

CHAPTER 1: INTRODUCTION

In his book entitled ‘What is Life?’ Erwin Schrödinger [1] discusses some aspects of fundamental processes taking place in biological systems employing concepts stemming from physics and chemistry. In this inspiring and vivid book he points out that life embraces basically two sorts of processes, the first one being associated to the so-called generation of *order out of order* and the second one to the emergence of *order out of disorder*. In the first point concerning the order out of order, the author discusses that the gene, as an aperiodic crystal with superior stability and coding capabilities, is responsible for a process that generates order out of order. The second point concerns the apparent contradiction between

the high degree of organization intrinsic to all living systems and the second law of thermodynamics, which states that in a closed system the entropy should be maximized and therefore disorder should prevail. This apparent antithesis between the disorder prescribed by the second law and the evolution towards highly organized states observed in living systems had been referred to as the Carnot-Darwin paradox [2].

Theoretical work by Prigogine and coworkers [3, 4] provided the basis for the understanding of how order can emerge out of disorder in far from equilibrium systems. They coined the term *dissipative structures* for open systems that are maintained in a time and/or space symmetry broken state, owing to the fluxes of energy and matter. Since no restrictive principle as the one given by the entropy maximization in the second law is present in far from equilibrium conditions, the apparent ‘contradiction’ referred to in the last paragraph is resolved. Dissipative or self-organized structures are maintained by exporting entropy to their environment. Indeed, the fact that life, as a far from equilibrium process, can develop and maintain very organized structures on the expense of the disorganization of the environment has been already recognized by Schrödinger [1].

The study of spontaneous emergence of spatiotemporal patterns, i.e., dissipative structures, has become an increasingly growing interdisciplinary field of research (see ref. [5] for a pictorial overview) during the last decades. From a chemical point of view, the spatially varying properties are usually thought of as being composed of several individually reacting elements that are coupled among each other. Examples of well-studied systems are the celebrated Belousov-Zhabotinsky reaction [6-10], heterogeneous catalytic reactions [11-22], and electrochemical reactions [23-28]. In all cases, far from equilibrium pattern forming systems are characterized by internal feedback loops and are mathematically described by nonlinear evolution equations [29, 30].

Feedback loops form especially easily in electrochemical systems, and, in fact, any electrochemical system can in principle display temporal symmetry breaking in the form of spontaneous current or potential oscillations in some parameter range when driven far from equilibrium. Although the very first chemical oscillation ever reported concerns the observation of potential oscillations during the iron dissolution [31], only recently the mechanisms underlying electrochemical oscillations were brought to light [23-25, 28].

Pattern formation in electrochemical systems occurs at the electrode/electrolyte interface and results from the interplay between interfacial kinetics and transport processes parallel to the electrode surface. The interfacial region exchanges energy and mass with the bulk electrolyte and the system is kept far from equilibrium by a constant supply of electrical energy from the surroundings to the electrode as schematically shown in Figure 1.1. This supply is usually realized via a potentiostat or a galvanostat. In the galvanostatic operation mode, the potential of the working electrode varies in order to keep a preset current value. In the potentiostatic operation mode the potential of the working electrode is controlled with respect to a reference electrode. In the scheme depicted in Figure 1.1, the electroactive species 'A' diffuses from the bulk solution to the electrode, adsorbs at the working electrode, where it is then oxidized to 'A⁺'. Finally the product 'A⁺' desorbs and diffuses from the reaction zone to the bulk solution.

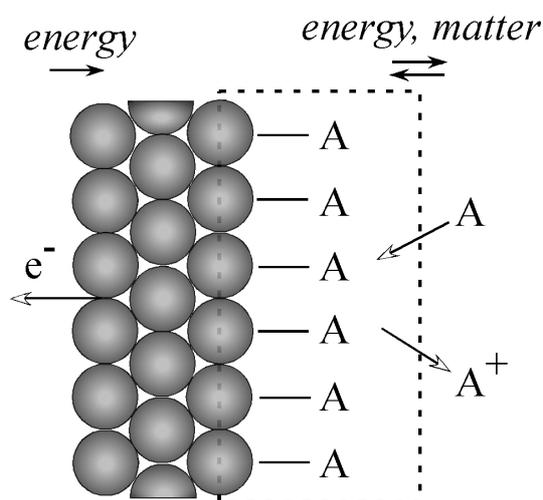


Figure 1.1: Schematics of the electrochemical interface as an open system in which electrons flow through the electrode/electrolyte interface and electroactive species flow through the reaction plane/bulk solution interface. Illustrated is the electrooxidation of A ($A \rightarrow A^+ + e^-$).

The unique opportunity of bringing together chemical and electrical properties makes electrochemical systems very suitable model systems for biological systems [26]. Actually, analogies between electrochemical and biological processes were recognized since the early days of the first experimental investigations in electrochemical systems as evidenced in the use of terms such as 'iron nerve' (i.e., the periodic passive to active transitions in the dissolution of iron in nitric acid) [32-35] and the 'mercury heart' (i.e., the oscillatory decomposition of hydrogen peroxide on mercury) [36-38].

In spatially extended electrochemical systems the individual elements composing the electrode are predominantly coupled through the electric potential in the electrolyte. The spatial range of this coupling can be intuitively understood as follows. Consider a perturbation of the interfacial potential at a particular location on the electrode. This perturbation causes a redistribution of the electric potential inside the whole electrolyte and thus also of the interfacial potential along the entire electrode. The amount of the redistribution, however, is larger close to the perturbation than further away from it. Thus, the perturbation makes itself felt over a large region of the electrode. Hence, the spatial coupling in electrochemical systems is long range or non-local. In contrast, in the case of a diffusional coupling, only neighboring sites of the perturbation are affected instantaneously, and thus, diffusion is local coupling. Besides being non-local, migration coupling is predicted to possess a further peculiarity. In a theoretical study, Mazouz *et al.* [39] showed that the range of the migration coupling can be experimentally changed by varying the distance between the counter electrode (CE) and the working electrode (WE). The possibility of changing the range of the migration coupling from a long range to a localized, diffusion-like coupling is a very interesting peculiarity that differentiates electrochemical systems from reaction-diffusion systems. However, no experimental investigation of this feature has been carried out so far.

In addition to migration coupling, a global coupling might be induced in electrochemical systems in both operation modes. In contrast to the migration coupling, the range of the global coupling does not depend on the position, i.e., a change of the state of a position at a particular location is felt by all other positions with the same strength. Furthermore, the global constraint is positive, or synchronizing, when the system is under galvanostatic control, and it is negative, or desynchronizing, under potentiostatic control if a part of the cell resistance between the CE and the WE is partially compensated [26, 40]. Global constraints are known to have a strong impact on pattern formation. Spatiotemporal phenomena in electrochemical systems that arise because of the global coupling have been reported. They include the development of stationary domains [40, 41], standing waves [42, 43], remote wave triggering [44] and pulses [43, 45]. Moreover, there was also a hint that much more complicated patterns might form at intermediate global coupling strengths [46, 47].

The main goals of the present thesis are (a) to experimentally verify the prediction that the range of the migration coupling varies with the distance between the CE and the WE, and (b) to systematically study the type of pattern that can arise owing to the global coupling and to explore the parameter region in which global coupling affects pattern formation. From a more general point of view, this thesis concerns the study of spatiotemporal pattern formation in an oscillatory system. This is of particular importance in view of the very few experimental studies in spatially extended oscillatory systems in contrast to many theoretical investigations available, mainly with the *complex Ginzburg-Landau equation* (CGLE) [48-52].

A prototype system, namely the oscillatory $\text{Pt|H}_2\text{SO}_4, \text{Cl}^-, \text{Cu}^{2+}|\text{H}_2$ system, was chosen since its homogeneous dynamics is well investigated [53] and also first experiments on pattern formation in the presence of global coupling were done with this system [47]. As preparatory studies it seemed advantageous to investigate the $\text{Pt|H}_2\text{SO}_4|\text{H}_2$ subsystem. In the course of these investigations, complex cyclic voltammograms were found, and since similar phenomena were reported in the literature but not understood, these phenomena were investigated in more detail.

The thesis is structured as follows. Basic concepts of nonlinear dynamics and its interface with electrochemical systems are introduced in chapter 2. In chapter 3 experimental details are given. The complex voltammetric response in the $\text{Pt|H}_2\text{SO}_4|\text{H}_2$ system is presented in chapter 4. Besides the experimental results, numerical simulations are also presented in this chapter. In chapter 5, the oscillatory $\text{Pt|H}_2\text{SO}_4, \text{Cl}^-, \text{Cu}^{2+}|\text{H}_2$ system is studied in the absence of any global constraint, and the influence of the range of the migration coupling upon the dynamics of the system is investigated. Chapter 6 presents the experimental equivalence between two different ways in which a negative global coupling can be induced into electrochemical systems under potentiostatic control. A systematic study of the influence of the strength of the negative global coupling on the spatiotemporal dynamics of the oscillatory $\text{Pt|H}_2\text{SO}_4, \text{Cl}^-, \text{Cu}^{2+}|\text{H}_2$ system is presented in chapter 7. Chapter 8 deals with composite patterns observed under stronger negative global coupling. They require a more complex kinetics than those in chapter 7 and result from the superposition of two different patterns. The main results are summarized in chapter 9.