

# THE MATHEMATICAL INVESTIGATION FOR THE MECHANISM OF THE ELECTROCHEMICAL OXIDATION OF PHENOLIC COMPOUNDS OVER CoO(OH) IN ALKALINE SOLUTION

V. Tkach<sup>1,2</sup>, S. C. de Oliveira<sup>2</sup>, G. Maia<sup>2</sup>, F.J. Anaissi<sup>3</sup>, R. Ojani<sup>4</sup>, U. Páramo-García<sup>5</sup>, O. Yelenich<sup>1</sup>, P.I. Yagodynets<sup>1</sup>

<sup>1</sup> Chernivtsi National University, 58012, Kotsyubyns'ky Str., 2, Chernivtsi, Ukraine

<sup>2</sup> Universidade Federal de Mato Grosso do Sul, Av. Sen. Felinto. Müller, 1555, C/P. 549, 79074-460, Campo Grande, MS, Brazil

<sup>3</sup> Universidade Estadual do Centro-Oeste, Setor de Ciências Exatas e da Terra, Departamento de Química, Laboratório de Materiais e Compostos Inorgânicos, Rua Simeão Varela de Sá, 03. CEP: 85040-080 – Guarapuava, PR, Brasil.

<sup>4</sup> University of Mazandaran, 47416-95447, 3<sup>rd</sup> km. Air Force Road, Babolsar, Islamic Republic of Iran

<sup>5</sup> División de Estudios de Posgrado e Investigación Instituto Tecnológico de Ciudad Madero, Calle Juventino Rosas y Jesús Urueta, Col. Los Mangos, C.P. 89440, Cd. Madero, Tamps., Mexico

\*Correspondence Author :E-mail: [nightwatcher2401@gmail.com](mailto:nightwatcher2401@gmail.com)

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## ABSTRACT

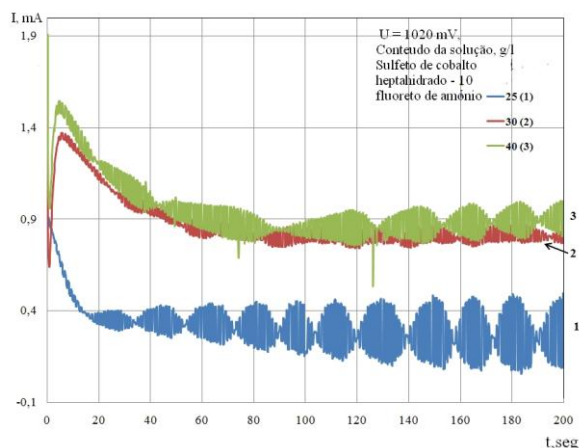
The mechanism for the electrochemical oxidation of phenolic compounds over cobalt(III)oxyhydroxide was suggested and mathematically analyzed, by means of linear stability theory and bifurcation analysis. The influence of pH on steady-state stability and reaction control has been investigated.

**Keywords:** phenolic compounds, quinonic compounds, electrooxidation, cobalt(III) oxyhydroxide, stable steady-state

## 1.INTRODUCTION

Phenolic and corresponding quinonic compounds are very important in organic synthesis and in biological systems [1 – 10], acting, for example, as antioxidants, neurotransmitters, hormones, not only in human, but also in animal and plant organisms. Their biological activity strongly depends on their concentration, thus, the problem of an analytic method, capable to detect precisely, rapidly and exactly is, without a doubt, an actual problem and electrochemical analytic methods are modern and outstanding alternative [11 – 32]. At the other hand, cobalt(III)oxyhydroxide is a modern inorganic material [33 – 40]. As a *p*-type semiconductor, it is seen as an alternative to titanium dioxide and may be used in corrosion protection, photoelectrocatalysis and as a surface for electrooxidation. So it would be an excellent catalyst for phenolic compounds' electrooxidation. The difficulties of its use [39 – 40] are the relatively high potential of its

electrosynthesis, problems of its stability in the presence of complex-forming substances and the electrochemical instabilities, capable to accompany either the  $\text{CoO}(\text{OH})$  electrosynthesis, or its dissolution, forming complex (See Fig. 1)



**Fig.1** Oscillatory behavior during the electrosynthesis of  $\text{CoO}(\text{OH})$  on platinum from  $\text{CoSO}_4$

In the majority of cases, such phenomena received merely phenomenological explanations. Even being based on logical arguments, it's feeling lack of a rigid theoretical base, given only by an analysis of a mathematical model, capable to describe the behavior of the system adequately. The modeling is also capable to predict the behavior of systems, yet not observed experimentally, and also to compare the behavior of the concrete system with the similar. So, the goal of this work is to suggest and analyze mathematically the mechanism for the electroanalytical function of  $\text{CoO}(\text{OH})$  in the process of the oxalic acid determination in strong alkaline media. Also we have the aim to compare it with the function of likely systems. We've already made some efforts to describe mathematically different electroanalytical systems, involving different active compounds (conducting polymers, small conjugated molecules and metallic nanoparticles) [41 – 63] and  $\text{CoO}(\text{OH})$  synthesis. So, this work is dedicated to the investigation the properties of  $\text{CoO}(\text{OH})$  as a surface for electroanalytical phenolic compounds oxidation in alkaline media, which haven't been studied well yet.

## 2.SYSTEM AND ITS MODELING

Cobalt(III) oxyhydroxide may be obtained electrochemically from the compounds of  $\text{Co}(\text{II})$  in alkaline medium:



At the other hand, moderately and strongly alkaline medium enhances the oxidation of phenolic compounds to correspondent quinones, according to the equation:



Taking this in account, it is possible to consider  $\text{CoO}(\text{OH})$  an excellent surface for phenolic compounds' oxidation, which has to be realized, according to the mechanism (3):



At the other hand, in strongly alkaline solution, the oxyhydroxycompound of cobalt (III) is dissolved to form a complex ion:



Taking in account the reaction mechanism (1, 3, 4), we introduce next variables:

$c$  – the phenolic compound concentration in the pre-surface layer,  $\theta$  – the  $\text{CoO}(\text{OH})$  surface coverage degree,  $a$  – the alkali concentration in the pre-surface layer.

To simplify the modeling, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also we suppose that the background electrolyte is in excess, so we can neglect the migration flow. The pre-surface layer thickness is assumed to be constant, equal to  $\delta$ , and the concentration profile of the analyte and the alkali, to be linear.

The *phenolic compound* enters the pre-surface layer by diffusion and then reacts with  $\text{CoO}(\text{OH})$ , yielding its quinonic derivative,  $\text{CoO}$  and water. It is also oxidized by direct reaction with hydroxyl-ions. Taking in account the first Fick's law and the modeling, related to the double electric layer (DEL), the balance equation for its concentration will be described as:

$$\frac{dc}{dt} = \frac{2}{\delta} \left( \frac{\Delta}{\delta} (c_0 - c) - r_3 - r_2 \right) \quad (5)$$

in which  $\Delta$  is the diffusion coefficient,  $c_0$  is the analyte bulk concentration and  $r_3$  and  $r_2$  are the rates of the reactions (3) and (2).

The *oxy-hydroxycompound of cobalt* is formed by electrooxydation (1) of the oxide, covering, at the starting point, the entire surface, in alkaline aqueous media. It reacts with the analyte and is dissolved in the strongly alkaline media (4) forming a hydroxyl complex. Thus, its balance equation will be described as:

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

in which  $\Gamma$  is the  $\text{CoO}(\text{OH})$  maximal surface concentration, and the parameters  $r$  correspond to the corresponding reaction rates.

The *alkaline hydroxyl* enters the pre-surface layer by alkali diffusion, participating in the reactions (1), (2) and (4). So, its balance equation will be described as:

$$\frac{da}{dt} = \frac{2}{\delta} \left( \frac{D}{\delta} (a_0 - a) - r_1 - r_2 - r_4 \right) \quad (7)$$

In which  $D$  and  $a_0$  is alkaline hydroxyl diffusion coefficient and bulk concentration.

The corresponding reaction rates may be calculated as:

$$r_1 = k_1 a (1 - \theta) \exp\left(\frac{F\varphi_0}{RT}\right), r_2 = k_2 c a^2 \exp\left(\frac{2F\varphi_0}{RT}\right) r_3 = k_3 c \theta^2 \quad r_4 = k_4 \theta a^3 \exp(-\beta\theta) \quad (8-11)$$

In which, the parameters  $k$  are rate constants of corresponding reactions,  $F$  is Faraday number,  $\varphi_0$  is the DEL potential slope, related to the zero-charge potential,  $R$  is universal gas constant,  $T$  is absolute temperature,  $\beta$  is the variable, describing the interaction of the adsorbed particles. In general, the system resembles the analogous cases for conducting polymers and inorganic materials. But, taking in account the amphotericity of  $\text{Co(III)}$  compounds, they dissolve in strongly alkaline media, which makes their behavior more complicated, and it is going to be discussed below.

### 3.RESULTS AND DISCUSSION

To investigate the electroanalytical behavior of  $\text{CoO}(\text{OH})$  in phenolic compound electrochemical detection in alkaline media, we analyze the differential equation system (5 – 7), describing the mechanism (1 – 4), taking in account the algebraic relations (8 – 11) using the linear stability theory. The Jacobian functional matrix, calculated for the steady-state, will be rewritten as:

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

$$\begin{aligned} a_{11} &= \frac{2}{\delta} \left( -\frac{\Delta}{\delta} - \frac{r_2}{c} - \frac{r_3}{c} \right) & a_{12} &= \frac{2}{\delta} (-2k_3 c \theta) & a_{13} &= \frac{4}{\delta} \left( -\frac{r_2}{a} \right) & a_{21} &= \frac{1}{\Gamma} \left( -\frac{r_3}{c} \right) \\ a_{22} &= \frac{2}{\delta} \left( -k_1 a \exp\left(\frac{F\varphi_0}{RT}\right) + k_1 a (1 - \theta) \alpha \exp\left(\frac{F\varphi_0}{RT}\right) - 2k_3 c \theta - k_4 a^3 \exp(-\beta\theta) + \beta k_4 a^3 \exp(-\beta\theta) \right) \end{aligned}$$

$$\begin{aligned}
 a_{23} &= \frac{1}{F\delta} \left( k_1(1-\theta) \exp\left(\frac{F\varphi_0}{RT}\right) - 3k_4\theta a^2 \exp(-\beta\theta) \right) a_{31} = \frac{2}{\delta} \left( -\frac{r_2}{c} \right) \\
 a_{32} &= \frac{1}{F\delta} \left( k_4 a \exp\left(\frac{F\varphi_0}{RT}\right) - k_4 a(1-\theta) \alpha \exp\left(\frac{F\varphi_0}{RT}\right) + 2k_3 c \theta - k_5 a^3 \exp(-\beta\theta) + \beta k_5 a^3 \exp(-\beta\theta) \right) \\
 a_{33} &= \frac{2}{\delta} \left( -\frac{D}{\delta} - k_1(1-\theta) \exp\left(\frac{F\varphi_0}{RT}\right) - 3k_4\theta a^2 \exp(-\beta\theta) - \frac{2r_2}{a} \right) \quad (13-21)
 \end{aligned}$$

The oscillatory behavior for this system, like the other systems with CoO(OH) electrosynthesis and electrochemical sensing with the coatings of active materials, is possible. The oscillatory behavior is realized in Hopf bifurcation conditions, requiring the presence of the positive elements in main diagonal of Jacobian matrix. Two elements of the diagonal may be positive, which are:

$$k_1 a(1-\theta) \alpha \exp\left(\frac{F\varphi_0}{RT}\right) > 0, \quad (22)$$

If CoO is strong reductant (which is viable in moderately and strongly alkaline solution) in the synthesis conditions, causing the positivity of the DEL potential slope  $\varphi_0$ , similarly to the other cases of electrochemical sensing with active mediators [41 – 63];

$$\beta k_5 a^3 \exp(-\beta\theta) > 0, \quad (23)$$

In the case of attraction of the adsorbed particles during the film dissolution and complex formation.

The steady-state stability requirement is derived by use of Routh-Hurwitz criterion. To avoid the appearance of huge expressions, we introduce new variables, and so the Jacobi matrix determinant will be rewritten as:

$$\frac{4}{F\delta^2} \begin{vmatrix} -\xi & -E + \Omega + \Lambda & -Z \\ \Omega + \Lambda & -Z & -\kappa \\ -Z & -\kappa & -s \end{vmatrix} \quad (24)$$

In which the new variables are parameters, describing the processes of the system.

Using the condition  $\text{Det } J < 0$ , that may be derived from the Routh-Hurwitz criterion, we obtain the steady-state stability requirement, rewritten as:

$$(-\kappa - s - \xi)(EZ - \Omega Z - \Lambda Z + Ep - \Omega p - \Lambda p + E\gamma - \Omega\gamma - \Lambda\gamma) < \xi(-\Omega p - \Lambda p - EZ - Ep - E\gamma) + s(EZ - Ep + \Omega p + \Lambda p) \quad (25)$$

It's possible to observe, that in this case, the steady-state will be stable, if the solution's pH is moderately alkaline (little value of the direct electrooxidation and dissolution parameters  $\xi$  and  $s$ ). It lowers the reaction rates of direct phenolic compound oxidation and CoO(OH) dissolution. Moreover, it reduces the influences of the electrochemical processes on DEL and promotes the repealing interaction of CoO(OH) adsorbed particles. The reaction, in this case, is controlled by the diffusion of the phenolic compound (because the hydroxyl diffusion in this system is more rapid). The steady-state stability concentrational influences may be represented in more detailed way on the table:

**Table :** The steady-state stability concentrational influences

Analyte concentration	Alkalinity	Analytical efficiency	Steady-state stability
Relatively high	Moderate, (pH<10,5; without excess)	Efficient	Favored
Relatively low	Moderate (pH<10,5; excess)	Efficient	Favored
-	Very high (pH>11)	Non-efficient, material destruction, direct compound oxidation	Non-favored by surface effects of dissolution

In the case of the equality of the mentioned influences to the stabilizing ones, the *monotonic instability*, which condition may be represented as (26)

$$(EZ - \Omega Z - \Lambda Z + Ep - \Omega p - \Lambda p + E\gamma - \Omega\gamma - \Lambda\gamma) = \xi(-\Omega p - \Lambda p - EZ - Ep - E\gamma) + s(EZ - Ep + \Omega p + \Lambda p) \quad (26)$$

It is revealed by N-shaped voltamperogram part. In the case of great *excess* of an alkali, relatively to the, the third variable disintegrates the system and the process will be described by the equation set (6 – 7) and the behavior will be more simple, but the stability of the system may be corrupt. Moreover, the concentration of the phenolic compounds may be neglected, so the main process will be the CoO(OH) dissolution. The analysis of this case will be described and discussed in our next works. In the case of autocatalytic behavior, characteristic for oxalate-ion, the equation system is modified, like it was described in [41 - 63]. The autocatalytic behavior modifies the Jacobian and causes the appearance of one more positive element in the main diagonal. It describes the oscillatory behavior in this case

#### 4.CONCLUSIONS

- The electroanalytical function of CoO(OH) in the electrochemical determination of phenolic compounds is efficient in moderately alkaline solutions. Concentrated alkaline solutions are capable to destroy the material and lead to electrochemical instabilities.
- The steady-state stability (and the reaction course) is defined in this system by rapid analyte diffusion and moderate alkalinity of the solution
- The oscillatory behavior for this system is possible and may be caused by electrochemical, surface and autocatalytic, if any, factors.
- The monotonic instability is realized in the case of the equality of the mentioned influences to the stabilizing ones.
- In the case of highly alkaline systems, the participation of the oxalate-ion in the system may be neglected, because the main process will be the CoO(OH) dissolution.

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