación de protones autocatalíticos los cuales participan en el proceso de electropolimerización)

Palabras clave: Polímeros conductores; compuestos heterocíclicos; acetonitrilo; pasivación de metales; oscilación electroquímica

Abstract

The electrochemical behavior of the system composed by heterocyclic compounds, in acetonitrile solutions, electropolymerized on iron and under passivation conditions was observed. A mathematical model was created in order to predict the most probable mechanism and the system behavior (including the determination of possible causes for the electrochemical instabilities). According to this model, it is possible to predict the conditions under which the system can act as an oscillator. In the systems with electropolymerization in ACN-water mixtures in acid media the electrochemical oscillations can also be caused by proton effect on the synthesis of a macromolecule (which manifests itself in autocatalytic proton formation and its participation in electropolymerization process).

Keywords: Conducting polymers; heterocyclic compounds; acetonitrile; metal passivation; electrochemical oscillations.

Introduction

The corrosion influences in our life every day because it causes the degradation and destruction of metallic details of instruments and devices¹⁻³. It is necessary to investigate the corrosion protection methods to reduce the influences of corrosion and money lose caused by it.

One of these methods is the surface protection by conducting polymer (CP) coatings synthesized by electrochemical polymerization of heterocyclic compounds (like pyrrole, thiophene, indole, etc.).

For the last decades the CP have been extensively studied, because they have vast and rich spectrum of use, beginning on the corrosion protective coatings^{2,4} and ending with

sensors and biosensors^{5,6}. Due to their liophobicity in most of the solvents^{1,2,4,7,8} they are capable to protect the metallic surface from degradation and, moreover, conduct the electric current.

But the synthesis of CP over active metals (like iron, aluminium, etc.) in aggressive conditions is difficult because the corrosion potential of mentioned metals is lower than the polymerization potential of some monomers^{2,9}. One of the methods to avoid this difficulty is to synthesize the polymers in absence of the active dissolution of the metal to be protected (for example, in dry acetonitrile). The passivation film forms itself over iron in dry acetonitrile under potentials comparable with polymerization potential of some monomers¹. The trans-

passive transition realizes itself during the film dissolution (according to the data of Li *et al.*¹ it is controlled mostly by surface reactions than by diffusion). The metal dissolution begins after addition of water in the acetonitrilic solution. If the concentration of water in the ACN-water mixture reaches 6%, or 3.1 M, the behavior of iron surfaces corresponds itself to the behavior in aqueous solutions. If the heterocyclic monomer is introduced to the system, after the film dissolution the surfaces in which the film was dissolved (and exposed to the aggressive media), occupy themselves with the monomer, that polymerizes itself to form the protecting polymer coating^{2,9}, which is very important.

To know the most probable mechanism of the electrochemical behavior of this system, we can construct the mathematical model capable to describe the electrochemical behavior of this system. Many systems with passivation, metal corrosion and electropolymerization of heterocyclic compounds were found to present the oscillatory behavior^{2-4,10-15}, but the mathematical model, capable to describe this process adequately has not developed yet.

In a recent report, Das *et al.*¹⁰ have observed the potential oscillations in galvanostatic mode for the polymerization of thiophene. They have explained this type of behavior by surface instability (figure 1)

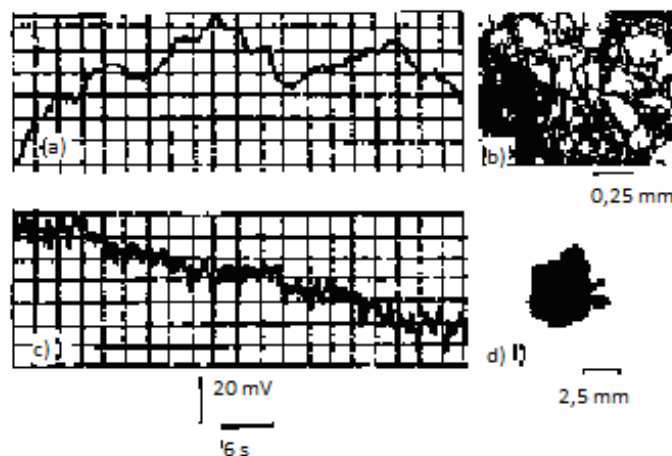


Fig. 1: Anodic potential oscillations, observed during the polymerization of thiophene in the presence of different dopants 4-TSS (a) y NaClO₄ (c) and the macromolecule's form in correspondent cases (b) (d). Reproduced from 10 with permission from CSIR-NISCAIR, New Deli, India.

The potential oscillations also were observed by Lemos Castagno², Ba-Shammakh⁴ and Das^{2,4,10-13} for the case with and without use of surfactants. The current oscillation during indole potentiostatic electropolymerization has been also observed³ (figure. 2).

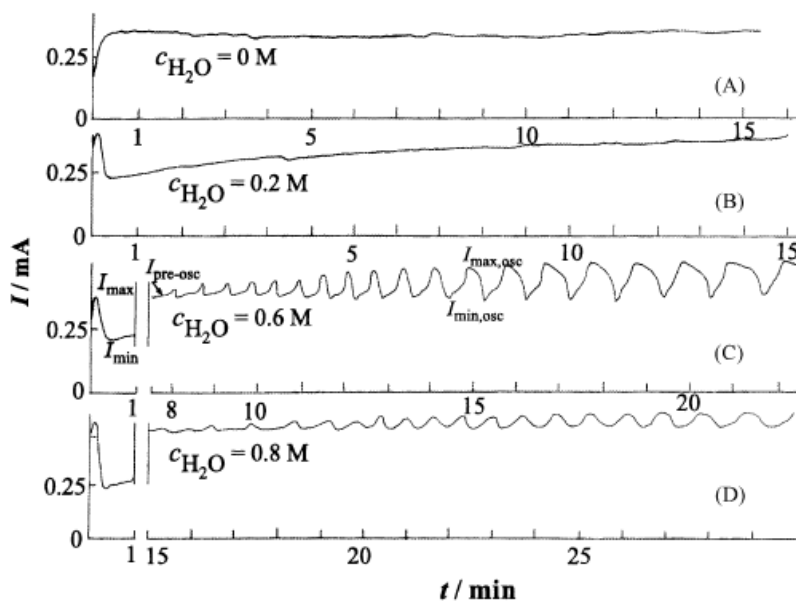


Fig. 2: The responses without (A, B) and with (C,D) current oscillations, obtained during indole electropolymerization in ACN-water mixtures in the presence of $[N(C_4H_9)_4][BF_4]$. Reproduced from 3 with permission from Elsevier, Amsterdam, The Netherlands.

The current oscillations were also obtained by Aoki *et al.*¹⁴ for a soluble polythiophene in the conditions of “The polythiophene paradox”. They have appeared in the system due to the factor of concurrence between polymer formation and dissolution. Different researchers have

found the causes for the oscillations to be different in different cases. So, the mathematical investigation, capable to find the general causes for the oscillations in the electropolymerization processes, has to be fundamental and one of the most difficult tasks of physical chemistry. It

may elucidate us to the mechanism of the temporal self-organization in the systems with electrochemical protection of the metal surface by electrochemical polymerization of one heterocyclic compound over it in aggressive conditions with the possibility to find the ways to intensify this process or the parameter values, which let us avoid the instabilities, undesirable in technological process.

Physically, this system consists of the stages:

- Monomer diffusion towards the surface
- Monomer adsorption and desorption
- Electrochemical polymerization of the monomer on the surface to form the protecting polymer coating
- Formation and dissolving of passive film
- Active metal dissolution, (in the section 2).

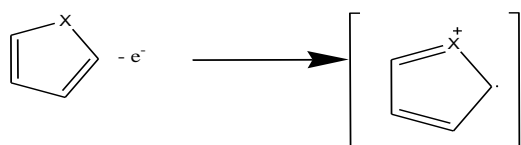
The mathematical model of the anodic electro-polymerization of one heterocyclic compound over iron covered with passive film

The mechanism of the electropolymerization of heterocyclic compounds.

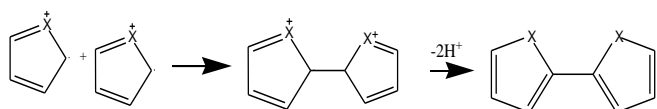
The explicit mechanism, capable to describe fully the electropolymerization of heterocyclic compounds has not described yet. The Sadki review article¹⁶ and the references therein describe the possible scenarios proposed for this process. The Diaz mechanism, proposed in 1979¹⁷, is the most acceptable in literature (modified with the Kim scenario¹⁸ in the modern literature¹⁰⁻¹⁵).

According to the Diaz mechanism the electropolymerization of heterocyclic compounds consists of such stages as:

- 1) Monomer oxidation to form cation-radical. π -radical is to form firstly, but it quickly isomerizes to form σ -radical with radical centre in the second position. The value of the resonance energy for the second position is more, than for the third

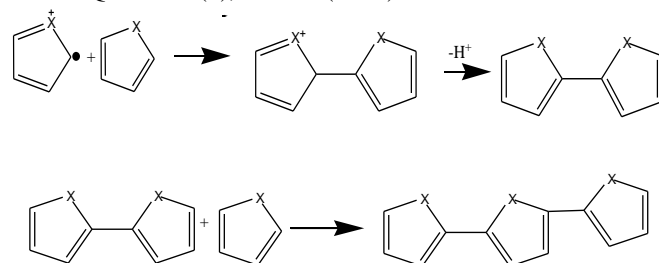


- 2) Dimer formation by two ways
 - Cation-radical recombination (Diaz's scenario):



- Electrophilic substitution (Kim's scenario)

- 3) Electrochemical dimer oxidation and chain propagation analogically to (1,2)



75% of rings in the resulting polymer are bonded in 2-2'-positions, but 3-3'-recombination of oligomer cation-radicals is also possible despite of steric difficulties. Autocatalytic growth of the chain is possible because oligomer or polymer oxidizes more easily than monomer due to cation-radical stabilization. Also autocatalysis can succeed in strong acid media¹⁹. It influences the electropolymerization, moreover, the pH is decreasing during the reaction, so proton formation is autodetermined.

The chose of the mode.

The electropolymerization of heterocyclic compounds may be realized potentiodynamically, galvanostatically and potentiostatically².

The potentiodynamic electropolymerization yields thin films, the properties of which depend on the potential margins chosen. The polymer tends to be partially overoxidized, and there may exist the "death points" in which the electropolymerization doesn't occur.

The galvanostatic electropolymerization in the majority of cases yields polymer dendrites¹⁶. It's difficult to be realized, because of the difficulty in finding of the value of the current density applied to the working electrode. Moreover, the polymer may partially overoxidize, when the electrode potential is higher than the overoxidation potential.

The potentiostatic electropolymerization is known to be most used in electrochemical syntheses of conducting polymer coatings. The polymerization potential for concrete monomer is easy to be determined from the CVAG and the working potential to be chosen is a little bit higher than the peak potential. So, in this work the process of the electrochemical polymerization of one heterocyclic compound in passivation conditions will be described in potentiostatic mode.

To describe mathematically this process in it we can introduce three variables

- c – monomer concentration in the pre-surface layer
- Θ_m – the coverage degree of the monomer
- Θ_f – the coverage degree of the passive film

The accepted suppositions

To simplify the mathematical model of this process we suppose that the liquid is stirring intensively (so we can

neglect the convective flow), the background electrolyte is in excess (so we can neglect the migration flow). The monomer concentration profile is linear, the diffusion layer thickness is constant and equal to δ .

The monomer in the diffusion layer

The monomer enters the layer by diffusion and also desorbing from the surface and leaves it adsorbing onto it, so the monomer concentration balance equation can be described as

$$\frac{dc}{dt} = \frac{2}{\delta} \left(v_{-1} - v_1 + \frac{D}{\delta} (c_b - c) \right) \quad (1)$$

in which v_1 and v_{-1} are monomer adsorption and desorption rates, c_b is the monomer bulk concentration, D is the diffusion coefficient.

The monomer on the electrode surface.

The heterocyclic monomer enters the surface adsorbing onto it and leaves it by desorption. It's also spent by electropolymerization. The monomer surface concentration balance equation can be described as:

$$\frac{d\Theta_m}{dt} = \frac{1}{\Gamma_{\max}} (v_1 - v_{-1} - v_2) \quad (2)$$

in which v_2 is the electropolymerization rate, Γ_{\max} is the maximal monomer surface concentration.

The adsorption, desorption and polymerization rates can be calculated as:

$$v_1 = k_1 \exp(\alpha_1 \Theta) c (1 - \Theta_m - \Theta_f);$$

$$v_{-1} = k_{-1} \exp(-\alpha_2 \Theta) (\Theta);$$

$$v_2 = k_2 \Theta \exp\left(-\frac{zF}{RT} \phi_0\right)$$

in which k_1 , k_{-1} and k_2 are constants of relative reactions, α_1 and α_2 describe the interactive forces between the adsorbed molecules z is the number of electrons transferred during the electropolymerization, T is the absolute temperature, R is the universal gas constant and ϕ_0 is the potential slope relative to the zero-charge potential.

The passive film on the surface

The passivation film is forming during the interaction of the metal with the air oxygen¹ and is dissolving itself in acetonitrile solution. The balance equation can be described as

$$\frac{d\theta_f}{dt} = k_3 \exp(\beta_1 \theta_f) (1 - \theta_f - \theta_m) - k_{-3} \exp(-\beta_2 \theta) \theta \quad (3)$$

in which k_3 and k_{-3} are film formation and dissolution constant, β_1 and β_2 are constants that describe the interaction of the molecules in the film.

Results and discussion.

We investigate the equation system (1-3) by using the linear stability theory[20]. The Jacobi functional matrix, the terms of which are calculated in the steady-state can be described as:

$$J = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

The terms of the matrix can be described as:

$$a_{11} = \frac{\partial F_1}{\partial c} = \frac{2}{\delta} \left(-\frac{D}{\delta} - \frac{v_1}{c} \right)$$

$$a_{12} = \frac{\partial F_1}{\partial \Theta_m} = \frac{2}{\delta} \left(\frac{v_{-1}}{1 - \Theta_m - \Theta_f} - \alpha_1 v_1 - \alpha_1 v_2 + \frac{v_{-1}}{\Theta_m} \right)$$

$$a_{13} = \frac{\partial F_1}{\partial \theta_f} = \frac{2}{\delta} \left(\frac{v_{-1}}{1 - \Theta_m - \Theta_f} \right)$$

$$a_{21} = \frac{\partial F_2}{\partial c} = \Gamma_{\max}^{-1} \frac{v_1}{c}$$

$$a_{22} = \frac{\partial F_2}{\partial \Theta} = \Gamma_{\max}^{-1} \left(-\frac{v_{-1}}{1 - \Theta_m - \Theta_f} + \alpha_1 v_1 + \alpha_1 v_2 - \frac{v_{-1}}{\Theta_m} - \frac{v_2}{\theta} - \alpha \frac{zF}{RT} v_2 \frac{\partial \phi_0}{\partial \theta} \right)$$

$$a_{31} = \frac{\partial F_3}{\partial c} = 0$$

$$a_{32} = -k_3 \exp(\beta_1 \theta_f)$$

$$a_{33} = \frac{\partial F_3}{\partial \theta_f} = \beta_1 v_3 - \frac{v_3}{1 - \Theta_f - \Theta_m} + \beta_2 v_{-3} - \frac{v_{-3}}{\Theta}$$

The stable steady-state

The characteristic equation of this system will be described as

$$l^3 + Al^2 + Bl + C = 0$$

in which

$$A = -(a_{11} + a_{22} + a_{33})$$

$$B = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} + \begin{vmatrix} a_{11} & a_{32} \\ a_{31} & a_{33} \end{vmatrix} + \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix}$$

$$C = - \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$$

To investigate the linear stability of this system we use the Rauss-Gurwitz criterion. It requires the main diagonal minors of Gurwitz matrix

$$\begin{pmatrix} A & 1 & 0 \\ C & B & A \\ 0 & 0 & C \end{pmatrix}$$

to be positive for stable steady-states. The members of the principal diagonal:

$$\Delta_1 = A,$$

$$\Delta_2 = \begin{vmatrix} A & 1 \\ C & B \end{vmatrix}$$

$$\Delta_3 = \begin{vmatrix} A & 1 & 0 \\ C & B & A \\ 0 & 0 & C \end{vmatrix}$$

We can see that $\Delta_3 = C\Delta_2$, so the the stability condition will be described as $C > 0$. We may analyze this system deeply, introducing new variables

$$\begin{aligned} -\frac{v_1}{C} &= G_1; & -\frac{v_{-1}}{1 - \Theta_m - \Theta_f} + \alpha_1 v_1 &= R_1; \\ & & \alpha_1 v_1 &= \kappa_1 \\ & & + \alpha_1 v_{-1} - \frac{v_{-1}}{\Theta_m} &= R_{-1} \\ \frac{v_2}{\theta} + \alpha \frac{zF}{RT} v_2 \frac{\partial \phi_0}{\partial \theta} &= R_2 & -k_3 \exp(\beta_1 \theta_f) &= G_3 \\ \beta_1 v_3 - \frac{v_3}{1 - \Theta_f - \Theta_m} &= R_3 & \beta_2 v_{-3} - \frac{v_{-3}}{\Theta} &= R_{-3} \end{aligned}$$

So, the Jacobian will be represented as:

$$DetJ = \frac{2}{\delta G_{\max}} \begin{vmatrix} G_1 - \frac{D}{\delta} & R_{-1} - R_1 & \kappa_1 - R_1 \\ -G_1 & R_1 - R_{-1} - R_2 & R_1 - \kappa_1 \\ 0 & G_3 & R_3 - R_{-3} \end{vmatrix}$$

Transforming the Jacobian we can obtain the steady-state stability condition as

$$(R_{-3} - R_3) \left(1 - \frac{D}{\delta G_1 R_2} (R_1 - R_{-1} - R_2)\right) < \frac{DG_3}{\delta G_1 R_2} (R_1 - \kappa)$$

or

$$R_{-3} - R_3 < \frac{\frac{DG_3}{\delta G_1 R_2} (R_1 - \kappa)}{1 - \frac{D}{\delta G_1 R_2} (R_1 - R_{-1} - R_2)}$$

So, the stationary state in this system is stable, when the difference between the passivation film formation and

dissolution factors is lower, than the critic parameter, the value of which is defined by adsorption, diffusion and polymerization factors (D , G_1 , R_1 , R_{-1} , R_2) and also the passivation factor itself (G_3).

We can see that this condition satisfies itself during the distractive interaction between adsorbed particles, which is defined by negative values of α_1 , α_2 , β_1 , β_2 . The negative values of the parameters β_1 and β_2 make the values of the expression on the left side of the inequality lower, and the negative values of parameters α_1 and α_2 make the rightwards' fraction bigger, which gives the possibility for this condition to be satisfied.

The oscillatory instability

Was described either for passivation systems, or for the electropolymerization systems and also in the coactions of both factors. It realizes itself in Hopf bifurcation conditions²⁰, that define the presence of complex radicals for characteristic equation, shown above. They require, that the terms of the main diagonal of the Jacobi matrix contain the positive addendums (that describe the positive callback).

It's obvious that the oscillatory behavior will be possible if α_1 , α_2 , β_1 and β_2 are positive (which, defining the possibility of R_1 and R_{-1} , describes the attractive interaction between adsorbed particles). The electrochemical oscillations in this case will be caused by cyclic change of electrochemical impedance, caused by cyclic change of the surface covering, so the responsible in this case is the surface instability, described by Das¹⁰⁻¹³ and Aoki¹⁴.

This surface instability favors the monomer adsorption, providing the positive callback in the adsorption process.

One more oscillation condition can be obtained in cause of the realization of

$$\frac{d\phi_0}{d\Theta_m} > 0$$

It is known²¹ that

$$\frac{\partial \phi_0}{\partial \Theta} = \frac{\phi_0 (K_0 - K_1) + K_1 \phi_1 + K_2 \phi_2}{K_1 \Theta_m + K_0 (1 - \Theta_m - \Theta_f) + K_2 \Theta_f}$$

In which K_0 , K_1 , K_2 are integral capacities for the parts of DEL, corresponding to the free part of the surface, the surface occupied by monomer and the surface occupied by the passive film, ϕ_1 and ϕ_2 are potential slopes of the corresponding parts of DEL relatively to zero-charge potential.

$$\text{Inputting the expression of } \frac{\partial \phi_0}{\partial \Theta}$$

to the corresponding member of Jacobian, we can obtain, that R_2 may be positive when φ_0 is negative. That can signify the oscillations during the anodic oxidation of strong reductants forming during the electropolymerization.

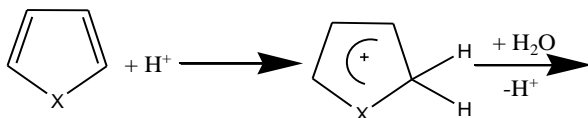
It explains the relation between the oscillations and dopant nature (the potential slope values in the presence of different dopants are different). More strong oxidant is dopant, lower is the value of φ_0 .

The monotonic instability defines system's behavior When the cyclic voltamperogram shows N-shaped curve.

It occurs in the conditions of $\text{Tr} < 0$, $\text{Det} = 0$. The principal condition is $\text{Det } J = 0$ (cause $\text{Tr} < 0$ realizes for nearly all the systems). Using the calculations, demonstrated above, we can show that it occurs in the condition of:

$$R_{-3} - R_3 = \frac{\frac{DG_3}{\delta G_1 R_2} (R_1 - \kappa_1)}{1 - \frac{D}{\delta G_1 R_2} (R_1 - R_{-1} - R_2)}$$

In this point multiple stationary states exist and the system chooses only one of them. It destroys after the change of the factor action. This model can be applied for all systems with passivation of metals during the electropolymerization in organic solvents without water, so the active metal dissolution does not occur.



In general, the procedures, used for this system is the same, that for the described above, so now it will be described briefly.

The monomer in the pre-surface layer.

Enters it by diffusion from the bulk and leaves from it participating either in the electropolymerization (according to the Diaz mechanism) or in the side reaction with protons (because it's acidophobic). The monomer balance equation can be described as

$$\frac{dc}{dt} = \frac{2}{\delta} \left(\frac{D}{\delta} (c_b - c) - v_p - v_a \right)$$

In which v_p is the polymerization rate and v_a is the rate of the reaction with protons (because it's side reaction).

Passive film.

Forms itself during the reaction of iron with water molecules and dissolves itself by chemical and electrochemical way reacting with protons. So, the balance equation will be described as:

The mathematical model of the anodic electro-polymerization of one heterocyclic compound over iron covered by passive film in ACN – H₂O mixtures in acid media.

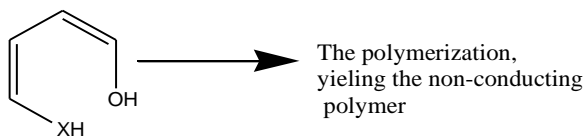
As it was described in the introduction, when the water is added to the solution, the iron begins to dissolve. The behavior of this system becomes more complicated.

To describe mathematically the system with the potentiostatic electropolymerization of one acidophobic heterocyclic compound, we can introduce three variables:

- c – the monomer pre-surface concentration
- Θ_f – the passive film coverage degree
- h – the pre-surface concentration of protons

supposing the mentioned above (page 100). Also (to simplify the modeling) we suppose that the electropolymerization is not foregone by monomer adsorption and that all the reaction of the protons are of the first order.

The side reaction of monomer (if it is furan or pyrrole) with proton is defined by its acidophobicity – electrophilic proton attack in the presence of water:



$$\frac{d\theta}{dt} = G^{-1} [v_f - v_{el} - v_q]$$

in which v_f is the film formation rate, v_{el} and v_q are chemical and electrochemical dissolution rate .

The protons

The protons reach the surface by diffusion. Their quantity increases during the electropolymerization process (according to the Diaz mechanism, mentioned above). Protons participate in chemical and electrochemical film dissolution and the side reaction (proton attack of the monomer). The proton balance equation can be described as:

$$\frac{dc}{dt} = \frac{2}{\delta} \left(\frac{D_2}{\delta} (h_b - h) + v_p - v_a - v_q - v_{el} - v_d \right)$$

in which D_2 is the proton diffusion coefficient, h_b is the proton bulk concentration, v_d is the metal dissolution rate.

The rates of the formation and dissolution of the film can be described as:

$$v_f = k_f \exp(\beta_1 \theta_f) (1 - \theta_f);$$

$$v_q = k_q \exp(-\beta_2 \theta) \theta h$$

$$v_{el} = k_{el} \exp(-\beta_2 \theta) \theta h$$

The metal dissolution, electropolymerization and side reaction rates can be described as:

$$v_d = k_d h;$$

$$v_p = k_p f(h) c \exp\left(-\frac{zF}{RT} \phi_0\right)$$

$$v_a = k_a hc$$

in which the function $f(h)$ manifests the influence of pH to the polymerization process.

Using the method, used above we can predict, that the oscillatory behavior in this system can be caused by attractive interaction between the molecules in the film,

One more factor is responsible to the oscillations in this system. It's the possibility of the autocatalytic proton effect on the electropolymerization. One of the addendums of the third matrix member can be positive if that describes the autocatalytic proton formation during the electropolymerization. According to the Diaz mechanism, it can succeed if the electropolymerization in acid media is autocatalytic.

Conclusions

We have described mathematically the electropolymerization of one heterocyclic compound on iron in acetonitrile solution in passivation conditions. The steady-state conditions were determined by Rauss-Gurwitz criterion. The oscillatory behavior can be caused by attractive interaction between the adsorbed particles of the monomer and the film and by anodic oxidation of strong reductants forming during the electropolymerization.

In the system with the electrochemical polymerization of one heterocyclic compound in ACN-H₂O mixtures in acid mode the electrochemical oscillations can also be caused by the autocatalytic proton effect on the polymerization process.

The system is temporal dissipative structure, existing by the monomer diffusion and stable polymer formation, capable to protect the surface from corrosion without dissolution (possible for the oxide (hydroxide) film).

References

1. FB Li, DH. Bremner, AE Burgess. Corrosion inhibition of copper by heterocyclic compounds- **Corr. Sci.**, **41**, 2317–2335 (1999).
2. KR Lemos Castagno, Electropolymerizacao de pirrol sobre a liga de alumínio 1100, Doctorate Thesis, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brasil (2007).
3. D Sazou. The dynamical behavior of the electrochemical polymerization of indole on Fe in acetonitrile-water mixture **Synth. Metals**, **130**, 45-54 (2002)
4. MS Ba-Shammakh.. Electropolymerisation of Pyrrole on Mild Steel for Corrosion Protection. MSc Thesis. King Fahd University of Petroleum & Minerals. Country? (2003).
5. VM. de Andrade. Confecção de biosensores através da imobilização de biocomponentes por electropolymerizacao de pirrol. Master Thesis, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brasil (2006).
6. A Ramanavicius, A Ramanaviciene, A Malinauskas, Electrochemical sensors based on conducting polymer— polypyrrol. **Electrochim. Acta**, **51**, 6025-6037 (2006).
7. J Roncali. Conjugated Poly(Thiophenes): syntesis, functionalization and applications. **Chem. Rev.**, **92**, 711–738 (1992).
8. TF Otero, AH Arévalo. Kinetic Studies of Polypyrrole Formation on DMF. **J. Braz. Chem. Soc.**, **5(3)**, 183-189 (1994).
9. AS Liu, MAS Oliveira. Electrodeposition of Polypyrrole Films on Aluminium from Tartrate Aqueous Solutions. **J. Braz. Chem. Soc.**, **18(1)**, 143–152 (2008).
10. I Das, NR Agrawal, SA Ansari, SK Gupta. Pattern formation and oscillatory electropolymerizaion of Thiophene. **Ind. J. Chem.**, **47A**, 1798-1803 (2008).
11. I Das, NR Agrawal, SK Gupta, RP Rastogi. Fractal Growth kinetics and Electric Potential Oscillations during Electropolymerization of Pyrrole **J. Phys. Chem.**, **113**, 5296–5301 (2009).
12. I Das, NR Goel, SK Gupta. Growth Patterns of Dendrimers and Electric Potential Oscillations During Electropolymerization of Pyrrole using mono and mixed surfactants. **J. Phys. Chem. B**, **114**, 12888–12896 (2010).
13. I Das, NR Agrawal, R Choudhary, SK Gupta. Fractal growth patterns and Oscillations in potential during electropolymerization of polyaniline with mono and mixed surfactants. **Fractals**, **3**, 317-328 (2011).
14. K Aoki, I Mukoyama. Competition between polymerization and dissolution of Poly(3-methylthiophene) Films. **Russ. J. of Electrochem.**, **3**, 319–324 (2004).
15. VV Tkach, VV Nechyporuk, YM Hrynda. The Behavior Investigation of Systems with Electropolymerization of Heterocyclic Compounds and Simultaneous Chemical Surface Polymerization. **J. Math. Sci. Eng.**, **5**, 462-467 (2011).

16. S Sadki, P Scotland, N Brodie, G Saboraud. The Mechanisms of Pyrrole Electropolymerization. **Chem. Soc. Rev.**, **29**, 283–293 (2000).
17. AF Diaz, JI Castillo, JA Logan, WY Lee, Electrochemistry of conducting Polypyrrole Films. **J. Electroanal. Chem**, **129**, 115–132 (1981).
18. KJ Kim, HS Sonh, JD Kim. Mechanism of Electropolymerization of Pyrrole in acid aqueous solutions. **Bull. Korean Chem. Soc.**, **9**, 248-251 (1988).
19. M Can, F Sevinb, A Yildizb. The effect of the proton on electropolymerization of the thiophene. **Appl. Surf. Sci.**, **210(3-4)**, 338-345 (2003).
20. J Wójtowicz, In JOM Bockris and B.E Conway (Eds). **Modern Aspects of Electrochemistry**, vol. **9**, Plenum Press, New York, 47-120 (1973).
21. MTM Koper. Far-from-equilibrium phenomena in electrochemical systems-PhD thesis, Universiteit Utrecht, faculteit Scheikunde. The Netherlands (1994)