Chapter 7: Summary

Spatiotemporal pattern formation through the interplay of chemical reactions and electrical effects is a wide-spread phenomenon. It occurs at biological membranes (*e.g.*, in nerve cells and muscle tissue), but has been most extensively studied in electrochemistry. The present work discussed self-organized spatiotemporal behavior in nonlinear electrochemical systems as exemplified by the electrocatalytic oxidation of formic acid on Pt.

The most important quantity for the kinetics of any electrochemical reaction is the interfacial potential (or double layer potential) at the electrode/electrolyte interface. It also constitutes an essential variable for almost all nonlinear phenomena observed in electrochemical systems. In this environment, the equations describing spatiotemporal patterns of interfacial potential are composed of a local (reaction) term and a part describing the spatial coupling through the electric field in the electrolyte. The spatial coupling through the electric field is termed migration coupling, and consequently, the evolution of the double layer potential is said to be described by a reaction-migration equation (RME).

Different geometries of the electrode setup give rise to different coupling properties. Using a ring as working electrode (sufficiently narrow to neglect radial patterns), all points of the working electrode are equivalent and affected equally by the external control as long as the reference electrode is placed symmetrically in the center of the ring; the sign of the long-range coupling is determined by the vertical distance between working and reference electrode. In contrast, on a ribbon electrode not all points are equivalent, moreover the coupling function diverges at the edges due to electrostatic effects. The symmetry of a ring

electrode was broken in the present work by either asymmetric placing of the reference electrode changing the local properties without introducing singularities in the coupling, or by insulating parts of the ring which introduces edge effects similar to the ribbon electrode while otherwise essentially preserving the equivalence of points along the azimuthal direction.

The experiments on pattern formation under galvanostatic or potentiostatic conditions were carried out with the formic acid oxidation on platinum electrodes in the presence of bismuth ions (Bi^{3+}) which enhanced the oxidation of formic acid at low potential and led to the high current oscillations over a broad potential region.

In chapter 3 potential oscillations in the electrocatalytic oxidation of formic acid with and without bismuth ions on a Pt ring electrode were investigated for symmetric geometry under galvanostatic conditions. Period-doubling and chaos (Feigenbaum scenario) were observed at fixed current. Characterization of the resulting chaotic attractors clearly suggested a *Shil'nikov* homoclinic orbit in the temporal behavior, at the same time the ring electrode remained always strictly in phase, demonstrating the occurrence of purely temporal chaos.

In chapter 4 an asymmetric condition was imposed on the ring electrode by removing the reference electrode from the central axis. We studied the effect of the asymmetrically placed reference electrode in the bistable and oscillatory regime. The transitions between active and passive state in the bistable regime were very similar to the symmetric situation, but in addition asymmetry-induced double metastability was obtained. New types of patterns were observed in the oscillatory region. Apart from periodic, spatially inhomogeneous oscillations, complex aperiodic behavior with more and less prolonged quiescent phases were observed. The latter phases are probably indicative of many coexisting attractors predicted earlier [34].

A ribbon electrode (chapter 5) has different dynamic regimes because the local effective resistance and the migration coupling depend on the different positions of the ribbon. Since the local effective resistance is smallest at the edges of the ribbon electrode, the local function diverges and the coupling strength increases at the edges. Using a short

distance between reference and working electrode, transitions *via* front propagation from passive to active states could be induced by a trigger electrode placed at one end of the ribbon, both locally and (by reversing the sign of the perturbation) at the opposite edge (remote triggering). For identical parameters, transitions from the active to the passive state as well as vice versa could be triggered (asymmetry-induced double metastability). Anti-phase edge oscillations for different positions of the reference electrode could be rationalized in terms of negative coupling and local inhomogeneity. On the other hand, in-phase edge oscillations were detected when the reference electrode was located far from the ribbon electrode, attributed to positive coupling. An asymmetrically placed reference electrode led to a patterned oscillation in which one side of the electrode oscillated with a frequency twice as high as the other side of electrode.

Chapter 6 focused on a pure edge effect, *i.e.*, insulated areas were introduced on an otherwise symmetric arrangement of the ring electrode and their effect on the pattern formation investigated. The basic pattern sequence for a symmetric ring (standing waves, travelling pulses, anti-phase oscillations with increasing voltage) had its analogues on ring electrodes which had 1, 2, or 3 small symmetrically placed insulated areas. Spontaneous emergence of active fronts always occurred at maximum distance from the conductor/insulator edges, in agreement with ribbon electrodes. Oscillations in-phase or out-of-phase at adjacent edges were comparable too, but differed in their relative parameter values from similar results on a ribbon. Some patterns on partially insulated ring electrodes did not have a counterpart in either ring or ribbon systems. These include period-doubled pulses and trapped oscillatory states, as well as the local velocity changes of travelling pulses due to the influence of the insulated parts. For not too broad insulated areas, travelling pulse waves accelerated near the insulators and jumped across them (s*altatory conduction*). This can readily be attributed to the fact that the coupling rises (and actually diverges) at a conductor/insulator interface. Consequently a pulse approaching an insulated area coupled very strongly to those parts of the electrode adjacent to the insulator and activated (or passivated) them much more rapidly than in regions far away from the insulated part. These findings may be of interest for certain biological systems (such as myelinated nerve axons).

The aim of the present work was to provide experimental evidence for the influence of the geometry and symmetry of the electrode setup on the dynamics of electrochemical reactions. The results were achieved by studying HCOOH electro-oxidation on Pt using different geometries of the working electrode, different electrode arrangements, and the introduction of symmetry-breaking insulated areas.