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Mechanisms of oscillation generation in anodic reactions catalyzed by Ag nanostructures

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Abstract

The kinetics of the anodic oxidation of the compounds that can interact with the oxidized states on Ag electrode surface (formaldehyde, etc.) have been simulated with the assumption that the chemical interaction controls the anodic reaction specifically catalyzed by Ag nanostructures. Computer simulation has shown that the superposition of the two mechanisms of the anodic oxidation — the direct electrochemical oxidation and the oxidation that comprises chemical interaction of the oxidizable solute with the oxidized electrode surface — can cause the oscillations of the potential at a galvanostatic control similar to the oscillations that were observed in the experiment.

Keywords: Potential oscillation; Electrochemical oxidation; Surface reactions; Computer simulation

1. Introduction

Oscillating reactions have become a widely used model object in the investigations of the self-organization and related nonlinear phenomena in the nonequilibrium systems [1,2]. The electrochemical oscillating reactions [3–13] may be of particular interest for the investigation and application of the nonlinear chemical dynamics, due to convenience of the electrochemical means of monitoring and control of the reaction kinetics. Owing to high sensitivity of the oscillating reactions to the status of the electrode surface (composition, roughness, crystallographic orientation) [7,10,13,14], they can also become a useful tool for investigation of inhomogeneous surfaces in catalysis. However, the knowledge

of the mechanisms of the oscillating reactions is insufficient to benefit from high potentiality of the electrochemical oscillations.

Structural inhomogeneity of the electrode surface is usually a necessary condition for the oscillation generation in the reactions with soluble reagents. The required status of metal electrodes may be attained by multiple cyclic anodic and cathodic pretreatment [6,14], which probably produces nonequilibrium nanophase (clusters and small metal particles) on the electrode surface [15]. Metallic phase catalyzes the reverse transformation of the nanophase [16], therefore the oscillating electrochemical reactions on metallic catalysts often lack reproducibility. Besides, the reaction on the metallic catalyst disguises the specific catalytic proper-

ties of the nanophase and thus hinders the disclosure of the oscillation mechanisms.

In order to eliminate the effect of the equilibrium metal phase in the oscillating reactions a special technique was developed based on the self-assembling of stable Ag and Ag–Pd nanostructures from the electrochemically generated unstable nonequilibrium nanophases on conducting SnO₂ films and glassy carbon electrodes [13,16,17]. At the nanophase content below 10¹⁵ atoms cm² Ag clusters generated on the nonmetallic conducting supports in aqueous media linked firmly by adsorbates and surface compounds forming stable nanostructured aggregates that may exceed 100 nm and attain various shapes [16]. The surface Ag atoms in the nanostructures oxidize more readily than in the metallic electrode, due to excess surface energy of the nanophase [13,16]. Partial surface oxidation favors interaction between the adjacent nanoparticles and prevents the nanostructures from further oxidation and transformation into the metallic phase. Besides high stability, nanostructures differ from the metal particles in electronic and catalytic properties [13,16].

The most interesting peculiarity of Ag and Ag–Pd nanostructures is their ability to support sustained electrochemical oscillations at the condition inappropriate for the oscillating reaction on a metal electrode, e.g. formaldehyde anodic oxidation in an alkaline medium proceeds with the oscillations of the potential at a galvanostatic control on Ag nanostructures, though the stationary potential is characteristic for this reaction when metallic Ag is used as a catalyst [13,16]. Similar oscillations were observed with bimetallic Ag–Pd nanostructures in anodic oxidation of hypophosphite ions [13,17]. As the surface metal atoms in the nanostructures alternately oxidized and reduced in the range of the electrode potential covered by the oscillations and the substrata of the oscillating reactions were capable of interacting with the oxidized electrode surface, the oscillations were assumed to result from the superposition of the direct anodic oxidation and the anodic reaction

mediated by chemical interaction of the solute with the oxidized surface atoms in the nanostructured catalyst [13,17].

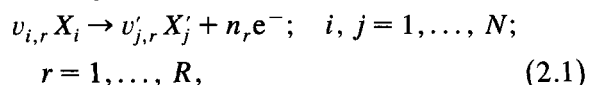
The goal of this work was to verify by means of computer simulation if the superposition of the two mechanisms (the direct anodic oxidation and the anodic oxidation that comprises chemical interaction of the oxidizable solute with the oxidized electrode surface) could actually cause the electrochemical oscillations at a galvanostatic control. As the peak of the anodic current was characteristic for the nanostructured catalyst in cyclic voltammetry [13], we have also examined the model for this peculiarity at a potentiodynamic control.

2. Model

2.1. Galvanostatic control

Typical current density in the oscillating anodic reactions on the nanostructured electrodes is 1–10 μA cm² at 0.1 M of the reaction substrate [13]. The diffusion control in the anodic reaction in this case may be ruled out and the concentration of the substrate may be considered invariable. We assume the activation control for all rates of the elementary electrochemical reactions except for the specific anodic reaction controlled by chemical interaction between the solute and the surface compound. The coulometry tests have confirmed resistance of the interior Ag in the nanostructures to anodic oxidation in the conditions of the oscillating anodic reaction. Therefore diffusion in the solid phase was also neglected (only the exterior layer of metal atoms in the catalyst was considered in the model). At these assumptions the dynamics of the oscillating reaction may be represented by the time dependencies of the surface concentrations.

Given the system of N reagents and R elementary reactions



the overall reaction rate can be expressed with the following general forms [18]

$$\frac{dX_m}{dt} = \sum_{r=1}^R (v'_{m,r} - v_{m,r}) \cdot k_r \cdot \prod_i$$

$$(X_i)^{v_{i,r}}; \quad m = 1, \dots, M, \quad (2.2)$$

where k_r is the rate constant of the elementary reaction with the number r and M is the dimension of the phase space (the number of the reagents whose surface concentrations should be considered in the model).

The constancy of the current density and the dependence of the reaction rate constants on the overpotential $E - E_{r(0)}$ give the additional equations:

$$F \cdot \sum_{r=1}^R n_r \cdot k_r \cdot \prod_i (X_i)^{v_{i,r}} = j, \quad (2.3)$$

$$k_r = k_{r(0)} \cdot \exp \left[\frac{n_r \cdot F}{R \cdot T} \cdot (E - E_{r(0)}) \right]. \quad (2.4)$$

The system of Eqs. (2.3) and (2.4) was solved symbolically for the potential E . The subsequent elimination of the variable electrode potential E in Eqs. (2.2) and (2.4) provided a numerical solution of the differential equations for a given reaction scheme and initial values of concentrations X_i , which gave phase trajectories with X_i used as phase coordinates and $E = f(t)$ dependence.

The partial current densities corresponding to the elementary electrochemical reactions have been calculated from the following equation:

$$j_r = F \cdot n_r \cdot k_r \cdot \prod_i (X_i)^{v_{i,r}}. \quad (2.5)$$

2.2. Potentiodynamic control

The supplement of the condition of the constancy of the potential scan rate

$$\frac{dE}{dt} = \text{scanrate}, \quad (2.6)$$

to Eqs. (2.2) and (2.4) makes the system of

$M + 1$ non-interacting ordinary differential equations with $M + 1$ variables. The simultaneous numerical solution of this system with Eq. (2.3) gives the potentiodynamic voltammogram.

2.3. Reaction scheme

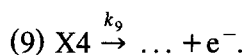
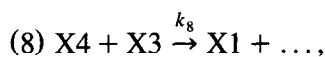
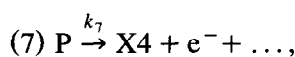
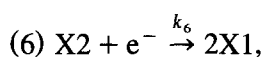
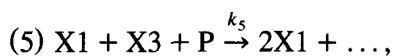
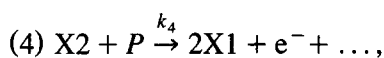
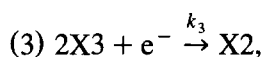
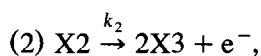
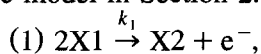
In order to concretize the model of the oscillations generation we consider the anodic oxidation of formaldehyde catalyzed by Ag nanostructures. On the metallic catalyst this reaction gives HCOO^- anions and H atoms; the latter form H_2 or oxidize into H_2O [19]. The anodic current on metallic Ag increases with the potential [13]. On the contrary, the anodic oxidation of formaldehyde on Ag nanostructures does not give gaseous hydrogen in the oscillating mode and the nanostructures exhibit maximum catalytic activity below the equilibrium redox potential of silver $E_{\text{Ag}^+/\text{Ag}}$ [13,17].

A combination of Ag(I) and Ag(0) gives a bifunctional active center on the partially oxidized electrode surface. In the Ag(0)Ag(I) center the Ag(I) site acts as the oxidizer that removes one hydrogen atom from the adsorbed CH_2O molecule or its ionized form $\text{CH}_2\text{O}(\text{OH})^-$, while the adjacent Ag(0) site catalyzes the electron transfer from the same particle in the electrochemical stage. In the nanostructured catalyst Ag(0)Ag(I) active center is not a merely statistical combination of Ag and Ag^+ , but rather a kind of a surface quasi-molecule which may be produced either by anodic oxidation of Ag(0) or cathodic reduction of Ag(I). In order to consider this peculiarity of the nanostructured catalyst, we assume $E_{r(0)}$ to be different in the above-mentioned anodic and cathodic reactions. Both reactions were supposed to be bidirectional, but the rate constants were assigned independently to the forward and reverse reactions to allow for major irreversibility.

Additionally, autocatalytic Ag(I) reduction to Ag(0) by the substrate of the oscillating anodic reaction was taken into account as the autocatal-

ysis is characteristic for Ag(I) interaction with formaldehyde and similar reducers [20].

With short symbols X1 for Ag(I), X2 for Ag(0)Ag(I) center, X3 for Ag(I), P for the anodic reaction substrate (formaldehyde, etc.) and X4 for chemically and electrochemically active product the oscillating reaction may be represented by the following reaction scheme which contains source substances and those products whose concentrations are required in the model in Section 2.1:



Reactions (1–4) and (6) are attributed solely to the nanostructured catalyst, while reaction (5) is a common autocatalytic Ag(I) reduction and reactions (7–9) represent slightly modified common mechanisms [19]. In the case of formaldehyde anodic oxidation X4 stands for atomic hydrogen, but generally it may represent any chemically and electrochemically active product of the anodic reaction (7). X4 is generated in the reaction (7) on the oxidized surface of the nanostructured catalyst, therefore X4 is partly consumed for X3 reduction in the reaction (8). The rest of X4 oxidizes anodically in the reaction (9). We observed H₂ evolution during formaldehyde anodic oxidation on Ag nanostructured catalyst only at high current densities that were inappropriate for the oscillating mode, therefore recombination of H atoms was not

taken into account in the model of the oscillations generation.

2.4. Constants

The potential scale was graduated in volts by using reasonable values for the parameters $E_{r(0)}$. The parameters $E_{1(0)}$ and $E_{2(0)}$, which may be regarded as standard redox potentials of the elementary electrochemical reactions (1) and (2), determine the potential range of the partially oxidized electrode surface, where the active center X2 can be formed both by the anodic oxidation of Ag(0) and cathodic reduction of Ag(I).

It has been known from cyclic voltammetry of Ag nanostructures [13,17] that a rather broad potential range (about half a volt) is characteristic for Ag oxidation on the surface of the nanostructures. It is not surprising, as the difference between standard redox potentials of metallic and atomically dispersed silver is even about 2.6 V [21].¹

−0.1 V versus AgCl/Ag was assigned to $E_{1(0)}$ and $E_{6(0)}$ and 0.3 V to $E_{2(0)}$ and $E_{3(0)}$ based on the experimentally evaluated potential range for oxidation and reduction of Ag in the nanostructures [13]. These assignments appeared to be significant for location of the simulated potential oscillations in the range that complied with the experiment. Because of lack of information on the values of rate constants, they were treated as dimensionless parameters of the model. For this reason arbitrary units were used for time, concentrations and current

¹ The usage of different standard redox potentials for metallic and highly dispersed silver is somewhat disputable, but it may be justified by the fact that Ag clusters and nanostructures cannot exist in the equilibrium with Ag phase in aqueous media. Besides, in view of the considerable difference between bulk silver and clusters in chemical properties, it is more convenient to treat clusters as particular chemical entities with respective standard redox potentials then make complicated corrections to a single standard redox potential for activities of Ag in the dispersed systems.

density. The constant $P = 1$ was used for the concentration of the substrate of the oscillating reaction.

The rate constant k_4 was assumed to be independent on the potential, similar to the rate constants of the non-electrochemical steps, as the rate of the electrochemical reaction (4) is determined by X2 chemical interaction with P.

3. Results and discussion

Several ranges for the rate constants that gave periodic solutions were found in the simulation of the oscillating anodic reaction. In all

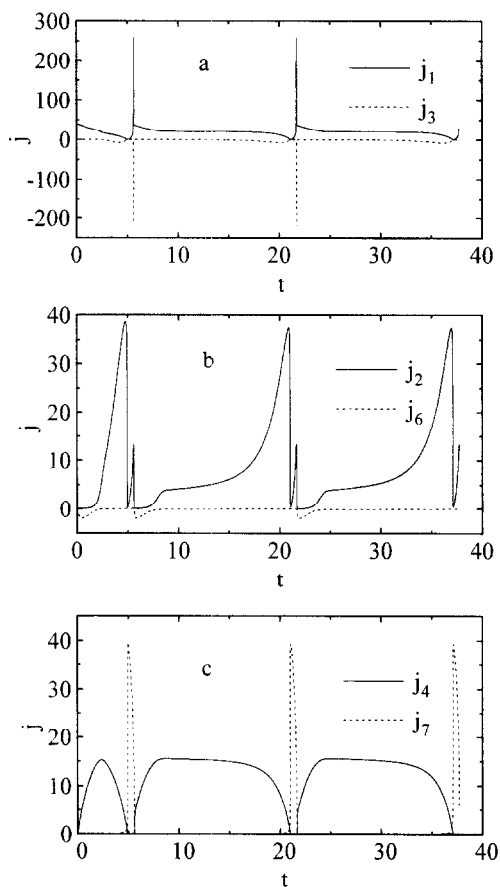


Fig. 1. The time dependence of the partial currents (a) j_1 , j_3 ; (b) j_2 , j_6 ; (c) j_4 , j_7 ; $j = 40$; $k_{1(0)} = 1 \cdot 10^{-4}$, $k_{2(0)} = 4 \cdot 10^{-3}$, $k_{3(0)} = 1 \cdot 10^{-4}$, $k_4 = 3.5 \cdot 10^{-4}$, $k_5 = 1$, $k_{6(0)} = 1 \cdot 10^{-3}$, $k_{7(0)} = 6 \cdot 10^{-4}$, $k_8 = 1 \cdot 10^{-4}$, $k_{9(0)} = 2 \cdot 10^{-4}$. The arbitrary units have been used for j and t .

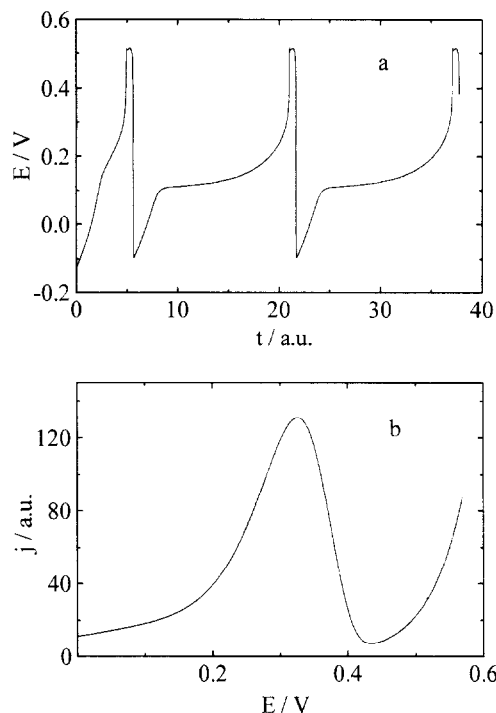


Fig. 2. (a) The dependence of the potential on the time and (b) the potential scanning voltammogram. The parameters are the same as in Fig. 1.

cases the sustained oscillations of the variables required that the rates of the reactions (4) and (5) were high enough to insure the regeneration of X1 from X2 and X3. This result complies with the experiment, as both substrates that support reproducible sustained oscillations in the anodic reactions on the nanostructured electrodes — formaldehyde and hypophosphite ions are efficient reducers for metal ions [20].

Fig. 1 shows typical patterns of the time dependencies of the partial current densities and Fig. 2a, Fig. 3a, c and Fig. 4a show various types of the time dependence of the electrode potential at a galvanostatic control. High amplitude potential oscillations are always asymmetric (the rise of the potential is much slower than the decrease), while the low amplitude oscillations may attain an almost sinusoidal form. We observed the same effect in the experiment. The analysis of the behavior of the model with different parameters at galvanostatic control has

shown that this effect is due to different contribution of the reactions (4) and (5) into the regeneration of X1 at different potentials. When the potential rises above $E_{2(0)}$ (0.3 V), reaction (4) terminates (Fig. 1c and Fig. 2a). After this point only reaction (5) can stop and reverse the rise of the potential. Though k_5 does not depend on the potential, the rate of this reaction strongly increases due to the increase in the production of X1 in the conjugated couple of the reactions (7) and (8). As the production of X3 in the reaction (2) also increases (Fig. 1b), the competition between reactions (2) and (5) proceeds at high rates. At appropriate k_5 the autocatalysis in the reaction (5) determines fast conversion of X3 to X1 with the corresponding fall of the potential to the initial low value. When k_5 is not high enough to reverse the production of X3, the potential may either oscillate with a low amplitude (if the current is low) (Fig. 3c) or attain the stationary value. The latter case is the

most common. Besides, the intermediate type of the behavior is characteristic for some combinations of parameters (Fig. 3a). In this case the oscillations damp at a constant current (Fig. 3a) and the corresponding phase trajectory curls approaching the focus (Fig. 3b). In the case of sustained oscillations the limit cycle attracts the phase trajectory, but the oscillating system may exhibit unusual behavior for some time before it reaches the limit cycle (Fig. 3c, d). The specific part of the trajectory is dependent on the initial conditions (the starting point in the phase space), while the limit cycle is characteristic of the set of the parameters of the model. Fig. 4 shows how the type of the behavior may vary with the parameters ($k_{1(0)}$ slightly decreases from Fig. 4a to b).

The oscillations of the potential are generally synchronized with the partial currents. However, due to the integral character of the potential the dependence of this variable on time

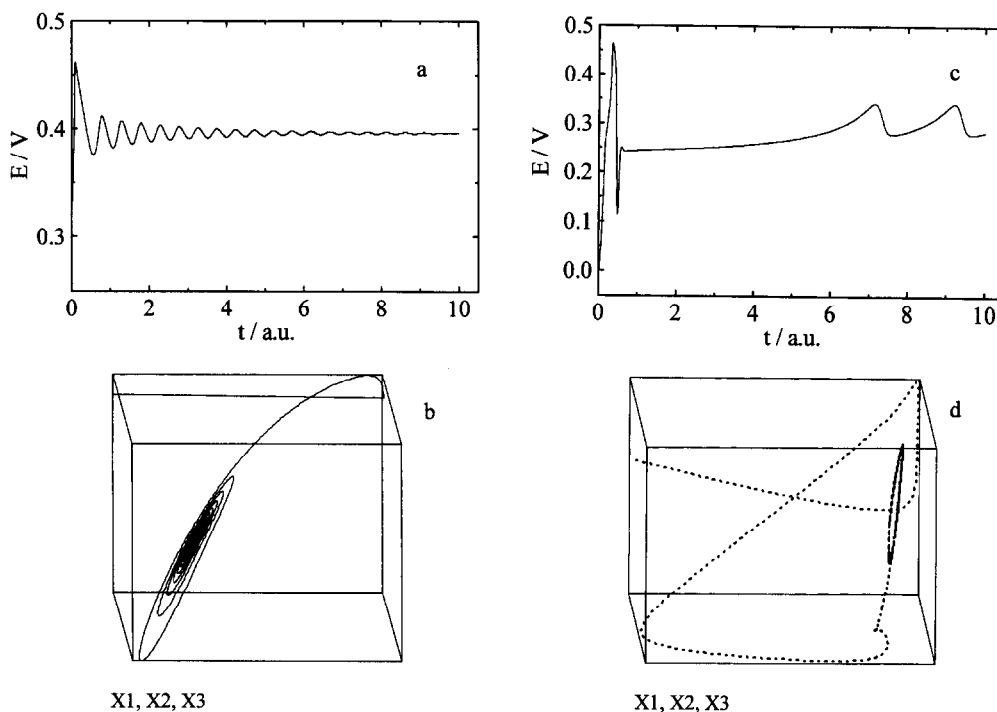


Fig. 3. (a), (c) The oscillations of the potential and (b), (d) the corresponding phase trajectories; $j=4$; (a), (b) $k_{1(0)}=1 \cdot 10^{-5}$, $k_{2(0)}=1 \cdot 10^{-4}$, $k_{3(0)}=3 \cdot 10^{-5}$, $k_4=1 \cdot 10^{-6}$, $k_5=8 \cdot 10^{-3}$, $k_{6(0)}=1 \cdot 10^{-4}$, $k_{7(0)}=2 \cdot 10^{-4}$, $k_8=2 \cdot 10^{-5}$, $k_{9(0)}=5 \cdot 10^{-10}$; (c), (d) $k_{1(0)}=8.5 \cdot 10^{-6}$, $k_{2(0)}=1.05 \cdot 10^{-4}$, $k_{3(0)}=3 \cdot 10^{-5}$, $k_4=2 \cdot 10^{-5}$, $k_5=1.32 \cdot 10^{-3}$, $k_{6(0)}=1 \cdot 10^{-4}$, $k_{7(0)}=2 \cdot 10^{-4}$, $k_8=2 \cdot 10^{-5}$, $k_{9(0)}=1 \cdot 10^{-11}$.

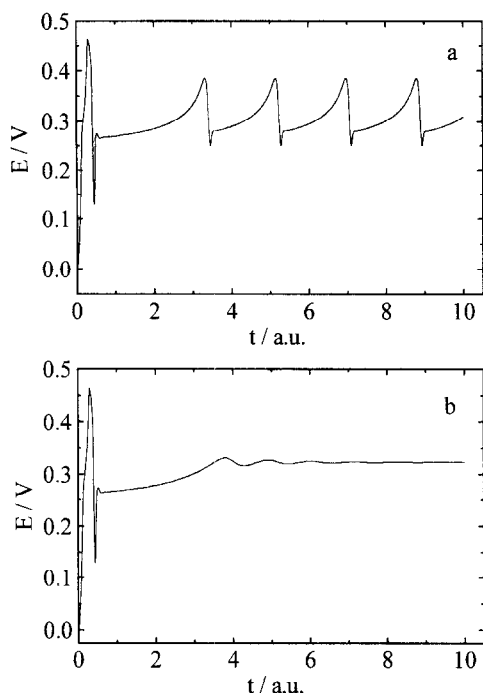


Fig. 4. The transition from the sustained to damped oscillations of the potential as a result of $k_{1(0)}$ variation; $j=4$; (a) $k_{1(0)}=1 \cdot 10^{-5}$, $k_{2(0)}=1.05 \cdot 10^{-4}$, $k_{3(0)}=3 \cdot 10^{-5}$, $k_4=1 \cdot 10^{-6}$, $k_5=1.32 \cdot 10^{-3}$, $k_{6(0)}=1 \cdot 10^{-4}$, $k_{7(0)}=2 \cdot 10^{-4}$, $k_8=2 \cdot 10^{-5}$, $k_{9(0)}=1 \cdot 10^{-11}$; (b) $k_{1(0)}=8.5 \cdot 10^{-6}$, $k_{2(0)}=1.05 \cdot 10^{-4}$, $k_{3(0)}=3 \cdot 10^{-5}$, $k_4=1 \cdot 10^{-6}$, $k_5=1.32 \cdot 10^{-3}$, $k_{6(0)}=1 \cdot 10^{-4}$, $k_{7(0)}=2 \cdot 10^{-4}$, $k_8=2 \cdot 10^{-5}$, $k_{9(0)}=1 \cdot 10^{-11}$.

approximates some fine structures observed in the partial current oscillations (Fig. 1b and Fig. 2a).

A typical voltammogram at linear anodic scanning of the potential is shown in Fig. 2b. The anodic current peak is similar to the peak that was observed in the experiment [13]. The characteristic peak is due to the reaction (4), which depends on the X2 and therefore decays at high potential.

Though the entire scheme that comprises reactions (1–9) is characteristic of the nanostructured catalyst, the participation of the oxidized electrode surface in the anodic reaction is not a unique property of the nanostructures; formaldehyde anodic oxidation can be also catalyzed by surface groups on the metallic Ag electrode [22]. However, the role of the surface groups on metallic Ag electrodes is not so significant.

Firstly, Ag oxidation commences at much higher potential on the surface of the metallic electrode; secondly, steric factor can favor the redox catalysis on the nanostructured surface; finally, the electronic properties of Ag nanostructures are somewhat different from those of the metallic Ag [13]. The oxidized nanostructures may be thus considered as a peculiar complex compound rather than the particles of the metal phase. Unlike oxidation of the metallic electrode, which may be considered as a localized surface effect, the oxidation and even chemical adsorption on the surface of the nanoparticle affects the properties of the whole particle.

4. Conclusions

The surface oxidation of the nanostructures formed by aggregation of the nonequilibrium metal nanophase may cause electrochemical oscillations, when the nanostructures are used as the catalyst of the anodic oxidation of the substances which can interact with the oxidized electrode surface. The oscillations of the potential and partial currents at a galvanostatic control result from the competition of the surface anodic oxidation with the reduction which proceeds in the electrochemical and non-electrochemical mechanisms.

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