

NON-EQUILIBRIUM ELECTROCHEMICAL PHENOMENA*

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Abstract – Research over more than 150 years has made clear that many electrochemical systems exhibit highly exotic behaviour. In the past few decades detailed dynamic studies of these interesting results often reveal oscillations, which vary from periodic to quasi-periodic to chaotic.

The application of *linear* theory of the irreversible thermodynamics to a variety of electrochemical problems demonstrates its utility, but the time evolution of certain phenomena must be modeled by *non-linear* equations to characterize their dynamic behaviour. The new ideas and solution methods in *non-equilibrium* phenomena, that are revolutionizing *dynamic systems theory*, provide the framework for understanding the nature of electrochemical dynamics. The extremely complex structures generated by certain systems, are analyzed in terms of *fractals*, one of the most rewarding scientific developments of recent years. The concept of fractal, their dimensions and the relations between fractal character of the phenomena and the dynamics of the processes are object of today's fundamental research.

In this work a quick overview is presented of some recent developments related to electrochemical dynamical systems. Attention is focused predominantly on the typical *tools* that are useful in the study of these systems. A summary of some oscillatory phenomena from different areas of electrochemistry is presented. Emphasis will be placed on those aspects that may prove beneficial for electrochemists.

INTRODUCTION

Electrochemical systems are known to show a variety of irregular steady-state and dynamic features. There is a great assortment of processes which can exhibit an exotic behaviour, such as oscillatory phenomena. Periodic electrode processes dates back to nineteenth century and induced transition to chaos have been reported already 30 years ago, long before similar phenomena have been recognized in non electrochemical systems.

Systematic both theoretical and experimental analysis of these electrochemical phenomena have aroused great interest. That study is carried out by means of the *dynamic systems theory*, which leads to find a number of regularities, using new concepts, such as dissipative structure or strange attractor. Some contradictory ideas can be reconciled if a *fractal geometry* is adopted.

In the last time many papers on these topics have appeared, frequently directed to specialist. A few popular publications give some information, but do not allow the non-specialist get an actual information of the matter in hand. The aim of this work is to point out as the theoretical speculation suggests an exciting experimental

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research in both fundamental and application fields of electrochemistry. They are illustrated using appropriate examples from recent literature on the subject. In the first section of this paper there is given a short exposure of irreversible thermodynamics concepts, and the second briefly presents, in the simplest possible way, the main ideas of *non-linear dynamics* and the concepts of *fractal geometry*. The last two sections give, respectively, an account of some recent developments on electrode oscillatory behaviour and fractal properties of a variety of electrochemical phenomena.

EVOLUTION CRITERIA

Equilibrium situations have been studied successfully by classical thermodynamics. However, systems where there is transport of energy and matter across the borders are very familiar. These open systems show frequently non-equilibrium behaviour, which study is the objective of the irreversible thermodynamics. The theory of irreversible thermodynamics is suitable for the study of processes in electrolyte systems, and the transfer of electric charge processes are better understood by application of this theory.

As it is well known, the second law of thermodynamics can be expressed formally in terms of change of *entropy*, S , in a system. In an *isolated* system the sum of all entropy changes is

$$dS \geq 0 \quad (1)$$

where the equality holds only for reversible processes. Then, an irreversible process yields an increase in the total entropy, and this entropy *production* leads to a dissipation of energy. The entropy of an isolated system increases until it reaches its maximum at equilibrium.

If the system can exchange energy with the environment, it is known as a *closed* system, and its behaviour is described by some state function, A or G , which values at equilibrium are minimum with respect any change of state.

The formulation of second law can be easily extended to *open* systems, in which energy as well as matter may be exchanged with surroundings. In this case, the change of entropy is composed of two terms

$$dS = d_i S + d_e S \quad (2)$$

where $d_e S$ is the transfer of entropy across the boundaries and $d_i S$ is the change of entropy corresponding to the processes occurring inside the system itself (see Fig. 1). For this later *entropy production*, the second law states that

$$d_i S \geq 0 \quad (3)$$

for any process.

If P is the rate of entropy production, it can be expressed in the form

$$P = \frac{d_i S}{dt} = \sum_k J_k X_k \geq 0 \quad (4)$$

where J_k is the flow associated with the irreversible k^{th} process and X_k the generalized force giving rise to this flow.

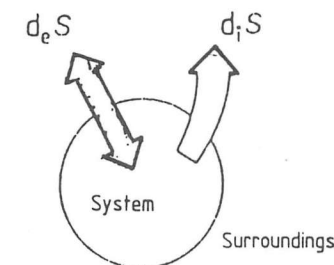


FIG. 1. Schematic representation of the entropy changes occurring in an open systems.

Linear behaviour. In a process at equilibrium, generalized forces vanish and there are no flows. These become

$$(J_k)_{eq} = 0 \quad \text{and} \quad (X_k)_{eq} = 0 \quad (5)$$

But close to equilibrium, forces are relatively weak, and the flows can be expanded in power series, from which, after neglecting the non significant terms, it is obtained the *linear* relation between fluxes and forces

$$J_k = \sum_l L_{kl} X_l \quad (6)$$

where L_{kl} is a coefficient, given by

$$L_{kl} = \left(\frac{dJ_k}{dX_l} \right) \quad (7)$$

These two last equations define the behaviour of a great number of irreversible phenomena which can be studied under this linear approximation. According Onsager's *reciprocity relation*, $L_{kl} = L_{lk}$, which establish connections between independent irreversible processes. Consequently, entropy production is both thermodynamic and kinetic quantity through thermodynamic forces and flows, respectively.

Thermodynamic analysis of steady state in linear range, under close to equilibrium conditions, shows that the system is directed towards a state of *minimum entropy*

production, P . The theorem of minimum entropy production, due to Prigogine, can be expressed in the form

$$\frac{dP}{dt} \leq 0 \quad (8)$$

where inequality and equality hold, respectively, for away from and at the steady state. During the evolution of the system from its initial state, the entropy production decreases and reaches a minimum at its stationary state. This is valid only if the phenomenological coefficients are supposed to be constant.

Non-linear behaviour. Certain phenomena cannot be described by linear thermodynamics because their non-linear development. Far from equilibrium, the steady state of the system is not stable, and the system goes over to a new steady state which may well have a different energy production. In this situation, as a consequence of instabilities, ordered structures in the system are formed. Under this conditions, equation (6) is not valid and equation (8) needs not be satisfied.

Prigogine proposed a new stability criterion. In the non-linear region, it is possible to arrive at

$$\frac{1}{2} \frac{\partial}{\partial t} (\delta^2 S) = \sum_k \delta J_k \delta X_k \quad (9)$$

where δJ_k and δX_k are, respectively, the deviations of J_k and X_k from the steady state. The right hand of this equation, which represents the *excess entropy production*, depends on the form of fluxes and forces. Near equilibrium $\partial P \geq 0$, as a consequence of the second law, but far from equilibrium the time derivative $\frac{1}{2}(\delta^2 S)$ needs to be positive. The non-equilibrium steady state becomes unstable as soon as $\delta^2 S$ becomes negative. It is remarkable that equation (9) is a sufficient and not a necessary criterion for the stability of a thermodynamic state.

As a result, both the distance from equilibrium and the non-linearity may be capable to driving the system to an ordered configuration. This is called *dissipative structure*, in contrast with the equilibrium *conservative structures*. Fig. 2 illustrates the two types of dynamical structures, showing area preservation or contractation to a single point in the phase space diagram.

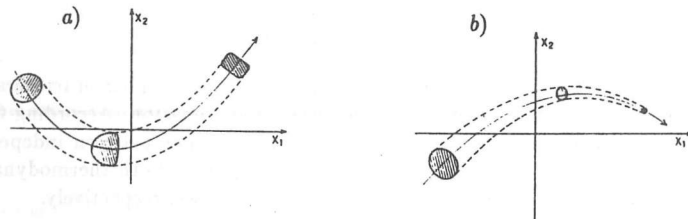


FIG. 2. Phase space diagrams of a) conservative and b) dissipative dynamic system.

DYNAMICS, CHAOS AND FRACTALS

The thermodynamic considerations in the previous section were independent of process mechanism and their dynamic behaviour. If *dynamics* is the study of change, a *dynamical system* must be a system whose state at any time can be characterized by a set of variables. If the dynamic law of a system is linear, its behaviour must be very simple. However, representative phenomena are not adequately described by linear dynamics.

Non-linear dynamics. The most familiar physical systems are governed by a complicated non-linear function of the state variables, and its temporal evolution will generally depend on the start conditions. The *non-linear dynamics* give powerful tools to a coarse description of the systems and to reveal the high complexity that their evolution can give rise.

To illustrate these ideas, consider a system embedded in a medium with which it exchanges some properties, X_i ; the time dependence of these properties can be expressed in the form

$$\frac{dX_i}{dt} = F_i(X_1, \dots, X_n; \lambda_1, \dots, \lambda_m) \quad (10)$$

where F represents the dynamic law. The evolution of the system is represented in a space by the state variables, which is called *phase space*, and this representation trace out the *trajectory* of the system. If initially far from equilibrium, variable X_i tends to it, in which the property attains $(X_i)_{eq}$ value.

In the vicinity of equilibrium, property deviation from its equilibrium value can be written

$$x_i = X_i - (X_i)_{eq} \quad (11)$$

which evolution is given by

$$\frac{dx_i}{dt} = - \sum_j \Gamma_{ij} \left(\frac{\partial \Phi}{\partial x_j} \right) \quad (12)$$

where Φ is a thermodynamic potential taking its minimum value at equilibrium and Γ_{ij} a symmetric matrix.

In a dissipative dynamic system, the phase space trajectory tends with time to a restricted region, as illustrated in Fig. 2. Such region is known as *attractor*, because a finite set of initial coordinates converge to it. The set of all initial conditions of trajectories that converge on a specific attractor defines a *catchment region* called *basin of attraction*. Fig. 3 represents schematically an attractor and its basin of attraction. Different types of attractors commonly observed in dissipative systems are shown in Fig. 4.

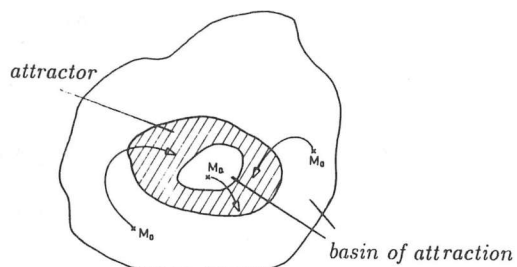


FIG. 3. Schematic representation of an attractor and its basin of attraction.

Special interest is found in *chaotic* attractors. In this case, the trajectory exhibits most of the features that one would associate with random functions, producing sensitive dependence on initial conditions and long-term unpredictability. To attempt to know where do trajectory points go and what do they do when they get there, mathematicians have developed techniques for obtaining information from experimental data to dilucidate the situation.

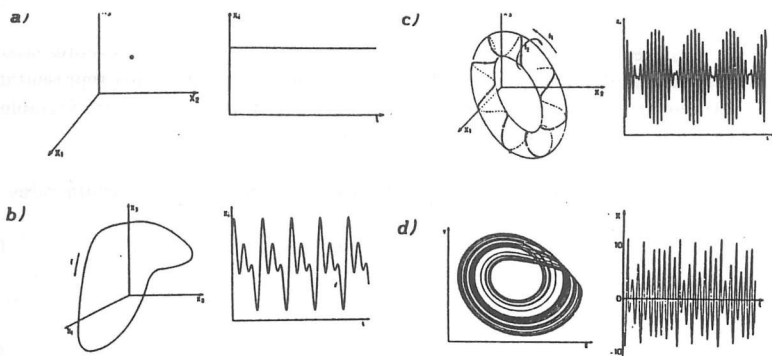


FIG. 4. Types of attractors: a) point attractor representative of a steady state, b) limit cycle attractor representative of a periodic regime, c) torus attractor representative of a quasi-periodic regime, and d) strange attractor representative of a chaotic regime.

The complexity of phase portrait in three or more dimensions can be reduced by a *mapping* of one or two dimensions, according Poincaré. A Poincaré section consists in a sequence of dots corresponding to the projection of the attractor trajectory at specific times. In this way, Poincaré mapping acts in a space of smaller dimensions than that of the phase space. As shown in Fig. 5, analysis of time oscillations leads to two-dimensional phase projection of trajectories onto the phase plane and the corresponding Poincaré section.

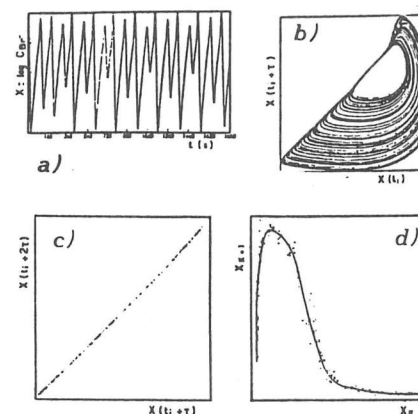


FIG. 5. Analysis of a chaotic system.

Routes to chaos. Sometimes, when an oscillating process is run, the observed oscillations are aperiodic. Amplitudes and periods of oscillations appear random. In general, a dynamic system can have more than an attractor, that is, different initial conditions can lead to different long time behaviours.

Transit from a stable to a chaotic regime is easily seen with the graphics of Fig. 6. These are based on the *difference* equation

$$X_{n+1} = a X_n(1 - X_n) \tag{13}$$

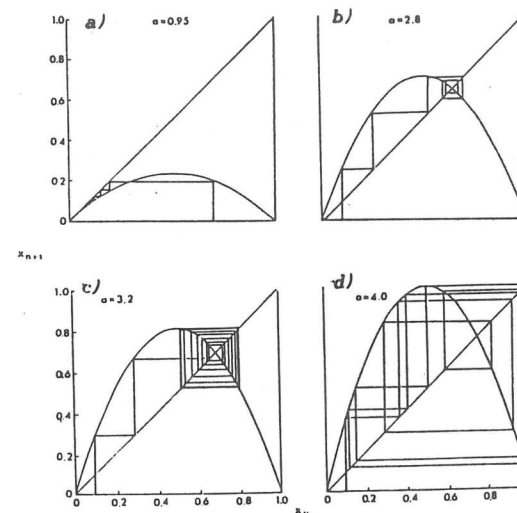


FIG. 6. Logistic maps for different values of parameter *a*, giving: a) zero, b) limit cycle, c) period doubling and d) no stable solution: strange attractor.

which generate the future value X_{n+1} of a variable X from its value X_n at the prior step n^{th} . The *logistic maps* show the curve of equation (13), the bisectrix line $X_{n+1} = X_n$ and a set of lines connecting successive iterations. Starting with some initial value, X_0 , the first point, X_1 is found where the line X_0 meets the curve; the next step is obtained moving to the bisectrix, from which X_2 can be found by going vertically to the curve. Depending on parameter a the different maps of the figure are obtained, with different solutions; for the highest a no stable solution is attained.

The mechanisms at origin of these different attractors is an *instability* and subsequent *bifurcation*. A bifurcations means the restructuring of a system, that occurs when the control parameter passes through a critical value, at which the unique solution branch loses its stability and new stable branches of solutions are generated. Fig. 7 represents a schematic bifurcation diagram.

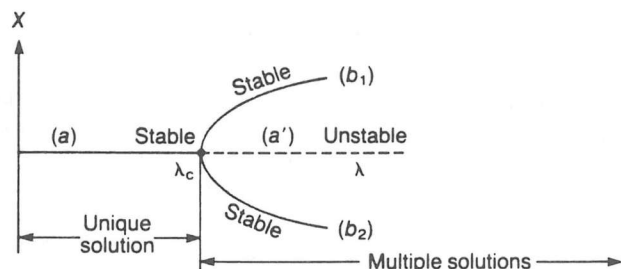


FIG. 7. Bifurcation diagram showing how the thermodynamic branch becomes unstable beyond a certain value of control parameter.

The bifurcated system oscillates between values, but on further increasing control parameter, a *cascade* of bifurcations occurs in the logistic map to result in a chaotic evolution.

Detailed analysis of the complex forms of strange attractors suggests their *fractal* nature. Order and chaos are usually regarded as antithetical concepts. But in nature chaos and structures showing a high degree of spatiotemporal order coexist. Indeed, chaotic and ordered structures arise from the same sort of non-linear laws and are often inseparable. The degree of order in chaos is generally expressed in terms of a fractal dimension.

Fractal patterns. Many familiar electrochemical phenomena are developed by non-equilibrium dynamics, through very complex processes, yielding patterns difficult to understand, and showing a fully random organization. The new concept of *fractal*, introduced by Mandelbrot, has contributed to obtain a detailed information on the properties and behaviour of such systems. In the last years, it has been appeared a large production of research literature on the topic.

The term fractal is applied to complex patterns, objects, curves, functions or sets,

to indicate both their infinitely broken structure and that they are characterized by a non-integer dimensionality. Dimension can be defined intuitively as a scaling of bulk with size. In geometrical terms, it is the exponent scaling an object's bulk with its size

$$bulk \propto size^{dimension} \quad (14)$$

where the *bulk* may correspond to a volume, a mass or a measure of information content and *size* is a linear distance. The relation

$$dimension = \lim_{size \rightarrow 0} \frac{\ln bulk}{\ln size} \quad (15)$$

gives the dimension.

The measure of any pattern is a function of the measuring unit size. For instance, the apparent length, L , of an irregular profile increases as the size of measuring unit, λ , decreases according to power law

$$L(\lambda) \propto \lambda^m \quad (16)$$

If $N(\lambda)$ is the number of line segments of length λ needed to cover the profile, the length is $L = N(\lambda) \lambda$, which becomes asymptotically equal L in the limit $\lambda \rightarrow 0$, independently of the measuring unit size. The profile fractal dimension, D , is given by the relation $D = 1 + |m|$. This procedure is known as *structured walk* method. A typical application is shown in Fig. 8 for a coastline.

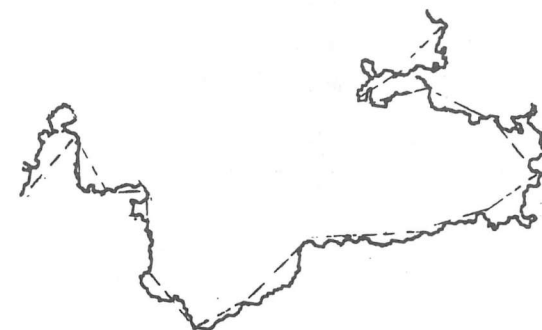


FIG. 8. Structured walk method for evaluating the fractal dimension of a rugged boundary.

In practice, fractal dimension can be determined counting the number of squares ("boxes") with edge length λ , needed to cover the profile as a function of λ . This method is called *box counting*, and it applies the scaling law

$$N(\lambda) \propto \lambda^{-D} \quad (17)$$

from which

$$D = \lim_{\lambda \rightarrow 0} \frac{\ln N(\lambda)}{\ln(1/\lambda)} \quad (18)$$

The dimension is computed graphically from log-log plots.

Frequently, the formation of a fractal object follows a deterministic rule. This is done in the forms of Fig 9 (a and b) and in many fractal structures developed by the mathematicians; the fractals of this kind are called *deterministic*. If the fractal object do not change by enlargement or reduction by an arbitrary factor, it shows *self-similarity*. This property is applicable only inside a range limited by the object size and its dimension. Many nature occurring fractals do not follow a deterministic rule, and are known as *stochastic* fractals (c). Under this conditions, the scalling takes a statistic meaning. To generalize the fractal concept to non-self-similar objects, it is introduced the concept of *self-affinity*, which is applied to structures showing self-similarity in a given space direction (d). Finally, the pattern (e) consists in a *multifractal* object, characterized by a large number of independent fractal dimensions.

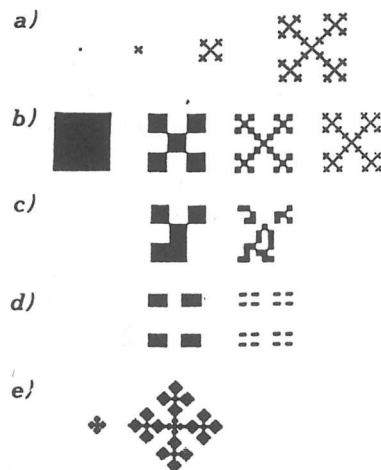


FIG. 9. Construction of fractals embedded into two dimensions: a) growing and b) by subsequent division to generate deterministic fractals, c) stochastic and d) self-affine fractals and e) multifractal objects.

It is today well accepted that the fractal dimension may be inappropriate for characterizing detailed structure of real patterns. For these multifractal structures the concept of *generalized* fractal dimension was introduced. The generalized fractal dimension is given by

$$D_q = \lim_{\lambda \rightarrow 0} \frac{1}{q-1} \frac{\ln \chi(q)}{\ln \lambda} \quad (19)$$

where

$$\chi(q) = \sum_{i=1}^{N(\lambda)} P_i(\lambda)^q \quad (20)$$

and P_i is the relative portion of the profile contained in the i^{th} cell, for $q = 0, 1, 2$, etc. Values of D_q increase slightly with q .

ELECTROCHEMICAL OSCILLATIONS

Open electrochemical systems advance to a definite steady state showing a variety of temporal behaviours. A large number of examples exhibits spontaneous oscillations. However, many of these observations, which now seems to be well recognized, have been regarded as curiosities or forgotten completely. New instrumental facilities and fiability of data obtained have favored dynamical analysis of oscillations. In this way, considerable material on periodical electrochemical phenomena recently has been collected and theoretically studied. Here there are only indicated some systems whose electrochemical oscillations have been observed and for which processes possible mechanisms have been proposed.

Many anodic processes exhibit oscillating behaviour. Observations of oscillations, often irregular, have been done in electrodisolution of metals. They have also been observed during electrocatalytic reactions as well as reduction processes. Most of these oscillations have been detected at electrodes on which anodic or cathodic surface layers can be formed. Typical electrochemical examples of oscillatory behaviour are presented in Fig. 10.

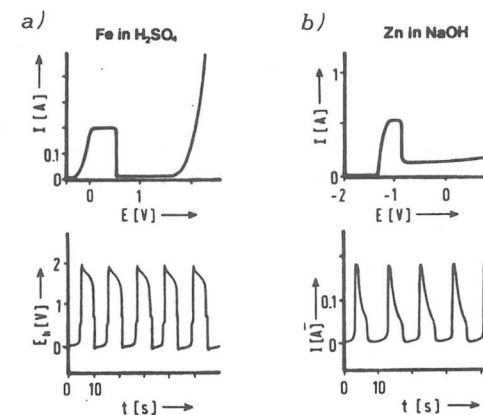


FIG. 10. Examples of electrochemical oscillations: a) galvanostatic potential and b) potentiostatic current oscillations.

Types of oscillating electrode processes. Electrochemical oscillations have been reported in connection with *anodic dissolution of metals*, such as iron, nickel and copper in acid media. Some experiments were done at potentiostatic conditions. The current is a function of the applied potential; at low potentials the current is steady, whereas for intermediate potentials it is oscillating, and by above certain potential values the electrode is passive. A summary for iron behaviour is given in Fig. 11 (Diem and Hudson, 1987). Comparison of potentiostatic and galvanostatic modes of operation is very useful for the study of bifurcations, as it was shown for nickel (Lev,

Wolffber, Stheintuch and Pismen, 1988). Copper has been investigated in phosphoric and chloride media (Albahadily and Schell, 1988; Bassett and Hudson, 1989). Effect of stirring condition has been recently reported for anodic behaviour of iron (D'Alba and Di Lorenzo, 1989).

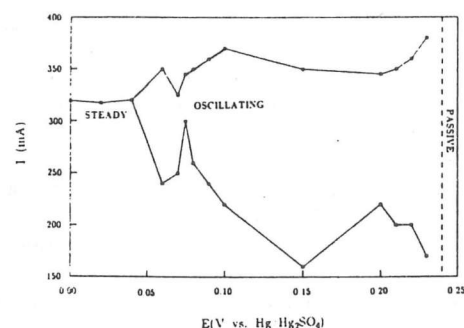


FIG. 11. Potentiostatic behaviour of iron: Upper and lower curves are maxima and minima, respectively, of the oscillations.

Oscillations have also been observed during *anodic oxidation of non-metallic species*, such as hydrogen or organic compounds. Non-steady behaviour of hydrogen electrooxidation has been known for sometime. Recently, kinetic equations describing potential oscillations due to coupling of hydrogen anodic oxidation with silver deposition/dissolution have been developed (Kodera, Yamazaki, Masuda and Ohnishi, 1988). Experimental results of periodic phenomena that accompany the anodic oxidation of formaldehyde (Xu and Schell, 1990) and of a mixture of formate and formic acid under galvanostatic conditions have been reported (Schell, Albahaduly, Safar and Xu, 1989).

Although most cases of electrochemical fluctuations were observed in anodic processes, several examples of *cathodic oscillatory reactions* have been reported. Recent works correspond to phenomena observed in galvanostatic reduction of hydrogen peroxide on platinum electrode in acid medium and during its reduction at chalcopyrite cathodes. In the last case, the reduction cause a remarkable corrosion of the electrode surface (Fetner and Hudson, 1990; Cattarin and Tributsch, 1990).

Cathodic electrodeposition of metals showed non-linear oscillations. It has been lately reported for zinc ion reduction at different electrolyte concentration and applied potential (Suter and Wong, 1989), see Fig. 12, or fixed current (Argoul and Arneodo, 1990). Since the interface is moving the oscillating signal displays a slow drift, which can be removed by Fourier filtering.

Models of oscillations. Models to explain the nature of the oscillatory electrochemical response were proposed some time ago. The availability of the techniques

in non-linear dynamics may result in a more complete analysis of the data in terms of phase portraits.

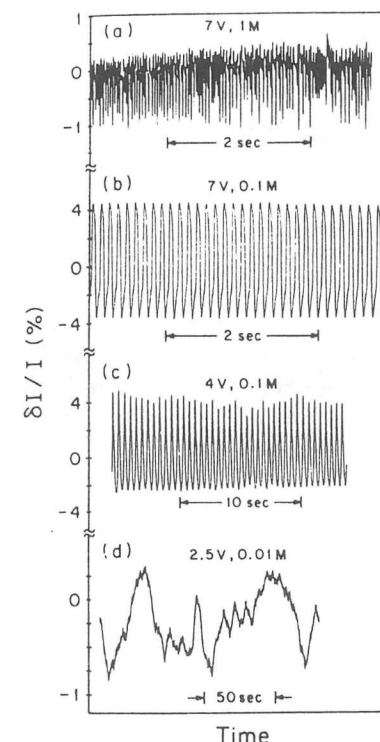


FIG. 12. Current oscillations observed at various concentrations and voltages in electrochemical growth of zinc dendrites.

Systems generating a stable *limit cycle*, corresponding to passivation of metals or hydrogen peroxide reduction have been reported. In this last case, on chalcopyrite cathodes, kinetic treatment developed in the phase space gives a limit cycle trajectory independent on the initial conditions (Cattarin and Tributsch, 1990). However, on platinum electrodes the complexity of oscillations shows that low-order *chaos* can be found for some parameters values (Fetner and Hudson, 1990).

During anodic dissolution of iron chaotic current oscillations were observed (Diem and Hudson, 1987). Copper electrodisolution, see Fig. 13, exhibits evidence for the sequence one-band chaos, two-band chaos, double torus, torus, limit cycles and steady state, where the thickness of a surface film acts as a slowly varying parameter (Bassett and Hudson, 1989). Complex behaviour of nickel anode dissolution has been recently

modelled as a chaotic dynamics (Lev *et al.*, Wolffber, Piesmen and Stehntuch, 1989). Fig. 14 shows the richness of compartments, which suggests a highly complex kinetic model for the electrochemical reaction.

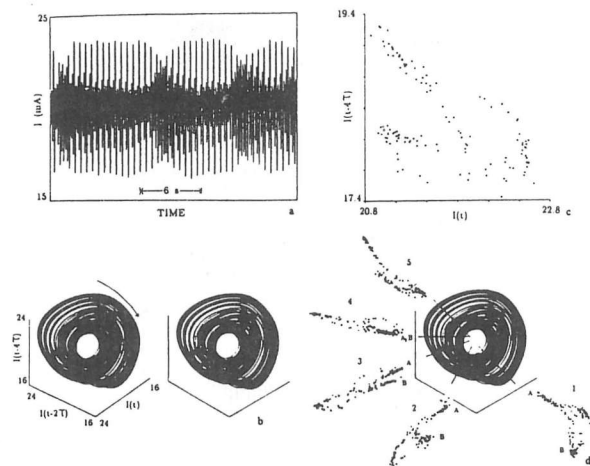


FIG. 13. Chaos on a broken toroidal structure: a) time series, b) attractor, c) Poincaré section and d) series of Poincaré sections, from copper dissolution experiments.

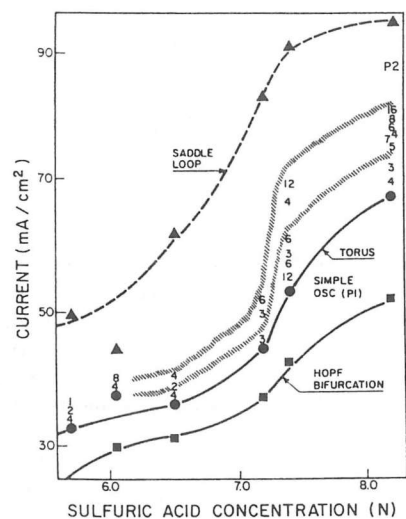


FIG. 14. Structure of the complex domain of nickel electrodisolution.

Electrochemical deposition has been found to produce a complex patterns, which growth process is different from other non-equilibrium spatio-temporal phenomena. Linear oscillations observed in electrochemical growth of zinc deposits have been reported (Sutter and Wong, 1989). The complexity of the patterns geometry is intricately connected with the dynamical evolution. The morphology is precursor to a chaotic dynamics, which Poincaré section demonstrates the low dimensional nature of this chaotic state (Argoul and Arneodo, 1990). Non-periodic oscillations observed for this system and the corresponding analysis are presented in Fig. 15.

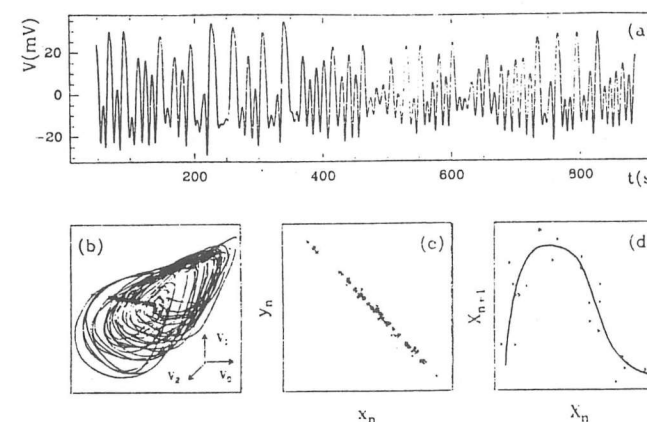


FIG. 15. Chaotic regime from potential measurements in electrochemical deposition of zinc: a) potential vs. time, b) phase portrait, c) Poincaré section and d) one-dimensional map.

FRactal PROPERTIES OF ELECTROCHEMICAL SYSTEMS

Application of fractal ideas to electrochemical phenomena is not a new topic. Fractal electrodes have been reported and its applicability to the study of faradaic impedance results is well known. Also, auto-similarity character of electrode surface, specially in battery electrodes, has been used to interpret the current efficiency. Particularly, studies on electrodeposition have become important because they supply patterns to test spatial models and the corresponding temporal dynamics.

Experimental electrochemical patterns. Electrochemical deposition has been found to produce a variety of patterns, ranging from orderly dendrites to random fractals (Matsushita, Sano, Hayakawa, Honjo and Sawada, 1984; Sawada, 1986). Simultaneous analysis of the statics and dynamics of fractal growing patterns provides

a quantitative characterization of the deposit and its dependence on the experimental conditions, respectively (Grier, Ben-Jacob, Clerke and Sanders, 1986; Sagués, Costa, Mas, Vilarrasa and López, 1991). Deposition onto a linear electrode provide further information about the growth and diffusion control model. The electrochemical polymerization from neutral species has also been exhibited interesting patterns (Kaufman, Nazzal, Melory and Kapitulnik, 1987).

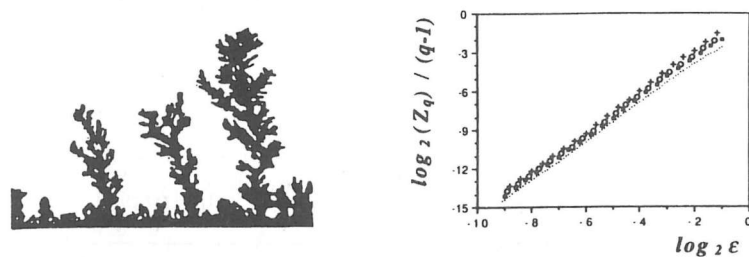


FIG. 16. Digitized images and plots used to calculate the generalized fractal dimension corresponding to electrodeposits of zinc.

The use of the generalized fractal dimension, D_q , is useful to discuss the self-similarity of experimental morphologies (Sagués, Mas, Vilarrasa and Costa, 1990). An application to zinc patterns is given in Fig. 16. When varying operation conditions, different textures are obtained. In the simple occurrence of uniform fractals with an uniform distribution, all generalized dimensions equal to fractal dimension. From time effect on deposit thickness the growth velocity is calculated (Costa, Sagués and Vilarrasa, 1991). Fig. 17 shows digitized images of copper electrodeposits taken at different times.

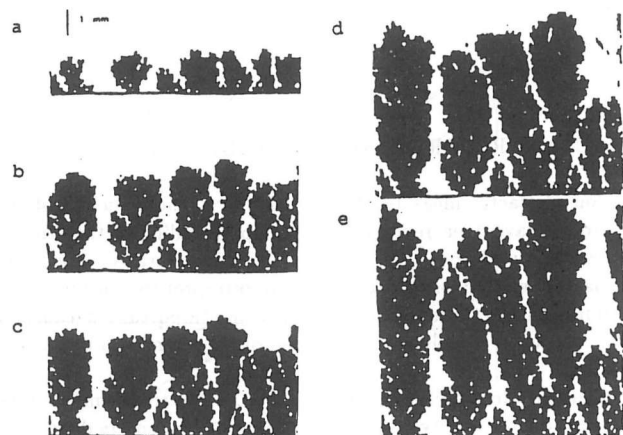


FIG. 17. Patterns of copper electrodeposits taken at 189, 430, 480, 720 and 900 s, respectively.

Electrodissolution of metals produces corroded surfaces, which morphologies are rarely uniform. The pits observed on this corroded surfaces have a variety of sizes and shapes. The fractal dimension concept can be applied to experimental pit boundaries (Costa, Sagués and Vilarrasa, 1991). The rugged boundary of a corrosion pit is shown in Fig. 18, as well as the practical determination of its fractal dimension.

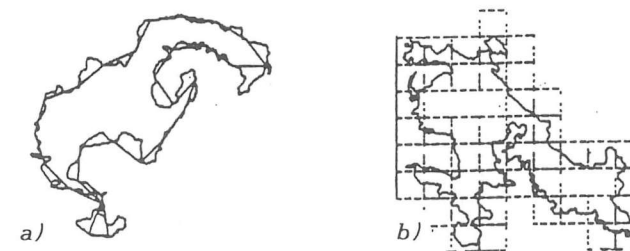


FIG. 18. Digitized micrograph of a pit showing schematically the practical utilization of a) structured walk and b) box counting methods to compute fractal dimensions.

Simulations of electrodeposits. Idealized computer simulations of many electrode processes have been carried out, in order to explore the physical structures formed on the electrode and to investigate the spatial and temporal behaviour of the system.

The character of experimental patterns presented in previous section is found to be similar to those obtained by diffusion-limited aggregation (DLA). This well-known model consists in a cluster growing from a seed particle by the addition of particles realised far from the cluster (Witten and Sander, 1981, 1983). Several algorithms for computer routines have been formulated to give rise to disorderly aggregates with no apparent symmetry (Sagués and Costa, 1989). Fig. 19 presents three clusters generated with different working conditions (Kertész and Vicsek, 1986).

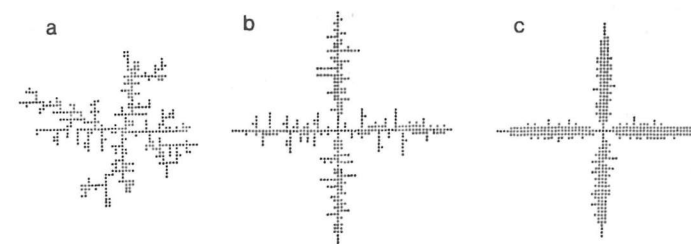


FIG. 19. Simulation of radial aggregates showing different morphologies: a) fractal, b) dendritic and c) needle patterns.

The morphology of these radial clusters changes from a typical random *fractal* structure to a *dendritic* growth and to a *needle* crystal, as a consequence of the competition between anisotropy due underlying square lattice and the fluctuations due to the random walks. A typical two-dimensional aggregate on a "linear" electrode is shown in Fig. 20, where the tenuous structure characteristic of fractal patterns is clearly reproduced.

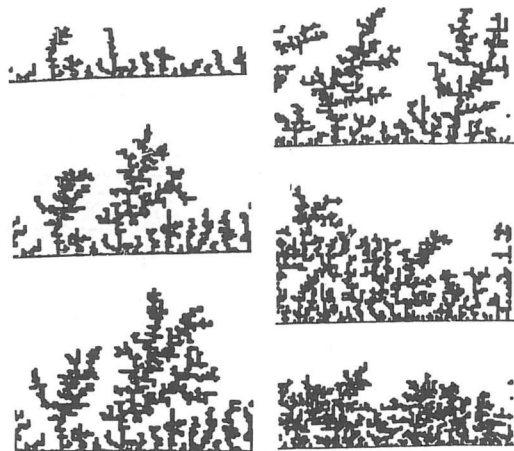


FIG. 20. Two-dimensional simulation of diffusion-controlled electrodeposition.

The effect of surface diffusion on the morphology of electrodeposited metal clusters has been studied, using square and hexagonal lattice models, which diagrams are outlined in Fig. 21 (T. Hepel, 1987).

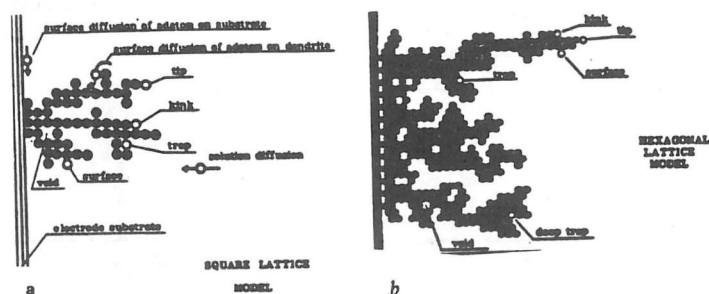


FIG. 21. Effect of surface diffusion on metal cluster: a) square and b) hexagonal lattice models.

Although it is not possible to cover all of the many results obtained in the last few years on non-equilibrium processes in the wide field of the electrochemistry, here it has been presented some both conceptual and experimental material, which can point out that electrochemistry is a fertile field for applications of theories of non-linear dynamics. However, it seems clear that there is a great need for further experimental work that can provide answers to many of the most theoretical questions and, consequently, this subject is in want of much more attention from researchers in electrochemistry.

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VOLTAMMETRIC BEHAVIOUR OF INSULIN-ZINC ON THE MERCURY INTERFACE

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SUMMARY

Insulin-zinc suspensions are more electroactive on the hanging mercury drop electrode (hmde) when the protein is in amorphous state. Reduction and reoxidation of disulphide bridges depend on the Zn(II) present in buffer solutions.

The influence of the insulin adsorption on the reduction process of zinc at the hmde, can be explained by variation of the exchange current density with a change in the surface fraction covered by the protein on the electrode.

INTRODUCTION

Insulin is found forming a monomer-dimer-hexamer system (1-3) in an aqueous solution. This type of association equilibria depends on its concentration, on the pH, on the temperature (4) and on the medium (5). The association constants which characterize the monomer-dimer and dimer-hexamer equilibria are $2.2 \times 10^4 \text{ M}^{-1}$ and $8.6 \times 10^5 \text{ M}^{-2}$