



The Mathematical Description of the Electro Polymerization of the Complex-Forming Monomers over Transition Metals

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ABSTRACT

The electropolymerization of a monomer, containing functional groups that form metallic complexes, over the transition metals, was described mathematically by the linear stability theory and bifurcational analysis. With the mathematical model, the influence of surface factors (monomer adsorption and desorption), electrochemical factors (influences in DEL) and complex formation factors on the electropolymerization process is evaluated.

Keywords: Metalorganic complexes; Conducting polymers; Electro chemical instabilities; Surface behavior; Stable steady-state

INTRODUCTION

The choosing of the monomer for the resulting conducting polymer is determined by how the polymer materials are going to be used. For example, the polymers, used as corrosion protecting coatings, have to be stable and adherent, and those used in sensors and biosensors must possess affinity to the analyte [1-25]. On the other hand, other monomers may have their electropolymerization on some metals accompanied by the complex formation. This phenomenon has already been observed during the electrochemical modification of the organic compounds and during their electropolymerization [26,27]. For the electrochemical modification this phenomenon may be considered as damaging for the final product yield. Nevertheless, for the synthesis of conducting polymers the complex formation contributes in the film adhesion, conductivity, color and electrochromism and also in electrocatalytic properties. Moreover, the electrochemical synthesis of conducting polymers in different modes has shown the possibility of electrochemical instabilities, accompanying it [28-38]. Although a phenomenological explanation may give logical interpretation to the causes of the instabilities, it can't have a rigid explanation. Moreover, such an interpretation is capable to explain only the concrete system, without pretensions to include the similar ones. A mathematical model, capable to describe adequately the processes in the system may eliminate both of the negative aspects of the phenomenological explanation. It is also able to make clearer the mechanism of the processes occurring there. We have already made different intentions to describe the different systems with the electropolymerization [39-54]. In this work, the mathematical modeling of the system with the electropolymerization of the monomer forming complexes with the electrode metal.

SYSTEM AND ITS MODELING

In order to describe the potentiostatic electropolymerization of a monomer, capable to form complexes, we use three variables:

c – the monomer pre-surface concentration;

θ – the monomer surface coverage degree;

χ – the complex surface coverage degree.

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 monomers enter in the pre-surface layer by means of its diffusion and by desorption from the surface and leave the layer by adsorption. So, its balance equation will be described as:

$$\frac{dc}{dt} = \frac{2}{\delta} \left(v_{-1} - v_1 + \frac{D}{\delta} (c_b - c) \right) \equiv F_1 \quad (1)$$

In which v_1 and v_{-1} are monomer desorption and adsorption rates, D is the diffusion coefficient and c_b the bulk concentration of the monomer. The monomer enters the surface by its adsorption and leaves it by desorption. It also participates in the anodic electropolymerization and complex formation, so its balance equation will be described as:

$$\frac{d\theta}{dt} = \Gamma_{t,\max} (v_1 - v_{-1} - v_2 - v_3) \equiv F_2 \quad (2)$$

In which $\Gamma_{t,\max}$ is the monomer maximal concentration, v_2 is the electrooxidative polymerization rate, and v_3 is the complex formation rate. The complex is formed by means of the monomer reaction of the monomer with the metallic surface and enters in the electropolymerization. Thus, its balance equation will be rewritten as:

$$\frac{d\chi}{dt} = \Gamma_{\chi,\max} (v_3 - v_2) \equiv F_3 \quad (3)$$

In which $\Gamma_{\chi,\max}$ is the maximal surface concentration of the complex. The adsorption and desorption rates may be described as:

$$v_1 = k_1 \exp\left(-\frac{(K_0 - K_1)\phi_0^2 + 2K_2\phi_0\phi_1}{2RT\Gamma_{\max 1}} \gamma\right) \exp(a(\theta_h)) c_h (1 - \theta - \chi)$$

$$v_{-1} = k_{-1} \exp\left(\frac{(K_0 - K_1)\phi_0^2 + 2K_2\phi_0\phi_1}{2RT\Gamma_{\max 1}} (1 - \gamma)\right) \exp(-a\theta) \theta$$

In which k_1 and k_{-1} are monomer adsorption and desorption constants, K_1 and K_0 are DEL capacitances, related to the free and covered parts of the surface, ϕ_1 and ϕ_0 are potential slopes, related to the zero charge potential. The electropolymerization speed may be described as:

$$v_2 = k_2 \theta^x \chi^y \exp\left(-\frac{zF}{RT} \phi_0\right)$$

In which k_2 is the reaction rate constant, x and y are reaction orders, z is the number of the electrons transferred, F is the Faraday number, R is the gas universal constant, T is the absolute temperature.

The complex formation rate is described as:

$$v_3 = k_3 \theta \exp(\beta_1 \chi)$$

In which β_1 is the coefficient of the attraction between the monomer and the metallic surface.

RESULTS AND DISCUSSION

The behavior of this system will be described by means of liner stability theory and bifurcation analysis. The steady-state Jacobian matrix elements for this system will be described as:

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

In which:

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

$$a_{12} = \frac{\partial F_1}{\partial \theta} = \frac{2}{\delta} \left(-\frac{\partial v_1}{\partial \theta} + \frac{\partial v_1}{\partial \theta} \right)$$

$$a_{13} = \frac{\partial F_1}{\partial \chi} = -\frac{\partial v_1}{\partial \chi}$$

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

$$a_{22} = \frac{\partial F_2}{\partial \theta} = \Gamma_{\max}^{-1} \left(\frac{\partial v_1}{\partial \theta} - \frac{\partial v_1}{\partial \theta} - \frac{\partial v_2}{\partial \theta} - \frac{\partial v_3}{\partial \theta} \right)$$

$$a_{23} = \frac{\partial F_2}{\partial \chi} = \Gamma_{\max}^{-1} \left(\frac{\partial v_1}{\partial \chi} - \frac{\partial v_2}{\partial \chi} - \frac{\partial v_3}{\partial \chi} \right)$$

$$a_{31} = \frac{\partial F_3}{\partial c} = 0 \quad a_{32} = \frac{\partial F_3}{\partial \theta} = \Gamma_{c,\max}^{-1} \left(\frac{\partial v_3}{\partial \theta} - \frac{\partial v_1}{\partial \theta} \right)$$

$$a_{33} = \frac{\partial F_3}{\partial \chi} = \Gamma_{c,\max}^{-1} \left(\frac{\partial v_3}{\partial \chi} - \frac{\partial v_1}{\partial \chi} \right)$$

In order to simplify the analysis of the matrix, avoiding the appearance of cumbersome expressions, we introduce new variables, so the determinant will be described as:

$$\frac{2}{\delta \Gamma_{\max} \Gamma_{c,\max}} \begin{vmatrix} -L - \kappa & -\Sigma_S & X_S \\ L & \Sigma_S - \Sigma_p - \Sigma_c & X_S - X_p - X_c \\ 0 & \Sigma_c - \Sigma_p & X_c - X_p \end{vmatrix}$$

Opening the brackets and applying the condition of $\text{Det } J < 0$, salient from the criterion, we obtain the steady-state stability requirement expressed as:

$$\kappa > \frac{L(\Sigma_c X_S - \Sigma_p X_S + \Sigma_c X_S + \Sigma_S X_c - \Sigma_S X_p - \tilde{A})}{\tilde{A}}$$

In which

$$\tilde{A} = \Sigma_S X_c - 2\Sigma_p X_c - 2\Sigma_c X_c - \Sigma_S X_p - \Sigma_c X_S + \Sigma_p X_S$$

This required is satisfied in the case of the kinetically-controlled process, in which the monomer diffusion is quicker than the chemical processes. This mode is easy to obtain and maintain in the reaction conditions. When the influences of the mentioned factors are equal, the monotonic instability is realized, and the condition of its appearance may be described as:

$$\kappa = \frac{L(\Sigma_c X_S - \Sigma_p X_S + \Sigma_c X_S + \Sigma_S X_c - \Sigma_S X_p - \tilde{A})}{\tilde{A}}$$

For the oscillatory instability to be realized, the presence of the positive elements in the main diagonal is necessary. The positive elements describe the positive callback.

In the main diagonal there are three elements, which may be positive:

- Σ_S , describing the attraction of the adsorbed particles;
- $-\Sigma_p$ describing the DEL influences of the electropolymerization process ($\varphi_0 < 0$);
- X_c describing the attraction between the growing film and the surface. The last factor was absent in the systems without complex formation. So, the mentioned process gives its impact to the oscillatory behavior.

CONCLUSION

The steady-state stability in this system is easy to obtain and maintain. The electrosynthetic process is kinetically controlled. The monotonic instability in this system is possible. The oscillatory instability may be caused not only by adsorbed particles' attraction and electrochemical DEL influences, but also by the attraction between the growing film and metallic surface.

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