



The mathematical stability study for the system of the CoO(OH) – overoxidized polypyrrole composite synthesis in the presence of fluor ions

V.Tkach^{1,2*}, S.C.de Oliveira², R.Ojani³, P.I.Yagodnynets¹, U.Páramo-García⁴

¹Chernivtsi National University, Kotsjubynskiy street 2, Chernivtsi 58012, Ukraine

²Universidade Nacional de Mato Grosso do Sul, Brazil

³University of Mazandaran, Islamic Republic of Iran

⁴Instituto Tecnológico de Ciudad Madero, Mexico

ARTICLE INFO: Received 17 May 2015; revised 03 January 2016; accepted 07 January 2016

Abstract: The potentiostatic synthesis of CoO(OH) – Overoxidized polypyrrole composite in the presence of fluor ions has been investigated mathematically. The corresponding mathematical model was described and analyzed by means of linear stability theory and bifurcation analysis. The steady-state stability requirements, like also oscillatory and monotonic instability conditions are derived.

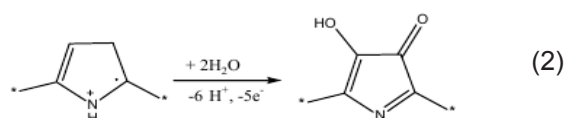
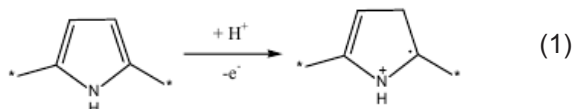
Keywords: Cobalt oxide-hydroxide, overoxidized polypyrrole, composite, fluoride, steady-state stability

INTRODUCTION

Oxy-hydroxycompound of cobalt, described by the formula of CoO(OH), is a very interesting material [1-3], that is viewed as an alternative to titanium dioxide in photo- and photoelectrocatalysis, for LEDs, and other optical devices, due to its intensively black color. It may also be used in corrosion-protecting coatings on some metal surfaces.

On the other hand, the conducting polymers (CP) are another class of attractive materials, extensively investigated during the last 5 decades [4-10], due to their capability to combine the properties of plastics with metal conductivity and facility in modification. They also have vast and rich use spectrum, beginning on corrosion protection and ending with sensors and biosensors [11-20]. So, the composite of CoO(OH) with conducting polymers must have interesting optical, electroanalytic and catalytic (including electrocatalytic) properties.

One of negative sides of the electrochemical synthesis of CoO(OH) from cobalt salts may be the Co²⁺ oxidation potential, superior to the overoxidation potential of some conducting polymers, like some polypyrroles, by the scheme:



Other negative side of the use of CoO(OH) is its instability in the presence of fluoride ions, which form the complex ions by reaction:



The synthesis may also be affected by electrochemical instabilities, accompanying both the synthesis of conducting polymers [21-30] and of CoO(OH) [31-32], like oscillations, represented in Figures 1-4.

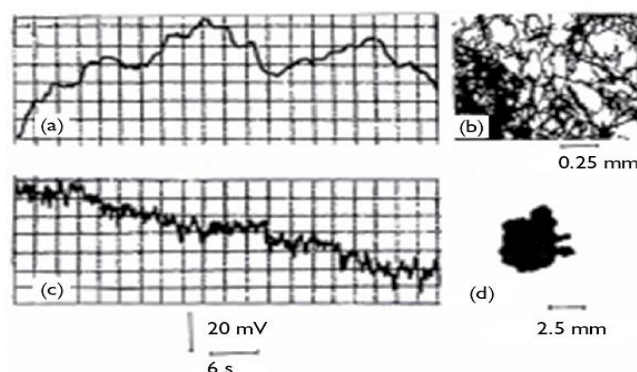


Fig. 1. The oscillatory behavior during the anodic electropolymerization of thiophene with two different background electrolytes-4-TSS (argentum 4-tolylsulphate) (a) and ZnSO₄ (c) and corresponding morphological changes (b,d). Reproduced from [22] with the permission of IN-SCAR, India

In the most part of reported works, these phenomena received purely phenomenological explanation, which besides of being logically argued, didn't have strong theoretical base, which may only be given by development and analysis of a mathematical model, capable to describe adequately the system's behavior. This modeling is also capable to describe the behavior of relative systems and also compare it with the

*corresponding author: e-mail: nightwatcher2401@gmail.com

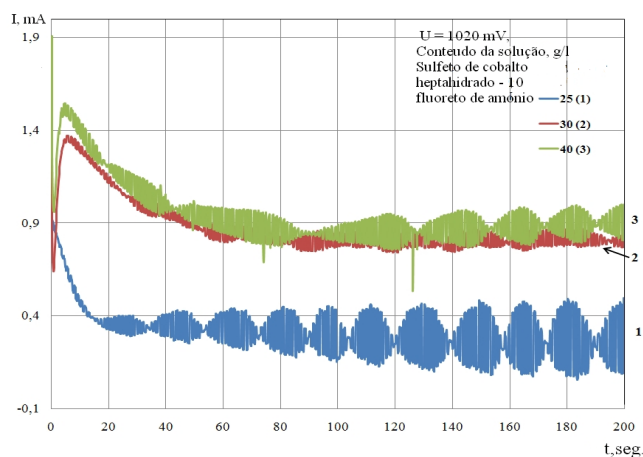


Fig. 2. The oscillatory behavior in current during the anodic synthesis of CoO(OH) in the presence of different concentration of ammonium fluoride. Reproduced from [31] with author's permission

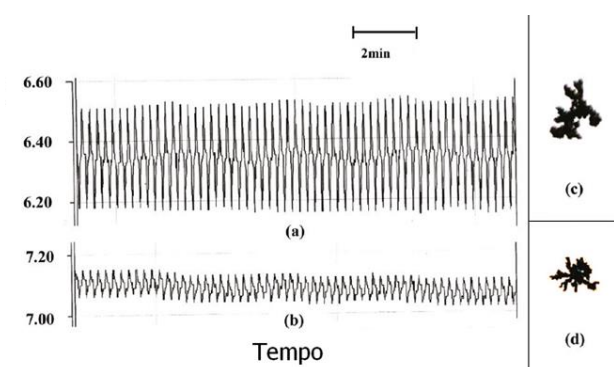


Fig. 3. The oscillatory behavior, observed during the electropolymerization of pyrrole in strongly acid media with (a) and without (b) the use of surfactants, (c) and (d) represent the surface modifications. Reproduced from [23] with the permission of Elsevier, the Netherlands.

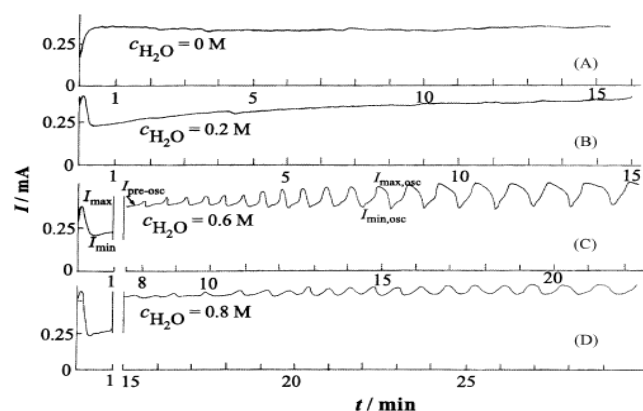


Fig. 4. The current responses, observed during potentiostatic electropolymerization of indole over iron in ACN-Water mixtures without (a, b) and with (c, d) oscillatory behavior. Reproduced from [24] with the permission of Elsevier, the Netherlands.

behavior of other systems with additional experimental essays.

We have made an effort to describe the behavior of analogous systems with electropolymerization and overoxidation of conducting polymers in different conditions [33-40] and electrosynthesis of CoO(OH) [41, 42]. So, in this work we continue this research

line and describe mathematically the potentiostatic synthesis of the CoO(OH)-overoxidized polypyrrole (OPPy) composite in the presence of fluoride ions and compare its behavior with the behavior of analogous systems, involving conducting polymers and CoO(OH).

System and its behavior: To describe mathematically the CoO(OH)-OPPy composite potentiostatic electro-synthesis in neutral solutions in the presence of fluoride, we introduce two variables:

- f - fluoride concentration in pre-surface layer;
- θ - the composite coverage degree.

To simplify the modeling, we assume that the reactor is stirred intensively, to neglect the convection flow, that the background electrolyte, containing the cobalt salt, is in excess, so we can neglect the migration flow. Also we suppose that the concentration profile of the fluoride is linear and the pre-surface layer is of constant thickness, equal to δ .

The fluoride-containing electrolyte enters the pre-surface layer by diffusion and leaves it, reacting with the composite film of CoO(OH)-OPPy. So, according to the Fick's first law and taking in account the DEL (double electric layer)-relative modeling coefficient, we may describe the fluoride concentration balance equation like:

$$\frac{dc}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (c_0 - c) - r_2 \right) \quad (4)$$

where:

- c_0 - a fluoride bulk concentration;
- r_2 - the reaction rate of composite destruction.

The composite is formed by the polypyrrole overoxidation in the presence of an excess of the salt of Co^{2+} as a background electrolyte (and we assume that at the beginning of the reaction the initial polymer covers the entire electrode surface), and then is destroyed, by reacting with fluoride-ion, so, the balance equation for its surface concentration may be described as:

$$\frac{d\theta}{dt} = \frac{1}{G} (r_1 - r_2) \quad (5)$$

where:

- G - the composite maximal concentration;
- r_1 - the reaction rate of its electrosynthesis.

The corresponding reaction rates may be calculated as:

$$r_1 = k_1 (1 - \theta) \exp \frac{zF\phi_0}{RT} \quad (6)$$

$$\frac{dc}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (c_0 - c) - r_2 \right) \quad (7)$$

where:

- k - reaction rate constants;
- z - the number of transferred electrons during the electrochemical processes;

$F=N_A \cdot e$ - the Faraday number;
 φ_0 - the DEL potential slope, compared to the zero-charge potential, calculated for the initial state of the surface;
 R - the universal gas constant;
 T - the absolute temperature;
 a - the variable, describing the interaction of adsorbed particles.

Generally, the equation set resembles the systems with overoxidation [29, 30] and CoO(OH) synthesis [31], but the behavior seems to be more simple than for the case of CoO(OH) synthesis, but more complicated, than for the case of common overoxidation. The behavior comparison will be discussed below.

RESULTS AND DISCUSSION

To analyze the system with the electrosynthesis of the composite CoOOH – OPPy in the presence of F^- , we investigate the equation set (4, 5) with the use of linear stability theory. The Jacobian functional matrix, described for the steady-state, will be rewritten as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \quad (8)$$

in which:

$$a_{11} = \frac{2}{\delta} \left(-k_2 \theta \exp(-a\theta) - \frac{\Delta}{\delta} \right)$$

$$a_{12} = \frac{2}{\delta} \left(-k_2 c \exp(-a\theta) + a k_2 \theta c \exp(-a\theta) \right)$$

$$a_{21} = \frac{1}{r} \left(-k_2 \theta \exp(-a\theta) \right)$$

$$a_{22} = \frac{1}{r} \left(-k_1 \exp \frac{zF\varphi_0}{RT} - b k_1 (1 - \theta) \exp \frac{zF\varphi_0}{RT} - k_2 c \exp(-a\theta) + a k_2 \theta c \exp(-a\theta) \right) \quad (9-12)$$

For the two-dimensional system, the stable steady-state requirements and main instabilities conditions may be described as:

Steady-state stability	Tr J < 0, Det J > 0
Oscillatory instability	Tr J = 0, Det J > 0
Monotonic instability	Tr J < 0, Det J = 0
Double instability	Tr J = Det J > 0

To simplify the analysis, we introduce new variables, for the Jacobian determinant to be described as:

$$\frac{2}{\delta G} \begin{vmatrix} -\kappa - \xi_1 & -\lambda \\ -\xi_1 & -\Lambda - \lambda \end{vmatrix} \quad (13)$$

In which:

$$\frac{\Delta}{\delta} = \kappa,$$

$$k_2 \theta \exp(-a\theta) = \xi_1,$$

$$k_2 c \exp(-a\theta) + a k_2 \theta c \exp(-a\theta) = -\lambda$$

$$-b k_1 (1 - \theta) \exp \frac{zF\varphi_0}{RT} - k_2 c \exp(-a\theta) = -\Lambda$$

As the condition Tr J < 0 is satisfied for the major part of cases in this system (κ and ξ_1 are always positive, Λ and λ are positive for the most cases), the main condition will be Det J > 0, or:

$$\frac{2}{\delta r} (\kappa \Lambda + \xi_1 \Lambda + \kappa \lambda) > 0 \quad (14)$$

It may be concluded, that the steady-state stability in this system is warranted by:

- the absence of strong influences in DEL of the electrochemical processes, maintaining Λ positive;
- the repelling interaction of adsorbed particles during the complex reaction with fluoride ions, maintaining the positive values of λ .

In the mentioned conditions, the steady-state will be stable and synthesis will be driven according to the Tafel conditions. The electrosynthesis is controlled by the diffusion of Co salt, as it is the slowest process.

The oscillatory behavior for this system is possible and will be realized in the main condition of Tr J = 0, or:

$$-\kappa - \xi_1 = \Lambda + \lambda \quad (15)$$

The expression on the left side of the equation is always negative, but the right side will be negative only in the case of the negativity of lambda parameters, which may be realized in the cases of:

$\Lambda < 0$ in the case of the strong influences of the composite synthesis on DEL. This cause is also valid for the electropolymerization (incl. the cases of "polythiophene paradox"), but not for the most potentiostatic overoxidation systems.

$\lambda < 0$ in the case of the presence of the attracting interaction of the adsorbed particles on the electrode surface, which makes the value of λ negative. This cause is valid for the electropolymerization of heterocyclic compounds and CoO(OH) electrosynthesis, but not for the most potentiostatic overoxidation systems. The amplitude of these oscillations will depend on the electrolyte composition (like on the Fig. 1 and 2), fluoride concentration and electrode surface.

The monotonic instability for the system is possible and may be realized in the conditions of:

$$\frac{2}{\delta r} (\kappa \Lambda + \xi_1 \Lambda + \kappa \lambda) = 0 \quad (16)$$

That may be transformed to:

$$\frac{2\kappa}{\delta r \xi_1} (\Lambda + \lambda) = -\Lambda \quad (17)$$

So, the monotonic instability in this system may occur, like in the electropolymerization systems and CoO(OH) synthesis systems, but contrarily to the most potentiostatic overoxidation systems. They occur in the specific value of the composite destruction reaction parameters ξ_1 and λ , so, in the case of the occurrence of this instability, the responsible process will be the reaction between the composite and the fluoride ions.

The double instability, or Takens-Bogdanov instability is also possible for this system. Imputting the value of λ of the equation (15) to (17), we obtain its condition like:

$$\frac{2\kappa}{\delta\Gamma\xi_1}(-\kappa - \xi_1) = -A \quad (18)$$

So, the double instability will occur in the specific value of the destruction rate, defined by fluoride diffusion and composite formation.

Autocatalytic behavior for this system may be possible in certain conditions (like the use of strongly acid media) and for this case the model (4, 5) will be changed. The autocatalytic behavior, if any, may be one more factor, responsible for the oscillatory behavior.

So, the model analysis shows, that the real synthesis of CoO(OH)-PPy composites will obey the general behavior features of diffusion-controlled systems. The stable steady-state is formed easily for the vast region of the parameters' values.

In the oscillatory mode, the time dissipative structure, analogous to the "predator-victim" oscillator, may be formed in the system. Its existence is maintained by cobalt salt diffusion (entrance of the entropy) and the stable composite formation (exit of the entropy).

CONCLUSIONS

1. For the most cases in this system, the steady-state is stable, and the steady-state stability is warranted by the absence of strong influences in DEL of the electrochemical processes, and the repealing interaction of adsorbed particles during the complex reaction with fluoride ions. When these conditions are satisfied, the reaction is diffusion-controlled.
2. The oscillatory behavior for this system is possible, being caused by surface and electrochemical factors. So, the presence of time dissipative structures in this system may be confirmed.
3. The monotonic instability in this system may occur and the responsible reaction will be the composite destruction by fluoride ions.
4. The Takens-Bogdanov instability in this system may occur in the specific value of the destruction rate, defined by fluoride diffusion and composite formation.
5. Autocatalytic behavior in this system, if any, will be responsible to the oscillatory behavior in it.

REFERENCES

1. Yang J., Liu H., Martens W.N., Frost R.L. (2010) Synthesis and characterization of cobalt hydroxide, cobalt oxyhydroxide, and cobalt oxide nanodiscs. *J. Phys. Chem. C.*, **114**, 111 - 119
2. Wang J.W., Kuo. (2013) Hierarchically porous cobalt oxyhydroxide derived from Morpho-butterfly wings: Preparation, characterization and carbon monoxide detection at low temperatures. *Phys. Stat. Sol.*, **210**, 494 - 502
3. Jagadale A.D., Dubal D.P., Lokhande C.D. (2012) Electrochemical behavior of potentiodynamically

deposited cobalt oxyhydroxide (CoO(OH)) thin films for supercapacitor application. *Mat. Res. Bull.*, **47**, 672

4. Sadki S. Scotland Ph., Brodie N., Saboraud G. (2000) The mechanism of pyrrole electropolymerization. *Chem. Soc. Rev.*, **29**, 283-293
5. Roncali J. (1992) Conjugated poly(thiophenes). *Chem. Rev.*, **92**(1992), 711-738
6. Ramoa S.D.A., Merlini C., Barra G.M.O., Soares B.G. (2014), Obtenção de nanocompósitos condutores de montmorilonita/polipirrol: efeito da incorporação do surfactante na estrutura e propriedades, *Polímeros*, **24**, 57-62 (in Portuguese)
7. Yamamoto T. (2010) Molecular assembly and properties of polythiophenes. *Asia Materials*, **2**, 54-60.
8. Ojani R., Raof J.B., Ahmady A., Hosseini S.R. (2013) Highly improved methanol oxidation onto carbon paste electrode modified by nickel particles dispersed into poly(2,5-dimethylaniline) film. *Casp. J. Chem.*, **2**, 45-57
9. deAndrade V.M. (2006) Confecção de biossensores através da imobilização de biocomponentes por eletropolimerização de pirrol, Tese de Mestrado em Engenharia. M.Sc. Thesis, UFRGS., Porto Alegre. (In Portuguese)
10. Tosar Rovira J.P (2008) Estudio de la inmovilización de oligonucleótidos a electrodos modificados de oro:polipirrol, y detección electroquímica de secuencias complementarias. Tesis de Licenciatura en Bioquímica, Universidad de la República, Montevideo. B.Sc. thesis (In Spanish)
11. Ramanavicius A., Ramanaviciene A., Malinauskas A. (2006) Electrochemical sensors, base don conducting polymer, polypyrrole. *Electrochim. Acta*, **51**(2006), 6025-6037
12. R. Singh. (2012) Prospects of organic conducting polymer modified electrodes: Enzymosensors. *Int. J. Electrochem.*, doi.org/10.1155/2012/502707
13. Zane D., Appetecchi G. B., Bianchini C. *et al.* (2011) An impedimetric glucose biosensor on overoxidized polypyrrole thin film. *Electroan.*, **23**, 1134-1141
14. McQuade T., Pullen A., Swager T.M. (2000) Conjugated polymer based chemical sensors. *Chem. Rev.*, **100**, 2537-2574
15. Ojani R., Raof J.B., Rahemi V., (2011) A simple and efficient electrochemical sensor for electrocatalytic reduction of nitrite based on poly(4-aminoacetanilide) film using carbon paste electrode. *J. Chin. Chem. Soc.*, **58**, 247-254
16. Schweiger B., Kim J., Kim Y.J., Ulbricht M. (2015) Electropolymerized molecularly imprinted polypyrrole film for sensing of clofibrac acid. *Sensors*, **15**, 4870-4889
17. Wang L., Xu H., Song Y. *et al.* (2015) Carbon fiber ultramicrodic electrode electrodeposited with overoxidized polypyrrole for amperometric detection of vesicular exocytosis from pheochromocytoma cell. *Sensors*, **15**, 868-879

18. Afkhami A., Gomar F., Madrakian T. (2015) Electrochemical sensor for Dapsone using molecularly imprinted polypyrrole membrane as a recognition element *J. Electrochem. Soc.*, **162**, 109-113
19. Montoya P., Mejía S., Gonçalves V.R. (2015) Performance improvement of macroporous polypyrrole sensor for detection of ammonia by incorporation of magnetite nanoparticles, *Sens. Act. B. Chem.*, **213**, 444-451
20. Alizadeh N., Ataei A.A., Pirsá S. (2015) Nanostructure conducting polymer polypyrrole film, prepared by chemical vapor deposition on the interdigital electrodes at room temperature under atmospheric conditions and its application as the gas sensor. *J. Iran Chem. Soc.*, **12**, 1585-1594
21. Liu A.S., Oliveira M.A.S. (2007) Electrodeposition of polypyrrole films on aluminium from tartrate aqueous solution. *J. Braz. Chem. Soc.*, **18**, 143-152
22. Sazou D. (2002) The dynamic behavior of the electrochemical polymerization of indole in acetonitrile - water mixtures *Synth. Met.*, **130**, 45-54
23. Das I., Goel N., Agrawal N.R., Gupta S.K. (2010) Growth patterns of dendrimers and electric potential oscillations during electropolymerization of pyrrole using mono- and mixed surfactants. *J. Phys. Chem.*, **114**, 12888-12896
24. Bzzaoui M., Bzzaoui E.A., Martins L., Martins J.I. (2002) Electropolymerization of pyrrole on zinc-lead-silver alloys' electrodes in neutral and acidorganic media. *Synth. Met.*, **130**, 73-83
25. Das I., Goel N., Gupta S. K., Agrawal N.R. (2012) Electropolymerization of pyrrole: Dendrimers, nano-sized patterns and oscillations in potential in presence of aromatic and aliphatic surfactants. *J. Electroanal. Chem.*, **670**, 1-10
26. Aoki K., Mukoyama I., Chen J. (2004) Polymerization and dissolution of polythiophene films. *Russ. J. Electrochem.*, **40**, 319-324
27. Das I., Agrawal N.R., Ansari S.A., Gupta S.K. (2008) Pattern formation and oscillatory electropolymerization of thiophene *Ind. J. Chem.*, **47A**, 1798-1803.
28. Ba-Shammakh M.S. (2002) Electropolymerization of pyrrole on mild steel for corrosion protection, Ph.D Thesis. King Fahd University of Petroleum and Minerals, Dharan, Saudi Arabia
29. Ba-Shammakh, M.S., Rahman, S.U., Abul-Hamayel M.A., Kahraman R. (2003) Thermal effects of pyrrole electropolymerization on mild steel. 203rd ECS Meeting, April 27-May 2, 2003, Paris, France. AC1. Organic and Bioorganic Electrochemistry General Session. No2468. <http://www.electrochem.org/dl/ma/203/pdfs/2468.pdf>
30. K.R. Lemos Castagno. (2006) Pattern formation and oscillatory electropolymerization of thiophene Tés. D.Sc. UFRS, Porto Alegre (Ph.D. Thesis in Portuguese)
31. Stadnik O. (2011) Synthesis, electrochemical and photoelectrochemical properties of the oxide-hydroxide compounds of cobalt. Diss. Kand. Chim. Nauk. Kyiv
32. Stadnik O., Ivanova N., Boldyrev Y. (2010) 218th Int. Electrochem. Soc. Meeting. Abstract 2240, <http://ma.ecsdl.org/content/MA2010-02/38/2240.full.pdf>
33. Tkach V., Nechyporuk V., Yagodynets' P. (2015) The mathematical description for the electropolymerization of furan, pyrrole and thiophene derivatives in alkaline media. *Med. J. Chem.*, **3**, 1122-1127
34. Tkach V., Nechyporuk V., Yagodynets' P. (2012) Eletropolimerização dos compostos heterocíclicos. Modelos matemáticos. *Ciê. Tecn. Mat.*, **24**, 54-58 (In Portuguese)
35. Tkach V., Nechyporuk V., Yagodynets' P. (2014) O estudo de estabilidade do processo da eletropolimerização de pirróis N-substituídos. *Proc. Quím.*, **8**, 49-56 (In Portuguese)
36. Tkach V., Nechyporuk V., Yagodynets' P., Hryhoryak M. (2012) A investigação do comportamento eletroquímico durante a síntese eletroreduziva de polímeros condutores na presença de catiões dos metais. *Cien. Tecn. Mat.*, **24**, 50-53 (In Portuguese)
37. Tkach V., Nechyporuk V., Yagodynets' P. (2013) As eletropolimerizações galvanostática e potenciodinâmica (em voltagem constante) dos compostos heterocíclicos e a sua descrição matemática. *Tecn. Met. Mat. Min.*, **10**, 249-256 (In Portuguese)
38. Tkach V., Nechyporuk V., Yagodynets' P. (2013) Descripción matemática de la síntesis electroquímica de polímeros conductores en la presencia de surfactantes. *Avan. Quím.*, **8**, 9-15 (In Spanish)
39. Tkach V., Nechyporuk V., Yagodynets' P. (2013) The general mathematical model for the oscillatory behavior of the electrochemical systems with electropolymerization of heterocyclic compounds in organic solvents in passivation conditions. *Avan. Quím.*, **8**, 97-104
40. Tkach V., Nechyporuk V., Yagodynets' P. (2013) Estudio matemático de las condiciones de estabilidad en la polimerización electroquímica de compuestos heterocíclicos en presencia de oxidantes. *Afinidad*, **70**, 73-77 (In Spanish)
41. Tkach V., Nechyporuk V., Slipenyuk O. (2012) A descrição matemática do fenômeno oscilatório durante a síntese eletroquímica dos filmes de oxi-hidroxi compostos de cobalto (III) e durante síntese dos compósitos deles com polímeros condutores. *Ecl. Quím.*, **37**, 72-76 (In Portuguese)
42. V.Tkach, V.Nechyporuk, O.Slipenyuk. (2012) Descrição matemática da síntese eletroquímica dos filmes de compostos oxi-hidroxi de cobalto (III) e durante a síntese dos compósitos deles com os polímeros condutores. Anais do II Encontro Internacional de Corrosão INTERCORR-2012, de 14 a 18 de maio de 2012, Salvador, BA, Comunicação 19 (in Portuguese)