

Theoretical Description for the Galvanostatic Electrode Pretreatment, Yielding Thiourea-Based Active Surface for Cathodic Conducting Polymer Deposition

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Abstract: The system with the electrode modification by thiourea basic derivatives for conducting polymer indirect cathodic deposition has been described from the theoretical point of view. The electrode pretreatment process has been analyzed using the linear stability theory and bifurcation analysis. It was shown that the steady-state is realized rapidly and provides efficient surface pretreatment. On the other hand, the oscillatory and monotonic behavior, in this case, is also possible due to the double electric layer capacitance changes during the doping stage and electrochemical reaction.

Keywords: conducting polymers; indirect cathodic electropolymerization; surface pretreatment; thiourea; stable steady-state.

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1. Introduction

Electropolymerization is one of the most used conducting polymer synthesis techniques [1–6]. The electrosynthesized polymers have some advantages while compared to the chemically synthesized polymers, like enhanced conductivity, flexibility, and versatility in modification for specific purposes and high sensing abilities. Depending on the participation of the monomer in the electrochemical stage, the electropolymerization may be direct or indirect.

The indirect electropolymerization, in which the electrochemical stage does not involve the proper monomer, but yields an active substance, promoting the chain formation and propagation, sometimes maybe more flexible than the direct one [5 - 6]. Independently on the monomer nature, it may be realized either cathodically or anodically. Moreover, it permits a one-stage realization of the processes like metal-polymer co-deposition, usually realized in two stages [7–10].

Nevertheless, in some cases the electropolymerization, be it anodic or cathodic, may require the electrode pretreatment [11-14], which may include not only physical or physicochemical processes like adsorption, chemical or electrochemical polish, but also be a complex process involving chemical and electrochemical stages (material doping, enzyme entrapment, graphene electrooxidation with further reduction, sulfide passivation). The aim of the electrode pretreatment is to enhance the polymer stability, adhesion, to modify by the proper way its behavior. If the electrosynthesis is indirect, the pretreatment may also be used to stabilize the initiating species.

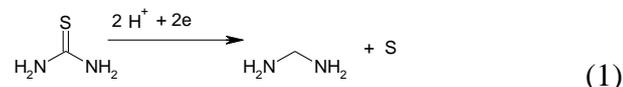
For example, thiourea and analogs, used to prevent the hydrogen evolution in cathodic processes and to augment the polymer adhesion, may be electrochemically reduced, yielding amino-mercaptans or elementary sulfur and diamines. Afterward, the resulting compounds may be doped by the initiating ion, preparing the surface for the electropolymerization process. These processes may be accompanied by the electrochemical instabilities (oscillatory and monotonic) [15 – 18], capable of causing drastic changes in the resulting polymer changes.

In this work, the theoretical description of the system described above is exposed. Through mathematical modeling and analysis, it is possible to investigate the steady-state stability conditions, like also to foresee the occurrence of electrochemical instabilities affecting the system. Also, the behavior of this system will be compared to similar ones [19–21].

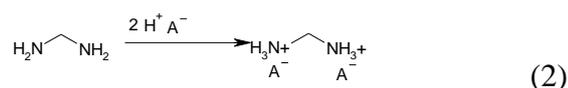
2. Materials and Methods

2.1. System and its modeling.

The surface pretreatment is realized in acidic media. By this, the thiourea is reduced to form the sulfur and methylene diamine, according to the reaction (1):



Methylenediamine is furtherly protonated in the presence of the anion, yielding a salt (2):



By this, the salt is formed, the conductivity is enhanced, and the hydrogen evolution is impeded.

Methylenediamine is used as a host matrix, yet doped by an ion, furtherly used as an initiator of the indirect electropolymerization process or even chemically assisted deposition. Thiourea may be easily substituted by thio- and semithiosquaraine dyes with basic nitrogen, mercaptoanilines, thiosemicarbazones, aminothiophenes, mercaptoazaarenes, and analogous compounds.

Due to the exposed, supposing the relative excess of the protons, the behavior of the system in galvanostatic mode will be described by three variables:

- c – the initiating ion concentration in the pre-surface layer;
- m – the undoped methylenediamine surface coverage degree
- q – the anode charge density.

To simplify the modeling, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also, we assume that the background electrolyte is in excess, so we can neglect the migration flow. The diffusion layer is supposed to be of a constant thickness, equal to δ , and the concentration profile in it is supposed to be linear.

The bivariate equation-set, describing the system will be exposed as:

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (c_0 - c) - r_d \right) \\ \frac{dm}{dt} = \frac{1}{M} (r_r - r_d) \\ \frac{di}{dt} = i - i_F \end{cases} \quad (3)$$

where Δ is diffusion coefficient, c_0 is the initiator bulk concentration in the pre-surface layer, i_F is Faradaic current, M is the methylenediamine maximal surface concentration, and the parameters r correspond to the reduction and doping rate, capable of being described as:

$$r_r = k_r (1 - m) \exp\left(-\frac{2F\phi_0}{RT}\right) \quad (4)$$

$$r_d = k_d m c^2 \exp(-\alpha m) \quad (5)$$

$$i_F = 2Fk_r (1 - m) \exp\left(-\frac{2F\phi_0}{RT}\right) \quad (6)$$

In which the parameters k are the correspondent rate constants, ϕ_0 is the potential slope in the double electric layer (DEL), α is the parameter, relating its capacitance to the doping degree, F is the Faraday number, R is the universal gas constant, and T is the absolute temperature.

As a matter of fact, this system will be similar to the systems with the electrochemical determination by doping and with the surface-assisted indirect electropolymerization [20 – 21]. Nevertheless, as we have chemical doping instead of electrochemical (like it was during the direct electropolymerization of a monomer in the presence of the initiating ion), the DEL influences of the process will be slightly different, as shown below.

3. Results and Discussion

In order to investigate the system with the electropolymerization surface pretreatment by thiourea reduction and doping of its product, we analyze the equation-set (3) by means of the linear stability theory. The steady-state Jacobian matrix members for this system may be exposed as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (7)$$

in which:

$$a_{11} = \frac{2}{\delta} \left(-\frac{\Delta}{\delta} - 2k_d m c \exp(-\alpha m) \right) \quad (8)$$

$$a_{12} = \frac{2}{\delta} \left(-k_d c^2 \exp(-\alpha m) + k_d m c^2 \exp(-\alpha m) \right) \quad (9)$$

$$a_{13} = 0 \quad (10)$$

$$a_{21} = \frac{1}{M} \left(-2k_d m c \exp(-\alpha m) \right) \quad (11)$$

$$a_{22} = \frac{1}{M} \left(-k_r \exp\left(-\frac{2F\phi_0}{RT}\right) - jk_r (1 - m) \exp\left(-\frac{2F\phi_0}{RT}\right) - k_d c^2 \exp(-\alpha m) + \alpha k_d m c^2 \exp(-\alpha m) \right) \quad (12)$$

$$a_{23} = \frac{1}{M} \left(-lk_r (1 - m) \exp\left(-\frac{2F\phi_0}{RT}\right) \right) \quad (13)$$

$$a_{31} = 0 \quad (14)$$

$$a_{32} = -2F \left(k_r \exp\left(-\frac{2F\phi_0}{RT}\right) + jk_r (1 - m) \exp\left(-\frac{2F\phi_0}{RT}\right) \right) \quad (15)$$

$$a_{33} = 2F \left(-k_r \exp\left(-\frac{2F\phi_0}{RT}\right) - jk_r (1 - m) \exp\left(-\frac{2F\phi_0}{RT}\right) \right) \quad (16)$$

$$a_{33} = -2F \left(lk_r(1 - m) \exp \left(-\frac{2F\varphi_0}{RT} \right) \right) \quad (17)$$

Observing the elements (8), (13) and (17), we may conclude that *the oscillatory behavior* in this system is possible. Moreover, its probability is enhanced in relation to the cathodic indirect solution-initiated electropolymerization [19], but is equal to that of the systems with the surface-initiated polymerization (to which the surface is hereby prepared) [20-21]. In galvanostatic mode, there are three elements capable of being positive, against two for potentiostatic mode. As in [20-21], the elements $jk_r(1 - m) \exp \left(-\frac{2F\varphi_0}{RT} \right) > 0$ if $j < 0$, related to the DEL influences on the electrochemical stage, and $\alpha k_a m c^2 \exp(-\alpha m) > 0$, if $\alpha > 0$, related to the DEL capacitance impact of the chemical doping, is responsible for oscillatory behavior. Another factor is described by the positivity of $-2F \left(lk_r(1 - m) \exp \left(-\frac{2F\varphi_0}{RT} \right) \right) > 0$ if $l < 0$. All of the mentioned factors act either during the assisted electropolymerization or during the surface pretreatment.

In order to investigate *the steady-state stability*, we apply the Routh-Hurwitz criterion to the equation-set (3). Avoiding the cumbersome expressions, we introduce new variables and, therefore, describe the Jacobian matrix determinant as:

$$\frac{4F}{\delta M} \begin{vmatrix} -\kappa - \mu & -\nu & 0 \\ -\mu & -\nu - \xi & -\lambda \\ 0 & -\xi & -\lambda \end{vmatrix} \quad (18)$$

Opening the brackets, we apply the Det $J < 0$ requisite, salient from the criterion and, resolving the inequation relatively to the electrochemical parameter λ , obtain the steady-state stability condition, expressed as (19):

$$-\lambda(\kappa\nu + 2\kappa\xi + \mu\xi - \nu\xi) < 0 \quad (19)$$

This inequation depicts either diffusion or kinetically controlled electrosynthetic system. It is warranted to be satisfied in the case of the fragility of the DEL influences of chemical and electrochemical stages. Really, the positive values of λ , ν , and ξ lead the left part of the inequation to more negative values, stabilizing the steady-state and leading to the appearance of a developed catalytic surface with “cabbage-like” morphology. It will provide the deposition of a similar polymer structure, as observed in [20–21].

The *monotonic instability* for this system is possible. It is defining the margin between stable steady-states and unstable states, and its conditions of appearance will be depicted as (20):

$$-\lambda(\kappa\nu + 2\kappa\xi + \mu\xi - \nu\xi) = 0 \quad (20)$$

While prepared, the pretreated surface may assist either the indirect electropolymerization or even chemically induced surface polymerization, depending on the monomer, synthesis conditions, and the dopant. While used in the indirect electropolymerization, the process will be described by the models, exposed in [20–21].

4. Conclusions

From the theoretical investigation of the assisted electropolymerization electrode pretreatment by thiourea reduction in the presence of an initiating dopant ion, it is possible to conclude that:

The electrode pretreatment is a diffusion-controlled process, in which the steady-state mode is easy to obtain and maintain.

The electrode pretreatment yields an active surface capable of supporting efficiently either electrochemical or chemical polymerization, augmenting the conductivity and adhesion of the resulting polymer.

The oscillatory behavior in this system is possible. As in the case of the surface-assisted indirect electropolymerization, it will be caused by double electric layer influences of both electrochemical stage and chemical doping reaction.

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Conflicts of Interest

The authors declare no conflict of interest.

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