Low Density and Elongation of Self-similar Periodic Islands in the Oscillatory Electrodissolution of Nickel

Baixa Densidade e Elongação de Ilhas Periódicas Auto Similares na Eletro-Dissolução Oscilatória de Níquel

Caio da S. Rodrigues,[a] Caio G. P. dos Santos,[a] Renan C. C. de Miranda,[a] Eduardo Parma,[a] Hamilton Varela[b] and Raphael Nagao[a,*]

[a] Institute of Chemistry, University of Campinas, 13083-970 Campinas, SP, Brazil
[b] Institute of Chemistry of São Carlos, University of São Paulo, 13560-970 São Carlos, SP, Brazil

Key words: nickel anodic dissolution, lyapunov exponent, isospike.

This work has been recently published: Rodrigues, C. S. et al. Phys. Chem. Chem. Phys., 2020, 22, 21823 - 21834. DOI: 10.1039/D0CP04238B

The oscillatory electrodissolution of nickel is one among several reactions utilized as a model-system to study the emergence of oscillations and pattern formation in electrochemical interfaces. In 1992, Haim and co-workers[1] modeled that system and since then many scientific studies have emerged based on this model. Besides, it is the first study to describe a well-detailed numerical investigation of the effect of control parameters on the complex dynamics of nickel dissolution.

The numerical integration was carried out by the 4th order Runge–Kutta method with a fixed time step of h = 0.1 and initial conditions of e = 2.0 (electrode potential), θ = 1.0 (coverage of NiOH + NiO) and η = 0.1 (coverage of NiO). We wrote the algorithm in C programming language that was parallelized to increase the calculation performance. The first four million integration steps were considered as transient and hence they were discarded. One million additional integration steps were taken, and from these time series, Lyapunov exponents and local minima (potential time series) were recorded. The parameters utilized were C_h = 1600, Γ_1 = 0.01, Γ_2 = 2, a = 0.3, b = $6x10^5$ and c = 10^3.

In our study, we provide a well-detailed and rigorous analysis of the effect of the external resistance and applied potential by simulating high-resolution phase diagrams based on the calculation of Lyapunov exponents based on Wolf's algorithm[2] and isospike diagrams. We could identify a strong dependence of the self-similar periodic islands, (structures called shrimps constituted by periodic islands within chaotic domains in the parameter space), with the control parameters resistance and potential, as showed in Figure 1. The shrimp-like structures become gradually elongated with an increase in control parameters.

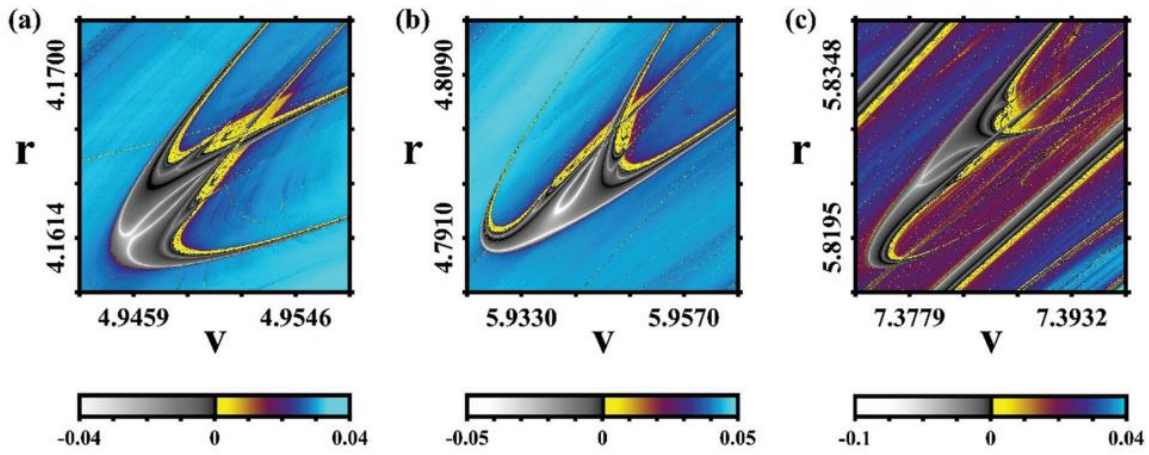

Figure 1: Lyapunov diagram in the (r, v) control space indicating chaotic and periodic regions of the panels (h)–(j) from Fig. 3 of reference 2. Chaos is marked by yellow-cyan scale and periodicity is denoted by white-black one.[3]

In addition, we have noticed a low density of periodic structures in the phase diagrams, as showed in Figure 2, in such a way that, ones were completely suppressed according to increase of resistance and potential values. Interestingly, period-doubling cascades were observed not only on the shrimps but also on the periodic bands.

It was also identified a problem with the model. As can be seen in Figure 3 b-e, the model displayed negative values for coverage of NiOH + NiO (θ) and it is related to the mass conservation utilized in the modelling procedure. It is well-known that coverage must lie in the interval of [0 1]. Currently, we are working and running some simulations in order to overcome this issue. Figure 3a shows a bifurcation diagram calculated at r = 4.1614 in the same interval of potential of Figure 2h. Figure 3a displays regions of periodicity alternated between chaos and two domains of periodicity attributed to the ‘‘body’’ and the ‘‘leg’’ of the shrimp. Each time-series (Figure 3b-e) is followed by its respective attractor in the e,θ-plane.[3]

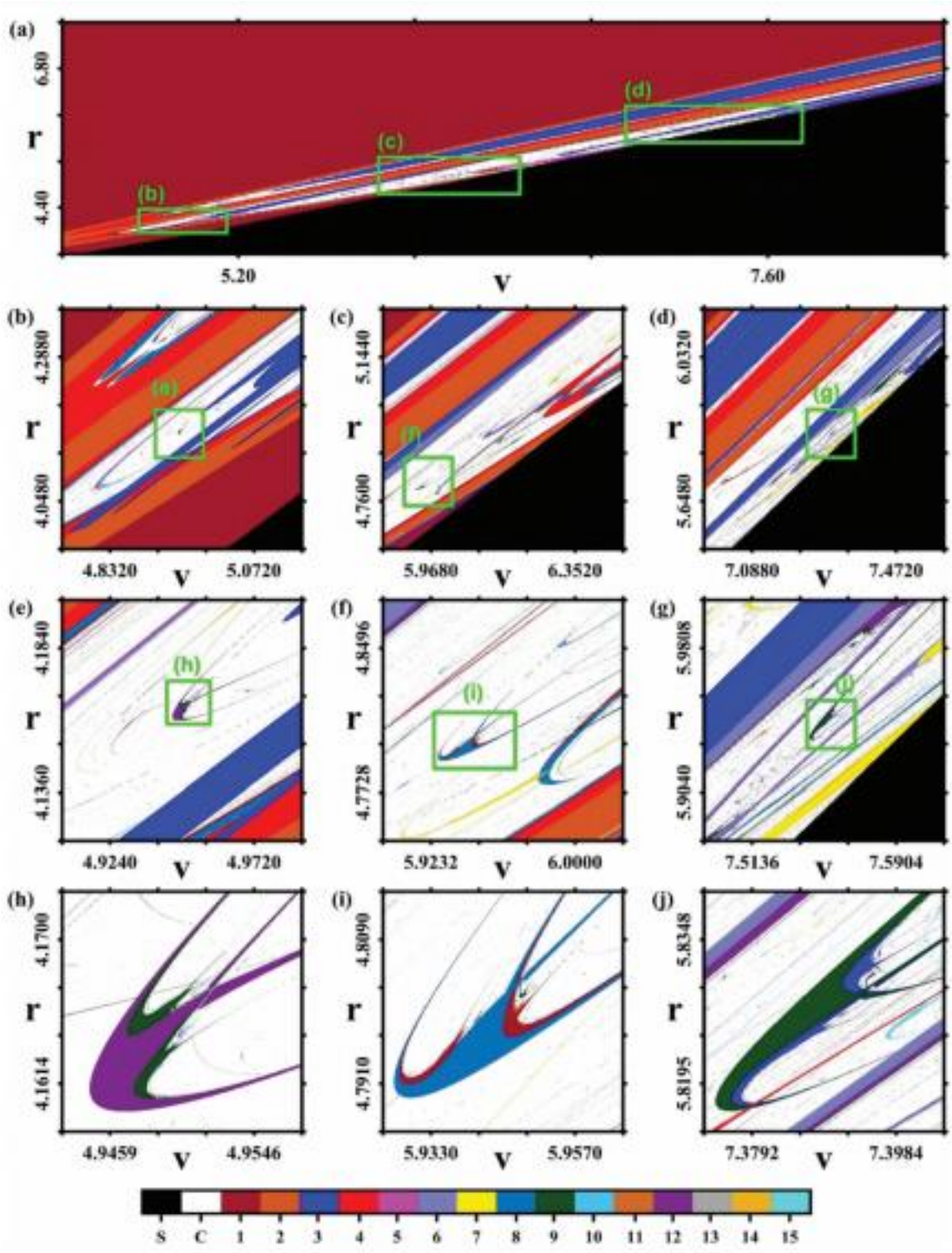

Figure 2: Isospike diagrams indicating the number of spikes per oscillation period. 15 different colours are attributed for a specific number of spikes and those which contain more than 15 spikes are plotted recycling the basic colours. Panel (a) is partial view from phase diagram and includes three domains (b)–(d) that are zoomed in (green box) to (e)–(g) and again to (h)–(j), respectively. In the periodogram colour bar, chaos (C) is shown as white and steady state (S) as black.[3]

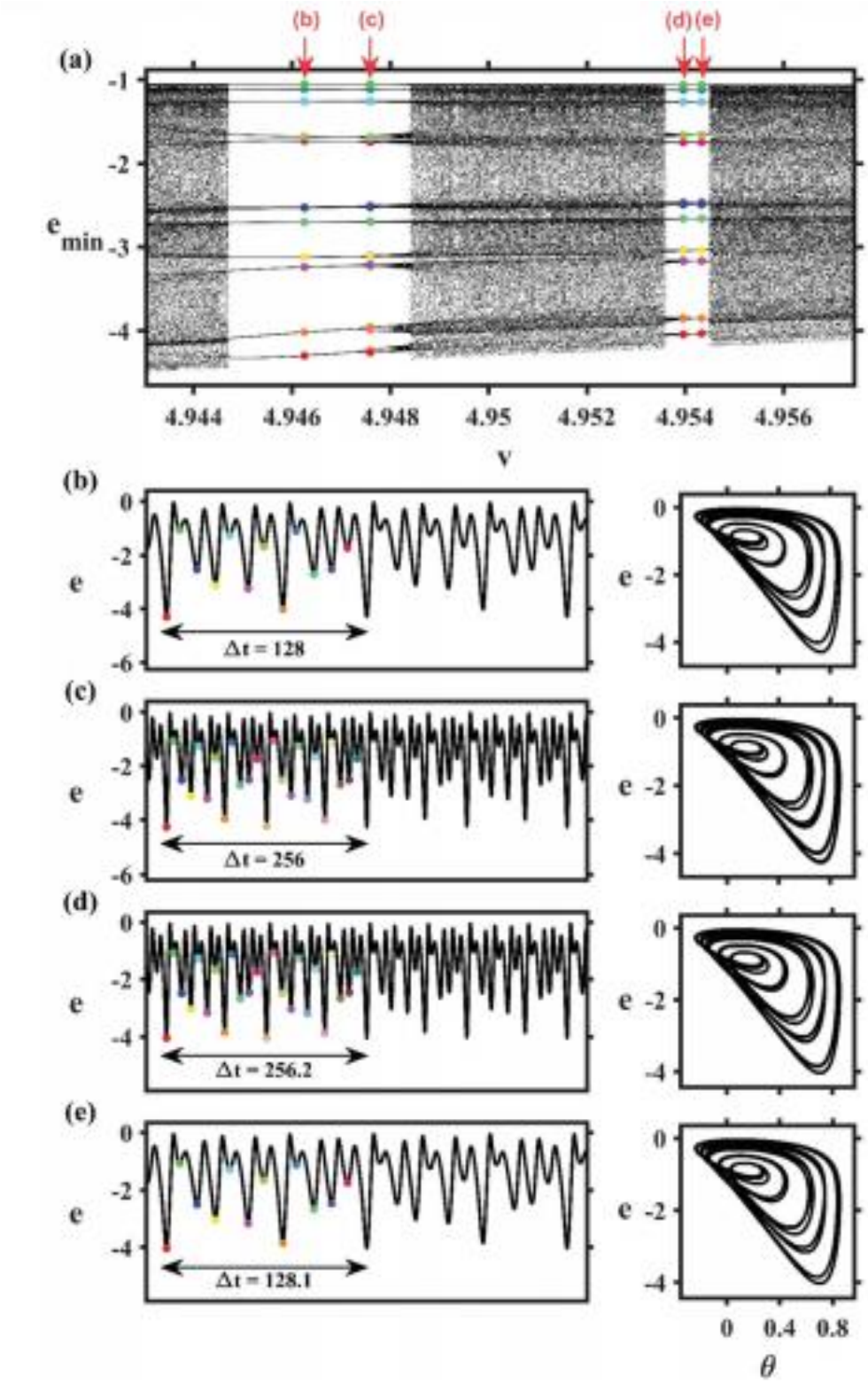

Figure 3: Bifurcation diagram calculated by recording the local minima related to the shrimp displayed in Fig. 2h at r = 4.1614. The panels (b) to (e) show different time-series and the respective limit cycle (e, y) corresponding to four values of potential (4.9462, 4.9476, 4.9540 and 4.9543). The coloured circles in the bifurcation diagram indicate the monitored minima also represented in the time-series.[3]

Acknowledgements:

C. S. R. (19/03273-4), E. P. (19/22202-0), H. V. (13/16930-7) and R. N. (16/01817-9) acknowledge support from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP); C. G. P. S. and R. C. C. M. acknowledge Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001; H. V. (306060/2017-5) and R. N. (405235/2018-6) acknowledge Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). The authors express their gratitude to the Centro Nacional de Processamento de Alto Desempenho (CENAPAD) located at Campinas for high-performance calculations and Dr Melke A. Nascimento for important suggestions to plot the Lyapunov exponents.

References:

[1] D. Haim, O. Lev, L. M. Pismen and M. Sheintuch. *J. Phys. Chem*. 1992, 96, 2676.
[2] A. Wolf, J. B. Swift, H. L. Swinney and J. A. Vastano. Determining Lyapunov exponents from a time series. *Physica D: Nonlinear Phenomena*. 1985, 16(3), 285-317.
[3] C. da Silva Rodrigues, C. G. P. dos Santos, R. C. C. de Miranda, E. Parma, H. Varela and R. Nagao. *Physical Chemistry Chemical Physics*. 2020, 22, 21823 – 21834. DOI: 10.1039/D0CP04238B.

*correspondent author e-mail: nagao@unicamp.br