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Theoretical Description for Ellagic Acid Electrochemical Oxidation and Electropolymerization

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Abstract: The theoretical description for ellagic acid electrochemical oxidation and electropolymerization has been suggested in this paper. The model includes the electropolymerization of ellagic acid in the presence of two of its low-molecular oxidation products. The correspondent mathematical model has been developed and analyzed using linear stability theory and bifurcation analysis. The analysis of the system has confirmed that the oscillatory behavior is more probable than in the simplest case of the electrosynthesis of the polymer of the electrochemically synthesized monomer. Nevertheless, the system is electrosynthetically efficient, yielding a polymer coating.

Keywords: ellagic acid; electrochemical oxidation; hydroquinonic compounds; electrochemical polymerization; conducting polymers; stable steady-state.

1. Introduction

Hydroquinone compounds constitute one of the most popular electrochemically active compound series [1–6]. They are useful for either electroanalytical or electrosynthetical points of view. For example, they may be a renewable material for conducting polymers and their dopants.

One of these compounds may be ellagic acid [7–9] (Fig. 1). It is a natural compound from pomegranate, known from the 5th Century BC. Its biological properties include antioxidant, anti-inflammatory, and hepatoprotective. Pomegranate is named by the seed-like pulp (from Spanish “grano” meaning “seed”) and gave the name to the Spanish city of Granada.

It is known that the alimentary properties of the pomegranate juice are dependent on different factors, including the location of the fruit growth, the age of the juice, and the condition of its storage [10, 11], and the ellagic acid is one of the markers of those properties, the reason why the electrochemical determination of the ellagic acid is actual [12–14].

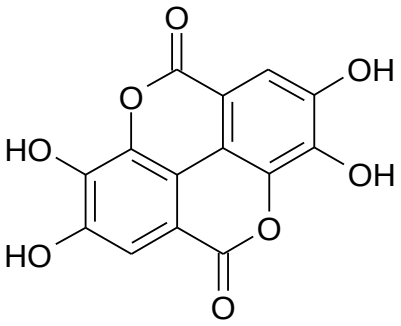

Figure 1. Ellagic acid.

Also, considering the ellagic acid composition, it is possible to conclude that it may serve as either monomer or dopant for conducting polymers, as it is characteristic of hydroquinone compounds [15–18].

Nevertheless, the ellagic acid electrochemical oxidation mechanism may be realized by two parallel mechanisms, each of which impacts the system's behavior. Moreover, this process tends to be accompanied by electrochemical instabilities, typical for this similar electrooxidation and electropolymerization systems [19, 20].

Therefore, the goal of this work is to describe the electrochemical behavior of ellagic acid theoretically during its electrochemical oxidation. It will be realized by the model development and analysis using linear stability theory and bifurcation analysis. Also, the system's behavior will be compared to those of similar systems [21–24]

2. Materials and Methods

2.1. System and its modeling.

The electrochemical oxidation routs for the ellagic acid may be depicted in Fig. 2:

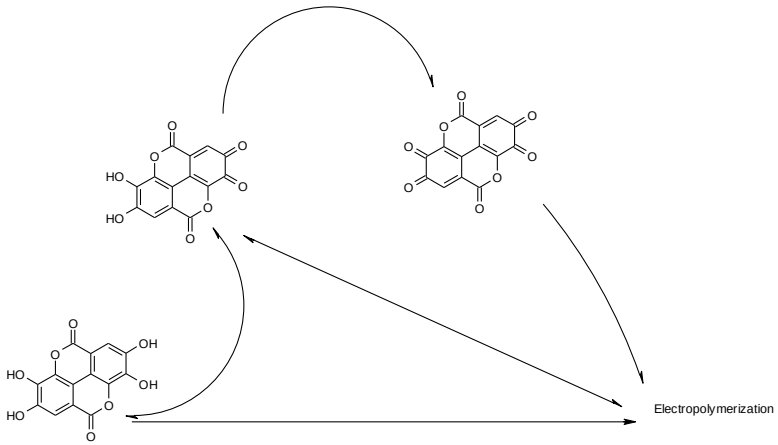

Figure 2. Ellagic acid electrooxidation scheme.

Being a hydroquinonic compound with two condensed hydroquinonic moieties, ellagic acid is electrooxidized gradually to the correspondent quinones. Another possible oxidation route is electropolymerization, known for dopamine and other hydroquinone compounds [15 – 18]. Either the reagent or both of the products are capable of entering the growing polymer chain.

Therefore, to describe the system with the electrochemical determination of ellagic acid, we introduce two variables:

q_1 – the first hydroquinone compound surface coverage degree;
q_2 – the second hydroquinone compound surface coverage degree.

Assuming that ellagic acid covers the entire electrode surface, we may describe the behavior of the system as:

$$\begin{cases} \frac{dq_1}{dt} = \frac{1}{Q_1}(r_1 - r_2 - r_p) \\ \frac{dq_2}{dt} = \frac{1}{Q_2}(r_2 - r_p) \end{cases} \quad (1)$$

Herein, Q_1 and Q_2 are the quinone compounds maximal concentrations, and the parameters r are the correspondent electrochemical reaction rates, calculated as:

$$r_1 = k_1(1 - q_1 - q_2)\exp\left(\frac{2F\varphi_0}{RT}\right) \quad (2)$$

$$r_2 = k_2 q_1 \exp\left(\frac{2F\varphi_0}{RT}\right) \quad (3)$$

$$r_p = k_p(1 - q_1 - q_2)^x q_1^y q_2^z \exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right) \quad (4)$$

Where the parameters k are the correspondent reaction rate constants, x y and z are the correspondent reaction orders for the electropolymerization reaction (the electron number $2(x + y + z) - 2$)may be derived from the classical Díaz electropolymerization mechanism), 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.

As this system is characterized by a chain of electrochemical systems, influencing the DEL and surface conductivity and impedance, the oscillatory behavior will be highly probable even in the simplest case. Nevertheless, the polymer has to be formed in an efficient manner, as shown below.

3. Results and Discussion

To describe the behavior of the system with the electrooxidation of ellagic acid yielding both quinone compounds and the polymer, we analyze the equation-set (1) using the linear stability theory. The steady-state Jacobian matrix members may be described as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \quad (5)$$

Herein:

$$a_{11} = \frac{1}{Q_1}\left(-k_1\exp\left(\frac{2F\varphi_0}{RT}\right) + jk_1(1 - q_1 - q_2)\exp\left(\frac{2F\varphi_0}{RT}\right) - k_2\exp\left(\frac{2F\varphi_0}{RT}\right) + jk_2 q_1\exp\left(\frac{2F\varphi_0}{RT}\right) + k_p x(1 - q_1 - q_2)^{x-1}q_1^y q_2^z\exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right) - yk_p(1 - q_1 - q_2)^x q_1^{y-1}q_2^z\exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right) + jk_p(1 - q_1 - q_2)^x q_1^y q_2^z\exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right)\right) \quad (6)$$

$$a_{12} = \frac{1}{Q_1}\left(-k_1\exp\left(\frac{2F\varphi_0}{RT}\right) + lk_1(1 - q_1 - q_2)\exp\left(\frac{2F\varphi_0}{RT}\right) - k_p x(1 - q_1 - q_2)^{x-1}q_1^y q_2^z\exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right) - zk_p(1 - q_1 - q_2)^x q_1^y q_2^{z-1}\exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right) + lk_p(1 - q_1 - q_2)^x q_1^y q_2^z\exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right)\right) \quad (7)$$

$$a_{21} = \frac{1}{Q_2}\left(k_2\exp\left(\frac{2F\varphi_0}{RT}\right) - jk_2 q_1\exp\left(\frac{2F\varphi_0}{RT}\right) + k_p x(1 - q_1 - q_2)^{x-1}q_1^y q_2^z\exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right) - yk_p(1 - q_1 - q_2)^x q_1^{y-1}q_2^z\exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right) + jk_p(1 - q_1 - q_2)^x q_1^y q_2^z\exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right)\right) \quad (8)$$

$$a_{22} = \frac{1}{Q_2}\left(-k_p x(1-q_1-q_2)^{x-1} q_1^y q_2^z \exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right) - zk_p(1-q_1-q_2)^x q_1^y q_2^{z-1} \exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right) + lk_p(1-q_1-q_2)^x q_1^y q_2^z \exp\left(\frac{(2(x+y+z)-2)F\varphi_0}{RT}\right)\right) \quad (9)$$

Avoiding the cumbersome expressions, we introduce new variables, rewriting the determinant as (10)

$$\frac{1}{Q_1 Q_2}\begin{vmatrix} -X-Y-Z & -S-Y \\ Y-Z & -Y \end{vmatrix} \quad (10)$$

The general singular point conditions for the bivariant systems may be joined in Table 1.

Table 1. The main singular point conditions for the bivariant systems.

Stable steady-state	Tr J<0, Det J>0
Oscillatory behavior	Tr J=0, Det J>0
Monotonic instability	Tr J<0, Det J=0

Herein,

$$Tr\,J = -\frac{1}{Q_1}(X+Y+Z) - \frac{Y}{Q_2} \quad (11)$$

$$Det\,J = \frac{1}{Q_1 Q_2}(XY + 2Y^2 + SY - SZ) \quad (12)$$

The Hopf bifurcation condition, correspondent to the oscillatory behavior, may be satisfied if the main diagonal Jacobian elements (6) and (9) contain positive elements, corresponding to the positive callback.

Two factors may be responsible for the oscillatory behavior in this case. Besides DEL influences of the electrochemical stages, leading to the cyclical changes in surface and DEL conductivities and impedances, the auto-promoted ellagic acid surface concentration decrease is also responsible for that type of behavior. The oscillation frequency and amplitude will be highly dependent on the background electrode composition and electrode nature. Mathematically, the oscillatory behavior condition for this system will be described as (13):

$$\begin{cases} -\frac{1}{Q_1}(X+Y+Z) = \frac{Y}{Q_2} \\ \frac{1}{Q_1 Q_2}(XY + 2Y^2 + SY - SZ) > 0 \end{cases} \quad (13)$$

As for the steady-state stability, its condition will be mathematically depicted as (14):

$$\begin{cases} -\frac{1}{Q_1}(X+Y+Z) < \frac{Y}{Q_2} \\ \frac{1}{Q_1 Q_2}(XY + 2Y^2 + SY - SZ) > 0 \end{cases} \quad (14)$$

The requisite (14) is satisfied in a somehow narrower topological parameter range than for similar systems. Nevertheless, it will remain wide, as the condition (14) is readily satisfied, if the kinetical parameters X Y, S, and Z are positive, describing the fragility of auto promoting and DEL destabilizing effects.

Really, putting X, Y, S, and Z >0, we may see that the left side of the first inequity of the set (14) will be more negative, and the left side of the left side of the second inequity of this set will be more positive. This will depict a kinetically controlled system with well-developed polymer surface formation.

The monotonic instability for this system depicts a margin between the stable steady-states and unstable states. It is correspondent to the N-shaped range of the steady-state voltammogram, and its condition will be described as:

$$\begin{cases} -\frac{1}{Q_1}(X+Y+Z) < \frac{Y}{Q_2} \\ \frac{1}{Q_1 Q_2}(XY + 2Y^2 + SY - SZ) = 0 \end{cases} \quad (15)$$

As for the polymer formed during the synthesis, it is also capable of being oxidized in certain conditions. The oxidation of the resulting polymer may be realized by either the quinone-hydroquinone mechanism or the polythiophene paradox mechanism. Either way, the equation-set (1) will be insufficient to describe this type of system, and the third equation, describing the polymer coverage degree, will be added to this set, transforming it into (16):

$$\begin{cases} \frac{dq_1}{dt} = \frac{1}{Q_1}(r_1 - r_2 - r_p) \\ \frac{dq_2}{dt} = \frac{1}{Q_2}(r_2 - r_p) \\ \frac{dp}{dt} = \frac{1}{P}(r_p - r_o) \end{cases} \quad (16)$$

The behavior of the system, described by the equation-set (16), will be even more dynamic. Its analysis will be described in our next works.

4. Conclusions

From the analysis of the system with the electrochemical oxidation and electropolymerization of ellagic acid, it has been possible to conclude that, despite the hybridity of the oxidation mechanism, the oxidation may be realized efficiently, yielding a well-developed polymer coating. The system is kinetically controlled. As for the oscillatory behavior will be more possible than for similar systems due to the action of two factors, providing the positive callback.

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Conflicts of Interest

The authors declare no conflict of interest.

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