The Mathematical Modeling for CoO(OH) – Poly(5-Amino-1,4-Naphthoquinone) Composite-Based Sensor for 1-Propenesulfenic Acid and Propanethial S-Oxide Detection in Food and Lacrimogenic Compositions

Volodymyr V. Tkach 1,2,*, Marta V. Kushnir 1, Vira V. Kopiika 3, Yuliia V. Yeshchenko 4, Olga V. Luganska 3, Zholt O. Kormosh 4, Yevgeniya V. Nazymok 5, Yana G. Ivanushko 5, Anzhelika F. Molodianu 5, Valentyna G. Ostapchuk 5, Svitlana P. Melnychuk 5, Mykola Ye. Blazheyevskiy 6, Karina V. Palamarek 7, Dina V. Fedorova 8, Silvio C. De Oliveira 2, Petro I. Yagodynets 1,*, Adriano O. Da Silva 9

1 Chernivtsi National University, 58000, Kotsyubynsky Str. 2, Chernivtsi, Ukraine
2 Universidade Federal de Mato Grosso do Sul, Av. Sen. Felinto. Müller, 1555, C/P. 549, 79074-460, Campo Grande, MS, Brazil
3 Zaporizhzhia National University, 69600, Zhukovsky Str. 66, Zaporizhzhia, Ukraine
4 Eastern European National University, 43000, Voli Ave., 13, Lutsk, Ukraine
5 Bukovinian State Medical University, 58001, Teatralna Sq., 9, Chernivtsi Ukraine
6 National Pharmaceutical University, 61000, Pushkinska Str. 57, Kharkiv, Ukraine
7 Chernivtsi Institute of Trade and Economics of Kyiv National University of Trade and Economics, 58012, Central Sq. 9, Chernivtsi, Ukraine
8 Kyiv National University of Trade and Economics, 02156, Kyoto Str. 21, Kyiv, Ukraine
9 Universidade Federal do Oeste do Pará, Campus Juriti, Rua V. de Souza Andrade, s/n, 68170-000, Juriti, PA, Brazil

* Correspondence: nightwatcher2401@gmail.com (V.V.T.); ved1988mid@rambler.ru (P.I.Y.);

Abstract: The theoretical description for 1-propenesulfenic acid and its isomer propanethial-S-oxide, substances, responsible for leek lacrimogenic activity, has been described theoretically. The process is realized anodically over a poly(naphthoquinone) – CoO(OH) composite. A model has been developed and analyzed using linear stability theory and bifurcation analysis. According to the model analysis, the ionic compound's transformation during the sulfenic acid oxidation may be responsible for the oscillatory and monotonic instability alongside the double electric layer (DEL) influences of the electrochemical stage. Nevertheless, the model's analysis shows that the electroanalytical process is efficient for determining both of the analytes.

Keywords: 1-propenesulfenic acid; propanethial-S-oxide; electrochemical sensors; cobalt (III) oxyhydroxide; electrochemical sensors; stable steady-state.

© 2020 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

As it is known, cutting crude onion, like also adding it into the food, leads to the tearing effect [1–3]. It is linked to the presence of the sulfurous organic compounds – 1-propenesulfenic acid and propanethial S-oxide. The acid is easily isomerized to the thioaldehyde S-oxide (Fig. 1).

Figure 1. 1-propenesulfenic acid isomerization to propanethial S-oxide.
Both substances are classified as irritant, possessing mild to moderate toxicity, which is much higher in excess [4–5]. Thus, the development of the methods for determining both of the substances is actual [6].

As both compounds contain sulfur in an intermediate oxidation state, it may be determined either cathodically or anodically. In the last case, a great variety of oxidants may be used, including conducting polymers [7–9], metallic nanoparticles [10–11], carbon materials [12–13]. Cobalt (III) oxyhydroxide, sole and in a composite with the conducting polymer [14–15] could be readily used for this purpose.

On the other hand, as the electrochemical instabilities are frequently observed in the organic molecules electrooxidation and electropolymerization [16–19], like also CoO(OH) electrosynthesis, the process of electrochemical determination of two sulfurous organic compounds in the presence of CoO(OH) and its composite with poly(5-amino-1,4-naphthoquinone) has to be thoroughly analyzed by theoretical means. Therefore, this work's goal is the mechanistic theoretical study of CoO(OH) – conducting polymer - assisted 1-propenesulfenic acid and propanethial-S-oxide determination with the development and analysis of the correspondent mathematical model. Also, the system's behavior will be compared to similar ones [20–21].

2. Materials and Methods

2.1. System and its modeling.

Schematically, the electroanalytical process is described in Fig. 2:

![Figure 2. The scheme of the electroanalytical process.](https://biointerfaceresearch.com/)

As seen from Fig. 1, both of the compounds are oxidized, yielding the hexavalent sulfur. The acid is oxidized by double bonds and sulfur atoms, yielding a hydroxysulfonic acid, much stronger than the initial sulfenic one. Therefore, forming a more ionic compound from a less ionic will influence the double electric layer (DEL) ionic force, conductivity, capacitance, and impedance, being responsible for the realization of electrochemical instabilities.

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

\[ s_1 \] – sulfenic acid concentration in the pre-surface layer; 
\[ s_2 \] – thioaldehyde oxide concentration in the pre-surface layer; 
\[ s_3 \] – CoO(OH) concentration in the pre-surface layer; 
\[ s_4 \] – CoO(OH) concentration in the composite layer; 
\[ s_5 \] – CoO(OH) concentration in the bulk layer.
c – cobalt (III) oxyhydroxide surface coverage degree.

In order to simplify the modeling, we assume that:
- the background electrolyte quantity is excessive in relation to the reacting substances so that we can neglect the migration flow and the oxidizing dopant oxidation change;
- the reactor is intensively stirred, permitting us to neglect the convection flow;
- the pre-surface layer concentration profile is linear, and it is of constant thickness, expressed as δ.

It is possible to prove that the differential equations’ set describing the system may be described as:

\[
\begin{align*}
\frac{ds_1}{dt} &= \frac{2}{\delta} \left( \frac{\Delta}{\delta} (s_0 - s_1) - r_i - r_{11} \right) \\
\frac{ds_2}{dt} &= \frac{2}{\delta} (r_i - r_{12}) \\
\frac{dc}{dt} &= \frac{1}{c} (r_2 - r_{11} - r_{12})
\end{align*}
\]  

(1)

Herein, Δ is the diffusion coefficient, s0 is the sulfenic acid bulk concentration, C is the cobalt oxyhydroxide maximal surface concentrations, and the parameters r are the correspondent reaction rates, calculated as:

\[
\begin{align*}
r_i &= k_i s_1 \exp(-a s_1) \\
r_{11} &= k_{11} s_1 c^4 \exp(-a s_1) \\
r_{12} &= k_{12} s_2 c^2 \\
r_2 &= k_2 (1 - c) \exp \left( \frac{F \phi_0}{RT} \right)
\end{align*}
\]  

(2) - (5)

The parameters are correspondent to k that are the reaction rate constants, a is the parameter relating the DEL capacitance with the sulfenic acid reactions, F=N_A*e stands for the Faraday number, \(\phi_0\) depicts the potential slope in a double electric layer, R is the universal gas constant, and T is the absolute temperature of the solution.

In this case, the system will be more dynamic than both CoO(OH)-assisted ionic compound determination and CoO(OH)-assisted isomerization monitoring due to the transformation of different organic sulfur ionic forms. These transformations have a strong impact on the systems’ behavior. Nevertheless, it doesn’t impede the system from being electroanalytical efficient, as shown below.

3. Results and Discussion

We observe the CoO(OH) – Poly(5-amino-1,4-naphthoquinone)-assisted 1-propenesulfenic acid and propanethial-S-oxide determination by analyzing the equation-set (2) by means of linear stability theory and bifurcation analysis. The steady-state Jacobian functional matrix members for this system may be described as:

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

(6)

Herein,

\[
\begin{align*}
a_{11} &= \frac{2}{\delta} \left( -\frac{\Delta}{\delta} - k_i \exp(-a s_1) + a k_i s_1 \exp(-a s_1) - k_{11} c^4 \exp(-a s_1) + a k_{11} s_1 c^4 \exp(-a s_1) \right) \\
a_{12} &= 0 \\
a_{13} &= \frac{2}{\delta} (-4 k_{11} s_1 c^3 \exp(-a s_1))
\end{align*}
\]  

(7) - (9)
\[ a_{21} = \frac{2}{\delta} (k_i \exp(-as_1) - ak_i s_1 \exp(-as_1)) \]  
\[ a_{22} = \frac{2}{\delta} (-k_{12}c^2) \]  
\[ a_{23} = \frac{2}{\delta} (-2k_{12}s_2c) \]  
\[ a_{31} = \frac{1}{c} (-k_{11}c^4 \exp(-as_1) + ak_{11}s_1c^4 \exp(-as_1)) \]  
\[ a_{32} = \frac{1}{c} (-k_{12}c^2) \]  
\[ a_{33} = \frac{1}{c} (-k_2 \exp \left( \frac{F\varphi_0}{RT} \right) + jk_2(1-c) \exp \left( \frac{F\varphi_0}{RT} \right) - 4k_{11}s_1c^3 \exp(-as_1) - 2k_{12}s_2c) \]  

Taking into account the addendums (7), (11), and (15), forming the Jacobian main diagonal, it is possible to confirm that it contains the elements capable of being positive, being, therefore, responsible for the positive callback, realizing the oscillatory behavior. Contrarily to the similar systems [20–21], in which the oscillatory behavior was caused by DEL influences of electrochemical process within the modifier and of the interaction between an ionic analyte and modifier, in this system, the DEL influence of isomerization, which transforms an ionic compound to a non-ionic, reducing the DEL ionic force. In contrast, the diffusion and sulfenic acid oxidation to sulfonic form augment it. By this, the changes in DEL ionic force, conductivity, impedance, and capacitance will be cyclical, providing the oscillatory behavior, which is mathematically condition of the positivity of the elements \( ak_i s_1 \exp(-as_1) > 0 \), \( ak_{11}s_1c^4 \exp(-as_1) > 0 \) and \( jk_2(1-c) \exp \left( \frac{F\varphi_0}{RT} \right) \). As DEL parameters' concrete values strongly depend on the background electrolyte composition, the oscillation amplitude will also be, as shown both experimentally and theoretically in [17–21].

As for the steady-state stability, in order to derive its requirement, we apply the Routh-Hurwitz stability criterion. Simplifying the determinant, we introduce new variables, rewriting it as:

\[
\frac{4}{\delta^2 c} \left| \begin{array}{ccc} -\kappa - \Xi - \Omega & 0 & -\Theta \\ \Xi & -\Lambda & -\Phi \\ -\Omega & -\Lambda & -\Xi - \Theta - \Phi \end{array} \right| \]  

Opening the straight brackets and applying the condition \( \text{Det } J < 0 \), salient from the criterion, we obtain the steady-state stability requisite, exposed as:

\[-\kappa(\Lambda \Omega + \Lambda \theta) - \Xi \Lambda \Omega - \Omega^2 \Lambda < 0 \]  

Which is warranted to be realized, if \( j<0 \) and \( a<0 \), defining the fragility of DEL influences of all chemical and electrochemical stages, capable of producing such influences. Really, in this case, the value of the expression to the left side of the equation (17) will be shifted to more negative values, stabilizing the system.

If the isomerization is relatively slow, the process will be either diffusion or kinetically controlled, as other processes are more rapid. On the other hand, if the isomerization is relatively rapid in the analysis conditions, diffusion will be the unique, controlling process.

As there are no side reactions capable of compromising the analyte and modifier stability are typical to this process, the steady-state stability will correspond to the linear dependence between the analytes’ concentration and the current in the system. Taking this into account, and considering that the steady-state stability is realized in the vast topological parameter region, the electroanalytical process may be considered as efficient.

The detection limit is defined by the margin between the steady stable-states and unstable states. Its condition is \( \text{Det } J = 0 \), or (18)
\[ -\kappa(\Delta \Omega + A\theta) - \varepsilon \Delta \Omega - \Omega^2 \lambda = 0 \]  

(18)

Suppose both of the isomers are ionic or yield ionic compounds during the electrooxidation. In that case, the electrochemical instabilities will be even more probable. The behavior of this system will be described in our next works.

4. Conclusions

From the theoretical analysis of the 1-propenesulfenic acid and propanethial S-oxide electrochemical determination, it was possible to conclude that the electroanalytical system will be generally efficient. Nevertheless, some of the behavior aspects will be strongly dependent on the supporting electrolyte composition. If the isomerization is rapid, the process will be diffusion controlled; if slow, it will be diffusion and kinetically controlled. As for the oscillatory behavior, it is possible, being caused by double electric layer influences not only of electrochemical stages and modifier-analyte chemical interactions but also of the isomerization of an ionic compound to a non-ionic form. The oscillation amplitude will be strongly dependent on the electrolyte composition.

Funding

This research received no external funding.

Acknowledgments

This research has no acknowledgment.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Moussa, Z.; Judeh, Z.M.A.; Ahmed, S. Nonenzymatic Exogenous and Endogenous Antioxidants. In: Free Radical Medicine and Biology. Open Access Peer-Reviewed Chapter, 2019.
2. Quesada, I.; de Paola, M.; Torres-Palazzolo, C.; Camargo, A.; Ferder, L.; Manucha, W.; Castro, C. Effect of Garlic’s Active Constituents in Inflammation, Obesity and Cardiovascular Disease. Current Hypertension Reports 2020, 22, https://doi.org/10.1007/s11906-019-1009-9
3. Kacjan Marsic, N.; Necemer, M.; Veberic, R.; Ulrih, N.; Skrt, M. Effect of cultivar and fertilization on garlic yield and allicin content in bulbs at harvest and during storage. Turkish Journal Of Agriculture And Forestry 2019, 43, 414-429.
4. Kot, M.; Olech, Z. Effect of Thermal Processing on Antioxidant Power and Thiosulfinate Content in Brussels Sprout Juices. Biotechnol. Food. Sci. 2017, 81, 83–92.
5. Patel, G.; Dalwadi, C. Cytotoxicity and Cellular Uptake of 5-Fluorouracil Loaded Methylcellulose Nanohydrogel for Treatment of Oral Cancer. Lett. Appl. NanoBioSci. 2021, 10, 1904–1918, https://doi.org/10.33263/LIANBS101.19041918.
6. Li, C.; Wang, Y.; Jiang, H.; Wang, X. Biosensors Based on Advanced Sulfur-Containing Nanomaterials. Sensors 2020, 20, https://doi.org/10.3390/s20123488.
7. Bagheri, A.; Hassan Marand, M. Voltammetric and Potentiometric Determination of Cu²⁺ Using an Overoxidized Polypyrrole Based Electrochemical Sensor. Russian Journal of Electrochemistry 2020, 56, 453-461, https://doi.org/10.1134/S1023193520060026.
8. Li, J.; He, Y.; Sun, Y.; Zhang, X.; Shi, W.; Ge, D. Synthesis of Polypyrrole/V2O5 Composite Film on the Surface of Magnesium Using a Mild Vapor Phase Polymerization (VPP) Method for Corrosion Resistance. Coatings 2020, 10, https://doi.org/10.3390/coatings10040402.
9. Koseoglugu, T.S.; Durgut, A. Development of a Novel Molecularly Imprinted Overoxidized Polypyrrole Electrode for the Determination of Sulfasalazine. Electroanalysis 2020, 32, 2072-2081, https://doi.org/10.1002/elan.202060036.
10. Kumar, Y.; Vashishtha, V.K.; Das, D.K. Synthesis of Perovskite-type NdFeO$_3$ nanoparticles and used as electrochemical sensor for detection of paracetamol. *Lett. Appl. Nanobiosci.* 2020, 9, 866–869, https://doi.org/10.33263/LIANBS91.866869.

11. Rajaram, R.; Kiruba, M.; Suresh, C.; Mathiyarasu, J.; Kumaran, S.; Kumaresan, R. Amperometric determination of Myo-inositol using a glassy carbon electrode modified with nanostructured copper sulfide. *Microchimica Acta* 2020, 187, https://doi.org/10.1007/s00604-020-04300-z

12. Xiang, H.; Cai, Q.; Li, Y.; Zhang, Z.; Cao, L.; Li, K.; Yang, H. Sensors Applied for the Detection of Pesticides and Heavy Metals in Freshwaters. *Journal of Sensors* 2020, 2020, https://doi.org/10.1155/2020/8503491.

13. Noori, J.S.; Mortensen, J.; Geto, A. Recent Development on the Electrochemical Detection of Selected Pesticides: A Focused Review. *Sensors* 2020, 20, https://doi.org/10.3390/s20082221.

14. Aguilera, L.; Aguiar, P.C.M.; Ruiz, Y.L.; Almeida, A.; Moreira, J.A.; Passos, R.R.; Pocrifka, L.A. Electrochemical synthesis of $\gamma$-CoOOH films from $\alpha$-Co(OH)$_2$ with a high electrochemical performance for energy storage device applications. *Journal of Materials Science: Materials in Electronics* 2020, 31, 3084-3091, https://doi.org/10.1007/s10854-019-02853-1.

15. Shamraiz, U.; Badshah, A.; Raza, B. Ultrafine $\alpha$-CoOOH Nanorods Activated with Iron for Exceptional Oxygen Evolution Reaction. *Langmuir* 2020, 36, 2223-2230, https://doi.org/10.1021/acs.langmuir.9b03293.

16. Das, I.; Goel, N.; Agrawal, N.R.; Gupta, Growth patterns of dendrimers and electric potential oscillations during electropolymerization of pyrrole using mono-and mixed surfactants. *J. Phys. Chem. B* 2010, 114, 12888-12896, https://doi.org/10.1021/jp105183q.

17. Das, I.; Goel, N.; Gupta, S.K.; Agrawal, N.R. Electropolymerization of pyrrole: Dendrimers, nano-sized patterns and oscillations in potential in presence of aromatic and aliphatic surfactants. *J. Electroanal. Chem.* 2012, 670, 1-10, https://doi.org/10.1016/j.jelechem.2012.01.023.

18. Bazzaoui, M.; Bazzaoui, E.A.; Martins, L.; Martins, J.I. Electropolymerization of pyrrole on zinc–lead–silver alloys electrodes in acidic and neutral organic media. *Synthetic Metals* 2002, 130, 73-83, https://doi.org/10.1016/S0379-6779(02)00101-7.

19. Tkach, V.V.; Nechyporuk, V.V.; Kushnir, V.M.; Yagodynets’, P.I. Descripción Matemática de la Electropolimerización de Monómeros, Modificados Electroquímicamente, *Afnidad*, 2015, 72, 218–222.

20. Tkach, V.V.; Kushnir, M.V.; Storoshchuk, N.M.; Ivanushko, Y. The Theoretical Description for the Confection of the Novel Thiourea-Based Active Surface for Cathodic Conducting Polymer Deposition. *Appl. J. Env. Eng. Sci.* 2020, 6, 143–148.

21. Tkach, V.; Kushnir, M.; Ivanushko, Y.; de Oliveira, S.; Reis, L.; Yagodynets’, P.; Kormosh, Z. The Theoretical Description for the Electrochemical Synthesis of Squaraine Dye Doped Conducting Polymer. *Appl. J. Env. Eng. Sci.* 2020, 6, 51–56.