

Full Paper

The Mathematical Stability Study of the Work of Isomerization Sensors, based on Conduction Polymers

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Received: 13 February 2014 / Received in Revised form: 10 June 2014 /

Accepted: 12 June 2014 / Published online: 30 June 2014

Abstract- The isomerization control, provided by a conducting polymer (CP) based electrochemical sensing coating, was described phenomenologically and mathematically (by using the linear stability theory and bifurcation analysis). The steady-state stability requirements and oscillatory and monotonic instabilities´ conditions were derived from the differential equation system analysis. The changes in model for different cases also were presented.

Keywords- Isomerization, Kinetic control, Conducting polymers, Electrochemical sensors, Linear stability theory

1. INTRODUCTION

Isomerization, as the reaction, in which one substance is converting to another, with the same atomic composition, but different structure, is a common phenomenon for many systems, generally in organic chemistry [1-3], being caused by different factors (the presence of different compounds, photocatalysis, electrocatalysis, etc). It may be realized by migration of electrons, atoms and functional groups. The isomerization reaction is usually of the first order.

The isomers' properties may be similar, but in many aspects they are different, because of the difference in their chemical structure, for example, salicylic acid is stronger, than its isomer and 4-aminoacridine is weaker base, than its 9-isomer.

Isomerization is the base of many processes to occur *in vivo* and *ex vivo*. So, the isomerization sensing is very important, because it can provide the kinetic control of this process (detect the quantity of the isomer formed, the isomerization velocity).

On the other hand, the conducting polymers, being one of the most studied compounds during the last 5 decades, attract more and more attention, because they are capable to combine the plastics' properties with the conductivity of metals and are modifiable by simple way [4-23]. The mentioned properties give them the vast and rich spectrum of use, beginning with the corrosion protective coating [9-12] and ending with sensors and biosensors [15-23] of different types. These sensors may be based not only on conducting polymers, but also on their composites.

The CP-based sensors may be of different types of action, and conducting polymer coating may play different role in them. In the direct electron transfer sensors, the coating plays the role of the active substance, according to the work scheme (Fig. 1):

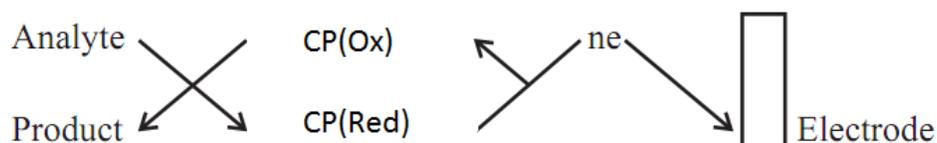


Fig. 1. The direct electron transfer CP-based electrochemical sensor function scheme

In this case, the conducting polymer molecule is modified by the functional group, capable to react specifically with the analyte. In general, the first reaction isn't oxy-reductive (although, for easy description, it's shown so on the scheme).

In the mediated transfer electrochemical sensors, the polymer coating plays the role of the mediator between the active substance (for example the fragment of enzyme) and transductor (electrode), according to the Fig. 2:



Fig. 2. The mediated electron transfer CP-based electrochemical sensor function scheme

In this case, the active substance may be entrapped, doped (accumulated) in the CP matrix or adsorbed over the coating. As it was shown experimentally [24] (being also possible to be

confirmed by means of mathematical modeling), in the last case the oxidation of the analyte is more efficient.

Both strategies may be used to construct the isomerization electrochemical sensors, based on conducting polymers, because the CP coatings are capable to separate isomers' oxidation signals, which may coincide on bare electrodes. In the first case, the scheme will be modified as:

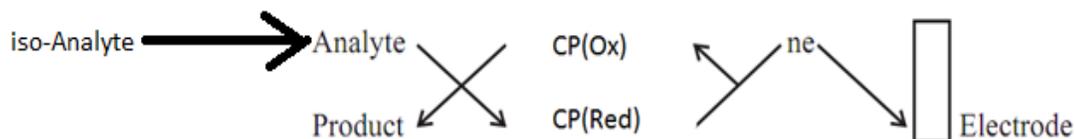


Fig. 3. The direct transfer CP-based electrochemical isomerization detecting scheme

The present scheme, valid for the case of the absence of the reaction between the initial isomer and conducting polymer, of the absence of the reaction between isomers and of the direct electron transfer may be considered the most simple scheme of CP-based isomerization detector.

The practical examples of such sensors may be:

- enantio-selective polymer-based sensors, based on signal separation of isomers, like [25], or on a specific reaction (mentioned in, for example [20]);
- the tautomer indicators, applicable for keto-enol tautomerism, based on polymers, substituted with functional groups, capable to react separately with one or another form (like the mentioned in the revision articles), which is suitable for the compounds in which both forms are stable.

Fortunately, the conducting polymer coatings are capable to separate the isomers' signals, which may coincide on bare electrodes, so it is possible to use the sensor on their base to detect the possible isomerization.

The phenomenological description of the sensing process, described above, may have satisfactory logical explanation, but a rigid mathematical base could make it more fundamental. It may be given by the mathematical model, capable to describe adequately the processes in the system. Moreover, the mathematical model is capable to give the exact requirements for the parameter region, in which the sensor gives the most precise results (steady-states' stability region) and the exact causes for different electrochemical instabilities, capable to accompany the detection process (not for one concrete system, but for series of similar systems). It's also licit to mention the prognostic function of mathematical modeling, giving the possibility to predict the behavior of the sensors that haven't designed yet.

The goal of our work is to develop and to analyze the mathematical model, capable to describe the system with the electrochemical isomerization direct transfer detector, based on specifically modified conducting polymer. This research gives the important information for the comprehension of the detection mechanism and to its detailed description.

We have already made some efforts to describe the behavior of different CP-based electrochemical sensors in different media [26-34]. So this work is the continuation of our research of the mathematical description of the CP-modification and its use in electrochemical sensors and biosensors.

2. SYSTEM AND ITS MODELING

For the modeling of the work of the isomerization CP-based direct electron transfer electrochemical sensor in potentiostatic mode (as in Fig. 3), we introduce three variables:

c_{iso} – the concentration of initial isomer in the pre-surface layer;

c – the concentration of the resulting isomer in the pre-surface layer;

θ – the coverage degree of the modified conducting polymer.

To simplify the modeling, we suppose that the reactor is stirred intensively, so we can neglect the convection flow, the background electrolyte is in excess, so we can neglect the migration flow, the diffusion layer concentrational profile is supposed to be linear and the layer thickness to be constant and equal to δ . Also we suppose that the solution *ab initio* is free of the resulting isomer and that the initial isomer doesn't react with the conducting polymer.

The isomerization used in the model may be not only simple electron migration, but also a more complicated migration process (in the case of the excess of the catalyzing substance). The initial isomer enters the pre-surface layer by diffusion and disappears by isomerization, so, taking in account the Fick's first law, the balance equation will be represented as:

$$\frac{dc_{iso}}{dt} = \frac{2}{\delta} \left(\frac{D}{\delta} (c_{iso0} - c_{iso}) - r_1 \right) \quad (1)$$

In which D is the diffusion coefficient, c_{iso0} is the initial isomer concentration in the bulk, r_1 is the isomerization rate, which is calculated as

$$r_1 = k_1 c_{iso} \quad (2)$$

in which k_1 is the isomerization rate constant.

The resulting isomer appears by isomerization and disappears reacting with the modified conducting polymer, so its balance equation will be represented as:

$$\frac{dc}{dt} = \frac{2}{\delta}(r_1 - r_2) \quad (3)$$

In which r_2 is the specific reaction rate that may be calculated as:

$$r_2 = k_2 c(1 - \theta) \quad (4)$$

in which k_2 is the specific reaction rate constant.

In the equations (1) and (3), the fraction $\frac{2}{\delta}$ is the modeling coefficient, referring to the bimolecular sub-layer, corresponding to double electric layer (DEL).

The conducting polymer is modified by the specific reaction and the modified form is transformed on the electrochemical stage, so the balance equation may be represented as:

$$\frac{d\theta}{dt} = \frac{1}{\Gamma_{max}}(r_2 - r_3) \quad (5)$$

in which Γ_{max} is the maximal surface concentration of the modified conducting polymer, r_3 is the electrochemical reaction rate, that can be calculated as:

$$r_3 = k_3 \theta \exp\left(\frac{zF\phi_0}{RT}\right) \quad (6)$$

in which k_3 is the electrochemical rate constant, z is the quantity of electrons transferred, $F = N_A \cdot e$, ϕ_0 is the potential slope, relative to the zero-charge potential, R the universal gas constant and T the absolute temperature.

3. RESULTS AND DISCUSSION

The behavior of this system will be investigated by linear stability theory. Jacobian functional matrix stationary elements for the differential equations' system (1, 3, 5), taking in account the equations (2, 4, 6) will be written 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:

$$a_{11} = \frac{\partial F_1}{\partial c_{iso}} = \frac{2}{\delta} \left(-k_1 - \frac{D}{\delta} \right) \quad (8)$$

$$a_{12} = \frac{\partial F_1}{\partial c} = 0 \quad (9)$$

$$a_{13} = \frac{\partial F_1}{\partial \theta} = 0 \quad (10)$$

$$a_{21} = \frac{\partial F_2}{\partial c_{iso}} = 0 \quad (11)$$

$$a_{22} = \frac{\partial F_2}{\partial c} = \frac{2}{\delta} (-k_2(1 - \theta)) \quad (12)$$

$$a_{23} = \frac{\partial F_2}{\partial \theta} = \frac{2}{\delta} (k_2 c) \quad (13)$$

$$a_{31} = \frac{\partial F_3}{\partial c_{iso}} = 0 \quad (14)$$

$$a_{32} = \frac{\partial F_3}{\partial c} = \frac{1}{\Gamma_{max}} (k_2(1 - \theta)) \quad (15)$$

$$a_{33} = \frac{\partial F_3}{\partial c} = \frac{1}{\Gamma_{max}} \left(-k_2 c - k_3 \exp\left(\frac{zF\phi_0}{RT}\right) - k_3 \theta \alpha \exp\left(\frac{zF\phi_0}{RT}\right) \right) \quad (16)$$

In which α is the coefficient, describing the dependence between ϕ_0 and θ , representing the influence of the electrochemical stage on DEL. It may be calculated from the capacitances of the parts of DEL as plain condenser.

The nullity of the elements a_{12} , a_{13} , a_{21} and a_{31} is caused by the absence of any reaction between the initial isomer, resulting isomer and conducting polymer.

To simplify the Jacobian, we introduce new variables, describing the influence of the main parameters on the system, so it will be rewritten as:

$$\frac{4}{\delta^2 \Gamma_{max}} \begin{vmatrix} -\kappa - k_1 & 0 & 0 \\ 0 & -X & \theta \\ 0 & X & -\theta - \Omega \end{vmatrix} \quad (17)$$

Using the Routh-Hurwitz steady-state stability criterion, described in [34-35] that may be rewritten as

$-\text{Det } J > 0$, we obtain the steady-state stability requirement as:

$$X\Omega(\kappa + k_1) > 0 \quad (18)$$

As the parameters X (first specific isomer reaction parameter, the second one, θ , disappears while the transition from (17) to (18)), κ (initial isomer diffusion parameter) and k_1 (isomerization rate constant, already mentioned) are always positive, the steady-state will be stable in the case of the positivity of the electrochemical reaction parameter Ω . Observing attentively the parameter Ω ,

$$\Omega = k_3 \exp\left(\frac{zF\phi_0}{RT}\right) + k_3 \theta \alpha \exp\left(\frac{zF\phi_0}{RT}\right) = k_3 \exp\left(\frac{zF\phi_0}{RT}\right) (1 + \theta \alpha) \quad (19)$$

We can simplify the stable steady-state condition to

$$1 > -\theta\alpha \quad (20)$$

That corresponds to the absence of the influences on DEL of the electrochemical reaction (in the case of the positivity of α) and, if it is characteristic to the system, to its fragility, comparing to the influence of the interaction between conducting polymer and transducer (in the case of the negativity of α). This condition is corresponding to the parameter region of linear dependence between electrochemical parameter and concentration and this region is vast, so we can affirm that, in theory, the CP-based isomerization detector in the conditions, described above, is exact.

A more profound steady-state stability analysis may give more information about the reaction control in the system. In general, three different experimental cases are capable to be observed in real isomerization sensing systems (as in the Table 1):

Table 1. The reaction rates' relations in real isomerization detective systems

Diffusion	Isomerization	Specific reaction
Slow	Rapid	Rapid
Rapid	Slow	Rapid
Rapid	Rapid	Slow

depending on reactions' kinetics and the concentrations of the substances (it is the factor that makes even a relatively slow reaction become rapid, as, for example, in [24] for the low methanol concentration). These factors are decisive for the system to choose the most stable of steady-states (stable or not) and the correlation between modeling and experimental observations are rejoined in table 2 (the lines corresponding to the table 1):

Table 2. The correlation between modeling and experiment

κ	k_1	X
Low	High	High
High	Low	High
High	High	Low

Putting in the values of constants, concentrations and reaction rates for concrete sensing system and using the expressions (8–16), we may know the details of its behavior in different analyte concentrations.

In the case of the equality of the influences of the electrochemical reactions on DEL, the monotonic instability occurs.

$$1 = -\theta\alpha \quad (21)$$

It is revealed on the N-shaped parts of voltamperograms and defines the saddle-node bifurcation (measure between the stable steady-states (stable node) and unstable states (saddle)). In this point the system exists in the multiplicity of the steady-states (each of them is unstable), choosing only one, that is destroyed by changing the reaction condition.

The oscillatory behavior occurs only (but not necessary) in the case of the presence of the positive elements in the Jacobian main diagonal (describing the positive callback). The only element, capable to be positive is $-\Omega$, in the case of

$$1 < -\theta\alpha \quad (22)$$

Which only may succeed, if α is negative, describing the influence of DEL of the electrochemical reaction on the third stage. This is the general case for the oscillatory behavior in all the systems with the use of the CP-based electrochemical sensors [25-33].

3.1. The case of autocatalytic stages

In the case of the autocatalysis on stage 1 (that is relatively rare case for an isomerization), the model is modified. The isomerization rate is described as:

$$r_1 = k_1 c_{iso} c \quad (23)$$

The Jacobian elements a_{12} and a_{21} are not equal to nil in this case, the element a_{22} is also changed:

$$a_{22} = \frac{\partial F_2}{\partial c} = \frac{2}{\delta} (k_1 c_{iso} - k_2 (1 - \theta)) \quad (24)$$

Giving the possibility of one more positive addendum in Jacobian main diagonal and one more cause for the oscillatory behavior, that is the autocatalytic isomerization.

3.2. The cause of the presence of the resulting isomer

The addendum, referring to the diffusion of the second isomer appears in the equation (3). The diffusion of the second isomer influences, in that case, the steady-states' stability.

4. CONCLUSIONS

The steady-states' stability in the systems with the CP-based electrochemical isomerization detectors is defined by the electrochemical stage and its influence on DEL. The increasing of the influence on DEL, relative to the interaction between the film and the electrode surface, leads the steady-state to its instability.

As the parameter region, corresponding to the steady-states' stability (linear dependence between electrochemical parameter and concentration), is vast, the CP-based isomerization detector may be used in the vast isomer concentration range with excellent response. The relation of the parameters' values may also define the most probable behavior for the concrete case in the concrete sensing system.

The equality of the influences of the electrochemical reaction on DEL and on electrode surface provokes the appearance of the monotonic instability.

The presence of time dissipative structure in the described systems has been confirmed. The oscillatory behavior may be caused by the influence of the electrochemical reaction on DEL and by autocatalytic stages (if any).

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