

## 8 Summary

This thesis deals with problems concerning two different aspects of electrode reactions, namely the ability of electrochemical reactions to spontaneously form patterns in space and time, and mechanistic aspects of electron transfer reactions in the presence and absence of an organic film. The main experimental methods used were surface plasmon resonance angle (SPRA) measurements and surface plasmon imaging (SPI).

The studies on pattern formation in electrochemical systems focused on two questions: According to a recent theoretical study, all electrochemical systems possessing an S-shaped current-potential curve spontaneously form Turing-type stationary potential and concentration patterns in wide parameter ranges. The Turing mechanism is a basic mechanism that leads to pattern formation, and it is possibly operative in some biological systems. Still, in chemical model systems it proved to exist only in exceptional cases. This makes the prediction of its widespread occurrence in electrochemical systems especially important. The first task of this thesis was to experimentally verify this prediction. The second topic was concerned with pattern formation in electrochemical systems with a negative global coupling on two-dimensional electrode surfaces. The impact of a global coupling on pattern formation is an interesting question from the nonlinear dynamics point of view, especially in the context of controlling or manipulating spatio-temporal systems such that they can be operated in a certain dynamic regime [129]. In addition, this topic is also from the electrochemical viewpoint of particular importance since an *IR* compensation – either through an electronic device incorporated in most commercial potentiostats or by minimizing the distance between the RE and the WE – introduces a negative global coupling into the system. If the uniform state becomes unstable owing to the global coupling (i.e., the *IR* correction), this has major consequences on the interpretation of global measurements which are no longer representative for the local dynamics.

The validation of the existence of Turing structures in electrochemical systems included the search for a suitable system, i.e., a system that possesses an S-shaped current-potential curve, whereby the two outer branches of the S should have sufficiently different resonance conditions for the surface plasmon excitation such that they can be easily distinguished by SP imaging. Since it is known that the adsorption of an organic molecule causes a pronounced shift of the SP resonance angle, it was tried to design a system with an S-shaped current-potential curve by superposing the adsorption/desorption of an organic molecule that undergoes a first-order phase transition from a densely packed ordered phase to a gas-like state with a low coverage and an electrochemical reaction. If the electron transfer reaction is inhibited by the organic adsorbate, the hysteresis that is connected with any first-order phase transition should yield an S- or Z-shaped current-potential curve, depending on whether the condensed state exists at lower or higher overpotential for the electrochemical reaction.

The design of the system was made in two steps. First, the adsorption of three organic molecules which were known to undergo a phase transition of the first order (thymine, coumarin and camphor) on Au(111) bulk single crystal electrodes were investigated on the Au(111) film electrodes which had to be used in the SP measurements. In particular, the shift of the SP resonance angle upon adsorption was studied. From these three molecules, camphor exhibited the clearest indication that the first-order phase transition also occurs on the Au(111) film electrode, and in addition exhibited the largest SP contrast between the bare and the camphor covered state. Hence, it was selected for the further experiments on the Turing structures.

As for the reaction species that should yield an S-shaped current-potential curve, five different electrochemical reactions were tested, namely, hexaminruthenium reduction ( $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ ), hexacyanoferrate reduction ( $\text{K}_3\text{Fe}(\text{CN})_6$ ), persulfate reduction ( $\text{K}_2\text{S}_2\text{O}_8$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and periodate reduction ( $\text{KIO}_4$ ). The hexaminruthenium reduction was not inhibited by the condensed camphor film. This might be due to a combination of the high reaction constant of this redox reaction and some imperfections of the film. During the hexacyanoferrate reduction a complicated interaction between camphor adsorption and the

electron transfer reaction that depended on various parameters was observed. Because of the prototype nature of the hexacyanoferrate redox reaction for a 'simple and fast' electron transfer reaction, further electrochemical and SPR investigations on this system were carried out with the aim to uncover the origin of the complex behavior (see below). The persulfate reduction current turned out to be very low in the potential region where the phase transition of the camphor film occurs, and thus this reaction was not suitable for our purpose. The  $\text{H}_2\text{O}_2$  oxidation in connection with camphor adsorption also turned out to involve complicated interactions between the adsorbed intermediated OH and the camphor film and was thus not applicable for our purpose. The periodate reduction finally was nearly completely inhibited by the condensed camphor film, and the current-potential curve exhibited the desired S-shaped characteristic. In addition, periodate reduction on Au(111) electrode without camphor turned out to possess an N-shaped current-potential characteristics. Furthermore, periodate reduction alone also exhibited a pronounced shift of the SP resonance with the potential. Hence, the system camphor-periodate/Au(111) was chosen for our investigation of Turing structures and its subsystem periodate/Au(111) was selected for the studies on two-dimensional pattern formation in the presence of global coupling.

In the camphor-periodate/Au(111) system, stationary potential patterns were indeed observed. The patterns manifested themselves in 'spot-like' structures of high camphor coverage that were surrounded by the nearly bare Au electrode. The number of spots depended on the concentration of periodate and the conductivity of the supporting electrolyte, suggesting that the patterns have an intrinsic wavelength that depends on kinetic parameters but not on the extension of the electrode, as it is characteristic for Turing patterns. Furthermore, the existence diagram of these stationary structures in the parameter plane spanned by the resistivity and the externally applied voltage was in excellent agreement with the theoretical predictions. This strongly suggests that the observed stationary patterns are indeed electrochemical Turing patterns. This finding also supports the prediction that Turing-like structures can be found in all electrochemical systems with an S-shaped current-potential characteristics in wide parameter regions.

As already mentioned, the second aspect of this thesis concerning pattern formation in electrochemical systems, namely the impact of a negative global coupling on the stability of the uniform state in an electrochemical system with an N-shaped current-potential curve, was studied employing the  $\text{IO}_4^-$  reduction on Au electrodes as a model system. This system turned out to be a typical N-NDR oscillator, i.e., the oscillations arise because in the region of the NDR the reaction becomes transport limited. All studies on the impact of negative global coupling on pattern formation in electrochemical systems that existed when these experiments were carried out, were done with quasi one-dimensional ring electrodes, and the global coupling was imposed by positioning the RE on the axis of and close to the WE. Pattern formation on two-dimensional electrodes in the presence of a negative global coupling had not yet been studied. A close RE in a case of a two-dimensional electrode introduces an asymmetric (i.e., weighted) global coupling, which complicates pattern formation. Hence, before this more complex situation is studied, it is desirable to investigate the symmetric case, in which the coupling is strictly global. To achieve this, an electronic device was used, which acts like a negative ohmic resistor (NID). Such a device also mimics the action of the  $IR$  correction of a potentiostat.

In the presence of the negative global coupling, instead of uniform oscillations the emergence of standing waves with a wave number 1 was observed in wide parameter regions. This confirmed the highly destabilizing properties of the negative global coupling. The symmetry breaking occurred exclusively along one spatial dimension, namely the longer side of the rectangular electrode. Two possible explanations are possible: Either the extension of the smaller side of the electrode was smaller than the characteristic length of the pattern, or this one-dimensional symmetry breaking is the dominant behavior of electrodes with aspect ratios much larger than 1. To clarify this question, further studies are necessary. Besides these symmetric oscillating patterns, also less symmetric spatiotemporal dynamics were observed in smaller parameter ranges. A comparison with simulations based on a prototype N-NDR model, which were stimulated by this study, showed that the basic features of the symmetric as well

as asymmetric patterns should, independent of the reaction under investigation, exist in all N-NDR oscillators.

Finally, owing to the importance of the reaction and the unexpected findings in connection with the search for a system with an S-shaped current-potential curve, the hexacyanoferrate redox system was studied in more detail in the presence and absence of camphor with surface plasmon resonance measurements. This method allowed the detection of a very small coverage of an adsorbate that formed during the electron transfer reaction. In connection with information that could be extracted from cyclic voltammetry, it was shown that in the camphor, hexacyanoferrate/Au system, camphor inhibits the reaction as long as the electrode potential is more negative than 0.2 V vs. Hg/Hg<sub>2</sub>SO<sub>4</sub>, the decrease in the reaction rate being more pronounced in electrolytes of low ionic strength (0.1 M and 0.02 M) than in those of high ionic strength (0.8 M). However, at more positive potentials the camphor film is displaced by polymeric hexacyanoferrate complexes. These complexes transform at longer reaction times and more positive potentials to Prussian White respectively Prussian Blue films. Also in the absence of camphor, the adsorption of a polymeric hexacyanoferrate compound was detected, once the electrode potential was positive to a threshold, which was lower than in the presence of the camphor film. From the strong tendency of Fe(CN)<sub>6</sub><sup>3-(4-)</sup> to form polymeric adsorbates, even at the low concentrations of Fe(CN)<sub>6</sub><sup>3-(4-)</sup> used in these studies, in neutral sodium perchlorate solution and at comparatively negative potentials, it can be concluded that hexacyanoferrate oxidation or reduction does not occur on a bare Au electrode under usually employed reaction conditions. Rather, already during the first cyclic voltammogram a hexacyanoferrate film starts to form if the potential is not kept at values considerably negative to the formal redox potential of this reaction. Furthermore, also care should be taken when using the Fe(CN)<sub>6</sub><sup>3-(4-)</sup> redox reaction as a probe for the characterization of organic monolayers adsorbed on electrodes, since the latter might be destructed by the adsorption of hexacyanoferrate complexes.