

Full Paper

The Mechanism of Electroanalytical Function of CoO(OH) in the Oxalic Acid Electrochemical Determination and its Mathematical Representation

Volodymyr V. Tkach,^{1,2,*} Sílvio C. de Oliveira,² Fauze J. Anaissi,³ Reza Ojani,⁴ Ulises Páramo-García,⁵ Olga Yelenich¹ and Petro I. Yagodynets¹

¹ Chernivtsi National University, 58012, Kotsyubyns'ky 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 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, Brazil

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

⁵ 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

* Corresponding Author, Tel.: +5521991809675

E-Mail: nightwatcher2401@gmail.com

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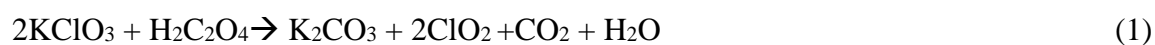
Abstract- The mechanism for the electroanalytical function of the cobalt oxyhydroxycompound in the electrochemical oxidation of oxalic acid was suggested. The mathematical model, describing this process, has been developed and analyzed by means of steady-state stability theory and bifurcation analysis. The behavior of the system was compared with the behavior of analogous systems. The steady-state stability requirements and oscillatory and monotonic instability conditions have been obtained. These instabilities may be caused by surface and electrochemical factor. The oscillation frequency and amplitude are pH-dependent, and the first parameter grows with pH. The pH-range of

electroanalytical sensing efficiency was also derived and it is corresponding to moderate alkaline solutions.

Keywords- Cobalt oxide-hydroxide, Electrocatalytic oxidation, Mechanistic analysis, Oscillatory behavior, Stable steady-state, Bifurcation analysis

1. INTRODUCTION

Oxalic acid and its derivatives are biologically important compounds [1]. They may be encountered in several plants like *Rumex Acetosa* [2] and participate in biochemical metabolic processes, like Krebs cycle [3]. It is also used in organic [4] and inorganic laboratory preparative synthesis of some compounds, like ClO_2 :



At the other hand, oxalates are toxic compounds, because of the calcium oxalate formation in kidney and renal tubules [5]. The toxicity depends on the concentration in the organism, for example, its human LD_{50} is 600 mg/kg. So, the development of precise, exact and clear methods of determination of oxalate concentration is still an actual task.

Many non-electrochemical [6–14] and electrochemical methods [15–21] of oxalate determination have been developed and, besides of some advantages, given by the first, the second ones are seen as more suitable, due to their low price, rapidity and efficiency.

The principal problems of the electrochemical sensors of different organic and small inorganic compounds [22–30] is the use of expensive metal electrodes (like platinum, gold and palladium), uncertain mechanism of electrochemical oxidation in different media, overvoltage, needed to be applied on bare metal electrodes, electrochemical instabilities, common during the electrooxidation of small organic molecules (including oxalic acid) and electropolymerization of heterocyclic compounds [31–40]. They may be resolved (partially or fully) by introducing of electrodes, chemically modified by substances, capable to participate in the electrochemical process as active substance and mediators, diminishing the overvoltage and the probability of electrochemical instabilities.

The modifying materials are chosen according to the analyte (the principle of the key and lock), electrochemical process (reduction or oxidation), sensing type, and concentration range. They may be organic, like conducting polymers, or ferrocene derivatives [41–45] and inorganic, like titanium dioxide, heteropolyanion and complexes [46–50].

Cobalt (III) oxyhydroxide is one of the novel inorganic materials, viewed as an alternative to titanium dioxide. It is a semiconductor of p-type, optically active material, also capable to be photo- and photoelectrocatalytic surface, due to its intensively black color [51–54]. It is generally obtained electrochemically, by electrolysis of a salt of cobalt (II) in

the presence of trace amounts of fluoride ions, for porosity reasons [55]. This electrochemical process is also accompanied by oscillatory behavior (Fig. 1).

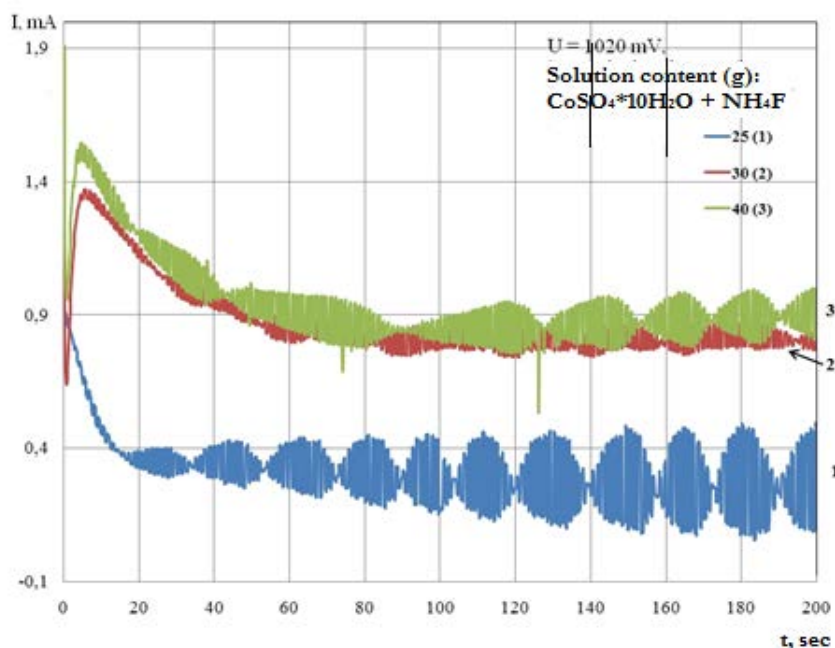


Fig. 1. Oscillatory behavior during the electrosynthesis of $\text{CoO}(\text{OH})$ on platinum from CoSO_4

The oscillation amplitude and frequency was different in different fluoride concentration, which may be referred to more active surface behavior (particle attraction) during the dissolution in the case of 3 (more fluoride), 2 and 1 (less fluoride).

In the major part of cases, such phenomena received merely phenomenological explanations. Despite of being based on logical arguments, it's feeling lack of a rigid theoretical base, given only by developed and analyzed 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) [55–68] and $\text{CoO}(\text{OH})$ synthesis. So, this work is the continuation of the investigation line, involving the work mechanism of different electroanalytical systems and also of the investigation of the properties of $\text{CoO}(\text{OH})$, the

analytical characteristics of which haven't been studied well yet. It is the continuation of the research, begun in [69], in which the oxalate electrochemical detection over CoO(OH) was experimentally described.

2. THE MECHANISM AND ITS MATHEMATICAL REPRESENTATION

As the oxalate determination is realized in alkaline media, the acid is transformed into its salt:



It is then oxidated over CoO(OH) by:



Cobalt (II) oxide is then electrooxidized, recovering the presence of CoO(OH)



Other side reaction, possible in strongly alkaline media is the dissolution, forming a complex ion:



Taking in account the reactions (3 – 5), we introduce next variables:

c – the oxalate-ion concentration in the pre-surface layer,

θ – the CoO(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 δ , and the concentration profile of the analyte and the alkali, to be linear.

The oxalate-ion enters the pre-surface layer by diffusion and then reacts with CoO(OH), yielding CO₂ and hydroxyl. 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:

$$\frac{dc}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (c_0 - c) - r_3 \right) \quad (6)$$

In which Δ is the diffusion coefficient, c_0 is the analyte bulk concentration and r_3 is the rate of the reaction (3).

The oxy-hydroxycompound of cobalt is formed by electrooxydation (4) of the oxide, formed in the reaction (3) in alkaline aqueous media. It is dissolved in the strongly alkaline media (5) forming a hydroxyl complex. Thus, its balance equation will be described as:

$$\frac{d\theta}{dt} = \frac{1}{\Gamma} (r_4 - r_3 - r_5) \quad (7)$$

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

The hydroxyl enters the pre-surface layer by alkali diffusion. It is also formed in the reaction (3), participating in the reactions (4) and (5). So, its balance equation will be described as:

$$\frac{da}{dt} = \frac{2}{\delta} \left(\frac{D}{\delta} (a_0 - a) - r_4 + r_3 - r_5 \right) \quad (8)$$

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

The corresponding reaction rates may be calculated as:

$$r_3 = k_3 c \theta^2 \quad (9)$$

$$r_4 = k_4 a (1 - \theta) \exp\left(\frac{F\varphi_0}{RT}\right) \quad (10)$$

$$r_5 = k_5 \theta a^3 \exp(-\beta\theta) \quad (11)$$

In which, the parameters k are rate constants of corresponding reactions, F is Faraday number, φ_0 is the DEL potential slope, related to the zero-charge potential, R is universal gas constant, T is absolute temperature, β 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 amphoterity of $\text{Co}(\text{III})$ compounds, they dissolve in strongly alkaline media, which makes their behavior more complicated.

3. RESULTS AND DISCUSSION

To analyze the electroanalytical behavior of $\text{CoO}(\text{OH})$ in oxalate electrochemical detection in alkaline media, we investigate the differential equation system (6–8), describing the mechanism (3–5), taking in account the algebraic relations (9–11) using the linear stability theory. The Jacobian functional matrix, calculated for the steady-state, will be rewritten as:

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

in which:

$$a_{11} = \frac{2}{\delta} \left(-\frac{A}{\delta} - \frac{r_3}{c} \right) \quad (13)$$

$$a_{12} = \frac{2}{\delta} \left(-2k_3c\theta \right) \quad (14)$$

$$a_{13} = 0 \quad (15)$$

$$a_{21} = \frac{1}{\Gamma} \left(-\frac{r_3}{c} \right) \quad (16)$$

$$a_{22} = \frac{1}{\Gamma} \left(-k_4a \exp\left(\frac{F\varphi_0}{RT}\right) + k_4a(1-\theta)\alpha \exp\left(\frac{F\varphi_0}{RT}\right) - 2k_3c\theta - k_5a^3 \exp(-\beta\theta) + \beta k_5a^3 \exp(-\beta\theta) \right) \quad (17)$$

$$a_{23} = \frac{1}{\Gamma} \left(k_4(1-\theta) \exp\left(\frac{F\varphi_0}{RT}\right) - 3k_5\theta a^2 \exp(-\beta\theta) \right) \quad (18)$$

$$a_{31} = \frac{2}{\delta} \left(\frac{r_3}{c} \right) \quad (19)$$

$$a_{32} = \frac{2}{\delta} \left(k_4a \exp\left(\frac{F\varphi_0}{RT}\right) - k_4a(1-\theta)\alpha \exp\left(\frac{F\varphi_0}{RT}\right) + 2k_3c\theta - k_5a^3 \exp(-\beta\theta) + \beta k_5a^3 \exp(-\beta\theta) \right) \quad (20)$$

$$a_{33} = \frac{2}{\delta} \left(-\frac{D}{\delta} - k_4(1-\theta) \exp\left(\frac{F\varphi_0}{RT}\right) - 3k_5\theta a^2 \exp(-\beta\theta) \right) \quad (21)$$

The oscillatory behavior for this system, like the other systems with CoO(OH) electrochemical synthesis 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:

$k_4a(1-\theta)\alpha \exp\left(\frac{F\varphi_0}{RT}\right) > 0$, if CoO is strong reductant in the synthesis conditions, causing the positivity of the DEL potential slope φ_0 , similarly to the other cases of electrochemical sensing with active mediators [56 - 68];

$\beta k_5a^3 \exp(-\beta\theta) > 0$, in the case of attraction of the adsorbed particles during the film dissolution and complex formation.

By the way, in the case of the work [55], the oscillatory behavior was caused by attraction of adsorbed particles during the film dissolution [70] by reaction:



Defining the film instability and pore formation in the presence of fluoride-ion. In this system, one of the cases for the oscillatory behavior is similar to the case of [55].

It's important to pay attention that the alkali concentration is included in the positive Jacobian addendums, so, the oscillations' frequency and amplitude depend of pH. The pH-dependence of the mentioned parameters will be analogous to the expressed on the curves (1-3) of the Fig. 1, due to analogy of two systems, so in highly alkaline solutions the oscillations will be of lower amplitude and more frequent.

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:

$$\frac{4}{\Gamma\delta^2} \begin{vmatrix} -\kappa - \xi & -\mathcal{E} & 0 \\ -\xi & -\mathcal{E} + \Omega + \Lambda & -Z \\ \xi & \mathcal{E} - \Omega + \Lambda & -Z - \gamma \end{vmatrix} \quad (23),$$

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

Using the inequality $\text{Det } J < 0$, we obtain the steady-state stability condition in the form of:

$$-Z(\kappa\mathcal{E} - \kappa\Omega + \kappa\Lambda - \xi\Omega - \xi\Lambda) - (Z + \gamma)(\kappa\mathcal{E} - \kappa\Lambda + \xi\mathcal{E} - \xi\Omega) < 0 \quad (24)$$

that may be transformed into:

$$-(Z + \gamma)(\kappa\mathcal{E} - \kappa\Lambda + \xi\mathcal{E} - \xi\Omega) < Z(\kappa\mathcal{E} - \kappa\Omega + \kappa\Lambda - \xi\Omega - \xi\Lambda) \quad (25)$$

$$-(Z + \gamma) < \frac{Z(\kappa\mathcal{E} - \kappa\Omega + \kappa\Lambda - \xi\Omega - \xi\Lambda)}{(\kappa\mathcal{E} - \kappa\Lambda + \xi\mathcal{E} - \xi\Omega)} \quad (26)$$

and, finally,

$$\gamma > -\frac{Z(\kappa\mathcal{E} - \kappa\Omega + \kappa\Lambda - \xi\Omega - \xi\Lambda)}{(\kappa\mathcal{E} - \kappa\Lambda + \xi\mathcal{E} - \xi\Omega)} - Z \quad (27)$$

It may be seen, that the steady-state stability (and the reaction course) is defined in this system by rapid alkali and analyte diffusion (high values of γ and κ) and by quick reaction of alkali, be it with CoO, or with CoO(OH) (high value of Z).

At the other hand, the high positive values of Ω (defining the strong influences of the electrochemical reactions on DEL) and Λ (defining CoO(OH) rapid dissolution with attracting interaction of adsorbed particles), yet discussed concerning the oscillatory behavior, drive the system to the less stable steady-states. Like in analogous systems [76–96], they do not favor the steady-state stability.

In the case of the equality of the mentioned influences to the stabilizing ones, the *monotonic instability*, which condition may be represented as (28):

$$\gamma = -\frac{Z(\kappa\mathcal{E} - \kappa\Omega + \kappa\Lambda - \xi\Omega - \xi\Lambda)}{(\kappa\mathcal{E} - \kappa\Lambda + \xi\mathcal{E} - \xi\Omega)} - Z \quad (28)$$

It is revealed by N-shaped voltamperogram.

In the case of *excess* of an alkali, relatively to the oxalate, 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 and stable. The analysis of this case will be described and discussed in our next works.

It may be shown from the analysis that the excess of alkali in moderately basic pH is favorable to detect low concentrations of oxalate. It may be shown on the table:

Table 1. The relation between analyte concentration, alkalinity of the solution and steady-state stability

Analyte concentration	Alkalinity	Analytical efficiency	Steady-state stability
Relatively high	Moderate, (7<pH<10,5; without excess)	Efficient	Favored
Relatively low	Moderate (7<pH<10,5; excess)	Efficient	Favored
-	Very high (pH>12)	Non-efficient, material destruction	Non-favored by surface effects of dissolution

In the case of highly alkaline systems, the participation of the oxalate-ion in the system may be neglected and the equation (6) leaves the equation set and the task stops to be electroanalytical, being now relative to the corrosion and material stability.

In the case of autocatalytic behavior, characteristic for oxalate-ion, the equation system is modified, like it was described in [55-68]. 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 oxalate 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 alkali and analyte diffusion (high values of γ and κ) and by quick reaction of alkali, be it with CoO, or with CoO(OH)
- The oscillatory behavior for this system is possible and may be caused by electrochemical, surface and autocatalytic, if any, factors. The pH of the solution influences their frequency and amplitude, and the first parameter grows with pH.
- 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.

REFERENCES

- [1] J. B. Cohen, Practical Organic Chemistry, Macmillan And Co. Ltd., London (1930) pp 368. [Online] available at:
http://library.sciencemadness.org/library/books/practical_organic_chemistry.pdf
Accessed at 8th of August (2015)
- [2] [Online] available at: <http://www.longwoodherbal.org/sorrel/sorrel.pdf>; Accessed at 8th of August (2015).
- [3] W.W. Cleland, and M. H. Johnson, J. Bio. Chem. 220 (1956) 595.
- [4] [online] available at:
<http://www.grandcircuitinc.com/sites/default/files/Howard%20Alliger%20%20An%20Overall%20View%20CI02.pdf> Accessed at 8th of August, 2015
- [5] M. Tsujihata, Int. J. Urol. 15 (2008) 115.
- [6] E. Yusenko, E. Polovintseva, A. Lyzhova, and A. Kalyakina, Proc. Latv. Acad. Sci. 67 (2013) 429.
- [7] H. Ilarsan, R. Palmer, J. Imsande, and H. Horner, Am. J. Bot. 84 (1997) 1042.
- [8] Q. S. Cao, Y. M. Ba, J. H. Luo, and Q. Dai, Act. Acad. Med. Sin. 37 (2015) 83.
- [9] J. Su, Y. Q. Sung, F. J. Huo, Y. T. Yang, and C. X. Yin, Analyst 135 (2010) 2918.
- [10] K. M. Lathika, K. V. Inamdar, U. Tarachandm, B. B. Singh, and K. G. Raghavan, Anal. Lett. 28 (1995) 425.
- [11] J. Kaloustian, A. M. Pauli, G. Pieroni, and H. Portugal, J. Therm. Anal. Calor. 20 (2002) 959.
- [12] W. Li, and G. P. Savage, Foods 4 (2015) 140.
- [13] X. Tang, N. V. Voskoboev, S. L. Wannarka, J. B. Olson, D. S. Milliner, and J. C. Lieske, Am. J. Nephrol. 39 (2014) 376.
- [14] V. Kalra, and C. S. Pundir, Ind. J. Biotechnol. 3 (2004) 52.
- [15] C. S. Pundir, and M. Sharma, J. Sci. Ind. Res. 69 (2010) 489.
- [16] S. Milardovic, Z. Grabaric, V. Rumenjak, and J. Marijana, Electroanalysis 12 (2000) 1051.
- [17] T. E. Benavidez, R. H. Capra, C. I. Álvarez, and A. M. Baruzzi, Electroanalysis 21 (2009) 837.
- [18] R. Chaudhary, and C. S. Pundir, Sens. Trans. 113 (2010) 127.
- [19] M. K. Sezgintürk, and E. A. Dinçkaya, Talanta 59 (2002) 545.
- [20] M. A. Rahni, and G. G. Guilbault, Anal. Chem. 58 (1986) 523.
- [21] J. Zhong, Z. Qi, C. Fan, G. Li, and N. Matsuda, Anal. Sci. 19 (2003) 653.
- [22] S. Balasubramanian, A. Revzin, and A. Simonian, Electroanalysis 18 (2006) 1885
- [23] Y. Z. Zhuang, C. F. Lin, H. H. Tsai, H. H. Liao, and R. L. Wang, Proc. Eng. 47 (2012) 1005.
- [24] K. Rovina, S. Siddiquee, and N. K. Wong, Sens. Bio. Sens. Res. 4 (2015) 16.

- [25] W. Kang, X. Pei, A. Bange, E. N. Haynes, W. R. Heineman, and I. Papautsky, *Anal. Chem.* 86 (2014) 12070.
- [26] Y. Zhang, M. Zhang, Z. Cai, M. Chen, and F. Cheng, *Electrochim. Acta* 68 (2012) 172.
- [27] C. Y. Na, K. Zhuo, and W. J. Kim, *Sens. Actuators B* 213 (2015) 329.
- [28] Y.T. Lee, J. Lee, H. Hwang, W. Lee, H. Bae, and S. Im, *Sens. Actuators B* 209 (2015) 490.
- [29] L. V. Mihajlovic, S. D. Nikolic-Mandic, and R. P. Mihajlovic, *J. Appl. Electrochem.* 39 (2009) 1917.
- [30] X. Lu, *Adv. Mat. Res.* 1006-1007 (2014) 811.
- [31] L. Hudson, and M. R. Bassett, *Rev. Chem. Eng.* 7 (1991) 108.
- [32] M. Pagitsas, and S. Dimitra, *Electrochim. Acta* 36 (1991) 1301.
- [33] A. J. Pearlstein, and J. A. Johnson, *J. Electrochem. Soc.* 136 (1991) 1290.
- [34] I. Das, N. R. Agrawal, S. A. Ansari, and S. K. Gupta, *Ind. J. Chem.* 47 (2008) 1798.
- [35] S. U. Rahman, and M. S. Ba-Shammakh, *Synth. Met.* 140 (2004) 207.
- [36] A. S. Liu, and M. A. S. Oliveira, *J. Braz. Chem Soc.* 18 (2007) 143.
- [37] D. Sazou, *Synth. Met.* 130 (2002) 45.
- [38] I. Das, N. Goel, N. R. Agrawal, S. K. Gupta, *J. Phys. Chem.* 114 (2010) 12888.
- [39] M. Bazzaoui, E. A. Bazzaoui, L. Martins, and J. I. Martins, *Synth. Met.* 130 (2002) 73.
- [40] I. Das, N. Goel, S. K. Gupta, and N. R. Agrawal, *J. Electroanal. Chem.* 670 (2012) 1.
- [41] Y. Meng, X. Zou, X. Huang, A. Goswami, Z. Liu, and T. Asefa, *Adv. Mater.* 26 (2014) 6510.
- [42] H. Shu, Applications of poly(3-hexylthiophene) thin film as a hydrazine-sensitive chemoresistor, M. Sc. Thesis, Auburn, Alabama (2006).
- [43] H. Beitollahi, S. Tajik, H. Kerimi-Maleh, and R. Hosseinzadeh, *Appl. Organometal. Chem.* 27 (2013) 444.
- [44] R. Ojani, J. B. Raoof, and S. R. Hosseini, *Electrochim. Acta* 53 (2008) 2402.
- [45] R. Ojani, J. B. Raoof, A. Ahmady, and S. R. Hosseini, *Casp. J. Chem.* 2 (2013) 45.
- [46] R. Ojani, J. B. Raoof, and P. S. Afagh, *J. Electroanal. Chem.* 571 (2004) 571.
- [47] R. Ojani, and E. Zarei, *J. Braz. Chem. Soc.* 24 (2013) 657.
- [48] L. Ruhlmann, and G. Genet, *J. Electroanal. Chem.* 568 (2004) 315.
- [49] B. Keita, I. M. Mbomekalle, L. Nadjjo, and R. Contant, *Electrochem. Comm.* 3 (2001) 267.
- [50] J. Obirai, and T. Nyokong, *J. Electroanal. Chem.* 573 (2004) 77.
- [51] J. Yang, H. Liu, W. N. Martens, and R. L. Frost, *J. Phys. Chem. C* 114 (2010) 111.
- [52] J. W. Wang, and Y. M. Kuo, *Phys. Stat. Sol.* 210 (2013) 494.
- [53] A. D. Jagadale, D. P. Dubal, and C. D. Lokhande, *Mat. Res. Bull.*, 47 (2012) 672.

- [54] O. Stadnik, N. Ivanova, Y. Boldyrev, 218th Int. Electrochem. Soc. Meeting. Abstract # 2240, [Online] available at: <http://ma.ecsdl.org/content/MA2010-02/38/2240.full.pdf> Accessed at 8th of August (2015).
- [55] O. Stadnik, Synthesis, Electrochemical and Photoelectrochemical Properties of the Oxide-hydroxide Compounds of Cobalt, Diss. Kand. Chim. N. – Kyiv. (2011).
- [56] V. Tkach, V. Nechyporuk, and P. Yagodynets, *Rev. Colomb. Cien. Quím. Farm.* 42 (2013) 30.
- [57] V. Tkach, V. Nechyporuk, and P. Yagodynets', *Anal. Bioanal. Electrochem.* 6 (2014) 273.
- [58] V. Tkach, V. Nechyporuk, and P. Yagodynets', *Rev. Colomb. Cienc. Quím. Farm.* 42 (2013) 215.
- [59] V. Tkach, H. Nascimento, V. Nechyporuk, and P. Yagodynets', *Rev. Col. Cienc. Quím. Farm.* 43 (2014) 196.
- [60] V. Tkach, B. Kumara Swamy, R. Ojani, M. Blanes, and P. Yagodynets, *Orbital. Elec. J. Chem.* 7 (2015) 1.
- [61] V. V. Tkach, R. Ojani, M. O. G. Espínola, P. Yagodynets', S. C. de Oliveira, *Química: ciência, tecnologia e sociedade* 3 (2014) 35.
- [62] V. Tkach, R. Ojani, V. Nechyporuk, P. Yagodynets, *Rev. Colomb. Cien. Quím. Farm.* 43 (2014) 35.
- [63] V. Tkach, R. Ojani, V. Nechyporuk, and P. Yagodynets', *Orbital. Elec. J. Chem.* 6 (2014) 142.
- [64] V. Tkach, R. Ojani, S. C. de Oliveira, O. I. Aksimentyeva, and P. I. Yagodynets, *Anal. Bioanal. Electrochem.* 7 (2015) 291.
- [65] V. Tkach, R. Ojani, V. Nechyporuk, and P. Yagodynets, *Rev. Colomb. Cien. Quím. Farm.* 44 (2015) 58.
- [66] V. Tkach, V. Nechyporuk, and P. Yagodynets', *Quím. Bras.* 7 (2013) 65.
- [67] V. Tkach, G. Maia, S. C. de Oliveira, *Quím. Mater.* 4 (2014) 7.
- [68] V. Tkach, R. Ojani, V. Nechyporuk, and P. Yagodynets, *Quím. Mater.* 44 (2015) 67.
- [69] A. Stadnik, E. M. Caldas, A. Galli, and F. J. Anaissi, *Orbital. Elec. J. Chem.* 7(2015) 122.
- [70] V. Tkach, V. Nechyporuk, and O. Slipenyuk, *Eclét. Quím.* 37 (2012) 74.