PhD Theses

Dynamical Instabilities in Electrochemical Systems

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I. INTRODUCTION AND THE AIM OF THE WORK

Electrochemical cells often exhibit instabilities that can result in temporal current/potential oscillations. These periodic phenomena are often observed, for example, in the anodic dissolution of certain metals under potentiostatic or galvanostatic conditions. In these far-from-equilibrium systems, due to the interaction of coupled nonlinear chemical and physical processes, complex dynamical behavior (e.g. bistability, periodic and chaotic oscillations) may evolve that can be described only by a large number of dynamical variables.

Our goal has been to study different nonlinear phenomena (and to understand their governing physicochemical principles) that may emerge due to the dynamical instabilities occurring in the copper-phosphoric acid electrochemical system under potentiostatic control. This goal is important for different reasons. First, the dynamical instabilities should generally be avoided in the industrial settings; therefore, we must learn about the laws of their origin. Another important reason is that our results can be quite useful for other research areas, for example, in medical research aimed at understanding the nonlinear dynamical phenomena of the human neuronal system. We considered it is also important to study the effect of different parameters on the dynamics (period, waveform etc.) of oscillating electrochemical systems in general. These parameters could be the concentration or temperature of the electrolyte, the surface coverage of the working electrode, the rotation rate of a disk electrode, or the resistance of an external resistor connected in series with the electrochemical cell. In our potentiostatic experiments, the most important control parameter is the circuit potential applied at the cell, and the easily measurable state variable is the current flowing through the electrode.

I have carried out my research in three well-defined topics.

The first topic aims at the detailed experimental investigation and modeling of birhythmicity (in other word, dynamical bistability) that I have studied earlier in my diploma thesis (2009). Importance of the topic is the following: in living organisms there are many rhythmic processes of different time scales that weakly interact. It is possible that the interaction between the units produces an internal delayed-feedback that can result in complex dynamical response.

The second topic is related to previous electrochemical experiments of our group using a rotating copper-disk electrode, of which an interesting and important question has emerged: what is the effect of the rotation rate on the period and waveform of the current oscillations. Although, rotating disk electrodes have been intensively applied in the past by many research groups to studying oscillatory dynamics of the electrochemical systems, we have found no literature record of the investigation on the effect of the rotation rate. Therefore, our research is not just new but it is aimed at providing a solution to this deficit. In achieving this goal, we have utilized the so-called nullcline-based method for characterizing nonlinear dynamical systems.

The third topic is related to the nullcline approach. The nullclines are special functional relationships between the essential dynamical variables of a system where the rate of change of a specific species is constrained to zero. Presently, no method is known to experimentally determine the nullclines in the state space of the system variables. Here, we propose and numerically test a nullcline-based technique which is capable of reproducing the temporal behavior of the system’s variables without the explicit knowledge of the system of differential-equations describing the dynamics.
II. EXPERIMENTAL METHODS
Applied model, experimental setup and numerical tools

1. The Koper-Gaspard dimensionless model of anodic electrodissolution
Koper and Gaspard developed a general model for negative differential resistance type electrochemical oscillators, such as the Cu-o-phosphoric acid system:

\[ \frac{dE}{dt} = \frac{V - e}{R} - 120k(e)u, \]  
\[ \frac{du}{dt} = -1.25d^{1/2}k(e)u + 2d(w - u), \]  
\[ \frac{dw}{dt} = 1.6d(2 - 3w + u), \]

where \( e \) is the dimensionless electrode potential, \( C_d \) is the double layer capacitance per surface area of the electrode, \( R \) is the series resistance of the cell, \( V \) is the circuit potential, \( d \) is the rotation rate of the electrode, \( u \) and \( w \) are the dimensionless concentrations of the electroactive species in the near surface and in the secondary diffusion layers, \( t \) is dimensionless time, and \( k(e) \) is the potential dependent rate constant defined as follows:

\[ k(e) = 2.5\Theta^2 + 0.01 \exp\left[0.5(e - 30)\right], \]

where \( \Theta \) is the surface coverage of the electrode which is a nonlinear function of the electrode potential:

\[ \Theta = \begin{cases} 1 & \text{ha } e \leq 35 \\ \exp\left[-0.5(e-35)^2\right] & \text{ha } e > 35 \end{cases}. \]

2. Experimental setup
Experiments were performed by using a standard three-electrode electrochemical cell equipped with a 5 mm diameter copper rotating disk electrode (W) (99,99%+, Radiometer EDI 101), a Pt-sheet counter electrode (C) (5 cm², Radelkis OH-9437), and a Hg/Hg2SO4/tel. K2SO4 (Radiometer Analytical, Ref.-621) reference electrode. A potentiostat was applied to set the potential between the working and the reference electrodes (Electroflex EF451 and Pine AFCBP1). The current was measured with an ammeter (accuracy 0,001 mA) built in the potenciostat. The sampling frequency for data acquisition was 200 Hz. The temperature of the cell was maintained with a circulating bath at the given values –5 °C ± 0,1 °C (Lauda RM6B). The electrolyte solution was 70 cm³ o-phosphoric acid (85 % Spektrum-3D). The surface of the copper disk was freshly polished by a series of wet sandpapers. (P180-P4000).

**Figure 1.** Three-electrode electrochemical system (C-counter electrode, W-working electrode, R-reference electrode)

To remove the oxide layer from the surface of the copper electrode, the potential was first set to 500 mV for 2 minutes then swept in several cycles between 0 and 750 mV with a scan rate of 10 mV/s. Next the series (ohmic) resistance \( R_s \) of the solution was
dynamical instabilities in electrochemical systems

Determined from impedance measurements. The series resistance of the electrolyte was usually 70 ± 5 ohm.

Before the feedback control experiments, the cell potential was set to \( V_{\text{H}} + 10 \text{ mV} \) for 2 hours (\( V_{\text{H}} \) is the potential at the Hopf-bifurcation point). By this time, the current oscillations stabilized assuring reproducibility. It is known, that oxygen does not affect the dynamics of the studied system. Therefore, no special treatment has been applied to remove dissolved air oxygen from the electrolyte.

3. Delayed-feedback control
For implementing the feedback control, the cell potential has been perturbed according to the following formula:

\[
\delta V(t) = K \left[ E(t) - E(t - \tau) \right],
\]

where \( \delta V(t) \) is the potential perturbation (feedback), \( K \) is the feedback gain, \( E(t) \) is the electrode potential, \( t \) is time and \( E(t-\tau) \) is the value of the electrode potential at \((t-\tau)\) where \( \tau \) is the delay time.

4. Numerical tools
The system of ordinary differential equations was solved numerically by using the XPPAUT program package. In most cases, the Gear method has been used (absolute error limit \( 10^{-6} \)). For the calculations of nullcline points the Runge-Kutta method has been applied.

III. NEW SCIENTIFIC RESULTS

1. Multirhythmicity has been found in the copper–phosphoric acid electrochemical system

1.1. Birhythmicity has been detected experimentally in the copper-phosphoric acid system by applying delayed feedback control.

Birhythmicity is the coexistence of two stable limit cycles with distinctly different periods at exactly the same conditions. In our case, it means current oscillations with two different periods at exactly the same parameter values including the feedback gain and the delay time. The observed period of oscillations depends on the prehistory of the system.

1.2. It has been found that there exists a critical delay time \( \tau_{\text{crit}} \) for the first appearance of birhythmicity and of the related hysteresis loop (Figure 2).

1.3. We have shown that the width of the hysteresis loop increases with the delay time (Figure 2).

1.4. It has been found that the larger the feedback gain, the smaller the critical value of the delay time (Figure 3).

The product of the feedback gain and the delay time is approximately unity:

\[
\kappa \tau_{\text{crit}} \approx 1
\]
1.5. **Trirhythmicity has been found at very large delay times (Figure 2).**

Trirhythmicity is the coexistence of three stable limit cycles with distinctly different periods at exactly the same conditions. In our case, it means current oscillations with three different periods at exactly the same parameter values including the feedback gain and the delay time. The observed period of oscillations depends on the prehistory of the system.

![Figure 2](image)

**Figure 2. Experiments:** the hysteresis loops of bi-, and trirhythmicity. Angular frequency of oscillations $\Omega$ at large control gain ($K = 0.12$) when the delay time is first increased (●) from 0 to 6 s then decreased back to 0 s (▲). $V_H = 120$ mV, $V_0 = 130$ mV, $R = 87$ Ohm; $T_0 = 1.24$ s. Three different oscillatory modes were observed at large feedback delay ($\tau > 4$ s). Oscillations with angular frequencies corresponding to the middle branch of the diagram (trirhythmicity, □) could be approached by perturbing the system from either the upper or lower branches. The points of the middle branch were traced by either increasing or decreasing the feedback delay time after the perturbation.

1.6. Based on the phase model we have predicted and then confirmed by experiments that there exists a linear relationship between the difference of the maximal and minimal values of angular frequencies and the control gain (Figure 3):

$$\Delta \Omega = \Omega_{\text{max}} - \Omega_{\text{min}} = 2\kappa = 2\beta K$$  \hspace{1cm} (8)

![Figure 3](image)

**Figure 3. Experiments:** testing the correlations (as predicted phase model) between $\Delta \Omega$, $K$, and $\tau_{\text{crit}}$ for birhythmicity at weak feedback. a) The difference between the maximum and minimum of the angular frequencies of the oscillations as a function of the control gain $K$. The slope of the fitted line is $2\beta = 48.38$ rad/s. b) Critical value of delay time as a function of control gain $K$. c) $K\tau_{\text{crit}}$ as a function of feedback gain $K$. 

4
2. New relationships have been found between the frequency (and waveform) of current oscillations and the rotation rate of the electrode

When studying the effect of rotation rate on the frequency, the resistance and cell potential had been adjusted in such a way that at the Hopf bifurcation the electrode potential was almost constant \( e_{ii} = -48 \pm 0.5 \text{ mV} \).

2.1. Based on numerical simulations we have predicted and then confirmed by experiments that frequency of current oscillations \( (\omega) \) is proportional to the square-root of the rotation rate \( (d^{1/2}) \) (Figure 4).

\[
\omega \propto d^{1/2}
\]  

(9)

Figure 4. Effect of rotation rate on the frequency of oscillations close to the Hopf bifurcation point. Inset: ln-ln plot giving slope 0.47 and 0.45. a): Experiment, b): Simulation)

2.2. The direct effect of the rotation rate on characteristics of the waveform and on the frequency of relaxation oscillations has been observed (Figure 5.).

Figure 5. Relaxation current oscillations at different rotation rates. Left (Experiments) a)–d): \( d = 1300, 1400, 1500, 1600 \text{ rpm} \). Right (Simulations) a)–d): \( \tilde{d} = 0.2; 0.4; 0.6; 0.8 \).
2.3. We have found that, although, the waveform of relaxation type oscillations strongly depend on the rotation rate, the position of the characteristic points (minimum, maximum and transition points) of the waveform does not change as the rotation rate is varied (Figures 5. and 6.).

Figure 6. Experiments: changes in the characteristics of the relaxation-type oscillations as the rotation rate is varied. Oscillation waveforms at different rotation rates: thick solid line: $d = 1300$ rpm; thick dashed line: $d = 1400$ rpm; thin solid line: $d = 1500$ rpm; and thin dashed line: $d = 1600$ rpm. The triangle and diamond indicate the upper and lower transitions.

3. Model independent method has been developed for the characterization of nonlinear dynamical behavior in electrochemical systems based on nullclines

The nullclines are special functional relationships between the essential dynamical variables of a system where the rate of change of a specific species is constrained to zero.

3.1. An adaptive control algorithm has been developed to calculate the points of e-nullcline.

The adaptive controller for the point of the e-nullcline are as follows:

$$V = V_0 + L(b - e), \quad (10)$$
$$\frac{db}{dt} = \lambda(b - e), \quad (11)$$

where $V$ is the circuit potential, $V_0$ is a set potential at which the nullcline points are sought, $L$ is the adaptive control gain, $b$ is the external control variable, and $\lambda$ is a control variable. The value of $\lambda$ defines a time scale at which $b$ traces the $e$ variable. When $b \equiv e$, no further perturbation takes place ($V = V_0$) and the constant value of $e$ gives one of the coordinates of the nullcline point in the $u$ vs. $e$ phase-space (Figure 7).

3.2. A proportional-differential (PD)-controller has been developed to obtain the other coordinate of the point of e-nullcline determined by the adaptive controller (Figure 7).

As the most suitable parameter for controlling $u$ values is the rotation rate, for the perturbation of $d$ the following formula has been applied:

$$d = d_0 + \alpha(u - u_0) + \beta \frac{du}{dt}, \quad (12)$$
where $d$ is the rotation rate, $d_0$ is the rotation rate at which the system is being investigated, $u_0$ is the setpoint, while $\alpha$ and $\beta$ are the proportional control gain and the derivative control gain.

3.3. An adaptive control algorithm has been developed to calculate the points of $u$-nullcline. The adaptive controller for the point of the $u$-nullcline are as follows:

$$d = d_0 + L(b - u), \quad (13)$$

$$\frac{db}{dt} = \lambda(b - u), \quad (14)$$

where $d$ is the rotation rate, $d_0$ is a set value at which the nullcline points are sought, $L$ is the adaptive control gain, $b$ is the external control variable, and $\lambda$ is a control variable. The value of $\lambda$ defines a time scale at which $b$ traces the $u$ variable. When $b = u$, no further perturbation takes place ($d = d_0$) and the constant value of $u$ gives one of the coordinates of the nullcline point in the $u$ vs. $e$ phase-space (Figure 7).

3.4. A proportional-differential (PD)-controller has been developed to obtain the other coordinate of the point of $u$-nullcline determined by the adaptive controller (Figure 7).

As the most suitable parameter for controlling $e$ values is the circuit potential, for the perturbation of $V$ the following formula has been applied:

$$V = V_0 + \alpha(e - e_0) + \beta \frac{de}{dt}, \quad (15)$$

where $V$ is the circuit potential, $V_0$ is the circuit potential at which the system is being investigated, $e_0$ is the setpoint, while $\alpha$ and $\beta$ are the proportional control gain and the derivative control gain.

3.5. We have shown that the nullcline-based method can be successfully applied to reconstruct the nonlinear dynamics of the oscillatory system (Figure 8).

By analyzing the motion of a phase point in the phase space and along the nullclines we could characterize the current oscillations both qualitatively and quantitatively.

3.6. We have shown that the nullcline-based method can be successfully applied to reconstruct the nonlinear dynamics of both the bistable and excitable system.
Figure 7. Simulations: Obtaining nullcline points using the control algorithm in the 2D model. Top row: The oscillatory behavior is suppressed by combination of adaptive control in variable $e$ using parameter $V$ and PD-control in variable $u$ using parameter $d$. The control is turned on at time $t = 0$ with parameters $\lambda = -0.1, L = 1, \alpha = -0.1, \beta = 0$, a): Variable $e$ vs. time. b): Variable $u$ vs. time. Bottom row: Theoretical nullclines (solid lines) and nullcline points obtained with control algorithm (markers). c): The $e$ nullcline points obtained with $\lambda = -0.1, L = 1, \alpha = -0.1, \beta = 0$. The $u_0$ parameter was varied between 15 and $-0.85$. d): The $u$ nullcline points obtained with adaptive control in variable $u$ using parameter $d$ and PD-control in variable $e$ using parameter $V$. $\lambda = -0.1, L = 1, \alpha = -0.15, \beta = -0.36$. The $e_0$ parameter was varied between 0.5 and 80. System parameters: $V_0 = 36.9778$, $R = 0.023$, $d_0 = 0.11913$

Figure 8. Simulations: Nullcline analysis of the 2D model and waveform prediction in the oscillatory region. Shown are the $e$ (thin curve with triangles) and the $u$ (thin curve with squares) nullclines, a numerically calculated oscillatory cycle (thick curve), and the nullcline model prediction (arrows). Markers are nullcline points obtained from control simulations.
IV. TOWARD POSSIBLE APPLICATIONS OF THE RESULTS

Electrochemical cells are widely applied and intensively studied examples of far-from-equilibrium dynamical systems. The parameters affecting the rate of electrochemical processes can be easily adjusted with high precision that allows the investigation of both the different nonlinear phenomena arising from the instabilities of the cells and also the physicochemical laws governing them.

The reported new results in the three studied topics have been achieved by a complex research strategy based on both experiments and model calculations, which, together with the novel methods applied for the interpretation of the results, may provide a well founded and useful starting point for similar strategies in areas beyond electrochemistry, for example, the interdisciplinary research on neuronal systems, muscle dynamics etc.

Our new results on delayed-feedback induced bi- and trirhythmicity may help in understanding the complex dynamics of weakly interacting biological systems with different times scales (e.g. the cardio-respiratory system); it is highly possible that the interaction of the units produces an internal delayed-feedback that can result in multirhythmicity similar to that found in our experiments. Deep understanding of such systems and their dynamics might help to control or even prevent life threatening situations.

Understanding the origin of multirhythmicity may also help in analyzing the dynamics of different adaptive biological systems, such as the self-tuned oscillator in the human auditory system.

In our experiment, we have demonstrated that by changing the rotation rate of the electrode we can control the rate of the diffusion from the bulk of the solution toward the surface of electrode resulting in controlled change in the period and waveform of current oscillations. Controlling diffusional transport may bring about similar effects in case of biological oscillators, which may give us a new „tool” for regulating biological processes.

Results of our numerical simulations indicate that the nullcline-based modeling approach can be successfully applied to recover the dynamical features of oscillatory, bistable or excitable systems without knowing the exact equations of motion. The importance of the nullcline-based method is underlined by the observation that the extension of the methodology to high dimensional systems is seemingly an important future goal for a number of top researchers of the field. This indirect, simple experimental method can provide important information on the dynamics of biological systems by reconstructing the trajectories of motion.

The importance and true value of the results of our basic research will be judged by the international community of researcher studying nonlinear dynamics or topics related to it.
V. SCIENTIFIC PUBLICATIONS

Published papers connected to the theses

T. Nagy, E. Verner, V. Gáspár, H. Kori, I. Z. Kiss
Delayed-Feedback Induced Multirhythmicity in the Oscillatory Electrodisolution of Copper
Chaos: An Interdisciplinary Journal of Nonlinear Science
2015
Impakt faktor: 1,954 (2014)

M. J. Hankins, T. Nagy, I. Z. Kiss
Methodology for Nullcline-based Model from Direct Experiments: Applications to Electrochemical Reaction Models
Computers and Mathematics with Applications
2013
Impakt faktor: 1,996 (2015)

M. Úrvölgyi, V. Gáspár, T. Nagy, I. Z. Kiss
Quantitative Dynamical Relationships for the Effect of Rotation Rate on Frequency and Waveform of Electrochemical Oscillations
Chemical Engineering Science
2012
Impakt faktor: 2,386 (2015)

I. Z. Kiss, T. Nagy, V. Gáspár
Dynamical Instabilities in Electrochemical Processes
Solid State Electrochemistry I: Electrodes, Interfaces and Ceramic Membranes, Ed. Vladislav V. Kharton, Wiley-VCH Verlag, Weinheim, Germany
Volume 2, 125-178. ISBN: 978-3-527-32638-9
2011
Presentations and posters connected to the theses

T. Nagy, E. Verner, V. Gáspár, H. Kori, I. Z. Kiss
Delayed-Feedback Induced Multirhythmicity in the Oscillatory Electrodecomposition of Copper
MTA Reaktiókinetikai és Fotokémiai Munkabizottsági Ülés, Siófok, Magyarország, 2014/05

M. Úrvölgyi, V. Gáspár, T. Nagy, I. Z. Kiss
Quantitative Dynamical Relationships for the Effect of Rotation Rate on Frequency and Waveform of Electrochemical Oscillations
4th European Science Foundation Conference on Functional Dynamics, Prága, Csehország, 2011/09 (Poster No. P21)

T. Nagy, V. Gáspár, H. Kori, I. Z. Kiss
Delayed-Feedback Induced Multirhythmicity in the Oscillatory Electrodecomposition of Copper
Oscillations and Dynamic Instabilities in Chemical Systems
Gordon Research Conference, Lucca (Barga), Olaszország, 2010/07 (off the record)
List of publications related to the dissertation

Foreign language international book chapter(s) (1)

   In: Solid State Electrochemistry II: Electrodes, Interfaces and Ceramic Membranes. Ed.:
   9783527326389

Foreign language scientific article(s) in International journal(s) (3)

2. Nagy, T., Verner, E., Gáspár, V., Kori, H., Kiss, I.Z.: Delayed feedback induced multirhythmicty in
   the oscillatory electrode dissolution of copper.
   Chaos. 29 (6), 064608-1-8, 2015. ISSN: 1054-1500.
   DOI: http://dx.doi.org/10.1063/1.4921694
   IF:1.954 (2014)

3. Hankins, M.J., Nagy, T., Kiss, I.Z.: Methodology for a nullcline-based model from direct
   experiments: Applications to electrochemical reaction models.
   DOI: http://dx.doi.org/10.1016/j.camwa.2012.11.016
   IF: 1.996
Dynamical Instabilities in Electrochemical Systems

DOI: http://dx.doi.org/10.1016/j.ces.2011.10.073
IF: 2.386

Total IF of journals (all publications): 6,336
Total IF of journals (publications related to the dissertation): 6,336

The Candidate's publication data submitted to the IDEa Tudósér have been validated by DEENK on the basis of Web of Science, Scopus and Journal Citation Report (Impact Factor) databases.

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