Full Paper

The Theoretical Evaluation of the Electropolymerization of Conjugated Compounds, Accompanied by their Electrocyclization

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Abstract- The theoretical evaluation of the electropolymerization of the *pi*-conjugated organic compounds has been given. The correspondent mathematical model has been developed and analyzed by means of linear stability theory and bifurcation analysis. It was shown that the presence of the electrochemical cyclization of conjugated compounds gives its strong impact on electropolymerization process, yielding the compounds with the possibility to enter the polymer chain as monomers. The cyclization may also be the cause of the oscillatory and monotonic instability in the system.

1. INTRODUCTION

The use of conducting polymers as electrode modifier for electrochemical analysis is one of the most important aspects of their application [1-10]. Combining the properties of plastics (versatility in shaping, flexibility, corrosion resistance, light weight) and metals (conductivity, magnetic properties) with the facility of modification [11-12], they take part in sensing processes either as active substances, or as mediators.

On the other hand, the electrochemical sensors provide the precise, exact, rapid and sensitive analysis of the concentration of toxic substances (like pesticides [13], chemical warfare [14]), pharmaceutically and biologically active substances [15-16], and phytoactive substances [17], which makes them rather important, because they are a modern and flexible instrument of analysis.

The conducting polymers may be synthetized either chemically, or electrochemically [18-21], but the electrochemical polymerization becomes more and more popular in the CP-synthesis for electroanalytical purposes, due to some reasons. Nevertheless, the electropolymerization of different compounds may be accompanied by additional processes like:

- Resulting polymer overoxidation. This phenomenon is known as "the polythiophene paradox" [22-25] and has been described for different monomers;
- Resulting polymer additional oxidation. Common, for example, for polydopamine, whose hydroquinonic groups are oxidized yielding their quinonic form [26];
- Electrocyclization, which is a one-molecule process, yielding the appearance of a new cyclic fragment (mostly, a heterocycle). Its possibility has been shown for dopamine [26] and isn´t discarded for diphenylamine derivatives electropolymerized in [27]. Another CP monomer, carbazole, is formed in the last case (Fig. 1):
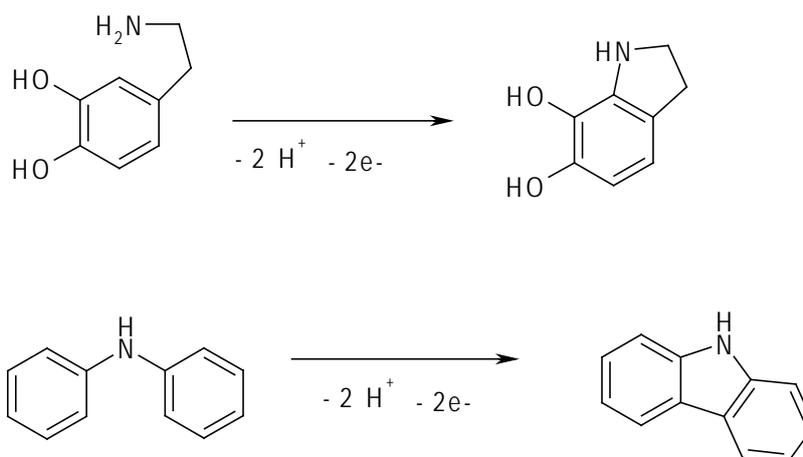
Fig. 1. The electrocyclization process for dopamine and diphenylamine

The electrocyclization is based on electrochemically promoted electrophilic substitution, as well, as the electropolymerization according to the Díaz mechanism, modified by Kim´s mechanism. It may be realized before, during and after electropolymerization, depending on the synthesis conditions. The electrocyclization product is generally more capable to be electropolymerized than the initial monomer.

Another problem is the presence of electrochemical instabilities, frequently accompanying the electropolymerization of different compounds [28-31]. The presence of electrocyclization may give its impact on the electrochemical instabilities, and its relation to a certain kinetic detail of the process is very important for the understandings of the process itself. 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 [32-35]. In this work, the mathematical modeling of the system with the electropolymerization of the monomer, capable to undergo the electrochemical cyclization during the electropolymerization process, will be described.

2. SYSTEM AND ITS MODELING

The potentiostatic electropolymerization of a compound, capable to undergo the simultaneous electrochemical cyclization, is, in fact a system with the copolymerization of two monomers, one of which is present on the surface, and another is obtained during an electroorganic procedure (electrocyclization).

So, the simplest model, described in [32] would not be compatible to this case, so we introduce three variables:

c – the monomer concentration in the pre-surface layer;
θ – the monomer surface coverage degree;
θ_c – the cyclization product 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.

It is possible to show that the system's behavior will be described by the trivariant system as:

$$
\begin{cases}
\frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) + r_{-1} - r_1\right) \\
\frac{d\theta}{dt} = \frac{1}{G}(r_1 - r_{-1} - r_2 - r_3) \\
\frac{d\theta_c}{dt} = \frac{1}{G*}(r_3 - r_2)
\end{cases}
\tag{1}
$$

In which Δ is the monomer diffusion coefficient, c_0 is its bulk concentration, G and G^* are the maximal concentrations of the monomer and its ciclization product, and the parameters are correspondent adsorption, desorption and reaction rates, described as:

$$r_1 = k_1(1 - \theta - \theta_c)c\exp(\alpha\theta), \tag{2}$$

$$r_{-1} = k_{-1}\theta\exp(-\alpha\theta), \tag{3}$$

$$r_2 = k_2\theta^x\theta_c{}^y\exp\left(\frac{nF}{RT}\phi_0\right) \tag{4}$$

$$r_3 = k_3\theta\exp\left(\frac{2F\phi_0}{RT}\right) \tag{5}$$

In which the parameters k are the correspondent rate constants, α is the parameter, describing the interaction of the adsorbed particles, n is the number of electrons, transferred during the electropolymerization, F is the Faraday number, ϕ_0 is the potential slope in double electric layer (DEL), related to the zero-charge potential, R is the universal gas constant and T is the absolute temperature.

The presence of electrochemical cyclization brings its strong impact to the steady-state stability, and this impact will be discussed below.

3. RESULTS AND DISCUSSION

In order to investigate the behavior of the system with the electropolymerization, accompanied by the electrocyclization of the correspondent monomer, we analyze the equation set (1-3) by means of the linear stability theory. The steady-state Jacobian functional matrix members for this case may be described as:

$$
\begin{pmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{pmatrix}
\tag{6}
$$

in which

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_1(1 - \theta - \theta_c)\exp(\alpha\theta)\right) \tag{7}$$

$$a_{12} = \frac{2}{\delta}\left(k_1\exp(\alpha\theta) - \alpha k_1(1 - \theta - \theta_c)\exp(\alpha\theta) + k_{-1}\exp(-\alpha\theta) - \alpha k_{-1}\theta\exp(-\alpha\theta)\right) \tag{8}$$

$$a_{13} = \frac{2}{\delta}\left(k_1\exp(\alpha\theta)\right) \tag{9}$$

$$a_{21} = \frac{1}{G}\left(k_1(1 - \theta - \theta_c)\exp(\alpha\theta)\right) \tag{10}$$

$$a_{22} = \frac{1}{G}\left(-k_1\exp(\alpha\theta) + \alpha k_1(1-\theta-\theta_c)\exp(\alpha\theta) - k_{-1}\exp(-\alpha\theta) + \alpha k_{-1}\theta\exp(-\alpha\theta) - \right.$$

$$\left. x k_2\theta^{x-1}\theta_c^{\;y}\exp\left(\frac{nF}{RT}\phi_0\right) - jk_2\theta^x\theta_c^{\;y}\exp\left(\frac{nF}{RT}\phi_0\right) - k_3\exp\left(\frac{2F\phi_0}{RT}\right) - jk_3\theta\exp\left(\frac{2F\phi_0}{RT}\right)\right) \quad (11)$$

$$a_{23} = \frac{1}{G}\left(-k_1\exp(\alpha\theta) - lk_2\theta^x\theta_c^{\;y}\exp\left(\frac{nF}{RT}\phi_0\right) - lk_3\theta\exp\left(\frac{2F\phi_0}{RT}\right)\right) \quad (12)$$

$$a_{31} = 0 \quad (13)$$

$$a_{32} = \frac{1}{G_C}\left(-x k_2\theta^{x-1}\theta_c^{\;y}\exp\left(\frac{nF}{RT}\phi_0\right) - jk_2\theta^x\theta_c^{\;y}\exp\left(\frac{nF}{RT}\phi_0\right) + k_3\exp\left(\frac{2F\phi_0}{RT}\right) + \right.$$

$$\left. jk_3\theta\exp\left(\frac{2F\phi_0}{RT}\right)\right) \quad (14)$$

$$a_{33} = \frac{1}{G_C}\left(-lk_2\theta^x\theta_c^{\;y}\exp\left(\frac{nF}{RT}\phi_0\right) + lk_3\theta\exp\left(\frac{2F\phi_0}{RT}\right)\right) \quad (15)$$

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:

$$\frac{2}{\delta\Gamma_{max\,1}\Gamma_{c,max}}\begin{vmatrix} -L-\kappa & -\Sigma_S & X_S \\ L & \Sigma_S-\Sigma_P-\Sigma_C & X_S-X_P-X_C \\ 0 & \Sigma_C-\Sigma_P & X_C-X_P \end{vmatrix}$$

Opening the brackets and applying the condition of 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 and electrochemical 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 DEL influences of the electrocyclization. The last factor was absent in the simplest electropolymerization systems. So, the mentioned process gives its impact to the oscillatory behavior.

4. CONCLUSION

From the analysis of the electrocyclization-accompanied electropolymerization it is possible to conclude that the steady-state stability in this system is easy to obtain and maintain. The electrosynthetical process is kinetically controlled. The monotonic instability in this system is possible; yet the oscillatory instability may be caused not only by adsorbed particles´ attraction and electrochemical DEL influences of the electropolymerization, but also by those of the electrochemical cyclization.

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