

The Theoretical Description of Cathodic Deposition of New Conducting Polymer Composite, Assisted by a Perrhenate of a Novel Triazolic Derivative

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Abstract:

The theoretical description of a new sandwich-like rhenium-based polymer composite cathodic electrodeposition has been given. The cathodic process is realized by perrhenate-ion electrochemical reduction to rhenium (IV) oxide, acting as an in situ formed oxidant for 3,4-dimethoxypyrrole polymerization. It is shown that the polymer deposition in this system is realized by more efficient manner than during the direct electropolymerization. The polymer composite has to have a well-developed morphology and enhanced conductivity by sandwich-like structure. The oscillatory behavior, in this case, is also possible, being caused by the DEL influences on both electrochemical and chemical stages of the process.

Keywords: conducting polymer composites; rhenium; assisted polymerization; electrochemical oscillations; stable steady-state

1. Introduction

The conducting polymers form one of the modern classes of organic materials, extensively studied during the last five decades [1 – 6]. Combining the properties of plastics with metallic conductivity, they obtain vast and rich spectrum of use, including the corrosion protecting coatings, supercapacitors, microwave absorber for telecommunication, stealth technology and environmental pollution [6], catalysts and active substances for sensors and biosensors. Conducting polymers may be used alone and in composites with metals and their compounds (oxides, oxihydroxides and insoluble salts).

One of these metals may be rhenium. It is added to different alloys in order to enhance their corrosion and thermal stability [7]. Rhenium

complex compounds re used as long-living catalysts for petroleum cracking, for fuel transformation in plane engines and in fuel cells. It is also used for complex compounds with catalytic properties [8 – 10]. One of the most known rhenium compounds is the famous $[\text{Re}_2\text{Cl}_8]^{2-}$ anion, in which the bond between two Rhenium atoms is quadruple (Fig. 1)

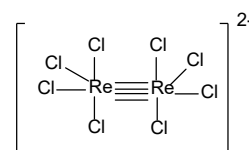


Figure 1. $[\text{Re}_2\text{Cl}_8]^{2-}$ structure.

Nevertheless, rhenium is considered as a rare element with its unique industrially-efficient mine on the island of Iturup (also known as Etorofu,

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controlled by Russia and claimed by Japan). Thus the problem of its recycling and regeneration is still actual [11].

The electrochemical synthesis of rhenium-polymer composite is usually realized in two stages, including direct electropolymerization and metal cathodic deposition from perrhenates on a yet formed polymer layer. However, some monomers with relatively low polymerization potential may also let the composite one-pot deposition, with ReO_2 formation as an *in situ* formed oxidant, polymerizing the monomer and reducing itself to the metallic rhenium. The synthesis is analogous to that described for pyrrole in [12].

It is possible to mention that the properties of polymers and based materials is dependent on the technique employed to obtain them. The polymerization conditions and critic phenomena, like monomer and initiator side reactions and electrochemical instabilities, capable to occur during the synthesis [13 – 16] also give their proper impact.

Thus, the practical use of new synthesis techniques is impossible without an *a priori* theoretical evaluation with the development and analysis of a mathematical model, capable to describe the behavior of the system. So, in this work, the possibility of rhenium-polymer sandwich-like composite cathodic deposition is described. The composite synthesis is given from the perrhenate of some novel triazolic derivatives [17 – 18] and 3,4-dimethoxypyrrole via ReO_2 *in situ* formation. It includes the development and analysis of the correspondent mathematical model in order to find the steady-state stability requisite and oscillatory and monotonic instability conditions. The comparison of the system's behavior with the similar ones [19 – 21] is also given.

2. System and its Modeling

The perrhenate immobilization on the cathodic surface is given by some novel triazolic derivatives, described in [17 – 18]. Possessing the pyridinic nitrogen atoms, the triazole is capable to form perrhenates (Fig. 2).

The perrhenate, in this case, is stabilized by the coordination bonds of rhenium atom with

pyridinic nitrogen atoms.

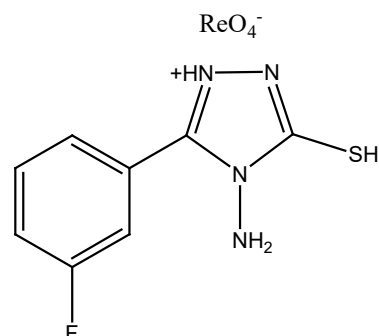
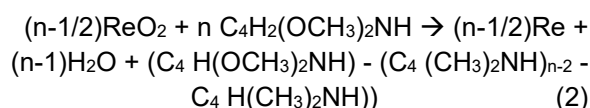
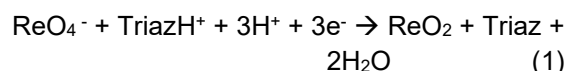


Figure 2. Triazolic perrhenate formation.

The composite electrodeposition is given in potentiostatic mode in relatively low cathodic potential module with insufficiently acidic solutions as following (1 – 2):



in which Triaz stands for the triazolic moiety.

In the composite, the Rhenium atom will be entrapped between the triazolic derivative and the polymer coating, yielding a sandwich-like structure (Figure 3).

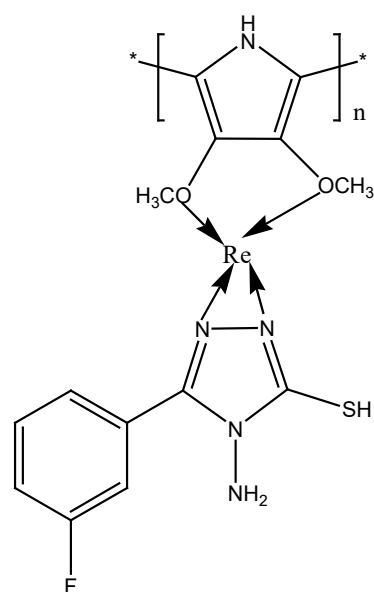


Figure 3. The composite structure.

This structure, along with the triazolic reinforcement, augments the electrical and

catalytic properties of the composite, like also the polymer adhesion on the cathodic surface.

Either the chemical or the electrochemical stages alter the ionic force of the pre-surface layer, like also the double electric layer (DEL) structure. These influences, as in [14-16, 19-21] may cause the oscillatory behavior in current. In potentiostatic mode, the cathode potential is fixed close to the potential of the electrochemical stage (1).

So, in order to describe the behavior of the system with potentiostatic rhenium-polymer sandwich-like composite cathodic electrodeposition, we introduce two variables:

c – 3,4-dimethoxypyrrrole concentration in the pre-surface layer;

μ – rhenium-dioxide triazole-stabilized particles coverage degree.

Simplifying 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 . The triazolium perrhenate is supposed to cover the entire cathode surface in the initial moment of the reaction.

It is possible to show that the system's behavior in potentiostatic mode will be described by the equation-set (3):

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (c_0 - c) - r_2 \right) \\ \frac{d\mu}{dt} = \frac{1}{G} (r_1 - r_2) \end{cases} \quad (3)$$

In which Δ and D are diffusion coefficients, c_0 is the monomer bulk concentration, G is the rhenium dioxide maximal surface concentration, and the parameters r are the reaction rates of the reactions (1) and (2), which may be exposed as:

$$\begin{aligned} r_3 &= k_3(1 - \mu) \exp\left(-\frac{F\varphi_0}{RT}\right) \\ r_4 &= k_4\mu^n c^{2n-2} \exp(-\alpha\mu) \end{aligned} \quad (4-5)$$

Being the parameters k correspondent reaction rate constants, F the Faraday number, φ_0 the potential slope, related to the zero-charge potential, α the parameter describing the DEL

influences of the ionic force changes during the polymerization, R is the universal gas constant and T is the absolute temperature.

In this system, the behavior is considered to be dynamic. Nevertheless, it is less dynamic than in the cases of the direct electropolymerization and direct rhenium electrodeposition [14 – 16, 19 – 21], which will be shown below.

3. Results and Discussion

In order to describe the electrodeposition of rhenium composite with triazolic derivative and poly (3,4-dymethoxypyrrrole), we analyze, by means of linear stability theory, the equation-set (3) along with the algebraic relations (4 – 5). The steady-state Jacobian matrix members will be rewritten as (6 – 10):

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \quad (6)$$

in which

$$a_{11} = \frac{2}{\delta} \left(-\frac{\Delta}{\delta} - (2n - 2)k_4\mu^n c^{2n-1} \exp(-\alpha\mu) \right) \quad (7)$$

$$a_{12} = \frac{2}{\delta} \left(-nk_4\mu^{n-1} c^{2n-1} \exp(-\alpha\mu) + \alpha k_4\mu^n c^{2n-1} \exp(-\alpha\mu) \right) \quad (8)$$

$$a_{21} = \frac{1}{G} \left(-(2n - 2)k_4\mu^n c^{2n-1} \exp(-\alpha\mu) \right) \quad (9)$$

$$a_{22} = \frac{1}{G} \left(-k_3 \exp\left(-\frac{F\varphi_0}{RT}\right) + \alpha k_3(1 - \mu) \exp\left(-\frac{F\varphi_0}{RT}\right) - nk_4\mu^{n-1} c^{2n-1} \exp(-\alpha\mu) + \alpha k_4\mu^n c^{2n-1} \exp(-\alpha\mu) \right) \quad (10)$$

The main conditions for stability and instabilities for bivariant systems may be exposed in the Table 1.

Table 1. The main stability and instability requirements for bivariant systems.

Stability aspect	Requirements
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

In order to avoid the cumbersome expressions, we introduce new variables, so the Jacobian determinant will be rewritten according to:

$$\frac{2}{\delta G} \begin{vmatrix} -\kappa_1 - W & -L \\ -W & -V - L \end{vmatrix} \quad (11)$$

As in [19 – 21], the oscillatory behavior (Tab. 1, line 3) in this system will be possible. Even being less probable than for direct electropolymerization, it will be caused by DEL influences not only of electrochemical reaction, but also of the ReO₂-assisted polymerization. These influences are described by the positivity of $\alpha k_3(1 - \mu) \exp\left(-\frac{F\phi_0}{RT}\right) > 0$ and $\alpha k_4 \mu^n c^{2n-1} \exp(-\alpha\mu) > 0$.

Both of the elements are responsible for the positive callback. The oscillations in this system are expected to be frequent and of small amplitude. Mathematically, the main condition for the oscillatory behavior will be rewritten as:

$$\frac{2}{\delta}(-\kappa_1 - W) + \frac{1}{G}(-V - L) = 0 \quad (12)$$

The steady-state stability requisite (Tab. 1, line 2) for this system will be described as:

$$\begin{cases} -\kappa - W - V - L < 0 \\ \kappa V + \kappa L + VL > 0 \end{cases} \quad (13)$$

And this condition will be warranted to be satisfied if the initiation parameter V and polymerization variable L are positive. This positivity is correspondent to the wide range of parameter values, in which DEL influences of the chemical and electrochemical stages are relatively fragile. From the electrosynthetic point of view, it means that the steady-state is formed easily, and the system is efficient. The electrosynthesis in this case will be diffusion-controlled, yielding a well-developed polymer composite.

The monotonic instability (Tab. 1, line 4) is

also possible in this system. It is correspondent to the N-shaped part of steady-state voltammogram and separates the stable steady-states from unstable states. Its condition is rewritten as:

$$\begin{cases} -\kappa - \Xi - \Omega - \Lambda < 0 \\ \kappa\Omega + \kappa\Lambda + \Xi\Lambda = 0 \end{cases} \quad (14)$$

The codeposition of rhenium and polymer may also occur if perrhenate-ion is present in the solution. For this case, the system will be described by a trivariant equation set, which will be shown in our next works.

4. Conclusions

From the cathodic synthesis of rhenium-polymer sandwich-like composite it is possible to conclude that:

- The formation of rhenium dioxide as an oxidant lets us codeposit rhenium and poly(3,4-dimethylpyrrole) efficiently, yielding a well-developed composite surface with catalytic properties;
- The electroanalytical process is diffusion-controlled, the steady-state is easy to maintain and obtain;
- The oscillatory behavior in this system is less probable than in the case of direct electropolymerization, but it is relatively probable, as there is more than one process influencing the double electric layer

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