Cathodic and anodic potentiostatic polypyrrole electrodeposition in strongly acid media. Theoretical and experimental comparison

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Two mathematical models describing cathodic and anodic polypyrroleelectrodeposition in strongly acid solution were developed, analyzed and compared with one another and with experimental data. The differences in the reaction mechanisms causing the difference in reaction kinetics, resulting polymer morphology and properties find their mathematical description. The probability of the realization of instabilities for cathodicelectrodeposition was also verified.

Keywords:polypyrrole, cathodicelectropolymerization, anodic electropolymerization, electrochemical instabilities, stable steady-state

INTRODUCTION

Conducting polymers (CP), being capable to combine the properties of plastics (flexibility, light weight, toughness, resiliency, versatility in shaping and corrosion resistance) with metal conductivity, and also being easily modified, have already found use in corrosion protection, optoelectronics, light-emission diodes (LEDs), electrochemical cells (e.g., electrochromic and fuel cells), optoelectronics and sensors [1 – 14].

The process is usually initiated by means of chemical or electrochemical monomer oxidation, followed by radical coupling (or electrophilic substitution) and chain propagation [2 – 5]. Chemical oxidation involves the use of oxidizing agents, usuallycations (Fe^{3+}, Cu^{2+}, NO^+) or anions (ClO_4^-, $S_2O_8^{2-}$) and electrochemical oxidation implies the use of anodically polarized electrodes (anodic electropolymerization [2,3]). The electropolymerization is predominantly used to obtain highly conductive coatings (because of thebetter coplanarity of the monomer rings and dopant intercalation [3, 15]), the thickness and morphology of which are easily controlled.

The cathodicelectropolymerization is less used, especially in the case of the monomers of 5-membered heterocyclic compounds [1, 15 – 18]. Two approaches may be used to deposit conducting polymers on a cathode – the electroreductivepolymerization and the use of *in situ* generated oxidants [1, 18]. The latter approach isnot

in fact an electroreductive polymerization, but chemical polymerization, initiated by electrochemically formed initiators.

In [1], polypyrrole was obtained by cathodic route, enabling the one-step synthesis of metal-polypyrrole composites. This was achieved by application of cathodic potential of -0,65 V versus an Ag/AgCl/4M KCl reference electrode in very specific conditions, coupling the reactions of electroreductive generation of an oxidizing agent, in this case nitrosyl cation,and oxidative polymerization of pyrrole. The summary reactions, yielding the cathodically deposited polypyrrole are given as:

$$NO_3^- + 4H^+ + 2e^- \rightarrow NO^+ + 2H_2O \quad (1)$$

$$(2n-2)NO^+ + nC_4H_5N \rightarrow C_4H_4N - (C_4H_3N)_{n-2} - C_4H_4N + (2n-2)NO + (2n-2)H^+ \quad (2)$$

The authors of [1] compared the morphology of the resulting cathodically obtainedpolypyrrolewith that obtained by anodic electropolymerization at +0,8 V in the same conditions. The cathodically synthetized polypyrrole presented more developed three-dimensioned surface, compared to the two-dimensional coating lacking mesoporosity,as shown in Fig. 1.

In [3] and articles cited therein the SEM images of similar structures of the anodically deposited polypyrrolewere also given, but such films were obtained in potentiodynamic mode, that wasnot applied for polypyrrole deposition, described in the first part of the article [1].

As reported by the authors of [1], the described polymerization method may allow the one-step

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preparation of a broad range of metals (theoretically including Ni (E^0=-0,4 V >-0,65 V), that has already gained its use in metal – CP composites acting as electrocatalysts and sensors for different compounds [19 – 21]).

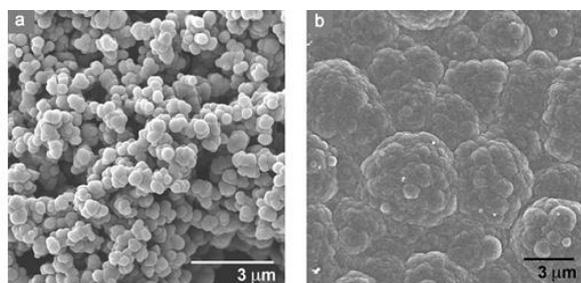**Fig. 1.**SEM images of cathodically (a) and anodically (b) synthetized polypyrrole from the same solution (0.4 M HNO$_3$ + 0.5M NaNO$_3$ + 0.2 M Py). Reproduced from [1] with the permission of Wiley-VCH Verlag GmbH &Co, Weinheim, Germany.

Another difference between the cathodic and the most used anodic electropolymerization is the influence of pH.According to [1], the efficient deposition of PPy films is possible at pH<1.5. On the other hand, according to [3], strongly acid media, although kinetically favoringthe electropolymerization, affect the morphology of the resulting conducting polymer, causing proton attacks and, in some cases, forming the poly(isopyrrole) form:
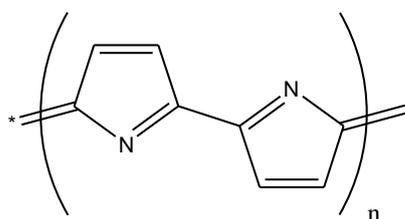
Also, during the anodic electropolymerization of pyrrole, thiophene and indole in strongly acid media the occurrence of electrochemical instabilities (oscillatory or monotonic) is possible [22 -31]. Some patterns of the oscillatory behavior (periodic, quasi-periodic and chaotic), observed in this systems, andthe morphology changes, accompanying such scenario, are represented inFig.2.

The authors of the works [22, 23] have compared the oscillatory patterns with the nature of the background electrolyte and observed the relations between polymer morphology and current thermodynamic state, describing the oscillatory behavior with surface instabilities. In the work [1], no electrochemical instabilities were observed, but this doesnot warrant that their occurrence (and, in consequence, the corresponding morphology changes) is impossible for the same synthesis in

different conditions (potential, acid or salt concentration, monomer concentration, nature of the electrode, etc.). To have the possibility to predict their occurrence and find their conditions, it is necessary to develop and analyze a mathematical model capable to adequately describe the processes in this system. This not only gives the possibility of prediction and explanation of the occurrence of electrochemical instabilities, but also enables the determination of clear stable steady-state requirements, or, better saying, of the most convenient synthesis.
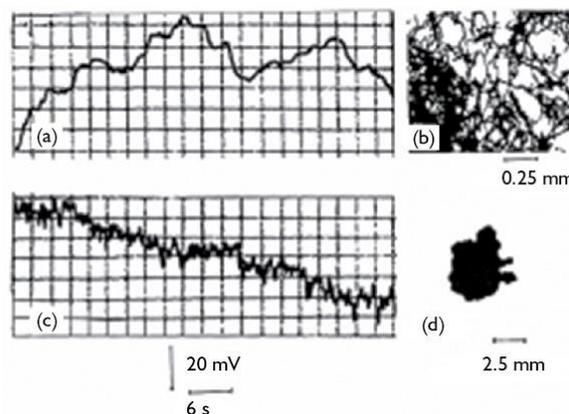

Fig.2. Oscillatory behavior during the anodic electropolymerization of thiophene with two different background electrolytes – 4 – TSS (a) and ZnSO$_4$ (b) and corresponding morphological changes (c,d). Reproduced from [22] with the permission of IN-SCAR, India
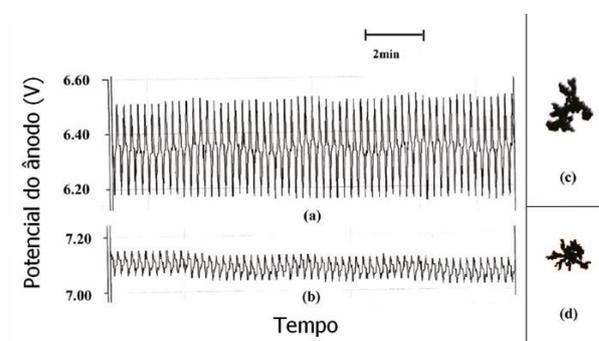

Fig.3. Oscillatory behavior observed during the electropolymerization of pyrrole in strongly acid media with (a) and without (b) the use of surfactants; (c) and (d) represent the surface modifications. Reproduced from [23] with the permission of Elsevier, the Netherlands.

Our group has already made some efforts to describe mathematically the electrochemical polymerization carried out by anodic route [32 – 42] and the conclusions of the modeling were in accordancewith the conclusions of experimental investigations. The comparative analysis of the mathematical models for cathodic and anodic polypyrrole depositions is an important part of the general comparison of the two methods. So, the goal

of our work was the construction and analysis of a mathematical model for polypyrrolecathodic deposition (section I) and the comparison of the models for cathodic and anodic deposition with one another and with experimental data as a part of the comparative kinetic investigation of the two synthetic routes (section II).
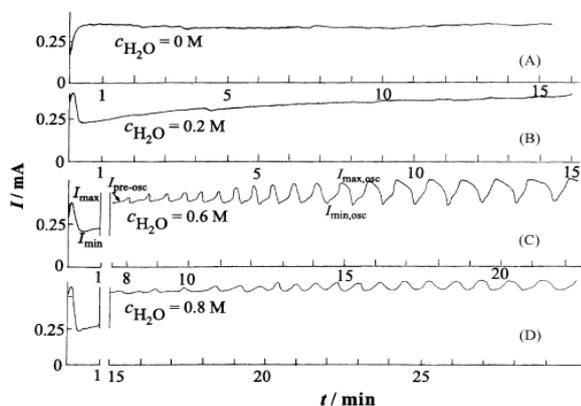

Fig. 4. Current responses observed during potentiostaticelectropolymerization of indole over iron in ACN-water mixtures without (a, b) and with (c,d) oscillatory behavior. Reproduced from [24] with the permission of Elsevier, the Netherlands.

SYSTEM AND ITS MODELING

As the process of the potentiostatic (E=-0,65 V) cathodicelectrodeposition of pyrrole described in [1] is pH-dependent, for its mathematical description we introduce three variables:

N –concentration of nitroso-cations in the pre-surface layer,

H –protons concentration in the pre-surface layer,

P –pyrrole concentration in the pre-surface layer.

In order to simplify the modeling, we suppose that (i) the reactor is intensively stirred, so we can neglect the convection flow;(ii) the background electrolyte containing NO_3^- ions is in excess, so we can not only neglect the migration flow influence, but also suppose its concentration as constant. Also we suppose that the concentration distribution of all substances in the pre-surface layer is linear and the thickness of the layer is constant and equal to δ.

Nitroso-cations are generated cathodicallyby strongly acidic media electrochemical reduction of NO_3^--ions, that in modeling (and also in the experimental conditions of [1]) are in excess. They are reduced during polymerization. So, the balance equation for their concentration may be written as:

$$\frac{dN}{dt} = \frac{2}{\delta}\left(r_i - r_p\right) \quad (3)$$

in which, r_i is the initiator generation rate, r_p is the polymerization rate, 2/δis the non-dimensional

modeling coefficient relative to the bimolecular double electric layer (DEL).

Protons are moving to the pre-surface layer by diffusion. Also they are generated in the process of electropolymerization. They participate in the process of nitroso-cations generation, may be cathodicallyreduced at the working potential and also may attack the acidophobicpyrrole molecules, yielding the non-conducting polymer, named "pyrrole red", by the mechanism, presented below:
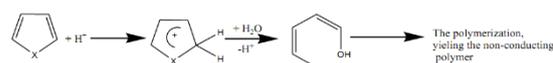
In this scheme X may be not only – NH, but also – O, because of the acid instability of furan and pyrrole.

Taking in account the excess of NO_3^- ions stabilizing the system, we can neglect this scenario, and also the protons' cathodic reduction, so, according to the Fick's first law, the balance equation for the protons' concentration may be described as:

$$\frac{dH}{dt} = \frac{2}{\delta}\left(\frac{D}{\delta}(H_b - H) - r_i + r_p\right) (4)$$

in which D is the protons' diffusion coefficient and H_b their bulk concentration.

Pyrrole monomer enters the pre-surface layer by diffusion and leaves it by polymerization. So the balance equation of its concentration, composed by taking into account the first Fick's law and modeling coefficient relative to DEL, may be described as:

$$\frac{dP}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(P_b - P) - r_p\right) \quad (5)$$

in which Δstands for pyrrole diffusion coefficient and P_b for its bulk concentration.

The respective reaction rates may be calculated as:

$$r_i = k_i H^w \exp\left(\frac{2F\xi\varphi_0}{RT}\right),$$
$$r_p = k_p N^x P^y (6-7)$$

in which w, x and y are protons,nitroso-ions and pyrrole reaction orders, depending on the polymerization mechanism, "2" in the expression (6) is the number of electrons transferred, ξis the transition number, $\varphi_0$is the potential slope, relative to the zero-charge potential, $k_i$and k_p are the rate constants for the respective reactions.

RESULTS AND DISCUSSION (SECTION I)

To analyze the behavior of the system with cathodic polypyrroleelectrodeposition, we analyze the differential equation system (3 – 5) by using

linear stability theory and bifurcation analysis. The Jacobi functional matrix steady-state elements may be calculated as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (8)$$

In which:

$$a_{11} = -\frac{2}{\delta} x k_p N^{x-1} P^y a_{12}$$

$$= \frac{2}{\delta} w k_i H^{w-1} \exp\left(\frac{2F\xi\varphi_0}{RT}\right)$$

$$a_{13} = -\frac{2}{\delta}\left(y k_p N^x P^{y-1}\right)$$

$$a_{21} = \frac{2}{\delta} x k_p N^{x-1} P^y a_{22}$$

$$= \frac{2}{\delta}\left(-\frac{D}{\delta}\right.$$

$$\left. - w k_i H^{w-1} \exp\left(\frac{2F\xi\varphi_0}{RT}\right)\right)$$

$$a_{23} = \frac{2}{\delta}\left(y k_p N^x P^{y-1}\right)$$

$$a_{31} = -\frac{2}{\delta} x k_p N^{x-1} P^y a_{32}$$

$$= \frac{2}{\delta} w k_i H^{w-1} \exp\left(\frac{2F\xi\varphi_0}{RT}\right)$$

$$a_{33} = -\frac{2}{\delta}\left(\frac{\Delta}{\delta} + y k_p N^x P^{y-1}\right) \quad (9-15)$$

Oscillatory behavior analysis. For the oscillatory behavior to be realized, the presence of the positive Jacobian main diagonal elements (describing the positive callback) is required, but, as it may be seen, the main diagonal elements a_{11}, a_{22} and a_{33} are negative, so, no oscillatory behavior, characteristic for the anodic electropolymerization, may be observed in this case, which is in accordance with the experiment described in [1].

Steady-state stability analysis. For the steady-state stability analysis, we use the Routh-Hurwitz stability criterion. To be derived, the main requirement is Det J <0. We introduce new parameters describing different aspects of the influences of the processes on the steady-state stability and the Jacobian determinant will be rewritten as:

$$\frac{8}{\delta^3}\begin{vmatrix} -\xi & \iota & -\chi \\ \xi & -\kappa_1-\iota & \chi \\ -\xi & \iota & -\kappa_2-\chi \end{vmatrix} (16)$$

Opening the brackets in (16) and resolving the inequation Det J<0, we obtain the stable steady-state requirement in the form of:

$$-\xi\kappa_1\kappa_2 < 0 \quad (17),$$

that is always satisfied, because all of the mentioned parameters may only have positive values in the conditions of synthesis. So, the steady-state stability is warranted by the high monomer and proton concentration (high values of the diffusion parameters κ_1 and κ_2) and also by the high concentration of nitroso-cations (ξ>>0). According to the experimental data described in [1], the cathodic polypyrrole deposition was efficient when the pH was low. In such conditions, the proton diffusion rate was high (κ_1>>0) and, taking into account the excess of nitrate-ions, the low pH made the concentration of nitroso-ions high too, satisfying the condition (ξ>>0).

As the condition (17) is always satisfied, the monotonic instability (requiring Det J=0) is impossible. So, the mathematical modeling confirms the optimal synthesis conditions, chosen for the synthesis of the cathodically deposited polypyrrole in [1]. The absence of surface and electrochemical instabilities also confirms the possibility of obtaining a well-developed 3-dimensional surface.

It is also important to admit that the excess of NO_3^- relatively to the proton concentration in this system acted as an important stabilizing factor, impeding the proton attacks on monomer and polymer molecules that would negatively influence the polypyrrole yield, steady-state stability and coating´s morphology. The steady-state stability analysis of the 4-dimensional system, including the balance equation for nitrate-ions, planned in our further investigations, may also give the "upper" and "lower" pH margin of the steady-state stability topological parameter region.

CONCLUSIONS (SECTION I)

In the system with the cathodic deposition of polypyrrole realized by electroreductive generation of oxidizing particles, the excess of precursor ion (in this case, nitrate-ion) is an important stabilizing factor providing convenient polymer electrodeposition.

When the concentration of precursor ions is maintained in excess, the system is maintained in a stable steady-state, which is in accordance with

experimental data. The low pH-condition may be interpreted in terms of satisfying rapid proton diffusion and nitroso-ions formation requirement.

Neither oscillatory, nor monotonic instability may be observed in this system, contrarily to the anodic electropolymerization. No time-dissipative structures, existing in the systems with anodic electropolymerization, exist in this case.

SECTION II. MATHEMATICAL MODEL FOR THE POTENTIOSTATIC ELECTROPOLYMERIZATION OF PYRROLE IN STRONGLY ACID MEDIA AND ITS COMPARISON WITH THE CASE OF CATHODIC ELECTRODEPOSITION

If the polarity of the working electrode is changed, the role of NO_3^- and protons, compared to the case of cathodic electrodeposition, is significantly different. In the case of potentiostaticelectropolymerization, nitrate-ion will play the role of a dopant, entering the polypyrrole matrix. The electrochemical polymerization will be accelerated by the dopant participation, but in this case, the monomer, like the conducting polymer molecule will be vulnerable to proton attacks, so it will lead to less developed morphology [3].

The most accepted mechanism for anodic electropolymerization of pyrrole (like other 5-atom heterocyclic aromatic rings) is that, proposed by Díaz and modified by Kim [3, 22,23]. It consists of cation-radical formation by monomer oxidation, chain propagation by coupling or electrophilic substitution,protonsexpulsion, dimer oxidation and coupling of the formed cation-radical with one of the monomer and so on. The anodic electrochemical polymerization of pyrrole is foregone by the monomer adsorption, dispensed in the case of cathodic electrodeposition, because pyrrole doesnot directly participate in the electrochemical process[1].

The mathematical model for the potentiostatic anodic electropolymerization of acidophobic monomers including pyrrole in strongly acid media has been already developed by us in [35]. Now we allocate here its description in order to make the comparison of the cathodic and anodic polypyrroleelectrodeposition from the same solution more clear.

To describe mathematically the electropolymerization of pyrrole in strongly acid media, we introduce three variables:

P – pyrrole concentration in the pre-surface layer;

T –coverage degree of pyrrole on the anodic surface;

H –protons concentration in the pre-surface layer,as supposed in section I.

It is possible to prove that this system may be described by the following system of differential equations:

$$\begin{cases} \dfrac{dP}{dt} = \dfrac{2}{\delta}\left(\dfrac{\Delta}{\delta}(P_b - P) + r_d - r_a - r_{ads}\right) \\ \dfrac{dT}{dt} = \dfrac{1}{\Gamma_{max}}(r_a - r_d - r_p) \\ \dfrac{dH}{dt} = \dfrac{2}{\delta}\left(\dfrac{D}{\delta}(H_b - H) + r_p - r_a\right) \end{cases}$$
$$(18 - 20)$$

in which r_{ads} and r_d are the monomer adsorption and desorption rates, $r_a$is the side reaction of the monomer with protons, Γ_{max} the maximal monomer surface concentration.

The reaction rates may be calculated as:

$$r_{ads} = k_{ads}\exp(\beta_1 T)(1 - T)P;$$
$$r_d = k_d\exp(-\beta_2 T)T;$$

$$r_a = k_a PH; \quad r_p = k_p f(H)T\exp\left(-\frac{zF}{RT}\phi_0\right); (21-24)$$

in which, the parameters k are the corresponding rate constants, f(H) is the function of the influence of proton attack on the electropolymerization process, β_1 and $\beta_2$are constants describing the attraction of the adsorbed particles, z the quantity of electrons transferred.

RESULTS AND DISCUSSION (SECTION II)

To analyze the behavior of the system with anodic electropolymerization and to compare it with cathodic electrodeposition, we investigated the equation system (18 – 20) by using the linear stability theory. The steady-state Jacobian functional matrix elements are represented as:

$$J = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{33} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (25)$$

in which

$$a_{11} = \frac{\partial F_1}{\partial P} = \frac{2}{\delta}\left(-k_{ads}\exp(\beta_1 T)(1 - T) - \frac{D}{\delta} - k_a H\right)$$

$$a_{12} = \frac{\partial F_1}{\partial T} = \frac{2}{\delta}\left(-k_a P\exp(\beta_1 T)((1 - T)T - 1) + k_d\exp(-\beta_2 T)(1 - T)\right)$$

$$a_{13} = \frac{\partial F_1}{\partial H} = -k_a P$$

$$a_{21} = \frac{\partial F_2}{\partial P} = \Gamma_{max1}^{-1} k_{ads}\exp(\beta_1 T)(1 - T)$$

$$a_{22} = \frac{\partial F_2}{\partial T} = \Gamma_{\max 1}^{-1} \begin{pmatrix} k_a P \exp(\beta_2 T)\big((1-T)\beta_1 - 1\big) - k_a \exp(-\beta_2 T)(1-T) - \\ -k_p f(H)T \exp\left(\frac{zF}{RT}\phi_0\right) - k_p f(H)T \exp\left(-\frac{zF}{RT}\phi_0\right) \frac{\phi_0(K_0 - K_1) + K_1\phi_1}{K_0(1-T) + K_1 T} \end{pmatrix}$$

$$a_{23} = \frac{\partial F_2}{\partial H} = \Gamma_{\max 1}^{-1}\left(-k_p P \exp\left(-\frac{zF}{RT}\phi_0\right) \frac{df(H)}{dH} \right)$$

$$a_{31} = \frac{\partial F_3}{\partial P} = -k_a H$$

$$a_{32} = \frac{\partial F_3}{\partial T} = k_p f(H)T \exp\left(-\frac{zF}{RT}\phi_0\right) + k_p f(H)T \exp\left(-\frac{zF}{RT}\phi_0\right) \frac{\phi_0(K_0 - K_1) + K_1\phi_1}{K_0(1-T) + K_1 T}$$

$$a_{33} = \frac{\partial F_3}{\partial H} = \frac{2}{\delta}\left(k_p P \exp\left(-\frac{zF}{RT}\phi_0\right) \frac{df(H)}{dH} - k_a P - \frac{D}{\delta} \right) \quad (26\text{–}34)$$

in which K_0 and K_1 are capacitances of the parts of DEL, referring to the free and monomer-covered parts of the surface.

As in the previous case, we simplify the Jacobian members, introducing the parameters, so, the matrix gains the form:

$$\frac{4}{\delta^2}\Gamma_{\max}^{-1} \begin{vmatrix} -u-v-\xi & -W & j \\ u & W-Z & -\kappa \\ -v & Z & \kappa-j-\rho \end{vmatrix} \quad (35)$$

Oscillatory instability investigation. Contrarily to the cathodic polypyrrole deposition, the oscillatory instability is possible for anodic electropolymerization, which has been proved experimentally [22 – 31]. The positive elements in the Jacobian matrix may be:

W in the case of attracting interaction of adsorbed particles (β_1, $\beta_2 > 0$). This confirms the surface instability and the polymer morphology changes, described in [22, 23].

Z in the case of DEL rearrangement occurring whilst the monomer is oxidized. This confirms the difference in oscillation amplitudes in the presence of different dopants, observed in [22, 23].

κ in the case of protons´ autocatalytic formation, previewed by Díaz mechanism for the case of proton attacks on a growing polymer molecule.

The oscillatory behavior is accompanied by the factors that make the polymer structure less developed, compared to that obtained in cathodic manner.

Steady-state stability. Using Routh-Hurwitz criterion, we obtain the steady-state stability requirement in the form of:

$$(-u-v-\xi)(W(\kappa-\rho) + Z\rho - Wj + Zj) + u(Zj + W(\kappa-\rho-j)) - v(W(\kappa-j) + Zj) < 0 \quad (36)$$

According to the inequation (36) the steady-state will be stable in the case of absence or fragility of influences on the electropolymerization process in

DEL (Z>0), repealing interaction of adsorbed particles (W<0) and higher value of the proton outlet reaction rates, compared to proton diffusion and electropolymerization. So, contrarily to the cathodic electrodeposition, the pH decrease doesnot favor the steady-state stability.

The critical values of the parameters expressed in (36) are corresponding to the saddle-node bifurcation, describing monotonic instability:

$$(-u-v-\xi)(W(\kappa-\rho) + Z\rho - Wj + Zj) + u(Zj + W(\kappa-\rho) - Wj) - v(W(\kappa-j) + Zj) = 0 \quad (37)$$

These parameter values correspond to the N-shaped fragment of the voltamperogram and describe the multiplicity of unstable steady-states, from which the system chooses one.

So, the model comparison may explain the differences in the mechanisms of the cathodic and anodic electrodeposition of pyrrole and the influences of different factors on the use of thementioned electrochemical techniques.

GENERAL CONCLUSIONS

1. The differences in morphology of polypyrrole obtained from the same solution by cathodic and anodic routes may be explained by the different roles of the protons and nitrate-ions in the processes. The difference in these roles explains the different behavior of the mentioned systems. In this case, pH decrease doesnot favor the steady-state stability.

2. Contrarily to the cathodic electrodeposition, for the anodic electropolymerization time-dissipative structures exist, being maintained by monomer and protons diffusion and polymer formation.

3. The oscillatory instability is caused by the action of surface, electrochemical and autocatalytic factor, which is in accordance with experimental data. The morphology changes, accompanying the electrochemical instabilities, may explain the appearance of a less developed surface, than in the case of cathodic electrodeposition.

4. The cathodic electrodeposition is a more efficient polypyrrole electrochemical synthetic technique in low-pH nitric acid solutions containing excess of nitrate-ions than the anodic electropolymerization. The comparative modeling of both processes confirms this fact.

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КАТОДНО И АНОДНО ПОТЕНЦИОМЕТРИЧНО ЕЛЕКТРО-ОТЛАГАНЕ НА ПОЛИПИРОЛИ В СИЛНО КИСЕЛА СРЕДА. ТЕОРЕТИЧНО И ЕКСПЕРИМЕНТАЛНО СРАВНЕНИЕ

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(Резюме)

Разработени са два математични модела описващи катодно и анодно потенциометрично електро-отлагане на полипироли в силно кисела среда. Изчисленията са анализирани и сравнени помежду си и с опитни данни. Разликите в реакционните механизми, причиняващи разлики в реакционната кинетика и в морфологията на полимерите и свойствата им намират своето обяснение в създадените модели. Потвърдена е вероятността на нестабилности при катодното електро-отлагане.