

Calculation of the Lyapunov Exponent and the Morphological Period in the Nickel Oscillatory Electrodissolution Time-Series

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Abstract

The electrochemical dissolution of nickel in acid medium was investigated under potentiostatic control by calculating the Lyapunov exponents with the aid of the Wolf's algorithm and comparing it with the morphologic periods. The model is described by three ordinary differential equations and was integrated by 4^o order Runge-Kutta numerical method. High-resolution Lyapunov diagrams were obtained by varying the parameters: external resistance and applied potential. Finger prints of the concept of universality, such as "shrimps", have been found in our simulations.

Key words:

Lyapunov Exponent, Nickel Electrodissolution, Chaos.

Introduction

Electrochemical systems present complex nonlinear behaviors such as stationary, quasi-periodic, periodic and chaotic according to applied parameters. Many examples of those dynamics are frequently observed in the electrochemical dissolution of non-noble metals in acidic media. The oscillatory anodic corrosion of nickel is one of the most important systems among them because of the robustness and rich variety of temporal patterns found in the "resistance vs. potential" domain. In fact, chaotic time-series has been modeled in this system and being mainly described by the coupling of reactive activation and surface passivation steps¹. Here, we focus our study in the proper characterization of the chaotic time-series by the use of the Lyapunov exponent and morphological period. The constructed bifurcation maps will allow the identification of the "shrimp" structures, leading to a direct comparison with the oscillation period².

Results and Discussion

The dimensionless model that describes the nonlinear electrochemical dissolution of nickel is composed by three differential equations³ with the independent variables: the electrode potential (v), the surface coverage of ($\theta - \eta$), and the surface coverage NiO (η). The system was controlled by a potentiostatic mode, varying the applied potential (v) and external resistance (r). Lyapunov exponents (λ) were calculated with the aid of the Wolf's algorithm. It basically represents if two nearby points of the time-series are moving away or converging in the phase space. In case of $\lambda > 0$, the time-series must present a chaotic behavior, otherwise, if $\lambda < 0$, the time-series is periodic. Figure 1 depicts a high-resolution diagram of 500x500 exponents numerically integrated by the 4^o order Runge-Kutta method with a step of 0.1. The total calculation, for each exponent, took 5×10^6 steps, discarding the first ones 4×10^6 as transient and using remaining to calculate the Lyapunov exponent. The colored scale tells about the magnitude of the largest Lyapunov exponent separated in two parts, that is, "yellow to red" represents the regions where the combinations of the parameters r and v induce a chaotic behavior and "black to white" represents those that have a periodic behavior. Interestingly, we found a peculiar profile, the so-called "shrimps", observed in many others nonlinear dynamic systems. Indeed, it has been used to verify the universality of chaos. The shrimps are made of islands of periodic oscillations surrounded by chaotic ones, where the white lines along them are expressed by very negative

exponents values. They usually appear in a fractal structuration - a non-Euclidean and invariant scale geometry. We have already calculated a period diagram of a phase space and currently, we are calculating to the same interval parameters of Figure 1. For that specific one, we found time-series with period-12, for the applied potential of 4.94592 and 4.95070, to external resistance of 4.16138 and 4.16670 respectively.

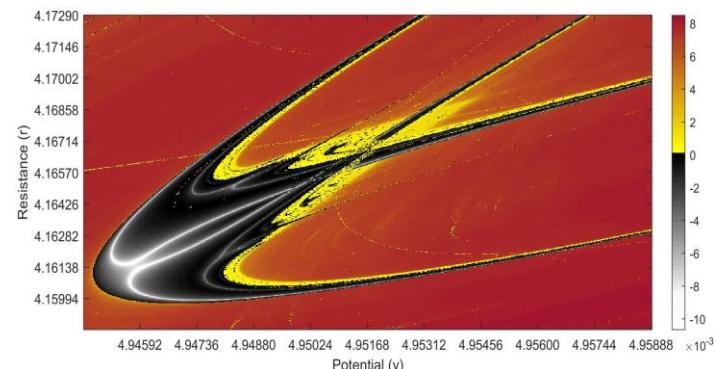


Figure 1. High-resolution Lyapunov diagram (500x500). Black to white scale denotes periodic regions with negative exponents and yellow to red scale denotes chaotic regions.

Conclusions

We have done a numerical study describing the nickel model through the calculation of the Lyapunov exponent and the morphological period. We reported shrimp-shaped structures that was found in this system corroborating with the universal nature of its appearance. We also intend to control the structuration by feedback techniques⁴ in order to understand how it will behave to the effect of potential feedback. We expected to obtain a diagram with high resolution and a better understanding of the potential and resistance relationships with the periodic islands within chaotic regions.

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