1 Introduction

The spontaneous formation of patterns from homogeneous initial conditions can be observed in many systems. Popular phenomena are regular cloud patterns or sand ripples [1], examples stemming from physics involve the formation of current filaments in gas discharge tubes and in semiconductor devices [2]. In chemical systems, the Belousov-Zhabotinsky reaction, in which malonic acid is oxidized to carbon dioxide by BrO_3^- in the presence of a Ce^{3+}/Ce^{4+} catalyst, is the prime example [3, 4]. In surface science, CO oxidation on platinum surface is the well studied system, which possesses very rich spatiotemporal pattern formation phenomena [5]. All these systems have in common that they are kept far from the thermodynamic equilibrium and that their evolution laws are nonlinear and fulfill certain requirements. Moreover, it could be shown that pattern formation in all these, from their nature, very different systems obeys unifying concepts [6, 7]. According to the same general rules, also many patterns in biological systems evolve [8]. The study of pattern formation in a particular system has thus always also an interdisciplinary aspect and helps to understand fundamental laws governing self-organization phenomena, which are an essential part of our animate and inanimate world. A field of science which deals with these interdisciplinary problems has developed during the last few decades as an independent discipline and is called 'Nonlinear Dynamics'.

Concentrating on chemical systems, the first published report of an oscillatory chemical reaction was in fact an electrochemical reaction. In 1828, Fechner described the potential oscillation generated by an iron electrode in a weak acidic solution [9]. In 1899, still long before the advent of nonlinear dynamics, Ostwald observed that the rate of chromium dissolution in an acid electrolyte periodically increased and decreased [10]. These early examples already point to the widespread prevalence of dynamical instabilities in electrochemical systems. In fact, today we know that practically any electrochemical system exhibits bistability or oscillation in certain ranges of the external parameters. The breakthrough in the understanding of the observed nonlinear phenomena in

electrochemical systems were only achieved within the last decade [11-17]. It could be shown that the key element causing the instabilities is the existence of a negative differential resistance (NDR) in the current-potential relation [11-17]. As outlined in chapter 2, the NDRs form very easily in electrochemical systems.

The interaction between the electrode reactions, which is inducing an NDR, and the spatial transport processes parallel to the electrode surface may induce spatial patterns. Understanding the different conditions, under which spatial pattern formation can be expected, and the different types of patterns that might emerge is a current focus of studies of nonlinear phenomena in electrochemical systems. It was shown that the transport process dominating the pattern formation in electrochemical systems is migration, i.e., the movement of ions in the electric field [18-22]. In contrast, in most chemical systems, pattern formation is the result of the interaction of nonlinear reaction kinetics and diffusion. Diffusion and migration possess different properties as far as the spatial coupling of different sites of the reacting medium is concerned, and, as a consequence, different spatial patterns will dominate. In this context, an especially exciting theoretical prediction had been made, before this thesis was taken up, and this is the existence of Turing-type patterns in an entire class of electrochemical systems.

'Classical' Turing patterns are stationary concentration patterns that emerge spontaneously due to the interaction of the local reaction kinetics and diffusion of the reacting species. Their central property is that they possess a defined wavelength which is exclusively determined by the kinetic parameters of the system, i.e., it is independent of the geometrical dimension of the system. The existence of such stationary concentration structures in chemical systems was predicted by Alan Turing as early as in 1952 in connection with possible mechanisms that participate in the early stages of morphogenesis. This intriguing idea prompted an experimental search for Turing structures in chemical systems after the first chemical oscillators were discovered [4]. However, the experimental validation of Turing structures was successful only 40 years later, and until today, there is only one especially designed chemical system in which Turing patterns were unambiguously proven to exist [23-27]. The problem in realizing these structures in chemical systems lies in the fact that two of the

species that are involved in the reaction mechanism have to have widely differing diffusion coefficients. However, in homogeneous aqueous reacting systems, diffusion coefficients of small molecules do not differ substantially from each other. In the above cited experimental example the difference in diffusion coefficients was 'artificially' brought about by employing a macromolecular indicator molecule that partially immobilizes one reacting species by reversible complexation.

According to [28], there is a class of electrochemical systems, namely systems with a so-called S-shaped current-potential curve, in which the electrode potential takes the role of the fast diffusing chemical species of the original Turing mechanism, also termed the inhibitor species. Since potential gradients lead to migration currents, the role of diffusion of the inhibitor of the 'classical Turing mechanism' is taken over by migration. In addition, it is shown that the characteristic rate of migration is always faster than that of diffusion such that the condition, which is hardly ever fulfilled in chemical systems, is fulfilled a priori in electrochemical systems with an S-shaped current-potential curve.

Thus, the initial task of this thesis was to experimentally verify the existence of Turing-like patterns in electrochemical systems. To do so, a method had to be employed with which the lateral potential distribution or adsorbate coverage can be imaged *in-situ* without disturbing the transport of reactants to the electrode or intervening with the reaction kinetics. Therefore, surface plasmon imaging (SPI), a method already established in the group was used, and that is one of the rare methods suitable for this type of *in-situ* measurements. Thus, the first task of this thesis was to find a system that possesses an S-shaped current–potential characteristics on Au or Ag film electrodes (the metal types required by SPI) and can be imaged by the SPI method.

Another central question in present studies on electrochemical pattern formation is the impact of a so-called global coupling on pattern formation. A system is said to be globally coupled if a local change of the system's state is instantaneously fed back to all other positions with the same strength. In electrochemical systems, a global coupling comes about owing to the control of the experiments, i.e., the

external circuit in which the electrochemical cell is embedded. For galvanostatic experiments this can be seen easily. In a galvanostatic experiment, the total current through the cell is kept constant. If there is a local fluctuation of, e.g., the electrode potential, which causes a change of the local current density, the total current will change too and, as a consequence, the galvanostat pumps charge into the double layer *everywhere along the electrode/electrolyte interface,* such that actual and set total current become coincided again. It is well known that such a global feedback can alter the stability of stationary states or oscillatory solutions [29]. As discussed below, also the (partial) compensation of the *IR* drop through the electrolyte introduces a global feedback into the electrochemical system [19, 30]. Theoretically, it was proved that the electronic *IR* compensation, which is built in many potentiostats, has the same effect as an electronic device in series to the working electrode that behaves like an ohmic resistor with *negative resistance* [31]. The second problem addressed in this thesis was the impact of such a negative impedance device on the dynamics of systems exhibiting a negative differential resistance in the current-potential characteristics, i.e. of systems that are known to exhibit, e.g., bistability and oscillations in the absence of spatial instabilities.

In the course of the search for a suitable system for the experimental validation of Turing patterns, the ferricyanide/ferrocyanide redox reaction in the presence or absence of an organic adsorbate was investigated. This redox system is widely used to test the quality of electrodes and the intactness of organic monolayers which inhibit the electron transfer between a redox species in solution and the electrode. These studies assume that the oxidation/reduction of ferrocyanide/ferricyanide are simple (outer sphere) charge transfer reactions that do not involve any further interaction between the redox species and the electrode. In our initial studies we obtained clear evidence that, even for very small concentrations of ferri- or ferrocyanide, adsorbates form on the electrode. Owing to the importance of this reaction, these studies were extended with the aim to obtain insight into the nature of the adsorbates as well as the conditions under which the adsorbates form.

The thesis is organized as follows: In the next chapter, chapter 2, a brief description of some concepts and general treatments related with the works in this thesis is given. Chapter 3 introduces the experimental techniques used and the procedures employed for electrode preparation. Chapter 4 discusses those systems which were tested during the search for a 'suitable' system with an S-shaped current–potential characteristics, with which the test for the existence of electrochemical Turing patterns could be performed. Chapter 5 focuses on the pattern formation studies in the selected system, which is periodate reduction on Au(111) in the presence of camphor. The impact of a negative impedance in the external electrical circuit on pattern formation during periodate reduction under potentiostatic control is investigated in chapter 6. Chapter 7 is devoted to the surface plasmon resonance angle (SPRA) studies of the ferricyanide/ ferrocyanide redox reaction on Au electrodes. Finally, the main results of the thesis are summarized in chapter 8.