The Mathematical Description for CoO(OH)-Assisted Hydroxylamine Electrochemical Determination in Neutral Media

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ABSTRACT: *The possibility of hydroxylamine electrochemical determination over a CoO(OH)-modified electrode, accompanied by complex-formation, has been studied from the theoretical point of view. The correspondent mathematical model has been developed and analyzed by means of linear stability theory and bifurcation analysis. It was shown that CoO(OH) may be applied as an efficient electrode modifier in the detection of hydroxylamine in neutral and slightly alkaline media. The electrochemical response has to be clear and easy to interpret. The possibility of the oscillatory and monotonic instabilities has also been verified.*

KEYWORDS: *Food safety; Hydroxylamine; Cobalt (III) oxyhydroxide; Electrochemical sensors; Stable steady-state.*

INTRODUCTION

The use of Chemically Modified Electrodes (CME) is one of the most interesting and modern tools in the electroanalytical chemistry [1 – 6]. Compared to the bare electrodes, they have some advantages, like:

- The rapidity of analytical response, compared with other analytical methods;
- Low cost of operation;
- Precisity and sensibility of response;
- Exactity in measures;
- Flexibility in construction and modification;
- Versatility in use;
- The affinity between the electrode modifier and the analyte.

On the other hand, hydroxylamine is one of the most used reducing agents [7-9]. It is an important intermediate in the nitrification processes [10-11]. It is also used in the pharmaceutical industry as a reagent for drug synthesis [12-14]. Nevertheless, it is well-known as a mutation agent, moderately toxic and harmful to human, animals, and even plants, even at a modest level [15-20]. Likewise, from the environmental, industrial and health viewpoints, development of a sensitive analytical method for determination of hydroxylamine in low level, is highly important [21-24], and the electrochemical methods would give it an excellent service.

As hydroxylamine is difficult to be oxidized on bare electrodes, the electrode modification is necessary. Many modifiers like graphene [25-26], conducting polymers [27-28], specific organic compounds [29-30] and metal nanoparticles [31-32] have been used. And the cobalt (III) oxyhydroxide CoO(OH), seen by many researchers as a substitute to titanium dioxide [33] and yet used in the detection of ascorbic acid [34], oxalic acid [34-35], phenolic and hydroquinone compounds [36], which are oxidized in similar conditions, as an electrode modifier, may be an interesting alternative.

On the other hand, its electroanalytical properties´ investigation has only begun, and a CoO(OH)-assisted electrochemical oxidation may confront the problems like:

- The indecision in the modifier mechanism of action;
- The compatibility of the modifier with the tissue or biological object (some modifiers, used *in vitro* may be non-compatible with *in vivo* sensing);
- The presence of electrochemical instabilities, accompanying both electrochemical synthesis of cobalt

(III) oxyhydroxide [37 – 38], and electrochemical oxidation and electrooxidation polymerization of organic molecules [39 - 42].

The mentioned problems may only be solved by means of an analysis of a mathematical model, capable to describe adequately the electroanalytical system. By modeling, it is also capable to compare the behavior of this system with that for the similar ones without any experimental essay.

So, the goal of this work is the mechanistic theoretic analysis of the possibility of hydroxylamine CoO(OH)-assisted electrochemical quantification. In order to achieve it, we realize the specific goals:

- The suggestion of the mechanism of the electroanalytical reaction consequence, leading to the appearance of an analytical signal;
- Development of the balance equation mathematical model, correspondent to the electroanalytical system;
- Analysis and interpretation of the model in terms of the electroanalytical use of the system;
- The seek for the possibility of electrochemical instabilities and for the factor, causing them;
- The comparison of the mentioned system´s behavior with similar ones [43 – 48].
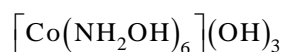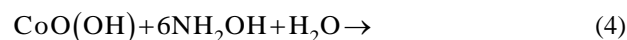
SYSTEM AND ITS MODELING

The mechanism of CoO(OH)-assisted hydroxylamine electrooxidation may be described as:

$$2NH_2OH + 4CoO(OH) \rightarrow 4CoO + N_2O + 5H_2O \qquad (1)$$

$$CoO + OH - e \rightarrow CoO(OH) \qquad (2)$$
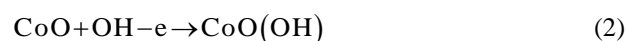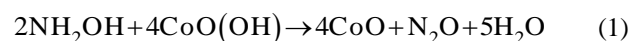
On the other hand, while in excess, hydroxylamine may form a complex [49] with the trivalent cobalt:

$$CoO(OH) + 6NH_2OH + 3H^+ \rightarrow \qquad (3)$$

$$\left[Co(NH_2OH)_6 \right]^{3+} + 2H_2O$$
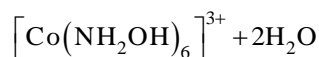
or, for a neutral solution,

$$CoO(OH) + 6NH_2OH + H_2O \rightarrow \qquad (4)$$

$$\left[Co(NH_2OH)_6 \right](OH)_3$$

The complex formation is more significant in acid media, in which hydroxylamine electrooxidation is very slow. But in neutral media, these processes may concur.

Research Article

Cobalt (III)oxyhydroxide may be dissolved, but the use of this reaction as electroanalytical may be discussed.

In order to describe the behavior of this system, we introduce two variables:

h – hydroxylamine pre-surface layer concentration;

θ – CoO(OH) surface coverage degree.

To simplify the modeling, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also, we assume that the background electrolyte is in excess, so we can neglect the migration flow. The diffusion layer is supposed to be of a constant thickness, equal to δ, and the concentration profile in it is supposed to be linear. It is also assumed that CoO covers the entire surface at the beginning of the reaction.

It is possible to show that the system's behavior may be described by a bivariant equation set as:

$$\begin{cases} \dfrac{dh}{dt} = \dfrac{2}{\delta}\left(\dfrac{\Delta}{\delta}(h_0 - h) - r_1 - r_4\right) \\ \dfrac{d\theta}{dt} = \dfrac{1}{G}(r_2 - r_1 - r_4) \end{cases} \qquad (5)$$

In which Δ is the diffusion coefficient, h_0 is the hydroxylamine bulk concentration, G is the CoO(OH) maximal surface concentration and the parameters r are the correspondent reaction rates, capable to be described as:

$$r_1 = k_1 h \theta^2 \qquad (6)$$

$$r_2 = k_2 (1 - \theta) \ \exp\left(\dfrac{F\gamma\theta}{RT}\right) \qquad (7)$$

$$r_4 = k_4 h^6 \theta \ \exp(-\alpha\theta) \qquad (8)$$

In which the parameters k_1, k_2, and k_4 are the correspondent rate constants, F is the Faraday number, α is the parameter, describing the CoO(OH) particles interaction during its dissolution, γ is the parameter, describing the influences of the electrochemical process to the double electric layer, R is the universal gas constant and T is the absolute temperature.

As the analyte reacts with the electrode modifier by hybrid mechanism, and both reactions may influence the process stability, the behavior of this system will be more dynamic, than in the case of the similar systems [43-48], which will be discussed below.

RESULTS AND DISCUSSION

In order to investigate the behavior of hydroxylamine CoO(OH)-assisted electrochemical detection in neutral media, we analyze the equation set (5) by means of linear stability theory. The Jacobian steady-state members for this case will be described as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \qquad (6)$$

in which:

$$a_{11} = \dfrac{2}{\delta}\left(-\dfrac{\Delta}{\delta}(h_0 - h) - k_1\theta^2 - 6k_4 h^5\theta \ \exp(-\alpha\theta)\right) \qquad (7)$$

$$a_{12} = \dfrac{2}{\delta}\left(-2k_1 h\theta - k_4 h^6 \exp(-\alpha\theta) + \qquad (8)\right.$$

$$\left. \alpha k_4 h^6 \theta \ \exp(-\alpha\theta)\right)$$

$$a_{21} = \dfrac{1}{G}\left(-k_1\theta^2 - 6k_4 h^5\theta \ \exp(-\alpha\theta)\right) \qquad (9)$$

$$a_{22} = \dfrac{1}{G}\left(-k_2 \exp\left(\dfrac{F\gamma\theta}{RT}\right) + \gamma k_2 (1-\theta) \exp\left(\dfrac{F\gamma\theta}{RT}\right) - \qquad (10)\right.$$

$$\left. 2k_1 h\theta - k_4 h^6 \exp(-\alpha\theta) + \alpha k_4 h^6 \theta \ \exp(-\alpha\theta)\right)$$

In order to simplify the analysis, avoiding the cumbersome expressions, we introduce new variables, so the Jacobian determinant will be described as:

$$\dfrac{2}{\delta G}\begin{vmatrix} -\kappa - \Xi & -\Lambda \\ \Xi & -\Sigma - \Lambda \end{vmatrix} \qquad (11)$$

The steady-state stability condition for a bivariant system is Tr J <0, Det J>0. In the case of the absence of the CoO(OH)-particles interaction, or their repulsion, like also in the case of the fragility of DEL influences of the electrooxidation, all main diagonal elements will have negative (positive with negative signs) values, satisfying the condition of Tr J<0. The requirement of Det J>0 will be, thus, satisfied. So the steady-state will be stable and, despite the possibility of CoO(OH)-dissolution, electroanalytical efficient. The possibility of the use of CoO(OH) as a sacrifice coating for hydroxylamine analysis in the conditions of complex formation isn't discarded. The linearity of the dependence between the electrochemical parameter and concentration is easy to maintain, as the steady-state in this system tends to be stable.

For most cases, the electroanalytical process is diffusion-controlled. It may be reaction-controlled if the electrode is small, and CoO(OH) is used as a sacrifice coating. Mathematically, the steady-state stability will be described as:

$$\begin{cases} -\kappa - \Xi - \Sigma - \Lambda < 0 \\ \kappa\Sigma + \kappa\Lambda + \Xi\Sigma > 0 \end{cases} \qquad (12)$$

The oscillatory behavior in this system is possible. Moreover, it is more probable, than in the simplest cases of the CoO(OH) use as an electrode modifier[43 – 48], as both electrochemical and surface instabilities are present. The Hopf bifurcation condition for this system may be described as:

$$\begin{cases} -\kappa - \Xi = \Sigma + \Lambda \\ \kappa\Sigma + \kappa\Lambda + \Xi\Sigma > 0 \end{cases} \qquad (14)$$

This condition may only be satisfied in the case of the positivity of the main diagonal elements $\gamma k_2(1-\theta) \quad \exp\left(\dfrac{F\gamma\theta}{RT}\right) > 0$, in the case of strong DEL influences of the electrochemical stage and $\alpha k_4 h^6\theta \quad \exp(-\alpha\theta) > 0$, in the case of the CoO(OH) adsorbed particles' attraction. The oscillation amplitude may depend on the analyte concentration and on the solution composition.

The monotonic instability in this system is also possible. Being correspondent to the detection limit, it is as:

$$\begin{cases} -\kappa - \Xi - \Sigma - \Lambda < 0 \\ \kappa\Sigma + \kappa\Lambda + \Xi\Sigma = 0 \end{cases} \qquad (14)$$

It is observed in the point of equality between stabilizing and destabilizing influences in DEL and on the electrode surface.

The use of *lightly alkaline media* drives the electroanalytical process to the major efficiency, as the complex-formation rate becomes very slow, and the hydroxylamine electrooxidation rate will be enhanced. So, this system becomes similar to those described in [43 – 48].

CONCLUSIONS

From the theoretical investigation of the possibility of CoO(OH) - assisted hydroxylamine electrochemical detection it is possible to conclude that:

- Despite of the hybridity of the mechanism, CoO(OH) may serve as an excellent modifier for hydroxylamine quantification. The stable steady-state is maintained easily;

- The system is electroanalytically efficient, even despite of the possibility of CoO(OH) analyte-promoted dissolution. The use of CoO(OH) as a sacrifice coating isn't discarded;

- The process is mostly diffusion-controlled, but if CoO(OH) is used as a sacrifice electrode, it may become reaction-controlled;

- The oscillatory behavior in this system is possible, being caused by both surface and electrochemical instabilities.

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