Article

The theoretical evaluation of the poly(3,4-dimetylpyrrole) cathodic electrodeposition assisted by manganate ions

Volodymyr V. Tkach[1,2*], Nataliia M. Storoshchuk[1], Lyudmyla V. Romaniv[1], Sílvio C. De Oliveira[2], Olga V. Luganska[3], Hélder Briosae Gala[4], Emílio Figueira Tchikuala[5], Petro I. Yagodynets´[1]

[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]*ZaporizhzhyaNationalUniversity, 69095, Zhukovs´kyStr.. 66, Zaporizhzhya, Ukraine*

[4]*Action4Touch, ActionB4Touch, Rua das Sudas, Bl. 1, R/C. Esq., 3770-067, Oiã, Aveiro, Portugal*

[5]*Universidade de Évora, 7000-671, Rua Romão Ramalho, 53, Évora, Portugal*

Abstract

The theoretical description of poly(3,4-dimethylpyrrole) cathodic electrodeposition in alkaline media has been reported for the first time. The electrochemical deposition of conducting polymer on cathode is realized by *in situ* formation of manganate-ions (MnO_4^{2-}) as oxidizing agents, and the proper polymer may be doped by hypomanagate, ions (MnO_4^{3-}). The stable steady-state in this system was established rapidly and efficiently, and the polymer surface has to be well developed. No electrochemical instabilities, typical for anodic direct electropolymerization, was observed.

Keywords. Conducting polymers, polypyrrole, cathodic electrodeposition, manganate ions, stable steady-state.

1. INTRODUCTION

Polypyrrole[1-6] is one of the most used conducting polymers during the 5 last decades. It was the first polymer to be obtained chemically[1] and electrochemically,[2] and has vast and rich list of applications, beginning from the corrosion-protecting coatings and ending with sensors and biosensors.[3-6]

Not only the proper polypyrrole, but also its 1, 3 and 4-substituted derivatives may be polymerized, yielding conducting polymers[3], which may even have certain advantages, while compared to a non-functionalized polypyrrole. For example, the introduction of donating groups makes the polymerization potential lower, reducing the use of electricity, augmenting its conductivity and, also, making more developed the polymer morphology, due to the impossibility of the collateral interactions α-β (2´-3´) between the monomeric units.[3] Nevertheless, one of the disadvantages of the use of the pyrrolic monomers is its instability in acidic media. In these conditions[1,3,4], it even becomes

polymerized, but yields non-conductive modifications, known as "pyrrole black"[1] and "pyrrole red".[4]

Taking into account the yet mentioned factors, like also the pH decrease during the classical Díaz electropolymerization process,[3] makes us look for the alternative methods for conducting polymer synthesis, capable either to yield polymers and composites the desired morphology, or to protect the monomer from the influence of the low hydrogen potential values.

The polypyrrole cathodic electrodeposition method, firstly described in Ref.,[7] according to the theoretical investigation,[8] satisfies both of the presented conditions, due to the steady-state stabilization by nitrate excess. Nevertheless, despite of the well-developed polymer morphology, achieved in Ref.[7] (Fig. 1), this methodology may be sensitive to the reagent addition order and to the electrode potential, which puts the question of the alternative more efficient and less sensitive deposition techniques.
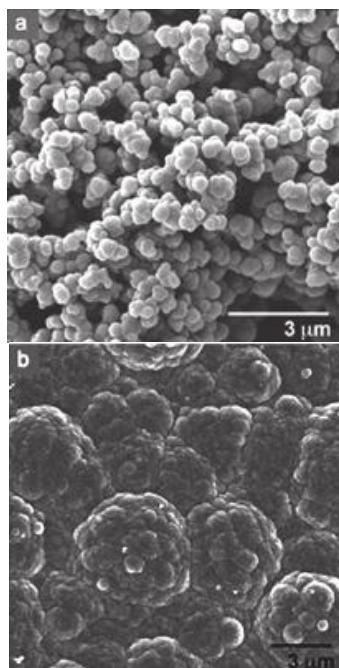
Figure 1: The SEM of the polypyrrole, obtained cathodically (a) and anodically (b) from the solution of 0.1 Py + 0.4 HNO₃ + 0.5 NaNO₃. Reproduced from Ref.[7] with the permission of Elsevier, The Netherlands

As the pyrrole is not capable to polymerize by electrochemical reduction, the polymerization is realized by *in situ* formation of the oxidants, as in Ref. [7] (Eq. (1-2):

$$NO_3^- + 4H^+ + 2e^- \rightarrow NO^+ + 2\,H_2O \qquad (1)$$
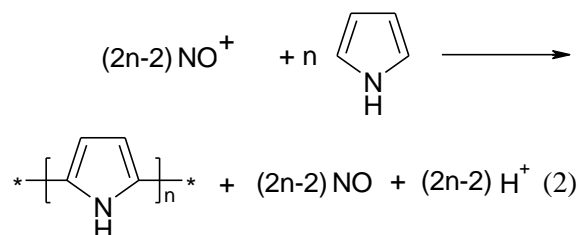
An interesting technique for poly(3,4-dimethylpyrrole) cathodic electrodeposition in basic media may be realized as assisted by *in situ* formed manganate ions. The morphology of the resulting polymer was different from those obtained by anodic direct electropolymerization in the same conditions.

These morphology changes may only be caused by mechanism divergences between two polymerization processes, and the development of new electropolymerization techniques requires us to propose a better deposition mechanism. Moreover, the electrochemical instabilities, characteristic for polypyrrole, polythiophene and polyindole anodic electropolymerization[9-13] (Fig. 2), although impossible for the case of Refs.[7-8] may be also capable to realize in the case of the cathodic deposition of polypyrrole.
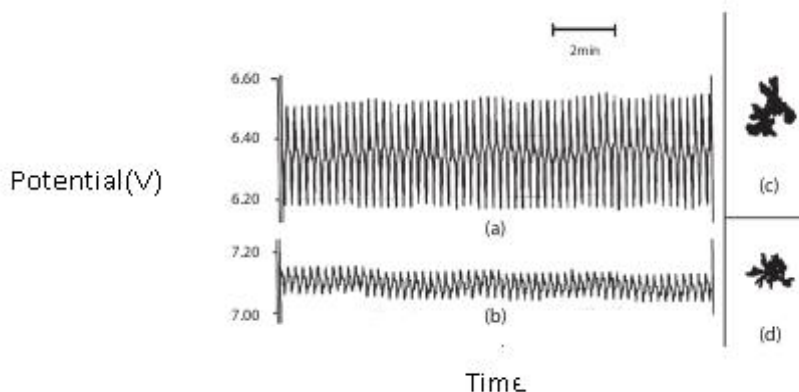

Figure 2: Potential oscillations, observed during the pyrrole electropolymerization in galvanostatic mode 3 in strongly acid media with (a) and without (b) surfactants and the surface changes (c) (d), accompanying the oscillatory electropolymerization

So, the goal of this work is to evaluate, from the theoretical point of view, the possibility of the cathodic poly(3,4-dimethylpyrrole) electrodeposition, assisted by manganate ions. For this purpose, we have to resolve following specific tasks:

- The suggestion of a mechanism, capable to describe adequately the sequence of chemical and electrochemical reactions, yielding the polymer;
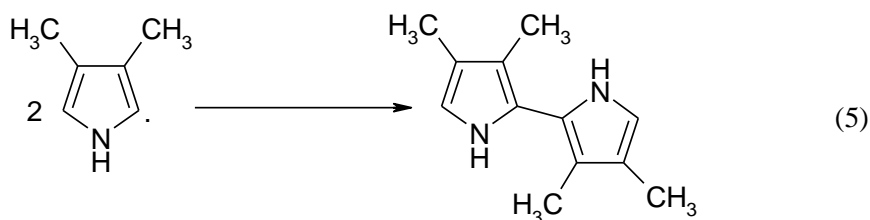
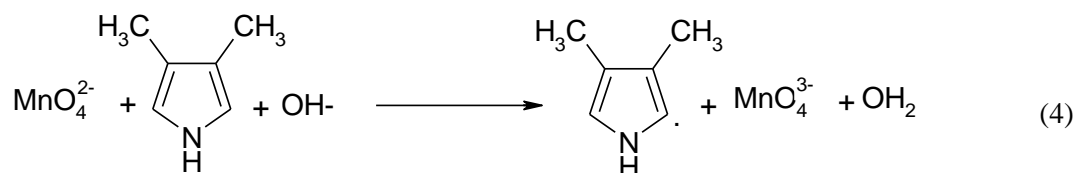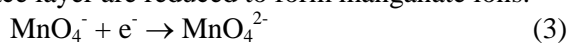- The development and analysis of the mathematical model based on the proposed mechanism;

- The evaluation of the system´s behavior, based on the model, with the accent on steady-state stability and occurrence of electrochemical instabilities

- The comparison of the behavior of this system with the anodic electropolymerization in the same conditions, described in Ref.[14]

SYSTEM AND ITS MODELING

The permanganate ions that presented in the pre-surface layer are reduced to form manganate ions:

$$MnO_4^- + e^- \rightarrow MnO_4^{2-} \qquad (3)$$

The manganate ions, in the presence of 3,4-dimethylpyrrole, are reduced to form manganate(V) ions and yielding the monomer radicals (4), which are, then, recombined:

(4)

(5)

The chain growth is, thus, continued by the classic mechanism, described in Refs.[1-6]

Permanganate ions may be present either in the solution, or on the electrode surface, as a dopant for another polymer or carbon material, by which the cathode is modified.

This work describes the simplest case with the permanganate, present in the solution. Taking into account the excess of the alkali, necessary to maintain both of the reactions, leading to the chain initiation, like also the potentiostatic mode, we introduce three variables:

c - concentration of poly(3,4-dimethylpyrrole) in the pre-surface layer;

p - concentration of permanganate in the pre-surface layer;

m - concentration of manganate 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 assume that the background electrolyte is in excess, so we can neglect the migration flow. The diffusion layer is supposed to be of a constant thickness, equal to δ, and the concentration profile in it is supposed to be linear.

It is possible to show that the behavior of the system will be described by the equation set as following (6):

$$\begin{cases} \dfrac{dc}{dt} = \dfrac{2}{\delta}\left(\dfrac{\Delta}{\delta}(c_0 - c) - r_4\right) \\ \dfrac{dp}{dt} = \dfrac{2}{\delta}\left(\dfrac{D}{\delta}(p_0 - p) - r_3\right) \\ \dfrac{dm}{dt} = \dfrac{2}{\delta}(r_3 - r_4) \end{cases} \qquad (6)$$

In which Δ and D are the diffusion coefficients, c_0 and p_0 are monomer and permanganate bulk concentrations, and the parameters r are the correspondent reaction rates, which may be calculated as:

$$r_3 = k_3 p \exp\left(-\frac{F\varphi_0}{RT}\right) \qquad r_4 = k_4 m^n c^{2n-2} \qquad (7\text{–}8)$$

In which the parameters k are correspondent reaction rate constants, F is the Faraday number, φ_0 is the DEL potential slope in the double, related to the zero-charge potential, n is the average number of the monomer units in the resulting polymer, R is the universal gas constant and T is the absolute temperature.

As mentioned in Refs.,[7,8] the behavior of the system will be different from that described in[18] for the anodic electropolymerization in alkaline media, which will give impacts on the polymer morphology, discussed below.

RESULTS AND DISCUSSION

In order to describe the behavior of the system with poly(3,4-dimethylpyrrole) cathodic electrodeposition, assisted by the redox-system $MnO_4^-/MnO_4^{2-}/MnO_4^{3-}$, we analyze the equation set (6) by means of the linear stability theory. The steady-state matrix members will be described as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \qquad (9)$$

in which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - (2n-2)k_4 m^n p^{2n-1}\right) \qquad (10)$$

$$a_{12} = 0 \tag{11}$$

$$a_{13} = \frac{2}{\delta}(-nk_4 m^{n-1} p^{2n-2}) \tag{12}$$

$$a_{21} = 0 \tag{13}$$

$$a_{22} = \frac{2}{\delta}\left(-\frac{D}{\delta} - k_3 \exp\left(-\frac{F\varphi_0}{RT}\right)\right) \tag{14}$$

$$a_{23} = 0 \tag{15}$$

$$a_{31} = \frac{2}{\delta}(-(2n-2)k_4 m^n p^{2n-1}) \tag{16}$$

$$a_{32} = \frac{2}{\delta}\left(k_3 \exp\left(-\frac{F\varphi_0}{RT}\right)\right) \tag{17}$$

$$a_{33} = \frac{2}{\delta}(-nk_4 m^{n-1} p^{2n-2}) \tag{18}$$

Taking into account the main diagonal Jacobian elements (10), (14) and (18), we may conclude that the main diagonal elements may only have negative values, which means that no *oscillatory instability,* characteristic for anodic electropolymerization,[9-14] is observed in this system.

In this system, either the monomer or the initiator is present in the solution, the chain is initiated in the pre-surface layer, and the cathode surface is only modified during the polymerization chain growth. On the other hand, in Ref.[14] it has been shown that the chain growth factors are not responsible for oscillatory and monotonic instabilities. Those instabilities are caused by surface (attraction of the monomer particles) and electrochemical factors, acting during the chain initiation.

Taking into account that the chain initiation is made in the pre-surface layer, the absence of the oscillatory instability is clearly justified. As the oscillatory instability influences the polymer surface morphology[9–10], the absence of surface instabilities, causing the oscillations during the anodic electropolymerization, makes the polymergrowth more stable, and the surface more developed.

In order to investigate *the steady-state stability*, we apply the Routh-Hurwitz criterion to the equation set (6). Avoiding the cumbersome expressions, we introduce new parameters, so the Jacobian determinant will be rewritten as:

$$\frac{8}{\delta^3}\begin{vmatrix} -\kappa_1 - \varXi & 0 & -\xi \\ 0 & -\kappa_2 - \varOmega & 0 \\ -\varXi & \varOmega & -\xi \end{vmatrix} \tag{19}$$

Applying the steady-state stability requirement Det J < 0, salient from the criterion, we obtain the stability condition, expressed as:

$$(-\kappa_2 - \varOmega)(\xi\kappa_1) < 0 \tag{20}$$

And this condition is always satisfied, as none of the parameters on the left side of the equation may be null or negative during the electropolymerization. It means that the stable steady-state in this system is

easy to obtain and maintain and, as there are no factors capable to compromise the polymer chemical stability, the steady-state stability is efficient from the electrosynthetical point of view. The polymer morphology has to be more developed than during the anodic electropolymerization and even during the anodic and cathodic electrodeposition, assisted on the surface.[15-17]

The electrochemical process is diffusion-controlled, and the monotonic instability, which had to be realized if Det J = 0 is not possible.

Yet is the permanganate ions are present on the surface, the system's behavior will be slightly different, as the surface will change its properties not only during the polymer chain growth, but also during the initiation process. The behavior of this system is more dynamic and will be observed in our next works.

CONCLUSIONS

By the analysis of the poly(3,4-dimethylpyrrole) electrochemical cathodic deposition in alkaline media, assisted by $MnO_4^-/MnO_4^{2-}/MnO_4^{3-}$ redox system, it is possible to conclude that:

- The electrochemical cathodic deposition is realized more efficiently that the anodic electropolymerization in the same conditions;

- The electrosynthesis process is diffusion-controlled, and the steady-state stability is easy to obtain and maintain;

- No oscillatory and monotonic instability, characteristic for anodic electropolymerization systems, are capable to be realized in this system;

- The polymer morphology was more developed than in the case of anodic electropolymerization.

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Corresponding author: **Volodymyr V. Tkach**

Chernivtsi National University, 58012, Kotsyubyns´ky Str., 2, Chernivtsi, Ukraine;
or
Universidade Federal de Mato Grosso do Sul, Av. Sen. Felinto. Müller,
1555, C/P. 549, 79074-460, Campo Grande, MS, Brazil
E-mail: nightwatcher2401@gmail.com.