











The Theoretical Description for the Reductive Indirect Electropolymerization of some Pyridinic Derivatives on Vanadium(III) Oxyhydroxide-modified Cathode

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Abstract: In this work, the theoretical description for the VO(OH)-assisted reductive electropolymerization of a pyridinic monomer or another heterocyclic monomer with one or more pyridinic nitrogen heteroatoms. The analysis of the correspondent mathematical model has confirmed the efficiency of the assisted electropolymerization and the enhanced process and surface stability related to the direct electropolymerization. The polymer surface is somehow more developed than in the case of direct electrochemical polymerization. As for the oscillatory behavior, it is less probable than for direct electropolymerization due to the absence of surface instability for indirect electropolymerization. The probability of the oscillatory behavior will be dependent on the ionization degree of the monomer.

Keywords: vanadium (III) oxyhydroxide; pyridine; reductive electropolymerization; indirect electropolymerization; anion-radical; electrochemical oscillations; stable steady-states.

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1. Introduction

Indirect electropolymerization [1–4], in other words, electropolymerization, is a process in which the monomer doesn't interact with the electrode but with the electrode reaction product. This change makes the electropolymerization process more flexible from the mechanistic point of view, providing a higher tunability of the resulting polymer properties.

In most cases, the electropolymerization (direct or indirect) is given by monomer oxidation, yielding cation-radical. Even if realized on the cathode, the cathodic reaction yields *in situ* an oxidant, attacking the monomer and creating the chain growth center as a radical cation. In some cases [5–7], the cathodic electropolymerization is given to the cathode by the

direct cathodic reaction. By this, the growth center is an anion-radical, which may also be created by an indirect cathodic or anodic reaction involving electrochromic materials.

Nevertheless, this type of polymerization is possible for the specific type of monomers. Most are 5- or 6-atom heterocyclic compounds with pyridinic nitrogen atoms with lone or condensed rings (pyrazoles, imidazoles, thiazoles, pyridines, quinolines, acridines, phenanthridines, *etc.*). Carbocyclic aromatic compounds with 2 or more accepting groups and azulenic derivatives may also polymerize by this mean. The electropolymerization is thereby given by nucleophilic mechanism, so the monomer units are linked via nucleophilic centers, not via electrophilic ones, as in direct anodic electropolymerization.

Their polymers may be used in corrosion protection, smart coatings, supercapacitors, and sensors. Also, they may be used to eliminate chlorogenic compounds like sucralose[8,9]. Moreover, indirect electropolymerization may be more economical and more “green” than direct one, as it may require reduced energy spending and involve monomers capable of being extracted from renewable fonts [10–14].

Even though direct anodic polymerization is generally used [15–21], it requires high anodic potential or specific oxidants for assisted polymerization. So, cathodic direct and assisted electropolymerization may be a suitable alternative, providing more developed polymer surfaces.

In this work, the theoretical description for the possibility of vanadium (III) oxyhydroxide-assisted cathodic electropolymerization of a pyridinic monomer via anion-radical formation has been realized. Vanadium (III) oxyhydroxide, in this case, changes the modification during the gradual anodic reaction, yielding a more active form, transferring the electron to the monomer, and provoking the polymer growth [8–21]. The system’s behavior will also be compared with that of similar systems [22–28].

2. Materials and Methods

The initiating VO(OH)-form is yielded by gradual vanadium dioxide reduction by:



The reaction (2) is, in fact, the initial stage of the trivalent vanadium reduction into bivalent, but it is unfinished in the synthesis conditions.

The electron transference, leading to chain initiation, will be thereby described as:



Therefore, to describe the behavior of this system, we introduce the trivariant equation-set of the next variables:

v – vanadium (III) oxyhydroxide less active modification surface coverage degree;

v^* – vanadium (III) oxyhydroxide more active modification surface coverage degree;

m – monomer pre-surface concentration.

Taking some assumptions [8,9,22–28], we describe the behavior of this system by a balance equation-set (4):

$$\begin{cases} \frac{dv}{dt} = \frac{1}{v} (r_1 - r_2) \\ \frac{dv^*}{dt} = \frac{1}{v^*} (r_2 - r_p) \\ \frac{dm}{dt} = \frac{2}{\delta} \left(\frac{M}{\delta} (m_0 - m) - r_p \right) \end{cases} \quad (4)$$

Herein, V and V^* are the maximal surface concentrations of the correspondent modifications of VO(OH), M is the monomer diffusion coefficient, m_0 its bulk concentration, and the parameters r are the correspondent reaction rates, calculated as:

$$r_1 = k_1(1 - v - v^*) \exp \frac{F\varphi_0}{RT} \quad (5)$$

$$r_2 = k_1 v \exp \frac{F\varphi_0}{RT} \quad (6)$$

$$r_p = k_p v^{*x} m^y \exp(-am) \quad (7)$$

Herein, the parameters k stand for the correspondent reaction rate constants, F is the Faraday number, φ_0 stands for zero-charge-related potential slope, R is the universal gas constant, T is the absolute temperature, and a is the variable describing the DEL influences of the polymerization stage, x , and y are the polymerization reaction orders.

If the monomer isn't significantly ionized during the electrochemical process, the exponential multiplier is turned to one, as the parameter a is reset to zero, and the reaction rate expression becomes simplified.

The oscillatory and monotonic instability in this system is more probable for ionic monomers and less probable for less ionic. Either way, it will be less probable, and the system will be more stable than direct polymerization in the same conditions, as shown below.

3. Results and Discussion

We investigate the behavior of VO(OH)-assisted cathodic reductive electropolymerization over vanadium (III) oxyhydroxide during modification reducing interchange by analyzing equation-set (4) by linear stability theory. The Jacobian matrix steady-state elements are described as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (8)$$

In which:

$$a_{11} = \frac{1}{V} \left(-k_1 \exp \frac{F\varphi_0}{RT} + jk_1(1 - v - v^*) \exp \frac{F\varphi_0}{RT} - k_1 \exp \frac{F\varphi_0}{RT} + jk_2 v \exp \frac{F\varphi_0}{RT} \right) \quad (9)$$

$$a_{12} = \frac{1}{V} \left(-k_1 \exp \frac{F\varphi_0}{RT} + lk_1(1 - v - v^*) \exp \frac{F\varphi_0}{RT} - lk_2 v \exp \frac{F\varphi_0}{RT} \right) \quad (10)$$

$$a_{13} = 0 \quad (11)$$

$$a_{21} = \frac{1}{V^*} \left(k_1 \exp \frac{F\varphi_0}{RT} - jk_2 v \exp \frac{F\varphi_0}{RT} \right) \quad (12)$$

$$a_{22} = \frac{1}{V^*} \left(lk_2 v \exp \frac{F\varphi_0}{RT} - xk_p v^{*x-1} m^y \exp(-am) \right) \quad (13)$$

$$a_{23} = \frac{1}{V^*} \left(-yk_p v^{*x} m^{y-1} \exp(-am) + ak_p v^{*x} m^y \exp(-am) \right) \quad (14)$$

$$a_{31} = 0 \quad (15)$$

$$a_{32} = \frac{1}{V^*} \left(-xk_p v^{*x-1} m^y \exp(-am) \right) \quad (16)$$

$$a_{33} = \frac{1}{V^*} \left(-\frac{M}{\delta} - yk_p v^{*x} m^{y-1} \exp(-am) + ak_p v^{*x} m^y \exp(-am) \right) \quad (17)$$

Observing the Jacobian main diagonal elements (9), (13), and (17), we may observe that all of them contain positive addendums related to the positive callback. Therefore, the Hopf bifurcation is possible, and the oscillatory behavior may be manifested in this system. It is caused by the DEL capacitance and conductivity impact of both electrochemical stages, leading to the initiator synthesis, like the initiated indirect electropolymerization.

They are described by the positivity of the elements $jk_1(1 - v - v^*) \exp \frac{F\varphi_0}{RT} > 0$ and $jk_2v \exp \frac{F\varphi_0}{RT} > 0$, if $j>0$, $lk_1v \exp \frac{F\varphi_0}{RT} > 0$, if $l>0$ and $ak_p v^x m^y \exp(-am) > 0$, if $a>0$. The action and the intensity of these factors are related to DEL capacitance and conductivity, which are directly related to background electrolyte composition (including pH). For this reason, the frequency and amplitude of the oscillations will be dependent on those factors, which have already been experimentally [22–24] and theoretically [25–28] proved.

Either way, the probability of the oscillatory behavior, in this case, will be much lower than for direct electropolymerization (anodic or cathodic), as the surface factor, which is manifested in the direct electropolymerization processes, does not play a significant part here. Therefore, adsorption instability isn't possible in this case, so the process is more stable.

To describe the *steady-state stability*, we apply the Routh-Hurwitz stability criterion to the equation set (4). We introduce new variables, rewriting the determinant as (18):

$$\frac{2}{\delta V V^*} \begin{vmatrix} -\Omega - \Sigma & -\Lambda - P & 0 \\ \Sigma & P - T & -E \\ 0 & -T & -\kappa - E \end{vmatrix} \quad (18)$$

To avoid cumbersome expressions.

Opening the brackets and applying the Det J<0 requisite, salient from the criterion, we obtain the stability condition, expressed as (19):

$$\Omega(T\kappa - P\kappa - PE) + \Sigma(T\kappa + \Lambda\kappa + PE) > 0 \quad (19)$$

Describing an efficient kinetically controlled system, in which the steady state is easily obtained and maintained, providing a well-developed polymeric coating synthesis. It may have excellent anticorrosive, catalytic, sensoric, and capacitor systems. Moreover, it is capable of retaining heavy metal cations and some chloroorganic compounds, like sucralose.

This makes the obtained process even more important, providing a simplified metal-polymer composite synthesis and chloroorganic compounds removal from wastewater.

As for monotonic instability, it delimits the stable steady-states and unstable states. Its condition may be described as Det J = 0, or (20):

$$\Omega(T\kappa - P\kappa - PE) + \Sigma(T\kappa + \Lambda\kappa + PE) = 0 \quad (20)$$

In some cases, the tetravalent vanadium may not be involved. Therefore, the process will be described by the equations (21 – 22):



By this, the equation-set becomes bivariate, and this process will be described in our next works.

4. Conclusions

From the theoretical analysis of cathodic indirect VO(OH)-assisted electropolymerization, it was possible to conclude that this process is an efficient kinetically controlled electrochemical system. The oscillatory behavior in this system is possible, and the oscillation frequency and amplitude depend strongly on the background electrolyte nature. Either way, the oscillatory behavior is less probable for the direct anodic or cathodic electropolymerization of the same monomer in the same conditions, providing a more economical and green process.

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Conflicts of Interest

The authors declare no conflict of interest.

References

1. Zhang, Y.; Huang, R.; Wang, X.; Wang, Z.; Song, B.; Du, Y.; Lu, Q.; Chen, X.; Sun, J. Facile large-scale preparation of vanadium pentoxide -polypyrrole composite for aqueous zinc-ion batteries. *Journal of Alloys and Compounds* **2022**, *907*, <https://doi.org/10.1016/j.jallcom.2022.164434>.
2. Chavan, U.D.; Prajith, P.; Kandasubramanian, B. Polypyrrole based cathode material for battery application. *Chemical Engineering Journal Advances* **2022**, *12*, <https://doi.org/10.1016/j.cej.2022.100416>.
3. Kondratiev, V.; Holze, R. Intrinsically Conducting Polymer Binders for Battery Electrodes. *Encyclopedia* **2022**, *2*, 1753-1762, <https://doi.org/10.3390/encyclopedia2040120>.
4. Tkach V.V.; Kushnir M.V.; Kopyika V.V.; Luganska, O.V.; Omelianchuk, L.O.; Yeshchenko, Y.V.; Kormosh, Z.O.; Kryvetskyi, V.V.; Kryvetskyi, I.V.; Kryvets, I.I.; Rusnak, V.F.; Banul, B.Y.; Gordiyenko, N.M.; Britsyna, Y.V.; Bagrii, K.L.; Strutynska, L.T.; Danyliuk, I.P.; de Oliveira, S.C.; Yagodynets, P.I.; Razhabova, D.B.; Niyazov, L.N. Theoretical Evaluation for the Assisted Electropolymerization of a Monomer, Obtained by an Indirect Electrochemical Synthesis. *Lett. Appl. NanoBioSci.* **2022**, *11*, 3605-3610, <https://doi.org/10.33263/LIANBS112.36053610>.
5. Sumisha, A.; Haribabu, K. Nanostructured Polypyrrole as Cathode Catalyst for Fe(III) Removal in Single Chamber Microbial Fuel Cell. *Biotechnol. Bioproc.* **2022**, *25*, 78–85, <https://doi.org/10.1007/s12257-019-0288-y>.
6. Samyn, L.M.; Babu, R.S.; Devendiran, M.; de Barros, A.L.F. Electropolymerization of p-phenylenediamine films on carbon fiber fabrics electrode for flexible supercapacitors: surface and electrochemical characterizations. *Ionics* **2020**, *26*, 3041-3050, <https://doi.org/10.1007/s11581-020-03562-0>.
7. Bagheri, A.; Hassani 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. Tkach, V.V.; Storoshchuk, N.M.; Oliveira, S.C.d.; Ivanushko, Y.G.; Nazymok, Y.V.; Luganska, O.V.; Yagodynets, P.I. The theoretical description for the sucralose electrochemical determination, assisted by poly(safranin) modified electrode. *Ukrainica Bioorganica Acta* **2021**, *16*, 34-37.
9. Tkach, V.V.; Kushnir, M.V.; de Oliveira, S.C.; Zavorodnii, M.P.; Brazhko, O.A.; Kornet, M.M.; Luganska, O.V.; Kopyika, V.V.; Ivanushko, Y.G.; Mytchenok, M.P. The Theoretical Description for a Sucralose Electrochemical Cathodical Determination over a 9-9'-Diacridyl-modified Electrode. *Orbital: The Electronic Journal of Chemistry* **2021**, *13*, 219–222.
10. Yu, P.-J.; Lin, Y.-C.; Lin, C.-Y.; Chen, W.-C. Enhanced mobility preservation of polythiophenes in stretched states utilizing thienyl-ester conjugated side chain. *Polymer* **2023**, *264*, <https://doi.org/10.1016/j.polymer.2022.125575>.
11. Akinay, Y.; Çolak, B.; Turan, M.E.; Akkuş, I.N.; Kazici, H.Ç.; Kizilçay, A.O. The electromagnetic wave absorption properties of woven glass fiber composites filled with Sb₂O₃ and SnO₂ nanoparticles doped mica pigments. *Polymer Composites* **2022**, *43*, 8784-8794, <https://doi.org/10.1002/pc.27061>.
12. Cao, Y.; Mohamed, A.M.; Mousavi, M.; Akinay, Y. Poly(pyrrole-co-styrene sulfonate)-encapsulated MWCNT/Fe–Ni alloy/NiFe₂O₄ nanocomposites for microwave absorption. *Materials Chemistry and Physics* **2021**, *259*, <https://doi.org/10.1016/j.matchemphys.2020.124169>.
13. Lan, L.; Li, Y.; Zhu, J.; Zhang, Q.; Wang, S.; Zhang, Z.; Wang, L.; Mao, J. Highly flexible polypyrrole electrode with acanthosphere-like structures for energy storage and actuator applications. *Chemical Engineering Journal* **2023**, *455*, <https://doi.org/10.1016/j.cej.2022.140675>.
14. Jang, H.J.; Shin, B.J.; Jung, E.Y.; Bae, G.T.; Kim, J.Y.; Tae, H.-S. Polypyrrole film synthesis via solution plasma polymerization of liquid pyrrole. *Applied Surface Science* **2023**, *608*, <https://doi.org/10.1016/j.apsusc.2022.155129>.

15. Bouabdallaoui, M.; Aouzal, Z.; El Guerraf, A.; Ben Jadi, S.; Bazzaoui, M.; Wang, R.; Bazzaoui, E.A. Influence of polythiophene overoxidation on its physicochemical properties and corrosion protection performances. *Materials Today: Proceedings* **2020**, *31*, S69-S74, <https://doi.org/10.1016/j.matpr.2020.06.067>.
16. Pinto Medeiros, M.F.X.; Leyva, M.E.; Alencar de Queiroz, A.A.; Maron, L.B. Electropolymerization of polyaniline nanowires on poly(2-hydroxyethyl methacrylate) coated Platinum electrode *Polímeros* **2020**, *30*, <https://doi.org/10.1590/0104-1428.02020>.
17. Yang, P.; Zhang, S.; Chen, X.; Liu, X.; Wang, Z.; Li, Y. Recent developments in polydopamine fluorescent nanomaterials. *Materials Horizons* **2020**, *7*, 746-761, <https://doi.org/10.1039/c9mh01197h>.
18. Liu, Y.; Wang, Y.; Meng, Y.; Plamthottam, R.; Tjiu, W.W.; Zhang, C.; Liu, T. Ultrathin Polypyrrole Layers Boosting MoO₃ as Both Cathode and Anode Materials for a 2.0 V High-Voltage Aqueous Supercapacitor. *ACS Applied Materials & Interfaces* **2022**, *14*, 4490-4499, <https://doi.org/10.1021/acscami.1c20922>.
19. Chepurayaya, I.; Smirnova, E.; Karushev, M. Electrochemically Active Polymer Components in Next-Generation LiFePO₄ Cathodes: Can Small Things Make a Big Difference? *Batteries* **2022**, *8*, <https://doi.org/10.3390/batteries8100185>.
20. Dong, R.; Zhang, T.; Liu, J.; Li, H.; Hu, D.; Liu, X.; Xu, Q. Mechanistic Insight into Polypyrrole Coating on V₂O₅ Cathode for Aqueous Zinc-Ion Battery. *ChemElectroChem* **2022**, *9*, <https://doi.org/10.1002/celc.202101441>.
21. Das, I.; Goel, N.; Agrawal, N.R.; Gupta, S.K. Growth Patterns of Dendrimers and Electric Potential Oscillations during Electropolymerization of Pyrrole using Mono- and Mixed Surfactants. *The Journal of Physical Chemistry B* **2010**, *114*, 12888-12896, <https://doi.org/10.1021/jp105183q>.
22. 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>.
23. Aoki, K.; Mukoyama, I.; Chen, J. Competition between Polymerization and Dissolution of Poly(3-methylthiophene) Films. *Russian Journal of Electrochemistry* **2004**, *40*, 280-285, <https://doi.org/10.1023/B:RUEL.0000019665.59805.4c>.
24. Tkach, V.V.; Kushnir, M.V.; de Oliveira, S.C.; Ivanushko, Y.G.; Tkach, V.O.; Mytrofanova, H.Y.; Zadoia, A.O.; Yagodynets, P.I.; Kormosh, Z.O.; Luganska, O.V. Theoretical Description for Copper (II) Electrochemical Determination and Retention on a 1 (2-pyridilazo)-2-naphthole-Modified Anode. *Lett. Appl. NanoBioSci* **2021**, *10*, 2078-2084, <https://doi.org/10.33263/LIANBS102.20782084>.
25. Tkach, V.V.; Storoshchuk, N.M.; Romaniv, L.V.; De Oliveira, S.C.; Luganska, O.V.; Gala, H.B.; Tchikuala, E.F.; Yagodynets, P.I. The theoretical evaluation of the poly(3,4-dimethylpyrrole) cathodic electrodeposition assisted by manganate ions. *Vietnam Journal of Chemistry* **2018**, *56*, 440-444, <https://doi.org/10.1002/vjch.201800027>.
26. Tkach, V.V.; Kushnir, M.V.; Storoshchuk, N.M.; Ivanushko, Y.G.; De Oliveira, S.C.; Yagodynets, P.I.; Kormosh, Z.O. The theoretical description for the confection of the novel thiourea-based active surface for cathodic conducting polymer deposition. *Applied Journal of Environmental Engineering Science* **2020**, *6*, 143-148, <https://doi.org/10.48422/IMIST.PRSM/ajees-v6i2.18543>.
27. Tkach, V.; Kushnir, M.; Ivanushko, Y.; *et al.*, The theoretical description for the electrochemical determination of 4-4'-dihydroxyazobenzene, assisted by a composite of squarain dye with cobalt (iii) oxyhydroxide in pair with cobalt (iv) oxide. *Appl. J. Env. Eng. Sci.* **2021**, *7*, 55-62, <https://doi.org/10.48422/IMIST.PRSM/ajees-v7i1.23046>.
28. Tkach, V.V.; Kushnir, M.V.; Storoshchuk, N.M.; Oliveira, S.C.D.; Luganska, O.V.; Kopyika, V.V.; Gala, H.B.; Baddouh, A.; Yagodynets, P.I. A descrição teórica da detecção eletroanalítica do letrozol, assistida pelo composto VO (OH)-polipirrol, obtido catódicamente. *Revista Colombiana de Ciencias Químico-Farmacéuticas* **2019**, *48*, 662-676, <https://doi.org/10.15446/rciquifa.v48n3.84985>.