Theoretical Aspects of the Electropolymerization of Some Hydroquinonic Derivatives

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Abstract: For the first time, the possibility of the electrochemical synthesis and polymerization of some novel modified naphthoquinone compounds has been described. The correspondent mathematical model has been analyzed by means of linear stability theory and bifurcation analysis. It has been shown that the electro organic synthesis may serve as an interesting substitution for Suzuki reaction for the synthesis of ferrocenyl naphthoquinone and its polymer. The oscillatory and monotonic instability, in this case, will be more probable than in the general electropolymerization case.

1. Introduction

Electrochemical polymerization is one of the most used conducting polymer synthesis techniques [1–10]. The electrosynthetized polymers have certain advantages, while compared to the chemically obtained macromolecules. These advantages include: enhanced conductivity, corrosion resistance, facility in the modification, tunability.

The most known conjugated conducting polymers contain alkine chains, carbo- and heterocyclic fragments in their moiety. While electrochemically synthesized, they are doped by a background electrolyte counter-ion or another counter-ion present in the solution. The monomer and electropolymerization techniques may be chosen according to the further use of the resulting polymer.

Recently, the Organic Chemistry group of the Yüzüncü Yil University of Van has obtained a novel ferrocenyl-substituted naphthoquinone derivative [11–12] (Fig. 1). The novel derivative has shown sensitivity to the concentration of hydrogen peroxide and may readily be used as a sensor. Nevertheless, the novel derivative has been obtained by a Suzuki-Miyaura reaction, requiring expensive catalysts and reagents. An electro organic synthesis used to yield

not only polymers but also their monomers [13–17]. From 1970th on, the monomer electrosynthesis techniques are developed to yield monomers and their polymers.
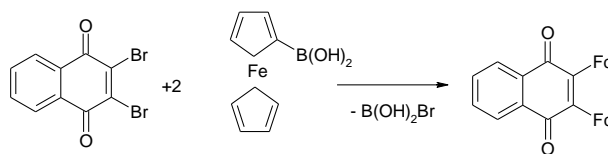

Figure 1. Chemical synthesis of the compound.

Nevertheless, the organic electrooxidation processes (including the electropolymerization) tend to be accompanied by electrochemical instabilities. These instabilities include the oscillatory changes in electrochemical potential and monotonic instabilities [18 – 25] and influence the polymer morphology and conductivity.

Thus, in order to investigate the parameter values, correspondent to the most efficient monomer and polymer formation, like also verify the possibility and probability of the electrochemical instabilities in this system, an *a priori* theoretical observation of the electrochemical system is necessary.

So, taking into account the above-mentioned statements, the goal of our work will be the theoretical description of the novel ferrocene naphthoquinones electrochemical synthesis as a substitute of the Suzuki reaction, with the further product polymerization.
In order to realize it, we achieve specific objectives as:
- to suggest the most probable mechanism for the sequence of chemical and electrochemical processes in the system;
- to develop the mathematical model, correspondent to the mechanism,
- by analysis of the model, to derive the steady-state stability conditions and oscillatory and monotonic instability requirements;
to compare the behavior of this system with that of the similar ones [25 – 28].

2. Materials and Methods

2.1. System and its modeling.

In the scheme of the electrochemical synthesis, 1,4-dihydroxynaphthalene is electrochemically oxidized in the presence of 2-chloroferrocene in the medium of carbonate buffer. By this, hydroquinone moiety is oxidized to the quinone one, and the ferrocenyl group integrates the naphthoquinone derivative, forming the monomer (Fig. 2).

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \qquad (1)$$

$$(2)$$
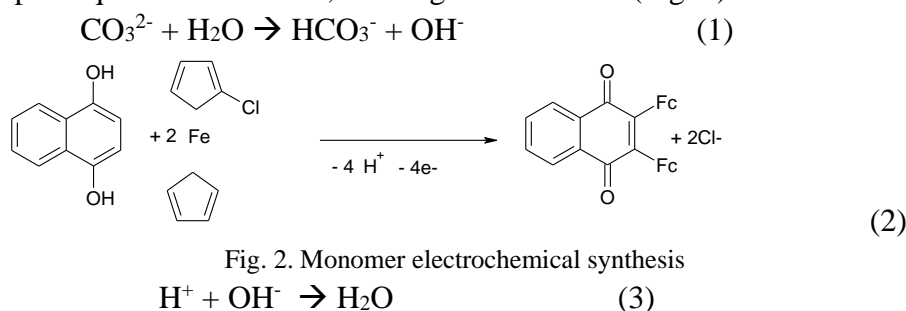
Fig. 2. Monomer electrochemical synthesis

$$H^+ + OH^- \rightarrow H_2O \qquad (3)$$

The carbonate buffer, added to the reaction medium, prevents the ferrocenyl moieties from acidolytic destruction during both synthesis and electropolymerization (both processes

expel protons and reduce the pH values) and also facilitates the hydroquinone to quinone oxidation.

The chain propagation is thus realized by cation-radical formation in the active ferrocenyl moiety and the non-substituted ring of the naphthoquinone fragment, yielding a highly conducting macromolecule, capable of being used in electroanalytic. The polymer morphological and magnetic properties have to be similar to those obtained in [29], but with enhanced conductivity.

Thus, in order to describe the electrochemical behavior of this system in galvanostatic mode, we introduce three variables:

f – chloroferrocene concentration in the pre-surface layer;

m – monomer concentration in the pre-surface layer;

q – anode charge density.

To simplify the modeling, we assume that:

- the background electrolyte is taken in excess so that we can neglect the migration flow and the oxidizing dopant oxidation change;

- the reactor is intensively stirred so that we may neglect the convection flow;

- the pre-surface layer concentration profile is linear, and its thickness is constant, equal to δ.

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

$$\begin{cases} \frac{df}{dt} = \frac{2}{\delta}\left(\frac{D}{\delta}(f_0 - f) - r_{ES}\right) \\ \frac{dn}{dt} = \frac{1}{N}\left(r_{ES} - r_p\right) \\ \frac{dq}{dt} = i - i_F \end{cases} \qquad (4)$$

Herein, D is the diffusion coefficient, f_0 is the ferrocene halide bulk concentration, N is the monomer maximal surface concentration i_F is the Faraday current and the parameters r are the monomer electrosynthesis and polymerization rates, capable to be calculated as:

$$r_{ES} = k_{ES}f^2(1-n)\exp\left(\frac{4F\varphi_0}{RT}\right) \qquad (5)$$

$$r_p = k_p n^m \exp\left(\frac{(2m-2)F\varphi_0}{RT}\right) \qquad (6)$$

The Faraday current may be calculated as:

$$i_F = 4Fr_{ES} + (2m-2)Fr_p \qquad (7)$$

Where the parameters k are correspondent reaction rate constants, m is the number of the monomer units in the polymer, F is the Faraday number, φ_0 is the potential slope, related to the zero-charge potential, R is the universal gas constant, and T is the absolute temperature of the solution.

Comparing to the potentiostat mode, described for the similar systems in [26], the behavior of this system will be a bit more dynamic. The polymerization kinetics and resulting polymer properties will be affected by this, according to the exposed below.

3. Results and Discussion

In order to investigate the galvanostatic electrosynthesis and electropolymerization of the novel ferrocenyl-substituted naphthoquinone, we analyze the equation-set (4) by means of the linear stability theory. The steady-state Jacobian matrix may be exposed like (8):

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

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{D}{\delta} - 2k_{ES}f(1-n)\exp\left(\frac{4F\varphi_0}{RT}\right)\right) \qquad (9)$$

$$a_{12} = \frac{2}{\delta}\left(k_{ES}f^2\exp\left(\frac{4F\varphi_0}{RT}\right) - jk_{ES}f^2(1-n)\exp\left(\frac{4F\varphi_0}{RT}\right)\right) \quad (10)$$

$$a_{13} = \frac{2}{\delta}\left(-pk_{ES}f^2(1-n)\exp\left(\frac{4F\varphi_0}{RT}\right)\right) \qquad (11)$$

$$a_{21} = \frac{1}{N}\left(2k_{ES}f(1-n)\exp\left(\frac{4F\varphi_0}{RT}\right)\right) \qquad (12)$$

$$a_{22} = \frac{1}{N}\left(-k_{ES}f^2\exp\left(\frac{4F\varphi_0}{RT}\right) + jk_{ES}f^2(1-n)\exp\left(\frac{4F\varphi_0}{RT}\right) - mk_pn^{m-1}\exp\left(\frac{(2m-2)F\varphi_0}{RT}\right) - jk_pn^m\exp\left(\frac{(2m-2)F\varphi_0}{RT}\right)\right) \qquad (13)$$

$$a_{23} = \frac{1}{N}\left(pk_{ES}f^2(1-n)\exp\left(\frac{4F\varphi_0}{RT}\right) - pk_pn^m\exp\left(\frac{(2m-2)F\varphi_0}{RT}\right)\right) \qquad (14)$$

$$a_{31} = -8Fk_{ES}f(1-n)\exp\left(\frac{4F\varphi_0}{RT}\right) \qquad (15)$$

$$a_{32} = 4F\left(k_{ES}f^2\exp\left(\frac{4F\varphi_0}{RT}\right) - jk_{ES}f^2(1-n)\exp\left(\frac{4F\varphi_0}{RT}\right)\right) + (2m-2)F(mk_pn^{m-1}\exp\left(\frac{(2m-2)F\varphi_0}{RT}\right) - jk_pn^m\exp\left(\frac{(2m-2)F\varphi_0}{RT}\right) \qquad (16)$$

$$a_{33} = -4F\left(pk_{ES}f^2(1-n)\exp\left(\frac{4F\varphi_0}{RT}\right)\right) - (2m-2)F\left(pk_pn^m\exp\left(\frac{(2m-2)F\varphi_0}{RT}\right)\right) \quad (17)$$

In order to derive the *steady-state stability* requirement, we apply the Routh-Hurwitz criterion to the equation-set (4). Avoiding the cumbersome equations, we introduce new variables, and the Jacobian determinant will be described as:

$$\frac{2F}{\delta N}\begin{vmatrix} -\kappa - \Lambda_1 & \Omega & -\Sigma \\ \Lambda_1 & -\Omega - \Xi & \Sigma - T \\ -4\Lambda_1 & 2\Omega + (m-1)\Xi & -2\Sigma - (m-1)T \end{vmatrix} \qquad (18)$$

Opening the brackets and applying the Det J<0 conditions, salient from the criterion, we obtain the steady-state stability condition, exposed as (19):

$$-\kappa(2\Xi\Omega + (m-1)\Omega T + \Xi(m-1)\Omega T + 2\Sigma T + \Xi(m-1)\Sigma + (m-1)\Xi T) - \Lambda\big(2\Xi\Omega + \Xi(m-1)\Omega T + 2\Sigma T + 2\Xi(m-1)\Sigma + (m-1)\Xi T + 4(-\Omega T - \Xi\Sigma)\big) < 0 \quad (19)$$

Describing a more dynamic system, while compared to those observed for potentiostat mode [25]. Taking into account the strong influences of both of the electrochemical processes on double electric layer (DEL) capacitance, ionic force and conductivity, like also the surface resistance, the cyclic changes of which may compromise the steady-state stability, the steady-state stability topological area will be more narrow than for the potentiostat mode.

If in [25], depending on the electrode size and monomer modifier concentration, the system could be only diffusion or only kinetically controlled, in galvanostatic mode, either diffusion or kinetics will influence the electrosynthesis process by equal manner.

Despite the above-mentioned factors, the monomer tends to be formed efficiently, as the topological stability area remains vast. The steady-state is easily stabilized. Nonetheless, the macromolecule morphology will be more dendritic and crystalline than film-shaped.

The *monotonic instability* for this system is possible. It is defining the margin between stable steady-states and unstable states, and its conditions of appearance will be depicted as (20):

$$-\kappa(2\Xi\Omega + (m-1)\Omega T + \Xi(m-1)\Omega T + 2\Sigma T + \Xi(m-1)\Sigma + (m-1)\Xi T) - \Lambda\big(2\Xi\Omega +$$
$$\Xi(m-1)\Omega T + 2\Sigma T + 2\Xi(m-1)\Sigma + (m-1)\Xi T + 4(-\Omega T - \Xi\Sigma)\big) = 0 \quad (20)$$

The oscillatory instability for this system, as in the similar ones [25 – 28] is possible. Moreover, it is even more probable than in [25], due to the presence of more than one factor defining the DEL capacitance.

As known, the Hopf bifurcation is realized if the Jacobian matrix main diagonal elements have positive elements, responsible for the positive callback. In these systems, elements, which may be positive are:

$jk_{ES}f^2(1-n)\exp\left(\frac{4F\varphi_0}{RT}\right) > 0$ if j>0, describing the positive callback, observed during the monomer synthesis. By this, the structure of the surface compound is changed with the enhance of its conductivity, leading to a favorable effect in a double electric layer;

$-jk_p n^m \exp\left(\frac{(2m-2)F\varphi_0}{RT}\right) > 0$ if j<0, describing the analogous effect during the electrochemical polymerization process, which is enhanced by the formation of charged intermediates (cation-radicals).

Other elements, capable of being positive are $-4F\left(pk_{ES}f^2(1-n)\exp\left(\frac{4F\varphi_0}{RT}\right)\right) - (2m-2)F\left(pk_p n^m \exp\left(\frac{(2m-2)F\varphi_0}{RT}\right)\right) > 0$, if p<0, describing the similar effects of the anode resistance.

We should mention that this model is only suitable for the polymerization in alkaline media, capable of neutralizing the pH decay, observed during the monomer synthesis and polymerization. If the pH is neutral or acidic, the ferrocene monomer and polymer suffer partial destruction, influencing the system's behavior and polymer morphology. This aspect will be described in one of our next works.

4. Conclusions

From the system with the new ferrocene naphthoquinonic derivative electrochemical synthesis and polymerization, it is possible to conclude that: The electrochemical synthesis of the novel ferrocene derivative of naphthoquinone may be a suitable substitution for the Suzuki reaction; n galvanostatic mode, the behavior of the system will be more dynamic than in potentiostat mode, due to double electric layer capacitance, ionic force, and conductivity, like surface resistance influences of both electrochemical stages; Also, in galvanostatic mode, the electrosynthesis will be either diffusion or kinetically controlled; The oscillatory instability will be more probable than for potentiostat mode, being caused by DEL influences of both electrochemical stages; Another factor responsible for this type of behavior will be the influence of both electrochemical stages on the anodic resistance.

Conflicts of Interest

The authors declare no conflict of interest.

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