



The Mathematical Description of the Electrochemical Function of Cp-Based Electrochemical Sensors, Based on Isomerizing or Exciting Conducting Polymers

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ABSTRACT

The behavior of CP-based electrochemical sensors, in which the conducting polymer is passing by excited or isomerized state, was analyzed mathematically. The correspondent model was investigated by means of linear stability theory and bifurcation analysis. It was detected that the isomerization (excitation) process may provoke the changes in the structure of double electric layer, capable to cause the oscillatory behavior. The stable steady-state stability depends not only on analyte diffusion and reaction, but also on isomerization (excitation) rate.

Keywords: Conducting polymers; Electrochemical sensors; Isomerization; Excitation; Stable steady-state; Life safety

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.

Nevertheless, the development of new analytical techniques, involving CP-based chemically modified electrodes encounters some difficulties, like:

- Indecision in the most probable mechanism for the modifier electroanalytical action (if it is an active substance, or mediator and in how it acts);
- The possibility of electrochemical instabilities (oscillatory or monotonic), characteristic for the electrooxidation of different organic and inorganic compounds (including the electropolymerization process) [18 – 20], and conducting polymers-based sensing [1 – 10, 20] and capable to give strong impact to analytical signal interpretation;
- The absence of a rigid theoretical base, describing the behavior of the analyte and the modifier.

A mechanistic theoretical investigation, including the development and analysis of a mathematical model, capable to describe the system's behavior, is an interesting manner to resolve all three mentioned difficulties and to predict the behavior of an electroanalytical system *a priori*. It also gives the possibility to compare the behavior of this system with that of similar ones without experimental essays.

Other problem encountered by the research is that some of conducting polymers, used in sensors [21 – 24] may be based on substances, capable to isomerize or excite (like colorants), and even a simple electronic

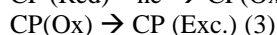
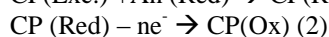
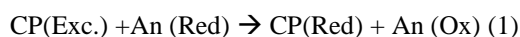
configuration change may be considered an excitation or isomerization. Such a process may give strong impact to the sensor behavior, so the general model, described in [25] for such case, isn't compatible to this type of systems, and the special model is required to be elaborated.

So, the general aim of this work is the theoretical mechanistic investigation of the CP-based sensor, based on isomerizing (exciting) conducting polymer. For this purpose, we resolve the specific objectives:

- Suggest the mechanism for this case;
- Develop and analyze the mathematical model, describing adequately this system;
- Interpret its conclusion, judging of the steady-state stability and possible electrochemical instabilities;
- Compare the behavior of this system with that of other CP- based sensors [25–28].

SYSTEM AND ITS MODELING

The mechanism for this type of CP-based electroanalytical system may be described as:



So, the electrode is reversible, but the cycle is more complicated, than in general case, described in [25 – 28], which will give strong impact on its behavior.

To describe it mathematically, we introduce three variables:

c – the analyte concentration in pre-surface layer;

θ – the coverage degree of the reduced CP form;

θ^* – the coverage degree of the oxidized CP form in ground state.

To simplify the modeling, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also we suppose that the background electrolyte is in excess, so we can neglect the migration flow. The pre-surface layer thickness is assumed to be constant, equal to δ , and the concentration profile of the analyte and the alkali, to be linear.

The analyte enters the pre-surface layer by means of its diffusion and reacts with the excited (isomerized) form of conducting polymer, forming its reduced form. Thus, its balance equation will be described as:

$$\frac{dc}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (c_0 - c) - r_1 \right) \quad (4)$$

in which r_1 is the rate of the reaction (1), c_0 is the analyte bulk concentration, Δ , its diffusion coefficient.

The conducting polymer is reduced from the excited (isomerized) form of its oxidized state, reacting with the analyte, and is then oxidized to form the “ground” form of its oxidized state. Thus, its balance equation will be described as:

$$\frac{d\theta}{dt} = \frac{1}{\Gamma} (r_1 - r_2) \quad (5)$$

in which Γ is the maximal concentration of CP and r_2 the rate of the reaction (2).

The ground-state oxidized form of conducting polymer is formed by the oxidation of its reduced form (reaction (2)) and then is excited (isomerized), by means of the reaction (3). So, its balance equation will be described as:

$$\frac{d\theta^*}{dt} = \frac{1}{\Gamma} (r_2 - r_3) \quad (6)$$

In which, r_3 is the rate of the reaction (3).

The correspondent reaction rates may be calculated as:

$$r_1 = k_1 c (1 - \theta - \theta^*) \quad (7)$$

$$r_2 = k_2 \theta \exp\left(\frac{nF\phi_0}{RT}\right) \quad (8)$$

$$r_3 = k_3 \theta^* \exp\left(\frac{\alpha\phi_0}{RT}\right) \quad (9)$$

in which the parameters k are corresponding reaction rate constants, n is the quantity of transferred electrons, F is the Faraday number, ϕ_0 is the potential slope, referring to zero-charge potential, R is the universal gas constant, T is the absolute temperature and α , the coefficient, describing the excitation (isomerization) effect on DEL.

In general features, the model resembles the analogous ones [25 – 28]. Nevertheless, as the isomerization (excitation) process influences the DEL strongly, it gives the great impact on the system's behavior, making the difference. The relation between this system and the similar ones will be discussed below.

RESULTS AND DISCUSSION

To investigate the behavior of the CP-based sensor, in which the conducting polymer isomerizes (excites), we analyze the equation set (4 – 6) by means of linear stability theory. The steady-state Jacobian functional matrix elements may be calculated as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (10)$$

in which:

$$a_{11} = \frac{2}{\delta} \left(-\frac{\Delta}{\delta} - k_1(1 - \theta - \theta^*) \right) \quad (11)$$

$$a_{12} = \frac{2}{\delta} (k_1 c) \quad (12)$$

$$a_{13} = \frac{2}{\delta} (k_1 c) \quad (13)$$

$$a_{21} = \frac{1}{r} (k_1(1 - \theta - \theta^*)) \quad (14)$$

$$a_{22} = \frac{1}{r} \left(-k_1 c - k_2 \exp\left(\frac{nF\varphi_0}{RT}\right) - jk_2\theta \exp\left(\frac{nF\varphi_0}{RT}\right) \right) \quad (15)$$

$$a_{23} = \frac{1}{r} \left(-k_1 c - pk_2\theta \exp\left(\frac{nF\varphi_0}{RT}\right) \right) \quad (16)$$

$$a_{31} = 0 \quad (17)$$

$$a_{32} = \frac{1}{r} \left(k_2 \exp\left(\frac{nF\varphi_0}{RT}\right) + jk_2\theta \exp\left(\frac{nF\varphi_0}{RT}\right) - jk_3\theta^* \exp\left(\frac{\alpha\varphi_0}{RT}\right) \right) \quad (18)$$

$$a_{33} = \frac{1}{r} \left(pk_2\theta \exp\left(\frac{nF\varphi_0}{RT}\right) - k_3 \exp\left(\frac{\alpha\varphi_0}{RT}\right) - jk_3\theta^* \exp\left(\frac{\alpha\varphi_0}{RT}\right) \right) \quad (19),$$

in which j and p are parameters, describing the relation between the DEL potential and electrode coverage.

Taking in account the expressions (11), (15) and (19), it is possible to see, that they contain positive elements, describing the positive callback. Thus, the oscillatory behavior for this system is possible. Moreover, it is more probable, than for the common case of CP-based sensors [25 – 28], due to the influence of isomerization (excitation) process.

The Jacobian main diagonal contains three positive elements against one for the common case:

$-jk_2\theta \exp\left(\frac{nF\varphi_0}{RT}\right) > 0$, when $j < 0$, and $pk_2\theta \exp\left(\frac{nF\varphi_0}{RT}\right) > 0$, when $p > 0$ which describes strong influences of the electrooxidation to the DEL capacitances. This factor is also characteristic for systems like [25 – 28], but in this system it is expressed more intensively.

$-pk_3\theta^* \exp\left(\frac{\alpha\varphi_0}{RT}\right) > 0$, when $p < 0$, describes strong influences of isomerization (excitation) to the DEL capacitances.

The coactions of two factors make the oscillations' frequency and amplitude dependent on the solution composition, but, in general, the oscillations have to be frequent and of little amplitude.

The *steady-state stability* in this system is seriously influenced by the CP isomerization.

To apply the Routh-Hurwitz criterion without operating cumbersome expressions, we introduce new variables, for the Jacobian determinant to be described as:

$$\frac{2}{\delta r^2} \begin{vmatrix} -\kappa_1 - X_1 & \Lambda & \Lambda \\ X_1 & -\Lambda - Y & -\Lambda - \Pi \\ 0 & \Sigma - \Xi & \Pi - \Sigma \end{vmatrix} \quad (20)$$

Resolving the inequation $\text{Det } J < 0$, we obtain the steady-state stability requirement, described as:

$$(-\kappa_1 - X_1)(-\Lambda\Pi - Y\Pi + \Lambda\Sigma + Y\Sigma + \Sigma\Lambda + \Sigma\Pi - \Xi\Lambda - \Xi\Pi) + X_1\Lambda(2\Sigma - \Xi - \Pi) < 0 \quad (21)$$

It is possible to prove, that, in the case of the positivity of the electrooxidation parameter Y and the negativity or (in some cases) nullity of the electrooxidation and isomerization parameters Π , Σ and Ξ , defining the fragility, or absence of DEL influences of electrochemical and isomerization (excitation) processes, the inequation (21) will be satisfied, and the steady-state will be stable. The steady-state stability is related with the linear part of electrochemical parameter – concentration curve. The stability zone for this case continues being vast, so the sensor is sensible.

The reaction is, generally, diffusion-controlled. But in high analyte concentrations it may be reaction-controlled and excitation controlled (because isomerization is, generally, a slow reaction). It is possible to join the obtained results in a table

Concentration	Diffusion	Reaction	Isomerization (Excitation)
Low	Slow	Rapid	Rapid
High	Rapid	Slow	Slow

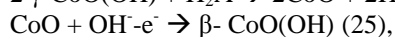
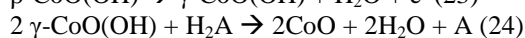
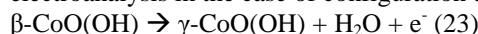
The *monotonic instability*, manifested by N-shaped voltamperogram part, for this system is possible. It is correspondent to the steady-state stability margin. Its condition is:

$$(-\kappa_1 - X_1)(-\Lambda\Pi - \Upsilon\Pi + \Lambda\Sigma + \Upsilon\Sigma + \Sigma\Lambda + \Sigma\Pi - \Xi\Lambda - \Xi\Pi) + X_1\Lambda(2\Sigma - \Xi - \Pi) = 0 \quad (22)$$

In this point the stable steady-states change themselves to unstable. It is correspondent to the detection limit.

Autocatalysis in this system may be possible (being more probable on the stage of electrochemical reaction). For this case, the model will be altered, as described in [25 – 28]. The oscillatory behavior will be caused by one more factor.

The *analogous systems* are also characteristic for inorganic modifiers. For example, for CoO(OH)-assisted electroanalysis in the case of configuration transformation:



and this model (with some corrections made) is also capable to describe these types of systems, which confirms the third theorem of similarity.

CONCLUSIONS

From the mechanistic investigation of the CP-based electrochemical sensors with the isomerization (excitation) of the polymer, it is possible to conclude that:

- The oscillatory behavior for this case is possible, being even more probable, than for general case of CP-based electrochemical sensor. It may be caused not only by DEL-influences of electrochemical reaction, but also by that of isomerization, or excitation.
- The steady-state stability is warranted by the fragility of DEL-influences of electrochemical reaction and isomerization. The topological stability zone is vast, and the sensor is very sensitive.
- The process is, in general, diffusion-controlled, but in high analyte concentration it may be also electrochemical reaction and isomerization-controlled.
- The monotonic instability for this system is possible. It defines the steady-state stability margin.
- The present model is capable to describe not only the present system, but also the analogous systems, including the inorganic substances. It confirms the third theorem of similarity.
- For the present model to be capable to describe exactly the behavior of autocatalyzing systems, adequate changes may be made.

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