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High-resolution phase diagrams of a generic electrochemical oscillator

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Introduction

Among chemically reacting systems, electrochemical ones probably comprise the most paradigmatic class, with examples ranging from electrodissolution of metals to electrocatalytic oxidation of small organic molecules. Dynamic instabilities in the form, for instance, of oscillatory current or potential response, are very common in most electrochemical systems. In particular for the case of fuel cell relevant reactions such as the catalytic electro-oxidation of hydrogen and small organic molecules, oscillatory dynamics seems to be the rule rather than the exception. However, the vast majority of numerical studies in those systems is focused on the investigation of some calculated time series and covers relatively small parameter regions. We report in this work a detailed numerical investigation of a minimal model of a generic electrochemical oscillator. Specifically, we compute high-resolution phase diagrams for an experimentally relevant section of the control (parameter) space.

Model

The study was carried with a generic model for an electrochemical system previously proposed by Krischer.[1]. The model describes the dynamics of HN-NDR electrochemical oscillators, which posses an N-shaped current-potential characteristic with partially hidden negative differential resistance. The model consists of three ordinary differential equations accounting for the temporal evolution of the double layer potential (ϕ), the concentration of electroactive species (c) and the surface coverage of an inhibiting specie (θ). In its non-dimensional form it reads:

$$\varepsilon \frac{d\phi}{dt} = -ck(\phi)(1-\theta) + \frac{U-\phi}{\rho} \qquad (1)$$

$$\mu \frac{dc}{dt} = -ck(\phi)(1-\theta) + 1 - c \qquad (2)$$

$$\frac{d\theta}{dt} = \theta_0(\phi) - \theta \qquad (3)$$

U is the applied voltage; parameter ε represents the capacitive term and determines the time scale of potential changes; ρ is the total resistance; μ determines the time scale of changes in concentration. The rate constant and equilibrium coverage are defined by k and θ_0 respectively,

$$k(\varphi) = 0.00002\varphi^3 - 0.0094\varphi^2 + 1.12\varphi$$

$$\theta_o(\phi) = \left[1 + \exp\left(\frac{\phi - \phi_o}{b}\right)\right]^{-1}$$

with b = 7.1204 and ϕ_o = 124.6.

Results and Discussion

The system of equations (1)-(3) was extensively studied by conventional bifurcation analysis, and found to oscillate in a considerably wide parameter range. In order to allow the comparison with experimental data, parameters ρ and U are the most straightforward to be investigated. We calculate high-resolution phase diagrams in the ρ versus U plane for a given set of parameters. The results are presented in terms of the Lyapunov exponents, and color-codified according to the magnitude of the largest nonzero exponent: regions of negative exponent (periodic solution) are given in grey scale, and defined the so-called order region, in opposite to chaotic ones. The positive values (chaotic oscillation) are indicated in a yellow-red scale. The color red indicates regions of strong chaos characterized by positive Lyapunov exponents of larger magnitude.

Figure 1(a) shows typical results for a selected region in the ρ versus U plane. It becomes apparent in this figure the structuring and self-similarity of the order domain within the chaotic background. Generally speaking, the order regions can be described as shrimp-like objects spread over the chaotic region at different scales. This is a rather universal behavior which has been reported for quite different systems (see [2] and references therein). Figure 1(b) displays the numerically estimated period distribution in the same parameter region given in (a). Here the chaotic region was deliberately set to zero and coded in white, the periodic states are given in color. Overall, most of the shrimps displayed in this region have periods of about 8, but it is noteworthy the structuring in the period distribution inside the shrimps. In the example of the main shrimp showed, periods smaller and larger than 8 appear in specific direction, mainly in the border between order and chaotic domains.

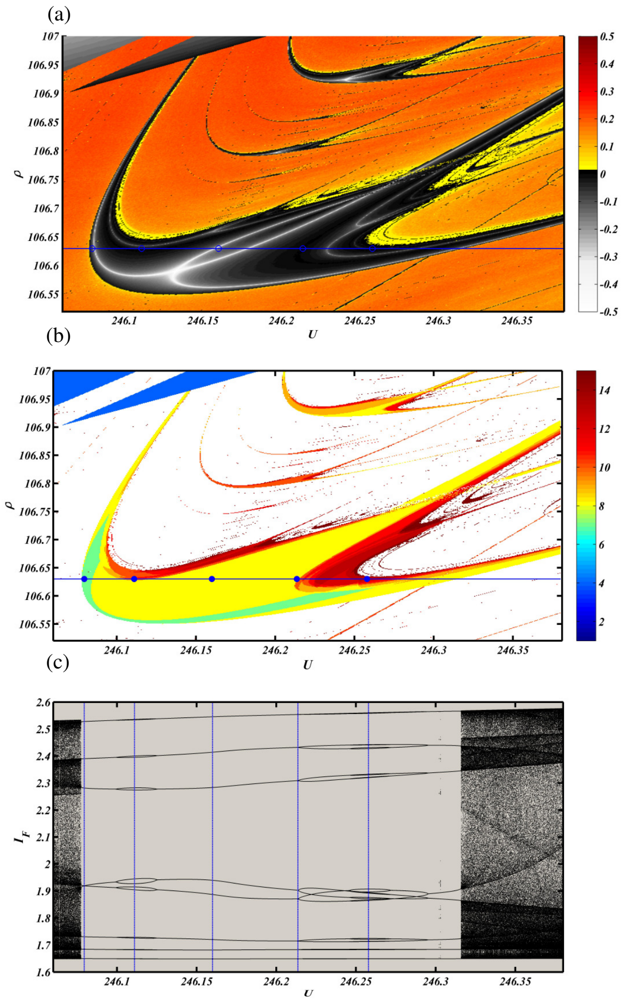

Figure 1: (a) High resolution Lyapunov diagram and (b) the corresponding diagram account for the period within the order region, in the plane ρ versus U. (c) conventional bifurcation diagram for the horizontal cut given in (a) and (b). $\varepsilon = 0.001$ and $\mu = 50$.

The conventional bifurcation diagram given in Figure 1(c), was obtained for different values of U along the horizontal cut in plates (a) and (b). The comparison between this diagram and the one given in (b) is straightforward. Moreover, it becomes rather clear the advantage of high-resolution phase diagram in the comprehensive description of the fine-structure in the two-parameter plane. Additional features of this analysis for the model presented will be published in due course [3].

Conclusion

We have described a numerical study of a generic model for an electrochemical oscillator. The analysis was carried out by means of an in-depth investigation of the high-resolution phase diagrams in a two-parameter plane. This is the first analysis of this kind for an electrochemical system, represented here by a minimal (3 ODE's) continuous-time autonomous model. Computation of Lyapunov exponents provided a detailed discrimination of chaotic and periodic domains and revealed the existence of intricate structuring of periodic domains embedded in a chaotic background. Shrimp-like periodic regions previously observed in other distinct systems were also clearly detected here, which corroborate the universal nature of the occurrence of such structures. In addition, we have also found a structured period distribution within the order region.

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