
UNSTABLE STATES AT INTERFACES OF SPHERICAL GEOMETRY¹

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Using the impedance spectroscopy method of bifurcation identification, the model conceptions have been worked out to establish a functional connection between the electrode dimensions, faradaic impedance, and Hopf instability of an electrochemical system with an electrocatalytic reaction on a spherical electrode surface under potentiostatic conditions. This mechanism has two bifurcation points (two bifurcation frequencies), where the steady-states of the system become unstable, and spontaneous oscillations appear. The calculations show that the bifurcation frequency depends on the electrode size and the thickness of the layer, from which electroactive species diffuse.

1. Introduction

The dynamical instabilities which cause spontaneous oscillations are widespread in physico-chemical systems (corrosion processes, deposition of functional coatings, dissolution-passivation, *etc.*) far from thermodynamic equilibrium [1,2].

In electrochemical systems, we can distinguish two types of instabilities. The first type is due to the chemical kinetics and is independent of the electrode potential, and the second type results from the combination of both chemical and electrochemical factors [3].

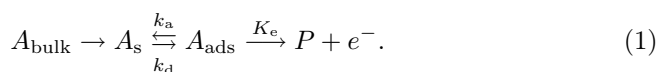
A graphic method for the identification of different bifurcations in electrochemical systems via impedance diagrams is well known [4].

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This article presents the analysis of an instability of the second type in an electrochemical system, in which the anodic oxidation occurs under potentiostatic conditions with the preceding stage of adsorption-desorption of the species being discharged. This model of electrocatalytic surface reaction was proposed in [5]. We consider this reaction in the case of a spherical electrode. The last one can be regarded in general as a spherical granule.

2. Electrocatalytic Reactions and Kinetic Equations at a Spherical Electrode

The anodic oxidation reaction under consideration is [5,6]:



The species of one sort (A_{bulk}) diffuse from the diffusive layer to the spherical electrode surface (A_{s}), on which they are adsorbed (A_{ads}) and electrochemically oxidized (P). It is assumed that the electron transfer step in reaction (1) is kinetically irreversible; k_{a} , k_{d} , and K_{e} are the rate constants of adsorption, desorption, and electron transfer.

The stationary current-potential relation and the faradaic impedance can be calculated with regard for the transport processes of electroactive species and the electrocatalytic processes on the spherical electrode surface. Neglecting the ohmic losses and the influence of a double layer, we can write the rates of adsorption-desorption

and electron transfer as follows:

$$\nu_1(t) = \Gamma k_a \exp(\gamma\theta(t)/2)C(R_0, t)(1 - \theta(t)) - \Gamma k_d \exp(-\gamma\theta(t)/2)\theta(t), \quad (2)$$

$$\nu_2(t) = \Gamma K_e(t)\theta(t) = \Gamma k_e \exp(\alpha f E(t))\theta(t). \quad (3)$$

Here, R_0 is the electrode radius, $C(R_0, t)$ is the concentration of electroactive species A at the electrode surface, $\theta(t)$ is the coverage of the electrode surface with the adsorbate, γ is the interaction parameter (the attraction constant), Γ is the maximum surface concentration, F is the Faraday's number, R is the gas constant, T is the absolute temperature, α is the symmetry factor of electron transfer in the direction of oxidation, E is the electrode potential, and $f = \frac{F}{RT} = 38.7 \text{ V}^{-1}$.

The equations for changes in the electrode surface coverage θ with the adsorbate and in the concentration $C(r, t)$ take the form

$$\Gamma \frac{d\theta}{dt} = \nu_1(t) - \nu_2(t), \quad (4)$$

$$\frac{\partial C(r, t)}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C(r, t)}{\partial r} \right) \quad (5)$$

with the boundary conditions

$$C(\delta, t) = C_0, \quad (6)$$

$$J_C(R_0, t) = -D \frac{\partial C(r, t)}{\partial r} \Big|_{r=R_0} = -\nu_1(t), \quad (7)$$

where J_C is the diffusion flux at the surface that is related to the adsorption-desorption rate, D is the diffusion coefficient, $\delta = R_0 + d$, d is the Nernst diffusion layer thickness, and C_0 is the bulk concentration of species A . The origin of coordinates coincides with the center of the sphere.

The faradaic current density, which is defined by the electron transfer rate, can be written as

$$i_f(t) = F\nu_2(t) = FT\Gamma k_e \exp[\alpha f E(t)]\theta(t). \quad (8)$$

Under steady-state conditions, i.e. when $d\theta/dt = 0$, $\partial C(r, t)/\partial t = 0$, one can obtain the stationary concentration at the electrode surface and the stationary electrode potential from Eqs. (4) and (5) with boundary conditions (6, 7), written as $J_C(R_0) = -m_C[C_0 - C_s(R_0)] = -\nu_1 = -\nu_2$:

$$C_s(R_0) = \frac{m_C C_0 + \Gamma k_d \theta_s e^{-\gamma\theta_s/2}}{m_C + (1 - \theta_s)\Gamma k_a e^{\gamma\theta_s/2}}, \quad (9)$$

$$E_s = (\alpha f)^{-1} \ln \left[\frac{m_C (C_0 - C_s(R_0))}{\Gamma k_e \theta_s} \right]. \quad (10)$$

Here, $m_C = \frac{D}{d} \left(1 + \frac{d}{R_0} \right)$. The potential is counted off from the zero-charge potential of the electrode free from species.

To calculate the faradaic impedance of the system in question, let us consider its dynamic behavior in the case of superimposing a small periodic signal $\Delta E(t) = \Delta E_0 e^{j\omega t}$, where $j = \sqrt{-1}$, ω is the angular frequency, on the stationary polarization potential E_s . In this case,

$$E(t) = E_s + \Delta E(t). \quad (11)$$

In response to this perturbation, the electrode surface coverage $\theta(t)$ oscillates about the stationary state,

$$\theta(t) = \theta_s + \Delta\theta(t), \quad (12)$$

where θ_s indicates the steady-state value of fractional coverage.

The faradaic current $i_f(t)$ and the concentration $C(R_0, t)$ oscillate according to (11) and (12) as follows:

$$i_f(t) = i_{fs} + \Delta i_f(E, \theta), \quad (13)$$

$$C(R_0, t) = C_s(R_0) + \Delta C(R_0, \theta). \quad (14)$$

The expression for the faradaic impedance in the space of Laplace transforms, $\bar{F}(s) = \int_0^\infty f(t)e^{-st}dt$, as a function of the complex frequency $s = \sigma + j\omega$ is given by

$$\bar{Z}_f(s) = \frac{\Delta \bar{E}(s)}{\Delta \bar{i}_f(s)} = \frac{\Delta \bar{E}(s)}{F \Delta \bar{\nu}_2(s)}, \quad (15)$$

since $\Delta \bar{i}_f(s) = F \Delta \bar{\nu}_2(s)$.

It is a response of the system to a low periodic signal imposed on the steady-state potential. After some calculations, one can obtain [7]:

$$\bar{Z}_f(s) = R_{ct} \times$$

$$\times \left\{ 1 + \frac{\partial_\theta \nu_2 [\sqrt{\tau_d s} \operatorname{cch} \sqrt{\tau_d s} + \lambda]}{\Gamma s [\sqrt{\tau_d s} \operatorname{cth} \sqrt{\tau_d s} + \lambda] - \partial_\theta \nu_1 [\sqrt{\tau_d s} \operatorname{cth} \sqrt{\tau_d s} + \frac{d}{R_0}]} \right\}, \quad (16)$$

where $R_{ct} = (\partial_E i_f)_s^{-1} = 1/F\Gamma\alpha f k_e \exp(\alpha f E_s)\theta_s$ is the charge-transfer resistance, $\lambda = \frac{d}{R_0} \left(1 + \frac{R_0}{D} \partial_C \nu_1 \right)$, and $\tau_d = \frac{d^2}{D}$. For convenience, partial derivatives are denoted as $\partial_x u = \partial u / \partial x$ and are equal to

$$\partial_\theta \nu_2 = \Gamma k_e e^{\alpha f E_s}, \quad \partial_C \nu_1 = \Gamma k_a e^{\gamma\theta_s/2} (1 - \theta_s),$$

$$\partial_{\theta}\nu_1 = \Gamma\{k_d e^{-\frac{\gamma\theta_s}{2}}[\frac{\gamma\theta_s}{2}-1] + k_a e^{\frac{\gamma\theta_s}{2}} C_s(R_0)[\frac{\gamma}{2}(1-\theta_s)-1]\}.$$

In order to pass from the Laplace space to the Fourier space, it is necessary to perform the substitution $s = j\omega$ in Eq. (16).

In our calculations, we ignore the electrolyte resistance and the double-layer impedance. In this case, the impedance of the model system under consideration is equal to the faradaic impedance.

3. Results and Discussion

Figure 1 shows the steady-state $i_{fs} - E_s$ curves for the model process (1) for different spherical electrode radii. The current-potential curve is N -shaped. The current magnitude is affected by two contrary factors: an increase in the potential and a decrease in the concentration of electroactive species in the near-electrode layer through the adsorption process, which is nonlinearly dependent on the potential. When the diffusion rate of electroactive species is equal to the rate of the processes occurring at the electrode, a maximum appears in the voltammogram. It is a consequence of the competition between the adsorption-desorption and diffusion processes. If the rate of consumption of reacting species predominates, the faradaic current decreases because of the insufficient delivery rate of species from the diffusion layer, whereas the potential increases. It is the region of the so-called negative differential resistance (NDR) [4], in which an instability usually arises. Such an N-NDR system may behave itself like activator-inhibitor systems [5,8], where the potential acts as an activator, and the concentration of electroactive species in the near-electrode layer acts as an inhibitor.

To study the linear stability of a nonlinear system near the stationary point, a well-known procedure consisting in the determination of Jacobian matrix eigenvalues [9] for the equations of state and a change in these eigenvalues at the potential change is usually used. For an electrochemical system under potentiostatic conditions, this is equivalent to studying the change in the faradaic impedance zeros at a change in the electrode potential. To establish a linear stability in an electrochemical system, the variation of the real parts s of the above $\bar{Z}_f(s)$ zeros depending on the electrode potential must be studied [5,6,10–12]. The sign of the real part of the faradaic impedance zero indicates the stability region of the stationary state under potentiostatic conditions. When the real part of the complex zero becomes positive, the stationary state becomes unstable.

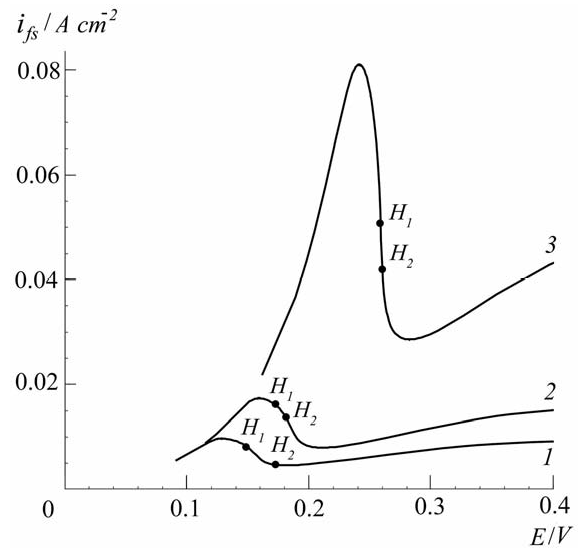


Fig. 1. Stationary polarization curves for a model process for various values of electrode radius R_0 (cm): (1) 0.01, (2) 0.001, (3) 0.0001. Parameters used in calculations: $\Gamma = 10^{-9}$ mol cm $^{-2}$; $\gamma = 8$; $\Gamma k_a = 0.1$ cm s $^{-1}$; $\Gamma k_d = 10^{-5}$ mol cm $^{-2}$ s $^{-1}$; $k_e = 10$ s $^{-1}$; $D = 10^{-5}$ cm 2 s $^{-1}$; $d = 10^{-3}$ cm; $\alpha = 0.5$; $C_0 = 10^{-5}$ mol cm $^{-3}$; $F = 96484$ C mol $^{-1}$; $R = 8.314$ J mol $^{-1}$ K $^{-1}$; $T = 295$ K

For our case, the impedance zeros are zeros of the numerator of Eq. (16):

$$(\Gamma s + \partial_{\theta}\nu_2)[\sqrt{\tau_d s} \operatorname{cth}\sqrt{\tau_d s} + \lambda] - \partial_{\theta}\nu_1[\sqrt{\tau_d s} \operatorname{cth}\sqrt{\tau_d s} + \lambda] + \frac{d}{R_0} = 0. \quad (17)$$

The numerical analysis of Eq. (17) shows that there are two Hopf bifurcations.

The Nyquist diagram, which characterizes the behavior of the faradaic impedance in the complex plane at the Hopf bifurcation point H_1 , consists of two distorted semicircles and passes through the origin of coordinates (Fig. 2). In the low-frequency range, there is an inductive loop with the negative real part of the faradaic impedance in the diagram. The point in the Nyquist impedance diagram, at which $\operatorname{Re}(Z(\omega)) = \operatorname{Im}(Z(\omega)) = 0$, corresponds to the threshold resistance, at which oscillations set up in the system [4].

The polarization resistance $Z_f(\omega \rightarrow 0)$ at the Hopf bifurcation point is negative.

The influence of the diffusion layer thickness manifests itself in the low-frequency range of negative impedance. The bifurcation frequency shifts to lower frequencies with increase in the thickness of the Nernst diffusion layer for spherical electrodes of the same radius.

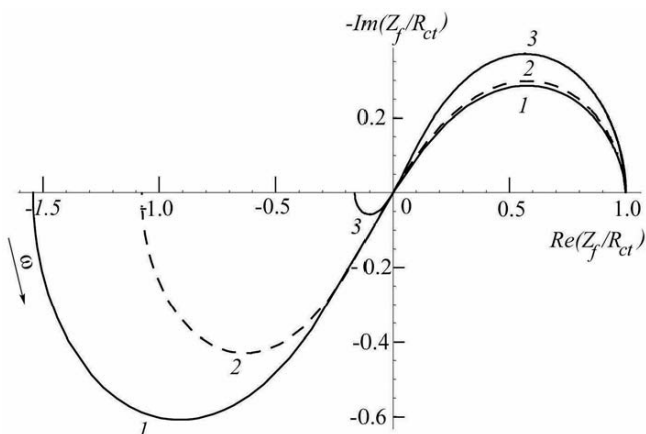


Fig. 2. Nyquist diagrams of the behavior of the faradaic impedance in the complex plane at the Hopf bifurcation point H_1 for various R_0 values (cm): (1) 0.01, (2) 0.001, (3) 0.0001

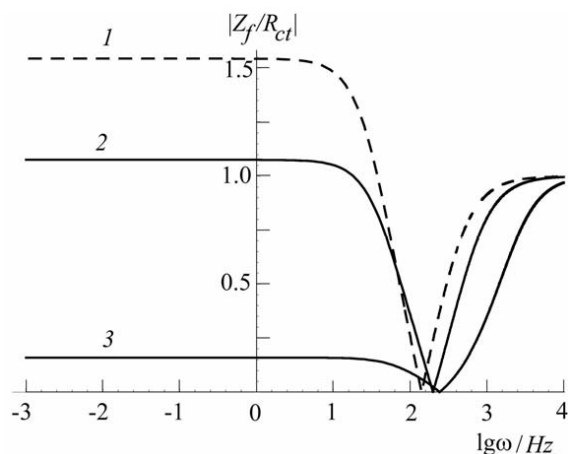


Fig. 3. Dependence of the faradaic impedance modulus, $|Z_f/R_{ct}|$, at the Hopf bifurcation point H_1 on $\lg \omega$ for various R_0 values (cm): (1) 0.01, (2) 0.001, (3) 0.0001

Dependence of the faradaic impedance modulus, $|Z_f/R_{ct}|$, on $\lg \omega$ (Bode diagrams) at the Hopf bifurcation point H_1 for spherical electrodes of various radii is shown in Fig. 3.

Nyquist faradaic impedance diagrams in the complex plane at various points of the current-potential curve in

Parameter values of an electrochemical system at the Hopf bifurcation point H_1

R_0 , cm	ω_H , Hz	θ_H	i_{tH} , A cm ⁻²	E_H , V	d , cm
0.01	141.44	0.563	0.008867	0.1443	0.001
0.001	198.78	0.513	0.01514	0.1768	0.001
0.0001	257	0.375	0.05345	0.2582	0.001
0.001	87.7	0.612	0.008327	0.1367	∞

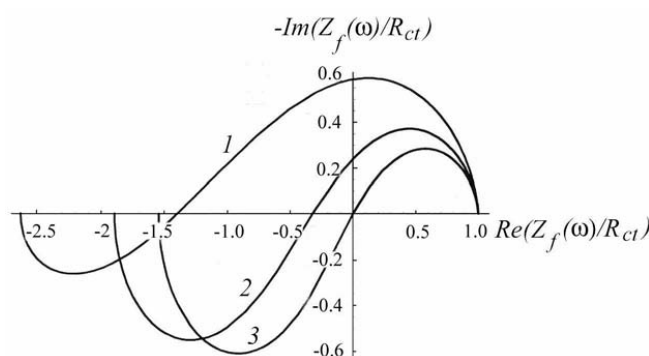


Fig. 4. Nyquist diagrams of the behavior of the faradaic impedance in the complex plane for various potential values along the stationary polarization curve ($R_0 = 0.01$ cm): (1) 0.139 V, (2) 0.142 V, (3) 0.144 V

the case of approaching the bifurcation point are shown in Fig. 4.

Parameter values of an electrochemical system at the Hopf bifurcation point H_1 at $\omega = \omega_H$ are listed in Table.

4. Conclusion

The electrochemical system with one sort of electroactive species under potentiostatic control exhibits oscillations when the faradaic impedance approaches its zero value from the side of the negative values of $\text{Re}(Z_f(\omega))$ as $(\omega \rightarrow \infty)$. The polarization resistance of the system has a negative value, $Z_f(\omega \rightarrow 0) < 0$ at the bifurcation values of parameters. The interaction of the mass-transfer and the adsorption-desorption processes depending on the electrode potential and proceeding to the charge transfer reaction determines the instability of the electrochemical system and gives rise to a negative impedance value. The potential region, where the instability appears, decreases with decrease in the electrode size. The dependence on the thickness of the Nernst diffusion layer is observed at low frequencies in the negative faradaic impedance region. In the case of semi-infinite diffusion, the region of the negative real part of the faradaic impedance increases in comparison with that in the case of the diffusion from a thin layer for the same radius.

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НЕСТАБІЛЬНІ СТАНИ НА МІЖФАЗНІЙ ПОВЕРХНІ СФЕРИЧНОЇ ГЕОМЕТРІЇ

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Резюме

На основі методу імпедансної спектроскопії для ідентифікації біфуркації розроблено модель, яка дозволяє встановити функціональну залежність між розміром електрода, фарадеевським імпедансом та нестійкістю Хопфа в електрохімічній системі з електрокаталітичною реакцією на поверхні сферичного електрода при потенціостатичних умовах. При такому механізмі існує дві точки біфуркації (дві біфуркаційні частоти), де стаціонарні стани системи стають нестійкими і виникають спонтанні коливання. Розрахунки показують, що значення біфуркаційної частоти залежать від розміру електрода та товщини шару, з якого дифундують електроактивні частинки.