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Theoretical Description for the Electrochemical Determination and Retention of Heavy Metals over the Overoxidized Polypyrrole by Complex Formation

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Abstract: An interesting electrochemical potentiodynamic amperometric heavy metal concentration monitoring system based on overoxidized polypyrrole has been proposed. A model describing the electrochemical behavior in potentiostatic mode of the system with metal complex oxidation during the formation has been developed and analyzed using linear stability theory and bifurcation analysis. It has been shown that the oscillatory behavior may occur more probably in this system than in similar ones due to the cyclical electrode surface impedance change during the chemical and two electrochemical stages. Nevertheless, this system may be efficient for heavy-metal concentration monitoring *in vitro* and *in vivo*.

Keywords: heavy metal cations; electrochemical sensor; overoxidized polypyrrole; electrochemical oscillations; stable steady-state.

1. Introduction

Heavy metal poisoning is one of the most problematic questions in toxicological and ecotoxicological investigations [1-7]. The monitoring of heavy metal concentration, like recycling and elimination, is of special concern due to their toxic effects, penetration via the food chains and persistence in the environment. Moreover, the chelating heavy metal cation concentration in the organism may be an important stress marker. Therefore, the development of a monitoring system for heavy-metal concentration, like their elimination from the environment, remains actual. The electroanalytical systems would serve as an interesting solution for this task [8–10].

On the other hand, polypyrrole [11–15] is one of the most used conducting polymers. It can combine the properties of plastics with metal conductivity and provide flexibility in modification and use. Although the overoxidized polypyrrole diminishes its conductivity, it becomes able to interact with chelating metal cations, yielding complex compounds, which is very important for metal concentration monitoring.

Nevertheless, the development of a new electroanalytical method, especially involving chemical and electrochemical stages, requires an a priori mechanistic theoretical analysis of the system's behavior, providing us the resolution of different kinetic and thermodynamic problems, including the branched mechanism for the electroanalytical process, oscillatory and monotonic instabilities, characteristic for the similar systems [16–22]. So, this work aims to continue the investigation of the possibility of heavy-metal cations determination and removal over an overoxidized conducting polymer coating. This aim will be achieved by developing and analyzing the correspondent mathematical model linked to the reaction mechanism. Also, the behavior of this system will be compared with that of similar ones [23 – 28].

In this case, a potentiodynamic constant-voltage mode behavior of this sensor will be described.

2. Materials and Methods

2.1. System and its modeling.

Herein, an interesting method for heavy metal electrochemical monitoring systems has been suggested and theoretically described. By this, a heavy metal chelating cation reacts with the overoxidized or specially modified conducting polymer, yielding a complex (Fig. 1).

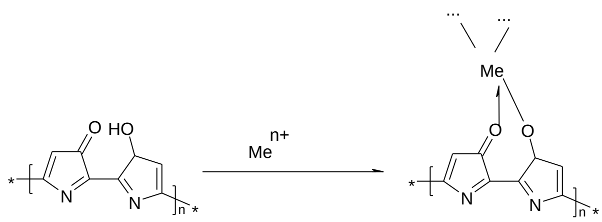

Figure 1. Conducting polymer-based heavy-metal concentration monitoring by cation recapture.

Depending on the metal properties, different types of behavior may be realized in this case. The simplest case has already been described by us in [28] for an amperometric sensor (working in potentiostatic mode), detecting a metal incapable of more than one valent state. In this case, we describe a system in which the metal complex, after formation, is also electro-oxidized, yielding another complex with another valent state. Therefore, this process will contain two electrochemical stages (the 1st and the 3rd) and one chemical, also influencing the double electric layer (DEL) (the 2nd).

So, in order to describe the behavior of this system, we introduce three variables:

m – metal-ion concentration in the pre-surface layer;

p – overoxidized polypyrrole surface coverage degree;

c – the low-valence metal complex surface coverage degree.

Taking into account some assumptions [26 – 28], we describe the system´s behavior by a trivariant equation set as:

$$\begin{cases} \frac{dm}{dt} = \frac{2}{\delta}\left(\frac{M}{\delta}(m_0 - m) - r_1\right) \\ \frac{dp}{dt} = \frac{1}{P}(r_O - r_1) \\ \frac{dc}{dt} = \frac{1}{C}(r_1 - r_2) \end{cases} \quad (1)$$

Herein, M is the heavy metal cation diffusion coefficient, m_0 is the heavy metal ion concentration in the pre-surface layer; P is the maximal surface concentration of the overoxidized polypyrrole, C is the maximal surface concentration of the low-valence polymer complex compound, and the parameters r are the correspondent reaction rates, calculated as (2 – 4):

$$r_O = k_O(1 - p - c)\exp\frac{nF\varphi_0}{RT} \qquad r_1 = k_1 pm \exp(-apm)$$

$$r_2 = k_2 c \exp\frac{mF\varphi_0}{RT} \qquad (2-4),$$

Where the parameters k are the correspondent reaction rate constants, a is the parameter capable of describing the relation between DEL and surface conductivity and structure, related to the complex compound formation, m and n are the numbers of the transferred electrons, φ_0 is the potential slope, related to the zero-charge potential, R is the universal gas constant, and T is the absolute temperature.

As there are two electrochemical stages, both capable of influencing the DEL, the electrochemical instabilities are more probable to occur in this system. Nevertheless, the electroanalytical process is efficient for both electroanalytical and electro-synthetical purposes, as shown below.

3. Results and Discussion

To describe the electrochemical behavior of the system with the electrochemical determination or retention of heavy metals by yielding an oxidizable overoxidized polypyrrole complex, we analyze the equation-set (1) using linear stability theory. The steady-state Jacobian matrix members for this system will be described as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (5)$$

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{M}{\delta} - k_1 p \exp(-apm) + ak_1 pm \exp(-apm)\right) \quad (6)$$

$$a_{12} = \frac{2}{\delta}(-k_1 m \exp(-apm) + ak_1 pm \exp(-apm)) \quad (7)$$

$$a_{13} = 0 \quad (8)$$

$$a_{21} = \frac{1}{P}(-k_1 p \exp(-apm) + ak_1 pm \exp(-apm)) \quad (9)$$

$$a_{22} = \frac{1}{P}\left(-k_O \exp\frac{nF\varphi_0}{RT} + jk_O(1 - p - c)\exp\frac{nF\varphi_0}{RT} - k_1 m \exp(-apm) + ak_1 pm \exp(-apm)\right) \quad (10)$$

$$a_{23} = \frac{1}{P}\left(lk_O(1 - p - c)\right) \quad (11)$$

$$a_{31} = \frac{1}{C}(k_1 p \exp(-apm) - ak_1 pm \exp(-apm)) \quad (12)$$

$$a_{32} = \frac{1}{C}\left(-jk_2c \exp\frac{mF\varphi_0}{RT}\right) \quad (13)$$

$$a_{33} = \frac{1}{C}\left(-k_2 \exp\frac{mF\varphi_0}{RT} + lk_2c \exp\frac{mF\varphi_0}{RT}\right) \quad (14)$$

Taking into account the main diagonal elements (6), (10), and (14), we may conclude that the *oscillatory behavior* in this system is possible. Moreover, taking into account the presence of one more electrochemical stage influencing the DEL, it is much more probable than in the neutral and basic media. It is known that the Hopf bifurcation in the trivariant systems may only be realized if some of the elements of the Jacobian main diagonal are positive, being related to the positive callback.

Besides the elements $ak_1pm \exp(-apm) > 0$, if a>0 and $jk_O(1-p-c) \exp\frac{nF\varphi_0}{RT} > 0$, if j>0, typical for the simplest case [28], the element, related to the DEL impact of the second electrochemical stage and complex compound transformation $lk_2c \exp\frac{mF\varphi_0}{RT} > 0$ if l>0 is also capable of being related to the oscillatory behavior. All of the mentioned factors may be responsible for the oscillatory behavior. The oscillation amplitude and frequency will be dependent on the solution composition (including the pH). Nevertheless, it is expected to be small, and the proper oscillations to be frequent.

As for the steady-state stability, in order to investigate it, we apply to the equation-set (1) the Routh-Hurwitz criterion. Avoiding the cumbersome expressions, we introduce new variables, rewriting thereby the Jacobian determinant as (15):

$$\frac{2}{\delta PC}\begin{vmatrix} -\kappa - \Xi & \Sigma & 0 \\ -\Xi & -\Omega - \Sigma & \Lambda \\ \Xi & -P & -\Phi \end{vmatrix} \quad (15)$$

Opening the brackets and applying the requisite Det <0, salient from the criterion, we obtain the stability condition, exposed as (16):

$$-\kappa(\Omega\Phi + \Sigma\Phi + P\Lambda) - \Xi(\Omega\Phi + 2\Sigma\Phi + P\Lambda - \Sigma\Lambda) < 0 \quad (16)$$

The requisite (16) describes an electroanalytical efficient detection process controlled by both diffusion and reaction kinetics. As no stages capable of compromising the analyte and (or) modifier in a side reaction are possible in this system, the steady-state stability will correspond to the linear dependence between the concentration and electrochemical parameter (in this case, the current).

The stability requisite is satisfied in a wide parameter range, although slightly narrower than for the simplest case. Therefore, the overoxidized polypyrrole may be an efficient electrode modifier for heavy metal determination and retention in potentiodynamic mode, even for the metal's multivalent states.

As for the detection limit, it is defined by monotonic instability. It defines the margin between the stable steady-states and unstable states. Its requisite is Det J =0, or (17):

$$-\kappa(\Omega\Phi + \Sigma\Phi + P\Lambda) - \Xi(\Omega\Phi + 2\Sigma\Phi + P\Lambda - \Sigma\Lambda) = 0 \quad (17)$$

The resulting material has a high tendency to be used as a catalyst for electroanalytical, electrocatalytic, and energy-converting systems. As for its electroanalytical function, it will be described in one of our next works.

4. Conclusions

From the analysis of the system with heavy-metal concentration monitoring on the overoxidized polypyrrole with the complex compound oxidation, it is possible to conclude that the overoxidized polypyrrole may be an efficient electrode modifier for the determination and monitoring of heavy metals concentration *in vivo* and *in vitro*. The electroanalytical process will be more dynamic than in the simplest case without additional complex compound oxidation. It is either diffusion or kinetically controlled, and the analytical signal is easy to interpret in a wide concentration range. On the other hand, the oscillatory behavior will be more capable of realizing than in the simplest case due to the influence of the additional electrochemical stage on DEL ionic force, conductivity, and surface impedance. Nevertheless, the electrochemical oscillations are realized far beyond the detection limit.

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Conflicts of Interest

The authors declare no conflict of interest.

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