In this thesis several aspects of self-organization phenomena in electrochemical systems are experimentally studied. The first aspect concerns temporal self-organization phenomena and deals with the question how complex, more precisely, higher periodic or aperiodic, current responses might occur in cyclic voltammetric experiments.

The other aspects are concerned with spatial pattern formation and cover two main problems, namely: (a) pattern formation in the oscillatory region of the electrode reaction, whereby the spatial coupling is exclusively due to the electric field of the electrolyte (migration coupling), and (b) the impact of an additional negative global coupling (NGC)
caused by the external control of the electrochemical reaction by means of a potentiostat on pattern formation of oscillatory electrochemical systems.

The experiments on the complex voltammetric responses were carried out with the hydrogen oxidation on platinum electrode in diluted sulfuric acid electrolyte, i.e., the Pt|H₂SO₄|H₂ system. The experiments on the spatial pattern formation were performed with the hydrogen oxidation in the presence of chloride and copper ions, the Pt|H₂SO₄,Cl⁻,Cu²⁺|H₂ system.

In chapter 4 the occurrence of complex voltammetric responses in the bistable Pt|H₂SO₄|H₂ system was presented. The observed periodic and aperiodic cyclic voltammograms are very similar to the ones previously reported during the electrooxidation of small organic molecules on platinum and palladium under comparable conditions. It was shown that, in contrary to earlier beliefs, the mechanism underlying the complex response does not necessarily require the occurrence of any reaction between carbon containing intermediates and surface oxide. Instead, the complex behavior results from the interplay between the negative differential resistance and the roughening process accompanying the surface oxide reduction followed by the relaxation of the rough surface. Theoretical simulations using a mathematical model comprising four ordinary differential equations further supported this conjecture. Considering the general nature of the conditions leading to the complex voltammetric responses, it was concluded that the observed phenomena should exist for a large variety of electrode reactions and electrode materials.

Chapter 5 launched the series of subsequent chapters on the spatiotemporal pattern formation in the oscillatory Pt|H₂SO₄,Cl⁻,Cu²⁺|H₂ system. In this chapter the system was studied in the absence of any global interaction. Hence, migration coupling, which is always present in electrochemical systems, was the only mechanism leading to a lateral communication along the ring electrode. The experiments were done for two distances between the CE and the WE, corresponding to two different ranges of the migration coupling. In both configurations a transition from periodic spatiotemporal structures to highly disordered spatiotemporal states was observed when increasing the applied voltage. These findings present one of the very rare (if not the first) experimental evidence of a transition into chemical turbulence in oscillatory media. Moreover, the impact of the localization of the migration coupling on the patterns could be clearly proven. The more localized the coupling
was, the more irregular were the spatiotemporal patterns and the smaller their characteristic wavelength.

The studies on the impact of a global coupling on the dynamic behavior of the Pt|H$_2$SO$_4$,Cl$^-$,Cu$^{2+}$|H$_2$ system started with the experimental verification of the global coupling in the presence of ohmic drop compensation. According to this theory, the NGC strength is a function of the compensated electrolyte resistance and the total cell resistance only, it does not depend on the way the compensation is achieved. This means, it is independent of whether a Haber-Luggin capillary or an electronic compensation is used. Comparing the spatiotemporal dynamics obtained when using a Haber-Luggin capillary and a negative impedance device inserted between the WE and the potentiostat, this prediction could be experimentally confirmed. This experimental verification is presented in chapter 6.

The influence of the strength of the NGC on spatiotemporal pattern formation in the Pt|H$_2$SO$_4$,Cl$^-$,Cu$^{2+}$|H$_2$ system was studied in chapter 7. The chapter is divided into two parts according to the copper concentration used. At lower copper concentration, at which the turbulent behavior was observed in the absence of NGC, the turbulence could be suppressed when even a weak NGC was added. When increasing the strength of the NGC, the following unusual scenario was observed: 2-PC of type I→2-PC of type II→IC→5-PC→pulses, whereby PC stands for phase clusters and IC for irregular clusters. The author is not aware of other experimental observation of periodic five phase clusters (resulting from a global constraint). At higher copper concentrations, the spatiotemporal patterns include target patterns (as well as their asymmetric version) at intermediate coupling strength, as well as modulated oscillations and pulses at low and high coupling strength, respectively.

Chapter 8 reports the observation of composite spatiotemporal patterns arising from the interaction between two negative differential resistances (NDRs), namely one owing to the Cl$^-$ adsorption at less positive potentials and one owing to the oxide formation at more positive potentials, in the presence of strong NGC and high applied voltages. The emergence of such patterns takes place at potentials at which oxide formation sets in. At these potentials and in the presence of NGC the electrode may split into two different regions, one being covered by oxide, the other one consisting of bare platinum. The novelty of the observed pattern is related to the development of spatiotemporal oscillations inside the active domain of the pre-patterned stationary state due to the (HN-NDR) oscillatory Pt|H$_2$SO$_4$,Cl$^-$,Cu$^{2+}$|H$_2$ system. The observed scenario is expected whenever there is a succession of two NDRs in the
$I/\phi_{DL}$ curve, as it is the case in many HN-NDR systems. Furthermore, the discussed mechanism should be a universal route leading to a sub-structuring of space in systems that experience a global coupling and possess at least two adjacent regions in parameter space which exhibit distinct dynamical instabilities, i.e., two distinct positive feedback loops.

The results are also of general nature and present an experimental contribution towards the understanding of spatiotemporal self-organization phenomena. From a more general point of view, this work provides further insight into the understanding of the collective dynamics of population of individual chemically active units, which are coupled either exclusively by migration or by migration and a global feedback.