Full Paper

The Mathematical Description for the CoO(OH)-Assisted Electrochemical Detection of Inositol in Alkaline Solutions

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Abstract- The possibility of the inositol CoO(OH)-assisted electrochemical detection in alkaline media has been evaluated 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 serve as a modifier for inositol electrochemical detection in alkaline media, participating in the electroanalytical process as a reducent. The electroanalytical process is diffusion-controlled. The possibility of oscillatory and monotonic instabilities has also been verified.

1. INTRODUCTION

The use of chemically modified electrodes (CME) is a very important step in electroanalytical chemistry [1-5]. Compared to the bare electrodes, they have some advantages, like: Rapidity, low cost, precisity, exactity, flexibility, versatility in use and affinity between the electrode modifier and the analyte.

On the other hand, inositol is a substance acting principally as an animal and human growth factor [6–8]. It is a cyclohexane-based hexol, glycose structure isomer (Fig. 1). Nine optical isomers are possible for inositol [9].
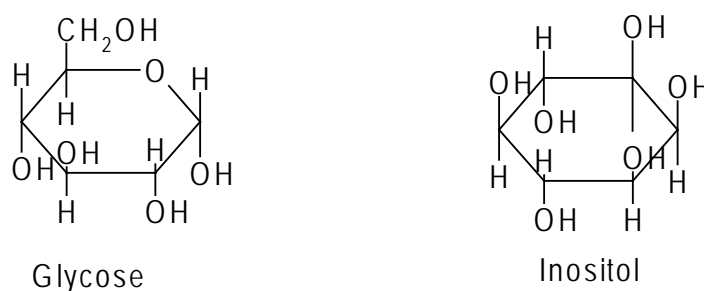
Fig. 1. Glycose (in pyranose form) and inositol

Sometimes it is classified as one of the vitamins of B complex (as vitamin B8) or as a vitamin-like compound [9-11]. It´s found in cell membrane phospholipids, plasma lipoproteins, and (as the phosphate form) in the nucleus with potential chemopreventive properties. As one of a number of intracellular phosphate compounds, inositol is involved in cell signaling and may stimulate tumor cell differentiation. It is also found in *Fabacea* (beans, peas) and some cereals (brown rice, wheat bran) and in nuts. It is water-soluble (can dissolve in water) and must be taken in every day. It maintains stable the cellular membranes and takes part in the impulse transmission in nerve tissue. It is also involved various biological processes like cellular membrane stabilization, insulin signal transduction[12], cytoskeleton assembly, nerve guidance, intracellular calcium concentration control[13], cell membrane potential maintenance[14], breakdown of fats[15] and gene expression. It is also being studied in the prevention of cancer [16]. Its lack in the organism [provokes different pathological states, among them, depression (during the inositol concentration in the cerebrospinal fluid) and in the eyes (its lack in tear liquor and in serum provokes retinopathy and even dry-eye syndrome *etc*) [17-19]. Side effects from inositol excess may be unlikely due to the fact that the body is well-adapted to its presence and involvement in biochemical processes. That said, the most common side effects reported by inositol users include: dizziness, headaches, gastrointestinal distress, and diarrhea (or loose stools) and hallucinations at high doses. [20]. So the development of a method, capable to detect inositol

concentration efficiently and rapidly is really actual [21], and the use of electrochemical methods for it would be an interesting proposal for it.

For now, only one work concerning inositol electrochemical detection is known [22]. The solution used for this purpose was alkaline, and the modifier used was the nickel-sodium hexacianoferrate. On the other hand, cobalt (III) oxyhydroxide, a material, thought by some researchers as an alternative to titanium dioxide [23-25], is one of the good candidates to electrode modifier for inositol electrochemical detection, as it has been used to quantify the compounds, capable to be oxidized in similar conditions (ascorbic acid, phenolic and hydroquinonic compounds, oxalic acid) in neutral and alkaline solutions [26-28]. Its electroanalytical efficiency has been already theoretically predicted for hydrazine [29], omeprazole [30], procarbazine [31], diquat pesticide [32] and many other compounds. As in cobalt(III) oxyhydroxide cobalt acts in middle oxidation state, it may act either as an oxidant (being transformed to CoO, $Co(OH)_2$ or Co^{2+}), or as a reducent (being oxidized in alkaline media to form CoO_2).

On the other hand, its electroanalytic 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 [33-34], and electrochemical oxidation and electrooxidative polymerization of organic molecules [35-38].

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 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 inositol $CoO(OH)$-assisted electrochemical quantification. In order to achieve it, we realize the specific goals:

- suggestion of the mechanism of the electroanalytical reaction sequence, leading to the appearance of 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 the similar ones [26-32].

2. SYSTEM AND ITS MODELING

In the case of inositol electrochemical detection, it is possible to use either the Co^{2+}/Co^{3+} or the Co^{3+}/Co^{4+} redox pair. As the analogous systems with the use of Co^{2+}/Co^{3+} pair have been already described theoretically by our group [28-32] and experimentally by Anaissi and coworkers [26-27], in this work, the case of the use of CoO(OH) as a reducent will be described.

In strongly alkaline media, CoO(OH) undergoes the oxidation, forming the tetravalent cobalt in the form of its oxide:

$$CoO(OH) + OH^- -e^- \rightarrow CoO_2 + H_2O \tag{1}$$

This reaction is realized with high anodic potential, compared with that for Ce^{3+}/Ce^{4+} redox pair.

As tetravalent cobalt is a strong oxidant, it oxidizes inositol with the cyclohexane ring destruction, in which cobalt(II) oxide is formed (2):

$$6CoO_2 + C_6H_6(OH)_6 + 6OH^- \rightarrow 6CoO + 6HCOO^- + 6H_2O \tag{2}$$

CoO(OH) is then restored by CoO electrochemical oxidation:

$$CoO + OH^- - e^- \rightarrow CoO(OH) \tag{3}$$

In hot alkaline solution, CoO(OH) may degrade, forming complex:

$$CoO(OH) + 3OH^- + H_2O \rightarrow [Co(OH)_6]^{3-} \tag{4}$$
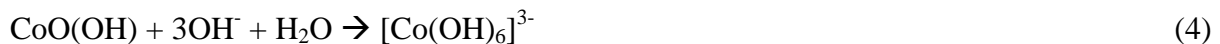
So, taking in account the excess of the alkali in the solution, we introduce three variables:

c – inositol concentration in the pre-surface layer;

θ – CoO(OH) surface coverage degree;

θ_{ox} – CoO$_2$ 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's also supposed that at the beginning of the reaction CoO covers the entire electrode surface.

Inositol enters the pre-surface layer by diffusion and then is oxidized according to the reaction (2). So, the balance equation for inositol may be described as:

$$\frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) - r_2\right) \tag{5}$$

In which Δ is the diffusion coefficient, c_0 is the inositol bulk concentration and r_2 is the rate of the reaction (2).

CoO(OH) is formed during the reaction (3) and disappears during the reactions (4) and (1). So its balance equation will be described as:

$$\frac{d\theta}{dt} = \frac{1}{G}(r_3 - r_1 - r_4) \tag{6}$$

In which G is CoO(OH) maximal surface concentration, r_1, r_3 and r_4 are correspondent reaction rates.

Cobalt dioxide is formed during the reaction (1) and disappears during the reaction (2). So its balance equation will be described as:

$$\frac{d\theta_O}{dt} = \frac{1}{G_O}(r_1 - r_2) \tag{7}$$

In which G is CoO(OH) maximal surface concentration, r_1, r_3 and r_4 are correspondent reaction rates.

The correspondent reaction rates may be described as:

$$r_1 = k_1\theta \exp\frac{F\varphi_0}{RT} \tag{8}$$

$$r_2 = k_2 c \theta_O^6 \tag{9}$$

$$r_3 = k_3(1 - \theta - \theta_O) \exp\frac{F\varphi_0}{RT} \tag{10}$$

$$r_4 = k_4\theta \exp(-\beta\theta) \tag{11}$$

In which the parameters k are correspondent reaction rate constants, F is the Faraday number, φ_0 is the potential slope in the double electric layer (DEL), related to the zero-charge potential, R is the universal gas constant, T is the absolute temperature and β is the variable, describing the interaction between the particles of CoO(OH) during its dissolution.

As cobalt is present in three oxidation states in this system, the behavior during the electroanalytical process is more complicated, than in the similar cases, described in [26-32], which will be discussed below.

3. RESULTS AND DISCUSSION

In order to describe the behavior of the electrochemical system with inositol CoO(OH)-assisted electrochemical detection, we analyze the equation set (5-7) by means of linear stability theory. The steady-state Jacobian functional matrix members may be described as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \tag{12}$$

in which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Lambda}{\delta}(c_0 - c) - k_2\theta_O^6\right) \tag{13}$$

$$a_{12} = 0 \tag{14}$$

$$a_{13} = \frac{2}{\delta}(-6k_2c\theta_O^5) \tag{15}$$

$$a_{21} = 0 \tag{16}$$

$$a_{22} = \frac{1}{G}\left(-k_3\exp\frac{F\varphi_0}{RT} + \alpha k_3(1 - \theta - \theta_O)\exp\frac{F\varphi_0}{RT} - k_1\exp\frac{F\varphi_0}{RT} - \alpha k_1\theta\exp\frac{F\varphi_0}{RT} - k_4\exp(-\beta\theta) + \beta k_4\theta\exp(-\beta\theta)\right) \tag{17}$$

$$a_{23} = \frac{1}{G}\left(-k_3\exp\frac{F\varphi_0}{RT} + \gamma k_3(1 - \theta - \theta_O)\exp\frac{F\varphi_0}{RT} - \gamma k_1\theta\exp\frac{F\varphi_0}{RT}\right) \tag{18}$$

$$a_{31} = \frac{1}{G_O}(-k_2\theta_O^6) \tag{19}$$

$$a_{32} = \frac{1}{G_O}\left(k_1\exp\frac{F\varphi_0}{RT} + \alpha k_1\theta\exp\frac{F\varphi_0}{RT}\right) \tag{20}$$

$$a_{33} = \frac{1}{G_O}\left(\gamma k_1\theta\exp\frac{F\varphi_0}{RT} - 6k_2c\theta_O^5\right) \tag{21}$$

Observing the expressions (13), (17) and (21), it is possible to see that the *oscillatory behavior* for this system is possible, as the main diagonal elements contain positive elements. Moreover, the oscillatory behavior will be more probable than for the similar cases involving CoO(OH) [26-32], due to the presence of two electrochemical processes against one, besides of the surface instability. So, the oscillatory behavior for this case is more probable than for the similar cases. The oscillations are expected to be frequent and of low amplitude.

In order to investigate the *steady-state stability* in this system, we apply the Routh-Hurwitz criterion to the equation set (5-7). Avoiding the cumbersome expressions, we introduce new variables, so now the Jacobian determinant will be rewritten as:

$$\frac{2}{\delta G G_O}\begin{vmatrix} -\kappa - \Xi & 0 & -\Lambda \\ 0 & -\Omega - P - \Sigma & -E - T \\ -\Xi & P & -T - \Lambda \end{vmatrix} \tag{22}$$

Opening the brackets and applying the condition Det J<0, salient from the criterion, we obtain the stability requirement, expressed as:

$$-\kappa(\Omega T + 2PT + \Sigma T + \Omega\Lambda + P\Lambda + \Sigma\Lambda + PE) - \Xi(\Omega T + 2PT + \Sigma T + PE) < 0 \tag{23}$$

And it is warranted to be satisfied in the case of the positivity of Ω, P, Σ and T, describing the fragility of DEL influences of the electrochemical process and the repulsion between CoO(OH) particles. The process is diffusion-controlled.

The steady-state is maintained stable easily. Nevertheless, its electroanalytical efficiency will depend on pH and electrode size. If the electrode size is relatively small in hot solutions with the concentrated alkaline media, the material will be destroyed, and the process won't be

electroanalytically efficient, although the steady-state remains stable. So, it is recommended to use relatively big electrodes with relatively cold solutions.

Being the requirements satisfied, the steady-state stability is correspondent to the linear dependence between the electrochemical parameter and analyte concentration, or, better saying, to the electroanalytical efficiency. This efficiency is maintained easily, so CoO(OH) may be an excellent electrode modifier for inositol electrochemical detection.

The *monotonic instability* in this system is possible, being caused by the equality between the stabilizing influences and the destabilizing ones of the electrochemical process influences on DEL. It is correspondent to the detection limit and its condition may be described as:

$$-\kappa(\Omega T + 2PT + \Sigma T + \Omega\Lambda + P\Lambda + \Sigma\Lambda + PE) - \Xi(\Omega T + 2PT + \Sigma T + PE) = 0 \qquad (24)$$

The use of Co^{III}/Co^{IV} redox pair for other analytes may also give simpler systems, which will be described in our next works.

4. CONCLUSION

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

- CoO(OH) may serve as an excellent modifier for inositol quantification, besides of the CoO_2 formation. The stable steady-state is maintained easily;
- The system is electroanalytically efficient, if the electrode size pH and temperature do not promote the rapid CoO(OH) dissolution. The electrode must be relatively big, and the solution temperature, relatively low;
- The process in this case is diffusion-controlled;
- The oscillatory behavior in this system is possible, being caused by DEL influences of the electrochemical process and surface instabilities, accompanying the dissolution;
- The monotonic instability in this system is also possible, being caused by the equality of the destabilizing influences in DEL to the stabilizing ones.

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