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MATHEMATICAL MODEL OF THE WORK OF THE MEDIATED CONDUCTING POLYMER SENSORS WITH THE USE OF THE POLYMERS OF HETEROCYCLIC COMPOUNDS

V, V. Tkach*, V. V. Nechyporuk, P. I.Yagodynets' e Yu. V. Meslyuk

ABSTRACT

The work of the mediated electrochemical sensors and biosensors with the use of polyheterocyclic compounds as mediators was mathematically described. Using the linear stability theory and bifurcation analysis we show, that the electrochemical oscillatory instabilities during the sensing act can be caused by changes in double electric layer (DEL) during the electrochemical oxidation of the reduced form of the mediator (which is based on polyheterocyclic compound). The stable steady-state conditions were found by using of Rauss-Gurwitz criterium. The critical value of the rate of the first chemical stage, for which the monotonic instability is possible, was also derived from general conditions.

Key words: Conducting polymers, electrochemical sensors, electrochemical instability, stable steady-state, oscillations.

RESUMEN

La función de los sensores y biosensores electroquímicos con el uso de los compuestos poliheterocíclicos como los mediadores fue descrita matemáticamente. Usando la teoría de la inestabilidad linear y análisis de bifurcaciones mostramos que las inestabilidades oscilatorias durante el acto de la detección pueden ser causadas por los cambios en la camada eléctrica dobla (CED) durante la oxidación electroquímica de la forma reducida del mediador (que es el compuesto poliheterocíclico). Las condiciones del estado estacionario estable fueron encontradas a través del criterio de Rauss y Gurwitz. El valor crítico para la velocidad de la primera etapa química, para el cual la instabilidad monotónica es posible, también fue derivado de las condiciones generales.

Palabras clave: Polímeros conductores, sensores electroquímicos, inestabilidad electroquímica, estado estacionario estable, oscilaciones electroquímicas.

INTRODUCTION

Electroanalytic chemistry being one of the most important branch of chemical sciences, that uses the investigations of electrochemistry in analytic purposes, attracts more and more scientists. Nowadays one of the main directions of electroanalytical investigation is the application of electrochemical methods of analysis in nanosensing and biosensing.

Among the electrochemical sensors being in use the conducting polymer sensors (CPS) of different scale and purpose of use have been gained more and more popularity because they are easily to be modified, the electrochemical signal is more or less clear and can be easily interpreted[1-4].

The conducting polymers can be used as active sensing compounds[2,3,4], catalysts, as well as mediators[1,3-6]. We may give the biosensor excellent selectivity if we modify it properly. One

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[*] 58012, Ukraine, Chernivtsi, Kotsyubyns'ky Str. 2., Chernivtsi National University.
Contact e-mail - nightwatcher2401@gmail.com

can modify the conducting polymers in sensing purposes by:

- Enzyme adsorption over the polymeric surface
- Chemical functionalization (it's possible to funcionalyze the either the polymer (yet synthetized) or the monomer (modifying it before the electropolymerization).
- Immobilization of the compound capable to implement the sensor functions (by doping[5,6] or entrapment[1]).

For example, the review article[3] describes the different types of polypyrrole-based electrochemical biosensors. One of examples of them, described in[3] were the PQQ-modified sensors with and without mediation.

The article[5] describes the direct electron transfer from GOx immobilized on polyphenantroline-modified glassy carbon electrode. The obtained sensor showed excellent selectivity on glucose and functioned as "direct response type" glucose biosensor.

The thesis[6] and the references within describe the preparation (either chemical or electrochemical) of sensitive modified golden and polypyrrole electrodes, capable to recognize the complementary sequences.

The thesis[1] indicates the practical use of the polythiophenes with bio-object entrapped in sensing. Sometimes overoxidized CP are used in sensing.

Nowadays the purpose of the CPS investigation is to find the cheap sensing electrodes capable to recognize selectively the specific compounds.

But sometimes, the sensing process may be undergone by some electrochemical instabilities. Sometimes their presence is important, because it shows the processes of the change in the resistance, caused by the formation or spending of some intermediate compounds; but in practice they are unnecessary. To find their conditions and the mechanisms of their appearance we describe mathematically the work of this sensor and analyze its mathematical model using the linear stability theory and bifurcation analysis.

We have already made an effort to describe mathematically the work of some types of CP sensor coatings obtained by electrochemical polymerization of heterocyclic compounds (for example, PQQ-modified unmediated CPS)[7]. Now our goal is to describe the work of the mediated CPS in which the conducting polymer plays the role of the mediator.

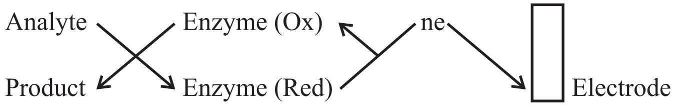
Finding of the stable and unstable steady-state conditions is necessary to find the parameter values in which the sensor function is better interpreted and so we can predict the working parameter values of the sensor.

THE SENSOR AND ITS MODELING

In this work we describe the sensor, that consists of active site of the enzyme (reacting with analyte), mediator (the medium link in the sensing process) and transducer (inert anode) .

One of the best examples of such sensors can be CP-mediated enzyme biosensor.

Enzyme is adsorbed over the CP matrix. In the cause of [6] the enzyme fragment was covalently attached to the CP molecule, so the sensor didn't need the mediator.



Now the sensing process consists of 3 stages.

1) The analyte oxidation

Analyte + Enz (ox) → Enz (red) + Product (chemical)

2) The oxidation of the reduced form of the enzyme:

Enz (red) + Med (ox) → Enz (ox) + Med (red) (chemical)

3) The electrochemical oxidation of the reduced form of the mediator:

Med (red) - ne^- → Med (ox) (electrochemical)

The conducting polymer in this sensing system implements the function of the mediating of the electron transfer between the reacting system (Analyte and enzyme) and the electrode. The work of this sensor will be described in potentiostatic mode.

To describe its work we use 3 variables:

C – the analyte concentration in pre-surface layer;
E – the surface concentration of the reduced form of the adsorbed enzyme
M – the surface concentration of CP mediator in reduced form.

To simplify the modeling we suppose that:

- The system is stirring intensively, so we can neglect the convective flow.
- The background electrolyte is in excess, so we can neglect the migration flow.
- The concentration profile in pre-surface layer is supposed to be linear and equal to δ.
- The thickness of the enzyme and polymer layers is supposed to be equal to the thickness of one molecule (as in ultrathin sensors and nanosensors).
- The chemical reactions are supposed to be of the 1st order for each substance.
- The enzyme orientation favours the diffusion and the electron transfer.

The analyte in the pre-surface layer

The analyte enters the pre-surface layer diffusing into it and turns to a product oxidizing itself on the 1st stage. So the balance equation for the analyte concentration in pre-surface layer will be described as:

$$\frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_b - c) - r_1\right) \equiv F_1$$

In which Δ stands for the diffusion coefficient, c_b stands for analyte bulk concentration and r_1 stands for the 1st stage rate.

The enzyme reduced form

Is forming itself during the analyte oxidation and oxidizes itself reacting with the mediator. So, the balance equation for the reduced form of enzyme can be described as:

$$\frac{dE}{dt} = r_1 - r_2$$

In which r_2 is the second stage rate.

We can rewrite this equation using the degree of coverage. So, the balance equation for the degree of coverage of the reduced form of enzyme is:

$$\frac{d\varepsilon}{dt} = \Gamma^{-1}{}_{\max 1}\left(r_1 - r_2\right) \equiv F_2$$

In which $\Gamma_{\max 1}$ is the maximally possible surface concentration of the reduced form of the enzyme on the polymer matrix. In this case we can understand θ as the reduction degree of the adsorbed enzyme, playing the role of the active site of the enzyme.

The concentration of the reduced form of the mediator

The chose of the CP, its synthesis and modification methods is provided by its function. The chosen CP has to implement the function of the mediator: It has to contain functional groups capable to oxidize the reduced form of the enzyme and capable to be oxidized electrochemically in work potential range (in this system in work potential) to form the oxidized form. The reduced form of the CP is formed by the 2nd stage and oxidizes itself electrochemically (finishing the electron transfer in sensing system) on the electrode surface. So the balance equation for the concentration of the reduced form of the mediator.

$$\frac{dM}{dt} = r_2 - r_3$$

In which r_3 is the electrochemical stage rate.

If we rewrite this equation, using the degree of coverage (or, to be more exact, the reduction degree of the mediator) μ:

$$\frac{d\mu}{dt} = \Gamma^{-1}{}_{\max 2}\left(r_2 - r_3\right) \equiv F_3$$

In which $\Gamma^{-1}{}_{\max 2}$ is the maximal surface concentration of the reduced form of the mediating CP over the metal surface.

$$r_1 = k_1 c(1-\varepsilon)\,;\quad r_2 = k_2\varepsilon(1-\mu)\,;\quad r_3 = k_3\mu\exp\left(-\frac{zF}{RT}\phi_0\right)$$

In which k_1, k_2 and k_3 are the unit rates of respective processes, z is the quantity of electrons transferred during the sensing process, F is the Faraday number ($F = N_A{*}e$), R is universal gas

constant, T is absolute temperature, φ_0 is the potential slope in DEL relatively to the zero-charge potential.
The electrode charge consists of the charge of the oxidized and reduced part of the surface:

$$Q = K_1(\varphi_0 - \varphi_1)\mu + K_0\varphi_0(1-\mu)$$

In which φ_1 is the potential slope between the parts of DEL, corresponding to the oxidized and reduced part of surface respectively, K_1 and K_0 describe the integral capacities of the respective parts of DEL.
So, the potential slope value depends of the mediator reduction degree and the derivative of the respecting function can be described as:

$$\frac{\partial \phi_0}{\partial \mu} = \frac{\phi_0(\mathrm{K}_0 - \mathrm{K}_1) + K_1\phi_1}{\mathrm{K}_1\mu + \mathrm{K}_0(1-\mu)}$$

RESULTS AND DISCUSSION

We describe the behavior in this system using the linear stability theory. The Jacobi functional matrix for this system can be described as:

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

In which:

$$a_{11} = \frac{\partial F_1}{\partial c} = \frac{2}{\delta}\left(-k_1(1-\varepsilon) - \frac{\Delta\alpha_1}{\delta}\right) \qquad a_{12} = \frac{\partial F_1}{\partial \varepsilon} = \frac{2}{\delta}k_1 c \qquad a_{13} = \frac{\partial F_1}{\partial \mu} = 0$$

$$a_{21} = \frac{\partial F_2}{\partial c_r} = \Gamma^{-1}_{\max 1}\left(k_1(1-\varepsilon)\right) \qquad a_{22} = \frac{\partial F_2}{\partial \varepsilon} = \tilde{A}^{-1}_{\max q}\left(-k_1 c - k_2(1-\mu)\right)$$

$$a_{23} = \frac{\partial F_2}{\partial \mu} = \tilde{A}^{-1}_{\max 1}\left(k_2\varepsilon\right)$$

$$a_{31} = \frac{\partial F_3}{\partial c} = 0 \qquad a_{32} = \frac{\partial F_3}{\partial \varepsilon} = \tilde{A}^{-1}_{c,\max}\left(-k_2(1-\mu)\right)$$

$$a_{32} = \frac{\partial F_3}{\partial \mu} = \tilde{A}^{-1}_{c,\max}\left(-k_2\varepsilon - k_3\exp\left(-\frac{zF}{RT}\phi_0\right) - k_3\mu\exp\left(-\frac{zF}{RT}\phi_0\right)\frac{\phi_0(\mathrm{K}_0 - \mathrm{K}_1) + K_1\phi_1}{\mathrm{K}_1\mu + \mathrm{K}_0(1-\mu)}\right)$$

Stable steady-state condition

The characteristic equation of this system will be described as

$$l^3 + Al^2 + Bl + C = 0$$

in which

$$A = -(a_{11} + a_{22} + a_{33})$$

$$B = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} + \begin{vmatrix} a_{11} & a_{32} \\ a_{31} & a_{33} \end{vmatrix} + \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix}$$

$$C = -\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$$

To investigate the linear stability of this system we use the Rauss-Gurwitz critetium. It requires the main diagonal minors of Gurwitz matrix

$$\begin{pmatrix} A & 1 & 0 \\ C & B & A \\ 0 & 0 & C \end{pmatrix}$$

to be positive for stable steady-states. The members of the principal diagonal:

$$\Delta_1 = A,\ \Delta_2 = \begin{vmatrix} A & 1 \\ C & B \end{vmatrix},\ \Delta_3 = \begin{vmatrix} A & 1 & 0 \\ C & B & A \\ 0 & 0 & C \end{vmatrix}$$

We can see that $\Delta_3 = C\Delta_2$, so the the stability condition will be described as C>0. Applying it to concrete sensor systems, we can calculate the concrete conditions of the stable steady-state. To make the Jacobian more compact, we introduce the next variables

$$-k_1\alpha_2(1-\varepsilon) = f\ ;\ \frac{\Delta}{\delta} = \kappa;\ k_1c = g;\ k_2(1-\mu) = h;\ k_2\varepsilon = s;$$

$$k_3 \exp\left(-\frac{zF}{RT}\phi_0\right) = u;\ k_3\mu \exp\left(-\frac{zF}{RT}\phi_0\right)\frac{\phi_0(\mathrm{K}_0 - \mathrm{K}_1) + K_1\phi_1}{\mathrm{K}_1\mu + \mathrm{K}_0(1-\mu)} = v;\ w = u + v;$$

It's obvious, that f is always negative, κ, g, h, s and u are always positive. The variable v can possess either positive or negative values and they depend on the system.

As the matrix members a_{13} and a_{31} in this case are equal to nil, the finding of the stable steady-state condition becomes more easy and so we can rewrite the stable steady-state condition as

$$fsw > \kappa(gs + gw + wh)$$

These parameter values correspond to the best sensor response. We can conclude, that the stability of the steady-state in this system is controlled mostly by the reaction of the first stage, by diffusion and by the rate of electrochemical stage.

The oscillatory instability
Realizes itself if the Hopf bifurcation conditions. To find the oscillatory points it's necessary to resolve the equation:

$$\frac{B_3}{B_1} - B_2 = 0$$

In which B_1 = -A; B_2= B; B_3= -C, and the necessary condition is B_2>0.
This necessary condition realizes itself if the principal diagonal of Jacobi matrix contains the positive addendums (that describe the positive callback). We can see, that the addendum

$$-k_3\mu \exp\left(-\frac{zF}{RT}\phi_0\right)\frac{\phi_0(\mathrm{K}_0 - \mathrm{K}_1) + K_1\phi_1}{\mathrm{K}_1\mu + \mathrm{K}_0(1-\mu)}$$

can be positive if φ_0 is negative (which succeeds during the electrochemical oxidation of strong reducents that possess dipole moment). The more strong reducent is analyte, the less is φ_0 (the potentials of three ORP are in the same potential range).
The oscillatory cycle forms itself due to the cyclic change of the surface conductivity. It changes during the chemical reactions and returns to t initial value after the electrochemical stage. This cycle repeats as the analyte is present in this system, so the oscillatory behavior in these systems is important.

The monotonic instability
In this system is also possible. Its conditions can be defined as Tr J<0, Det J =0. As the condition Tr J <0 realizes for the majority of the systems, we can pay attention to the main condition Det J = 0. It realizes in the conditions of

$$f = \frac{\kappa(gs + gw + wh)}{ws}$$

In this point in this system exist the multiple steady-states, from which the system chooses one only and it destroys itself if the conditions change. The monotonic instability succeeds in the critical value of the first stage rate.

CONCLUSIONS

- The work of the mediated electrochemical sensors and biosensors, based on CPs, in potentiostatic mode was mathematically described. The mathematical model was analyzed using the linear stability theory and bifurcation analysis

- The stable steady-state condition can be found by using Rauss-Gurwitz criterion. The stability of steady-states is mostly controlled by analyte diffusion, the first stage and electrochemical stage.
- The oscillatory instability in this system can succeed if the analyte is strong reducent.
- The monotonic instability for this system is also possible in the critical value of the first stage rate, which can be derived from general conditions.

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