Theoretical Evaluation for the Assisted Electropolymerization of a Monomer, Obtained by an Indirect Electrochemical Synthesis

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Abstract: In this work, the possibility for indirect electropolymerization of a monomer synthesized by an indirect electrosynthesis has been evaluated. Based on the reaction mechanism, the correspondent mathematical model has been developed and analyzed using linear stability theory and bifurcation analysis. It has been shown that in the case of indirect monomer electrosynthesis and electropolymerization, the polymer deposition is far more stable than for direct participation of the monomer in the electrochemical stage. The surface tends to be more developed. Yet, the electrochemical oscillations are expected to be less probable than in the case of the direct anodic process.

Keywords: conducting polymers; electropolymerization; indirect cathodic electrodeposition; electrochemical oscillations; steady stable-state.
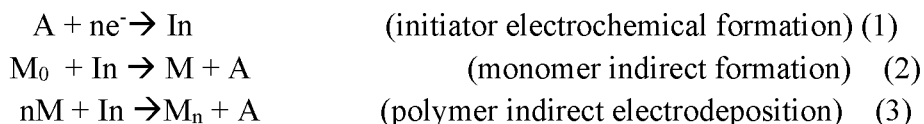
1. Introduction

Electropolymerization is one of the most used synthetic techniques for conducting polymers [1–10]. It consists of conducting polymer deposition over an electrode surface in an electrochemical process.

Electropolymerization may be direct or indirect. In the first case, the monomer is oxidized or reduced directly, provoking a chain initiation and propagation. In the second case, the electrochemical stage yields a chain initiator, reacting with the monomer, yielding a polymer. The second path provides a more flexible conducting polymer formation, like in [11-15]. For example, this is the unique possibility for polypyrrole and polythiophene formation on the cathode.

In some cases, not only polymer but also a monomer may be formed by indirect electrosynthesis. Thus, the electrochemical system will be described by an electrochemical and two chemical reactions (1 – 3). If we consider, for simplicity, a cathodic process, it will be described as:

$$A + ne^- \rightarrow In \quad \text{(initiator electrochemical formation) (1)}$$
$$M_0 + In \rightarrow M + A \quad \text{(monomer indirect formation)} \quad (2)$$
$$nM + In \rightarrow M_n + A \quad \text{(polymer indirect electrodeposition)} \quad (3)$$

As a matter of fact, the monomer, which undergoes an indirect electropolymerization on a specifically modified cathode, is also synthesized analogously, yielding a polymer. These processes may be accompanied by electrochemical instabilities (oscillatory and monotonic) [16, 17], capable of causing drastic changes in the resulting polymer changes.

In this work, the theoretical description for the system described above is exposed. By the 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 [18–21].

2. Materials and Methods

2.1. System and its modeling.

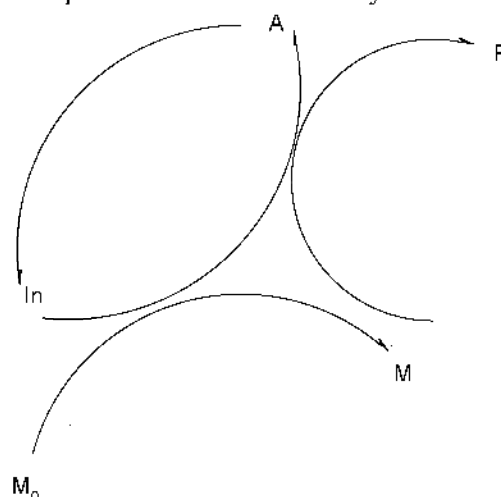Schematically, the exposed electrochemical system will be described as on Fig. 1:

Figure 1. The scheme of the indirect monomer and polymer electrochemical synthesis.

Taking this into account, to describe the behavior of the system, we introduce three variables:
c – monomer precursor concentration in the pre-surface layer;
m – monomer concentration in the pre-surface layer;
v – chain initiator surface coverage degree.

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

It is possible to show that the behavior of the electrochemical process will be described as (4):

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) - r_m\right) \\ \frac{dm}{dt} = \frac{2}{\delta}(r_m - r_p) \\ \frac{dv}{dt} = \frac{1}{V}(r_i - r_m - r_p) \end{cases} \qquad (4)$$

Herein, Δ is the diffusion coefficient, c_0 is the precursor bulk concentration, V is the chain initiator maximal surface concentration, and the parameters r are the correspondent reaction rates, calculated as:

$$r_m = k_m c v \qquad (5)$$
$$r_p = k_p m^n v \qquad (6)$$
$$r_i = k_i(1 - v)\exp\left(-\frac{zF\varphi_0}{RT}\right) \qquad (7)$$

The parameters k are the correspondent rate constants, z is the number of the transferred electrons, φ_0 is the potential slope in the double electric layer (DEL), F is the Faraday number, R is the universal gas constant, and T is the absolute temperature.

In this work, the simplest system, in which the monomer doesn´t contain ionic functional groups capable of influencing DEL, is investigated. Therefore, the oscillatory behavior will be caused uniquely by the behavior on the electrochemical stage, and the polymer deposition will be realized in an efficient manner, as shown below.

3. Results and Discussion

To investigate the indirect cathodic electropolymerization behavior of an indirectly synthesized monomer, we analyze the equation-set (4), taking into account the algebraic relations (5 – 7), using linear stability theory. The steady-state Jacobian matrix members for this system will be exposed as (8):

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

in which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_m v\right) \qquad (9)$$
$$a_{12} = 0 \qquad (10)$$
$$a_{13} = \frac{2}{\delta}(-k_m c) \qquad (11)$$
$$a_{21} = \frac{2}{\delta}(k_m v) \qquad (12)$$
$$a_{22} = \frac{2}{\delta}\left(-nk_p m^{n-1} v\right) \qquad (13)$$
$$a_{23} = \frac{2}{\delta}\left(k_m c - k_p m^n\right) \qquad (14)$$
$$a_{31} = \frac{1}{V}(-k_m c) \qquad (15)$$

$$a_{32} = \frac{1}{V}\left(-nk_p m^{n-1} v\right) \qquad (16)$$

$$a_{33} = \frac{1}{V}\left(-k_i \exp\left(-\frac{zF\varphi_0}{RT}\right) + jk_i(1-v)\exp\left(-\frac{zF\varphi_0}{RT}\right) - k_m - k_p m^n\right)(17)$$

As in [13, 14], *the oscillatory behavior* for this system is possible, and it will be caused uniquely by influences of the electrochemical reduction stage on DEL capacitances, described by the positivity of main-diagonal element $jk_i(1\text{-}v)\exp\left(-\frac{zF\varphi_0}{RT}\right)$ (positive main-diagonal elements describe the positive callback). The oscillations are expected to be frequent, and their amplitude will strongly depend on the background electrolyte composition, including pH.

Yet if those influences aren't strong enough to influence the system's behavior, *the steady-state stability* is safeguarded. It may be proved as shown below. To investigate the steady-state stability in this system, we apply the Routh-Hurwitz stability criterion to the equation-set (4). Avoiding the cumbersome expressions, we introduce new variables, rewriting the determinant as (18):

$$\frac{4}{\delta^2 V}\begin{vmatrix} -\kappa - \varXi & 0 & -\varLambda \\ \varXi & -P & \varLambda - \varSigma \\ -\varXi & -P & -\varOmega - \varLambda - \varSigma \end{vmatrix} \qquad (18)$$

Opening the brackets and applying the Det J<0 conditions, salient from the criterion, we obtain the steady-state stability requisite, exposed as (19):

$$-(\kappa - \varXi)(2P\varLambda + P\varOmega) < 2\varLambda\varXi P \qquad (19)$$

Considering that all of the parameters mentioned in the inequation (19), accept of $\varOmega$, are always positive, the right side of the expression (19) is always positive, and the left side is always negative if $\varOmega$ is maintained positive. As the parameter $\varOmega = k_i \exp\left(-\frac{zF\varphi_0}{RT}\right) - jk_i(1-v)\exp\left(-\frac{zF\varphi_0}{RT}\right)$ is positive for the negative values of j, defining the fragility of the influences of the electrochemical stage on DEL ionic force, conductivity, and impedance, the steady-state stability condition is warranted to maintain stability if $\varOmega$ is positive.

This defines an efficient conducting polymer deposition. The material is formed as a well-developed cabbage-like film, centered on the active sites of the initiator formation.

The conductivity of the polymeric material will be strongly dependent on both the monomer or initiator nature.

If the initiator has non-metallic nature (for example, nitrite, sulfite), the polymer adhesion over the cathode surface is augmented, but the conductivity remains diminished. Changing the electrode polarity, the polymer is doped, preserving both the high conductivity of a doped CP or the developed surface of a cathodically deposited conducting macromolecule.

Yet if the initiator has metallic nature (manganese, vanadium, rhenium, and other, generally d- and f-element derivatives), the electropolymerization yields, in fact, a hybrid material with highly developed catalytic properties. It may be additionally doped by changing the polarity.

As for the proper electrosynthesis process, it is either diffusion or kinetically controlled.

The *monotonic instability* in this system is possible. It is manifested by an N-shaped fragment of the voltammogram. Its condition for this case is Det J =0, or (20):

$$-(\kappa - \varXi)(2P\varLambda + P\varOmega) = 2\varLambda\varXi P \qquad (20)$$

This model describes the case in which the cathodic reaction, yielding chain initiator, is realized on the surface. If the reaction is realized in the solution, the electrochemical reaction will not be accompanied by oscillatory and monotonic stability, as shown in [13].

4. Conclusions

From the theoretical evaluation of the indirect electrochemical polymerization of an indirectly electrosynthetized monomer, it has been possible to conclude that the indirect electropolymerization of an indirectly electrosynthetized monomer tends to be more stable than the direct electrooxidation of the precursor and the monomer in the same conditions. As for the polymerization, it yields a well-developed macromolecule, with a cabbage-like morphology, centered on an initiator generation active sites. The electrochemical process tends to be either diffusion or kinetically controlled. The conductivity of the polymer depends on either monomer or initiator nature due to the possibility of metal-polymer formation in the case of metal derivative used as an initiator. The oscillatory behavior in this system is possible but less probable than for direct electropolymerization. It is only caused by the double electric layer influences of the electrochemical stage.

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Conflicts of Interest

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