

Effects of External Current Constraint on the Belousov-Zhabotinskii System Measured by a Pt Electrode

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The Belousov-Zhabotinskii system measured by a Pt electrode is investigated under external electrode current constraint. A dynamical analysis of the electrode reaction phase has been made by means of a linearized stability criterion valid for three-variable system. It turns out that limit cycle oscillatory regime and dynamical behaviors of the electrode reaction phase have been degenerated under periodical electrode current.

Key Words : Belousov-Zhabotinskii system, External electrode current constraint, Limit cycle oscillations, Numerical simulations, Systematic-dynamical analysis

Introduction

Belousov-Zhabotinskii (B-Z) reaction has been the subject of a number of experimental and theoretical investigations, and great advances have been made in the research work.^{1,2} However, an inert electrode is always used as a probe in the experiment to observe and measure the dynamical behaviors of B-Z reaction system.^{3,4} Thus, the complex-phase electrochemical reaction system arises, which involves the electrode B-Z reaction system and the bulk phase B-Z reaction system. Meanwhile, oscillations can appear in the bulk phase of the complex-phase system under certain conditions.⁵ Therefore, the system belongs to a special kind of electrochemical oscillation system. The systematic-dynamical investigation of this complex-phase system not only extends the research scope of the B-Z reaction, but enriches the research work of electrochemical oscillation. To begin with, this article establishes the dynamical model of electrode B-Z reaction system on the basis of Oregonator model; Secondly, temporal self-organization appearing in the electrode reaction phase has been discussed under stationary current constraint and periodical current constraint while the bulk phase is at a steady state. Finally, we will give a short concluding remarks.

Results and Discussion

Systematic-Dynamical Analysis of Electrode B-Z Reaction System. Usually, the dynamic behaviors of B-Z reaction are monitored by a Pt electrode measuring system. However, the pure chemical reaction steps must be coupled with the electrochemical reaction steps and diffusion steps because of the discharge of ceric ion at the electrode surface. As a result, the whole system consists of two subsystems: bulk phase and electrode reaction phase.

On the basis of Oregonator model⁶ and electrode process dynamics,⁷ the dynamical model of coupled system is proposed in Table 1 (we only consider diffusion coefficient

Table 1. Dynamical model of the coupled system

Basic steps in the electrode reaction phase	Diffusion processes	Basic steps in the bulk phase
$A + Y \xrightarrow{k_1} X + P$	$X \xleftarrow{D_1} X'$	$A + Y' \xrightarrow{k_1} X' + P$
$X + Y \xrightarrow{k_2} 2P$	$Y \xleftarrow{D_2} Y'$	$X' + Y' \xrightarrow{k_2} 2P$
$A + X \xrightarrow{k_3} 2X + 2Z$	$Z \xleftarrow{D_3} Z'$	$A + X' \xrightarrow{k_3} 2X' + 2Z'$
$2X \xrightarrow{k_4} A + P$		$2X' \xrightarrow{k_4} A + P$
$Z \xrightarrow{k_5} hY$		$Z \xrightarrow{k_5} hY'$
$Z + e \xleftarrow{k_f/k_b} Ce^{3+}$		

of intermediates).

Where $A \equiv BrO_3^-$; $P \equiv HOBr$; $X \equiv HBrO_2$ (electrode phase); $Y \equiv Br^-$ (electrode phase); $Z \equiv Ce^{4+}$ (electrode phase); $X' \equiv HBrO_2$ (bulk phase); $Y' \equiv Br^-$ (Bulk phase); $Z' \equiv Ce^{4+}$ (bulk phase); k_i ($i = 1 \sim 5$) is rate constant for B-Z chemical reaction. It is considered to be the same constant in the two reaction phase, for the effect of electrochemical reaction on k_i can be ignored. The stoichiometric factor h is expendable parameters that is allowed to vary.^{6,8} k_f and k_b , which are anode and cathode rate constants for electrochemical reactions, take the following forms⁷:

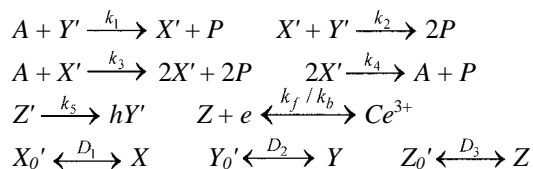
$$k_f = k^0 \exp(-\alpha n F \phi / RT) \quad k_b = k^0 \exp((1-\alpha) n F \phi / RT) \quad (1)$$

Where ϕ is the electrode potential with respect to some reference electrode; k^0 is rate constant for $\phi = 0$; α is the cathodic transfer coefficient; n is the number of electron transfer.

Because diffusion contribution to the bulk phase can be neglected compared with that to the electrode phase, only pure chemical reactions occur in the bulk phase. We regard chemical reactions in the bulk phase as the classical B-Z reactions.

Meanwhile, on the premise of neglecting diffusion contributions, the effects of external electrode current on the bulk phase can also be neglected. In this article, we put our

emphasis on the dynamic analysis of electrode reaction phase under the condition that the bulk phase is at a stable steady state. Thus, the dynamic model of electrode reaction phase is as below:



Where (X_0', Y_0', Z_0') is the stable steady state of bulk phase, which can be obtained when the right functions of evolution equation of bulk phase are equivalent to zero. According to the electrode processes, electrode current density can be expressed as below⁷:

$$i = nF\{C_0k_f - C_Rk_b\} \quad (2)$$

From Equation (1) and Equation (2), the evolutionary equation of the electrode reaction phase can be rewritten as:

$$\begin{aligned} dX/dt &= k_1AY - k_2XY + k_3AX - 2k_4X^2 + D_1(X_0' - X) = F_1 \\ dY/dt &= -k_1AY - k_2XY + hk_5Z + D_2(Y_0' - Y) = F_2 \\ dZ/dt &= 2k_3AX - k_5Z - i/F + D_3(Z_0' - Z) = F_3 \end{aligned} \quad (3)$$

Where i is the external electrode current density.

Systematic-Dynamical Analysis of Electrode B-Z Reaction System Controlled by Constant Electrode Current. Linear stability and bifurcation analysis are mathematical techniques useful for the study of nonlinear dynamical systems: information on the stability and dynamical behavior of the system can be obtained by changing the parameters.

By means of a linear stability analysis of the steady state of evolution equation (3), the Jacobian matrix takes the form:

$$J = \begin{vmatrix} \frac{\partial F_1}{\partial X} & \frac{\partial F_1}{\partial Y} & \frac{\partial F_1}{\partial Z} \\ \frac{\partial F_2}{\partial X} & \frac{\partial F_2}{\partial Y} & \frac{\partial F_2}{\partial Z} \\ \frac{\partial F_3}{\partial X} & \frac{\partial F_3}{\partial Y} & \frac{\partial F_3}{\partial Z} \end{vmatrix}_0 = \{a_{ij}\}_0$$

where

$$\begin{aligned} a_{11} &= -k_2Y_0 + k_3A - 4k_4X_0 - D_1; & a_{12} &= k_1A - k_2X_0; & a_{13} &= 0; \\ a_{21} &= -k_2Y_0; & a_{22} &= -k_1A - k_2X_0 - D_2; & a_{23} &= hk_5; \\ a_{31} &= 2k_3A; & a_{32} &= 0; & a_{33} &= -k_5 - D_3. \end{aligned}$$

The characteristic equation of the Jacobian matrix is as follows:

$$w^3 - Tw^2 + \delta w - \Delta = 0 \quad (4)$$

Where $T = a_{11} + a_{22} + a_{33}$

$$\delta = a_{11}(a_{22} + a_{33}) + a_{22}a_{33} - a_{12}a_{21}$$

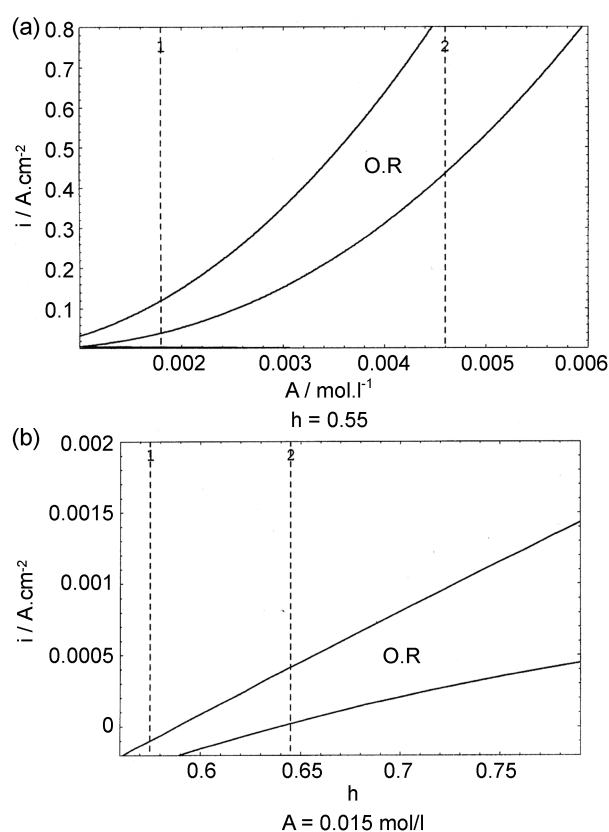


Figure 1. Limit-cycle oscillatory regimes of electrode reaction phase in parameters' plane. $k_1 = 1.34 \text{ M}^{-1}\text{s}^{-1}$; $k_2 = 1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $k_3 = 0.8 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$; $k_4 = 4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$; $k_5 = 1 \text{ M}^{-1}\text{s}^{-1}$; $D_i = 10^{-5} \text{ cm}^2\text{s}^{-1}$; $C = 0.0001 \text{ mol/L}$.

$$\Delta = \det(a_{ij})$$

According to Hanusse criterion valid for the appearance of limit-cycle oscillations in three-variable system,⁹ it is very favorable for occurrence of limit-cycle oscillation if:

$$\begin{aligned} \Delta &= -4T^3\Delta + \delta T^2 - 27\Delta^2 + 18T\delta\Delta - 4\delta^3 < 0; & T < 0; \\ T\delta - \Delta &> 0 \end{aligned} \quad (5)$$

Obviously, in the isothermal chemical system, the rate constant $k_i (i = 1 \sim 5)$ is unchangeable. In addition to the model parameter h , the other adjustable parameters are the initial concentration of BrO_3^- and the external electrode current density i . Through a lot of numerical calculations, the parameter regimes for occurrence of limit-cycle oscillations in the electrode reaction phase are depicted in Figure 1.

Figure 1 demonstrates that when we control the electrode current density i at a certain value, limit cycle oscillations can emerge in the electrode reaction phase under the condition that the bulk phase is at a steady state.; The regimes in Figure 1 between two dashed lines 1 and 2 are the limit-cycle oscillatory regimes of the bulk phase; Regimes marked O.R are where limit-cycle oscillations can appear in the electrode phase.

Effects of Periodical Current Constraints on the Dynamic Behavior of Pt Electrode Phase. If we exert a sinusoidal electrode current $i - i_0 + \varepsilon \sin[wt]$ on the electrode

B-Z system, the evolution equation (3) is rewritten as:

$$\begin{aligned} dX/dt &= k_1AY - k_2XY + k_3AX - 2k_4X^2 + D_1(X_0' - X) = F_1' \\ dY/dt &= -k_1AY - k_2XY + hk_5Z + D_2(Y_0' - Y) = F_2' \\ dZ/dt &= 2k_3AX - k_5Z - (i_0 + \varepsilon \sin[wt])/F + D_3(Z_0' - Z) = F_3' \end{aligned} \quad (6)$$

Obviously, electrode B-Z reaction system has become a heteronomy dynamical system. Linear stability methods useful for autonomic dynamical systems are helpless.¹⁰ Under small periodical constraint approximation (namely, $\{k_i (i = 1 \sim 5)\} \gg w$ and $\varepsilon \ll i_0$), we will investigate the stability of the dynamical system. The so-called small periodical constraint approximation means that the amplitude of external periodical constraint is very small and changes slowly, which can be regarded as a slow variable relative to other variables of the chemical reaction. Thus, the system will evolve on the periodical change of electrode current constraint and will reach at a steady state. The steady state is the function of the changing external periodical constraint. Therefore, we can consider the small periodical electrode current as a temporal parameter and make linearized stability analysis for evolution equation (6). In this case, we expand the Jacobian matrix around the reference state i_0 , and take the first order term.

$$J'_{(i=i_0+\varepsilon \sin(\omega t))} = \begin{vmatrix} \frac{\partial F_1'}{\partial X} & \frac{\partial F_1'}{\partial Y} & \frac{\partial F_1'}{\partial Z} \\ \frac{\partial F_2'}{\partial X} & \frac{\partial F_2'}{\partial Y} & \frac{\partial F_2'}{\partial Z} \\ \frac{\partial F_3'}{\partial X} & \frac{\partial F_3'}{\partial Y} & \frac{\partial F_3'}{\partial Z} \end{vmatrix}_{i=i_0} = \{a_{ij}'\}_0$$

The corresponding matrix elements can be written:

$$\begin{aligned} a_{11}' &= -k_2Y_0' + k_3A - 4k_4X_0' + \frac{\partial a_{11}}{\partial i} \Big|_{i=i_0} \\ a_{12}' &= k_1A - k_2X_0' + \frac{\partial a_{12}}{\partial i} \Big|_{i=i_0} \quad a_{13}' = 0 \\ a_{21}' &= -k_2Y_0' + \frac{\partial a_{21}}{\partial i} \Big|_{i=i_0} \\ a_{22}' &= -k_1A - k_2X_0' + \frac{\partial a_{22}}{\partial i} \Big|_{i=i_0} \quad a_{23}' = hk_5 \\ a_{31}' &= 2k_3A \quad a_{32}' = 0 \quad a_{33}' = -k_5 \end{aligned}$$

The characteristic equation of Jacobian matrix takes the form:

$$\lambda^3 - T'\lambda^2 + \delta'\lambda - \Delta' = 0$$

where

$$\begin{aligned} T' &= a_{11}' + a_{22}' + a_{33}'; \\ \delta' &= a_{11}'(a_{22}' + a_{33}') + a_{22}'a_{33}' - a_{12}'a_{21}'; \\ \Delta' &= \det(a_{ij}') \end{aligned}$$

When we carry out the linear stability analysis and also we consider the property of the sine function, the parameter values satisfying the condition of the limit-cycle oscillations

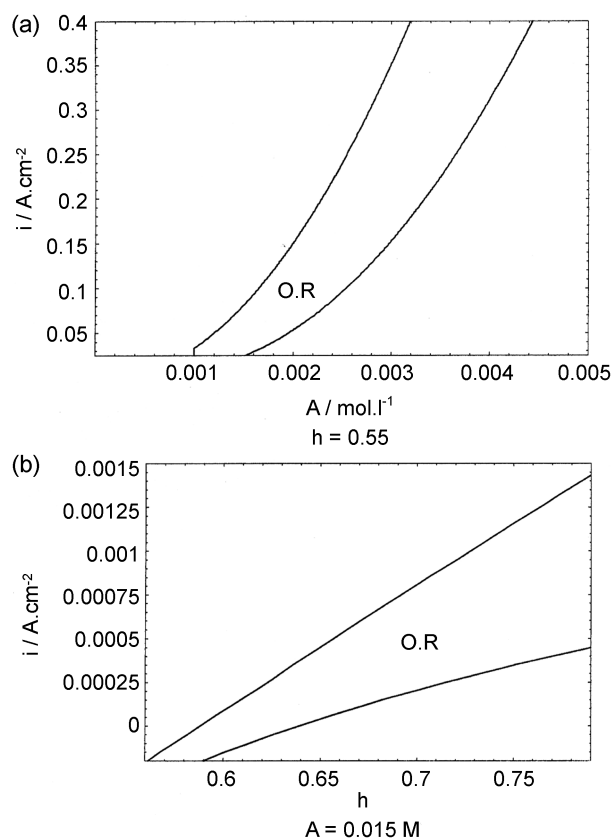


Figure 2. Regimes of dynamic behaviors of B-Z electrode chemical system perturbed periodically. $k_1 = 1.34 \text{ M}^{-1}\text{s}^{-1}$; $k_2 = 1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; $k_3 = 0.8 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$; $k_4 = 4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$; $k_5 = 1 \text{ M}^{-1}\text{s}^{-1}$; $\varepsilon = 0.001$; $D_{i(i=1,2,3)} = 10^{-5} \text{ cm}^2\text{s}^{-1}$; $C = 0.0001 \text{ M}$.

must fulfill the following conditions:

$$\begin{aligned} T < 0; T\delta - \Delta > 0; 18T\delta\Delta - 4T^3\Delta + T^2\delta^2 - 4\delta^3 - 27\Delta^2 < 0; \\ (\sin[wt] = -1) \end{aligned}$$

By means of numerical calculations, the parameter regimes for occurrence of limit-cycle oscillations in the electrode phase have been depicted in Figure 2. Regime marked "O.R." in Figure 2(a) is the limit-cycle oscillatory regime in A-i plane; Figure 2(b) shows limit-cycle oscillatory regime in h-i plane.

According to Equation (2), for the electrode processes: $Z + e \xrightarrow{k_f/k_b} Ce^{3+}$, we can obtain the following equation:

$$i = F\{Zk_f - (C - Z)k_b\} \quad (7)$$

where Z is the concentration of Ce^{4+} ; C, which is assumed to be a constant during the experiment, is the concentration sum of Ce^{4+} and Ce^{3+} at the electrode surface.

Combining Equation (1) and Equation (7), electrode potential is related to electrode current density by the following expressions:

$$\varphi = -\frac{2RT}{nF} \ln \left[\frac{\frac{i}{nFk_0} + \sqrt{\frac{i^2}{n^2F^2k_0^2} - 4Z(Z-C)}}{2Z} \right] \quad \left(\text{For } \alpha = \frac{1}{2} \right) \quad (8)$$

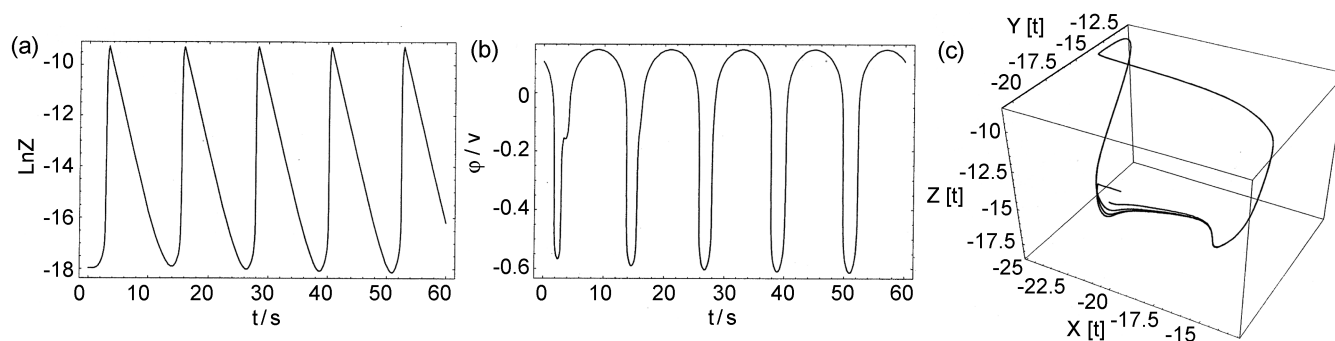


Figure 3. Response to the external periodical electrode current. $A = 0.015 \text{ M}$, $h = 0.6$; $i_0 = 0.00083 \text{ A.cm}^{-2}$; $w = \pi/6$; $\varepsilon = 0.0001$.

We choose groups of parameters to make numerical integration simulation in the oscillatory regimes. It turns out perturbing a focal steady state with periodical electrode current leads to response of limit-cycle oscillation, as is shown in Figure 3(a) and Figure 3(b). Figure 3(c) shows that evolution of the system from different initial values can trap into an invariant limit cycle.

The limit cycle oscillatory frequency of X, Y and Z within the regimes cannot change with the external constraint, but the dynamical behaviors of electrode potential are very complex under periodical constraint.

From Equation (8), the electrode potential is linked not only with the electrode current density i but with $[Ce^{4+}]$. Therefore, electrode potential oscillations are the combining effect of external periodical constraint and periodical oscillations of $[Ce^{4+}]$. We have chosen different values of i_0 , ε and ω to simulate dynamical behaviors of the electrode

potential. The results are shown in Figure 4. Dynamical behaviors in the electrode reaction have been simulated under different frequencies ω , see Figure 4(a). Figure 4(b) has shown dynamical behaviors of the electrode potential under different magnitude of the steady-state current, i_0 . Also, the dynamical behaviors of the electrode potential under different values of amplitude, ε , have been depicted in Figure 4(c). It has been found that the magnitude of i_0 can have a severe effect on oscillatory amplitude of the electrode potential and initial oscillatory electrode potential (Figure 4(b)); Different values of external current frequency can lead to the occurrence of biperiodicity and multi-periodicity of electrode potential (Figure 4(a)); The amplitude of external electrode current, ε , can affect oscillatory mode of electrode potential ϕ , which can be seen clearly in Figure 4(c).

Out of the regimes the electrode reaction phase is not at a steady state, but oscillate with the same frequency as that of

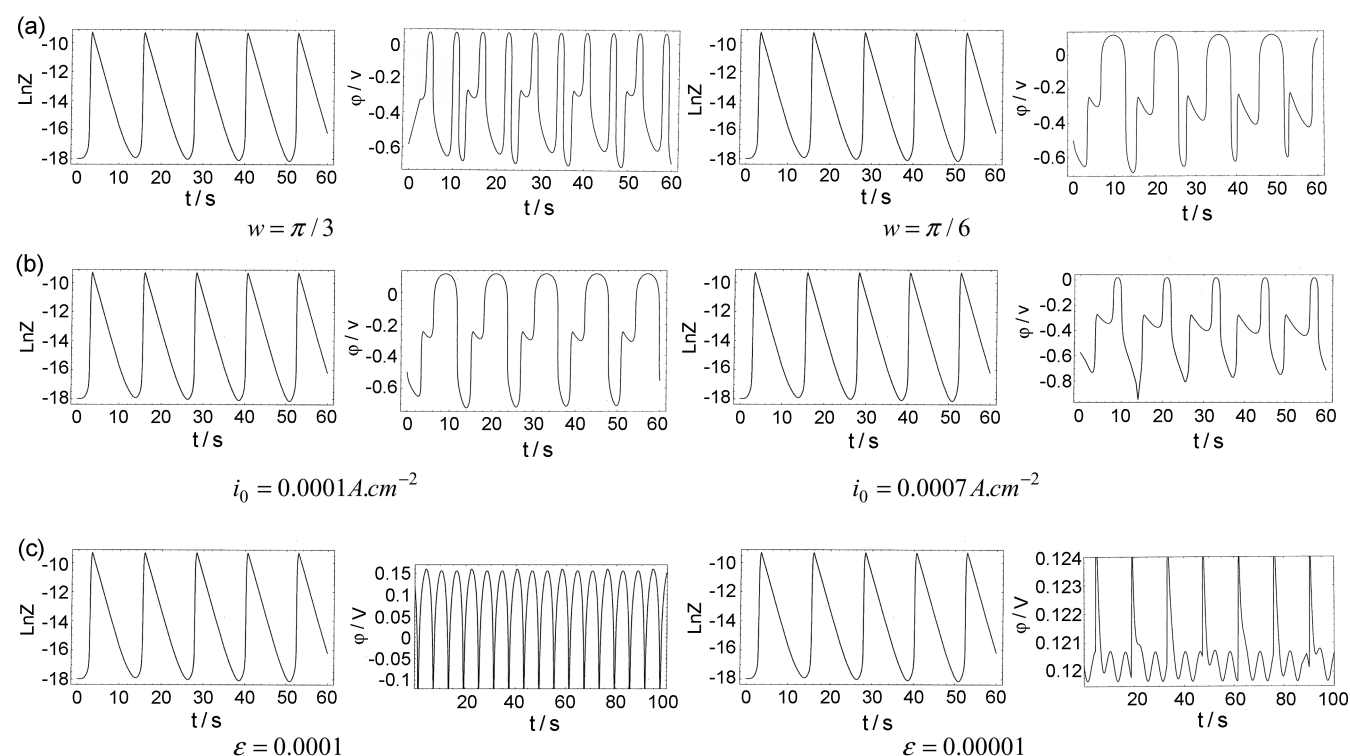


Figure 4. Limit cycle oscillations of the electrode reaction phase under different external parameters.

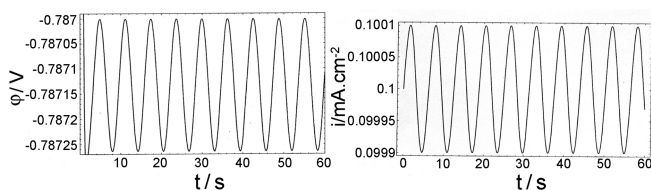


Figure 5. Time series of electrode current potential of the electrode reaction phase and the external electrode current constraint ($A = 0.001 \text{ M}$; $h = 0.55$; $i_0 = 0.1 \text{ A}\cdot\text{cm}^{-2}$; $w = 1$; $\varepsilon = 0.0001$).

the external electrode current constraint, see Figure 5. Obviously, this kind of oscillations is different from that of limit cycle oscillation within the oscillatory parameters regime. Further experimental investigations will appear in our forthcoming papers.

Conclusion

In general, electrode measuring system is used to observe dynamic behaviors of B-Z reaction. This article investigates the effects of small periodical current constraint on electrode B-Z coupled system. It is concluded that the dynamic behaviors of the bulk phase of this system cannot be affected by external current constraint. However, new dynamic behaviors can arise in the electrode reaction phase. By means of linear stability analysis of three-variable system, the parameter regimes of appearance of limit cycle oscillation in the electrode reaction phase have been calculated. Within the regimes the oscillatory behaviors of

X, Y and Z cannot be affected by external constraint, but the external constraint can have a great influence on the behaviors of electrode potential; Out of the regimes the electrode phase is not at a steady state but oscillate with the same frequency as the external constraint. This research work is helpful to further qualify the accuracy and reliability of detection of pure B-Z reaction monitored by an inert electrode.

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