Chapter 10

Summary and Outlook

"Der andere Umstand, über welchen es mir nöthig scheint, noch einige Worte hinzuzufügen, betrifft die Frage, wie sich die Möglichkeit solcher Umkehrungen überhaupt mit der elektrochemischen Theorie vereinigen läßt. Man sollte nämlich meinen, daß, sobald der elektrische Gegensatz zwischen den beiden Metallen durch die Veränderungen auf Null herabgekommen ist, dieser neutrale Zustand sich fort und fort erhalten müßte. Daß dies nicht wirklich der Fall ist, deutet wohl sehr bestimmt dahin, daß es der elektrische Gegensatz nicht allein ist, welcher bei Trennung und Bildung chemischer Verbindungen ins Spiel kommt, sondern daß auch andere, jedem Körper eigenthümliche Beschaffenheiten, die wohl hauptsächlich in dessen Cohäsionszustand und gebundener Wärme liegen möchten, hierbei modifizierend mitwirken. Die bestimmte Art jedoch, wie dies geschieht, liegt leider nur zu sehr für uns noch im Dunkeln."

M.G.Th. Fechner, Jahrbuch der Chemie und Physik, **53**II (**1828**) 150

Initial situation

For a long time, baffling spatiotemporal self-organization phenomena in electrochemistry under far-from-equilibrium conditions ('dissipative structures') have left chemists in a state of cluelessness as to the underlying physical origins. Recently, however, a general framework regarding the conditions for the occurrence of temporal electrochemical instabilities, i.e. primarily kinetic oscillations, has successfully been advanced [23, 27]. Still, a countless number of mechanistic hypotheses are being put forward for individual oscillating electrochemical reactions disregarding the recent theoretical progress [135, 131, 125].

Spatial phenomena on electrified interfaces - even though long known - only recently became the focus of more and more research activities, however are still rather poorly understood. This is because the number of reactions known to exhibit patterns, especially among *electrocatalytic* systems, is limited. In particular, the nature

of the spatiotemporal patterns observed in electrocatalysis so far is rather simple [36, 27, 189] compared to that known from other chemical pattern-forming systems [51, 187, 87, 185, 186, 194].

Finally, research activities emphasizing the practical usefulness of self-organizing regimes in electrochemical systems had largely been neglected to date. This will gradually change in the near future, as the mechanistic fundamentals are sufficiently resolved.

The present work

The primary goal of the present thesis was to contribute to the knowledge and understanding of spatiotemporal dynamics in electrochemical, particularly electrocatalytic, systems. Primary emphasis was placed on three issues: **(1)** A number of individual oscillatory electrocatalytic systems, such as the formic acid oxidation or the iodate reduction, were characterized experimentally, followed by the development of detailed kinetic models in order to reproduce the complex experimental dynamics. Thereby a clear understanding of the mechanistic origins was achieved, and predictions concerning experimental regimes became possible. **(2)** Spatiotemporally periodic patterns on the electrode interface were for the first time observed in an electrocatalytic reaction system. Moreover, counter-intuitive 'remote triggering' of propagating waves provided important insight in the coupling mechanisms operating in electrochemical systems in general. **(3)** A comprehensive categorization scheme for electrochemical oscillators based on mechanistic criteria was suggested. The scheme compiles and compares relevant knowledge on the origin and manifestation of oscillatory behavior in electrochemistry. Moreover, a practical experimental procedure for the rapid mechanistic classification was put forward involving dynamical feedback control techniques, the usefulness of which for distinguishing chemical mechanisms was demonstrated experimentally in an electrocatalytic oscillator.

(1) In chapters 4 and 5, the electrocatalytic formic acid oxidation on Pt single crystals was investigated. This reaction has recently attracted considerable attention, since it is known to be a crucial intermediate step during the oxidation of methanol on noble metal catalysts, which recently has gained enormous technological importance in the context of fuel-cell related applications [251]. The oscillatory oxidation of formic acid was characterized by voltammetric measurements on low-index single crystals Pt(100), Pt(110) and Pt(111) in acidic solutions. The three crystal faces exhibited distinct behavior concerning the shape, the period and the potential range of the current oscillations. Apart from simple period-1 oscillations, mixed-mode oscillations were found on Pt(100) which transformed into period-1 oscillations upon sufficiently strong stirring. Voltammetric studies of the CO oxidation subsystem preceded the formic acid experiments in order to stepwise increase the complexity of the systems under investigation. Chapter 5 focused on the development of a detailed chemical reaction mechanism for the formic acid oxidation under the conditions employed in chapter 4. The mechanism was based on the classical dual-path hypothesis advanced by Capon and Parsons [122, 152] and intentionally kept as simple as possible: Following recent experimental findings, linear CO was assumed as sole surface

poison, no vacant site requirement was included in the oxidation of CO and quasi-reversible OH poisoning was taken to account for decreasing reaction rates at higher overpotentials. Structural surface changes were intentionally neglected as there was no evidence for their dynamical relevance. The model was developed stepwise, first for CO oxidation, then for formic acid oxidation, in order to minimize the number of parameter to be fitted to experimental data. For the first time it was evidenced by kinetic simulations using realistic parameters that the dual-path mechanism is in fact able to reproduce all relevant experimental features near and far from equilibrium such as steady states, the oscillatory regimes, the mixed-mode regimes, the oscillatory wave shapes, the bifurcation diagrams as well as the stirring behavior [153, 72]. The rate of surface poisoning alone was found to be sufficient to account for the structural dependence of the shape of the oscillations on the single crystals. Thus, the dual-path mechanism can now be regarded not only as chemical plausible but also as kinetically consistent with oscillatory experimental data. A mechanistic analysis revealed the presence of two oscillatory subnetworks, one belonging to the NDR and the other to the HNDR oscillatory category. In parameter regions where both oscillators were operating, complex dynamics such as mixed-mode or aperiodic behavior was observed.

Chapter 8 deals with the experimental and theoretical investigation of the electrocatalytic reduction of IO_3^- in alkaline solutions on noble metal electrodes. Even though oxyhalogen anions have long been known to be involved in a great number of self-organizing chemical systems, e.g. in the Belousov-Zhabotinskii reaction [252], oscillations during the catalytic reduction of IO_3^- at an electrified interface were only reported about a decade ago. The oscillatory iodate system exhibited both potentiostatic and galvanostatic oscillations. In contrast to previously studied oscillators (formic acid, hydrogen oxidation), however, the bifurcation sequence from stable to oscillatory and back to stable behavior with increasing outer potential/current was reversed insofar as the soft (hard) bifurcation occurred at high (low) absolute overpotentials or current densities. The reaction exhibited a N-shaped current/potential profile. In addition, impedance spectroscopy revealed the presence of a hidden negative differential resistance. Crucial for the mechanistic clarification was the observation that oscillations were accompanied by vivid hydrogen evolution. First, a simple prototype model accounting for only the iodate reduction was developed on the basis of the previously studied NDR skeleton models. From cyclic voltammetry in comparison with iodide adsorption isotherms it was concluded that the origin of the negative differential resistance must lie in an electrostatic repulsion rather than a surface blocking due to iodide adsorption. Then, upon superposition of an additional faradaic term accounting for the hydrogen bulk evolution, i.e. a second current carrying reaction independent of the iodate concentration, the NDR model was shown to transform into a model for a HNDR oscillator with the bifurcation sequence reversed just as found in experiments. Based on these specific dynamical features, the mechanistic analysis finally led to the introduction of the IO_3^- subgroup within the HNDR oscillator group. Importantly, the theoretical finding that a simple NDR oscillator becomes of the HNDR type in the presence of an additional 'independent' current carrier provided plausible explanations for a whole class of electrochemical oscillators.

At the same time, previously discussed convective mechanisms for the occurrence of oscillatory behavior in the iodate systems were invalidated.

(2) Experimental spatiotemporally self-organizing structures on electrified interfaces as well as the nature of electrochemical spatial couplings were the focus of chapter 6. Employing a circular array of potential microprobes for the imaging of spatial potential inhomogeneities, the experiments set out to observe complex inhomogeneous potential distributions ('potential patterns') along a polycrystalline Pt ring electrode during the electrocatalytic formic acid oxidation in an acidic electrolyte. The reference electrode was placed in the center of the ring, while the counter electrode was a second concentrical ring electrode with larger diameter. First, the evolution of the instantaneous potential profile was monitored when the local system dynamics exhibited bistability. In agreement with earlier electrochemical studies in bistable media [35, 36], propagating fronts which were locally triggered by activating perturbations exhibited accelerating sharp interfaces connecting a high potential (low current density) state with a low potential (high current density) state. Surprisingly, however, propagating waves could also be triggered at remote distances applying local passivating perturbations. This counter-intuitive nonlocal phenomenon turned out to be unique for the electrochemical migration coupling and has never been described before. For oscillatory local dynamics, patterns periodic in space and time could be observed ('standing wave', 'antiphase oscillations'). And finally, highly complex spatiotemporally aperiodic regimes were measured for slightly different electrolyte concentrations. The existence of inhomogeneous potential patterns was found to be drastically contingent upon the absence of any ohmic series resistance often used to facilitate kinetic oscillations in electrochemistry [64, 153]. Regarding the electrochemical coupling mechanisms operating in the electrocatalytic system, the experimental findings clearly suggest the presence of a positive short-range, but negative long-range coupling across the electrolyte solutions in the absence of an external ohmic resistance.

J. Christoph recently proposed an integral formalism for the description of the reaction-migration currents occurring at electrified interfaces [40] which allowed for the analytical calculation of the shape (range and strength) of the electrochemical migration coupling across the electrolyte between two points on the electrode surface. For the simple experimental geometry the kinetic model favorably reproduces the observed phenomena such as local and remote triggering. This was owing to the shape of the analytical coupling function consistently showing negative (positive) values for points on opposite (the same) sides of the ring electrode. The apparently nonlocal 'remote triggering' effect was shown to be a consequence of the extremely fast electrical migration coupling compared to the time scale of chemical reactions. Adding a slow chemical species, the model also exhibited more complex behavior such as standing waves or antiphase oscillations. Upon applying a sufficiently large external resistance the model predicts the disappearance of negative long-range coupling just as observed in the electrocatalytic experiments.

Apart from the excellent correspondence between model and experimental data, the present study indicates the feasibility of a deliberate control of spatial pattern formation on electrochemical interfaces through experimentally accessible parameters.

(3) In chapter 7, primary stress is placed on the deliberate control of the dynamical state of electrocatalytic oscillators by means of feedback techniques; it is also shown that the feedback methods provide valuable mechanistic information and, therefore, are extremely useful for the distinction of electrochemical mechanisms. In particular, unstable foci were to be stabilized by means of a feedback of experimentally accessible, time-dependent variables (control variables) on certain experimental parameters (control parameters) with the system parameters unchanged after successful control.

First, in the oscillatory hydrogen oxidation in the presence of electrosorbing cations and anions as well as in the formic acid oxidation on Pt electrodes, it was shown that the delay-free feedback of the instantaneous time-derivative of the total current on the outer applied potential leads to time-periodic regimes of varying amplitudes rather than to the stabilization of a steady state. From numerical modeling and analytical calculations these findings could be confirmed. It could further be shown analytically that the stabilization of the steady state under these conditions is a sufficient condition for the presence of an electrochemical oscillator where the double layer potential is nonessential (strictly potentiostatic oscillator). This behavior was related to the special form of the equations for charge conservation usually employed in electrochemical modeling. If, however, the instantaneous value of a *chemical* species was fed back on the outer potential or current, in contrast, the stabilization of the unstable foci is possible. This was demonstrated experimentally in the galvanostatic oxidation of hydrogen in a ring-disk arrangement where the instantaneous time derivative of the bromide coverage was deduced from the ring signal. Essentially what the latter feedback does is the experimental determination of an off-diagonal element of the Jacobian which can be used for the discrimination of oscillatory electrochemical mechanisms and the determination of the dynamical role of individual species.

Finally, chapter 9 set out to provide a general mechanistic categorization of electrochemical oscillators compiling relevant data from previous studies as well as from the preceding chapters. Four principal classes of electrochemical oscillators are distinguished depending on the mechanistic role of the double layer potential ϕ. Class I oscillators involve ϕ as nonessential variable, while in Class II ϕ acts as essential, yet non-autocatalytic variable. In Classes III and IV, finally, ϕ plays its 'usual' role as dominant autocatalytic and hence essential variable. Emphasis was also placed on a direct comparison between the classes with respect to their experimental voltammetric, impedance and bifurcation behavior.

Numerical studies on strictly potentiostatic oscillators (Class I) evidenced that care should be taken where an immediate classification on the basis of impedance data is concerned [74]. Strictly potentiostatic oscillators allow for virtually all possible shapes of impedance plots and therefore need to be identified first, for instance, by using the method described in chapter 7. A rather exotic group of oscillators was that with S-shaped voltammetric I/ϕ profiles (Class II) where the double layer potential serves as the slow essential variable. Then, based on the investigations given in chapters 5 and 8 as well as previous studies on electrocatalytic oscillators [27], it appeared appropriate to subdivide the large group of HNDR oscillators (Class IV) into three subgroups according to their mechanistic 'ingredients' responsible for

oscillations. It is worth noting that the concept of 'dependent' and 'independent' current carriers has significantly contributed to the extension and refinement of the classification scheme insofar as it allowed a rather precise formulation of the dynamical requirements of NDR and HNDR oscillators.

Chapter 9 concluded with an experimental operational procedure for a systematic classification of unknown electrochemical oscillators. This practical procedure of classification is to serve as an initial approach towards an identification of dynamical elements or roles of species; it can then be followed by a much more conscious search for detailed chemical steps necessary for the model to comply with experimental data.

Outlook

There are a number of reasons why self-organizing electrochemical systems will continue to be popular paradigms for the experimental study of far-from-equilibrium phenomena, whether to test theoretical predictions or to search for original experimental dynamics. One reason already mentioned for this lies in the marked deviations from thermodynamic equilibrium which are usually applied when conducting interfacial electrode processes. Electrochemistry also offers several system variables and parameters which are easily accessible and easy to control. Finally, nonlinearities are inherently present in faradaic electrode processes and the mechanistic requirements for the occurrence of spontaneous patterns, e.g. oscillations, are moderate. As demonstrated in chapter 7, spatial electrochemical patterns exhibit qualitatively new phenomena due to migration couplings across the electrolyte adding to reaction and diffusion. Sophisticated theoretical modeling by J. Christoph [40] has predicted a tremendous richness of spatial electrode dynamics yet to be discovered in experiments.

The scanty number of spatial studies in electrocatalysis clearly testifies that the liquid/solid interface of electrocatalytic systems often requires more sophisticated imaging techniques compared to other complex chemical systems such as surfaces under UHV conditions, in particular where a continuous monitoring of two-dimensional electrode surfaces is concerned [36, 253]. However, it is exactly these real conditions that might make complex spatiotemporal behavior in electrocatalysis appealing, since the gap between academic and technological electrochemistry is rather narrow.

Generally, in the near future, electrochemists working in the field of spatiotemporal patterns will have to face increasing expectations as to the practical usefulness of nonstationary or inhomogeneous chemical states, which in turn will increase the incentive to think about situations where complexity is superior to stationarity. There are links in abundance:

Obviously, periodic behavior in time samples a wide range of phase space offering the possibility of a sustained self-recovering of certain surface conditions. This appears plausible, for instance, in the context of the periodic poisoning and de-poisoning during spontaneous oscillations in the oxidation of fuels (cf. chapter 4 and 5) which may even result in increased average current density compared to stationary conditions. In ref. [125] it was demonstrated that a periodic perturbation of a galvanostatic stationary state resulted in the sustained decrease of surface poisoning indicated by the considerable decrease in the average surface potential.

Conversely, if stationary behavior is required, but becomes inaccessible due to spontaneous instabilities, control methods may help to extend the range of stationary states. This can also be rationalized by the voltammetric profile of the hydrogen oxidation: At potentials near the maximum current densities on the anodic branch, the stationary states tend to become unstable, but can be stabilized by appropriate feedback methods.

Concerning electrodissolution systems, it is well conceivable that perfect controllability of stationary spatial patterning with respect to the reaction rate of an electrodissolution/electropolishing reaction may be exploited for a deliberate microstructuring of electrode surfaces. Such a self-organized lithographic process may have favorable properties compared to common photo- or electronbeam-litographic techniques owing to easy handling.

Another conceivable way to leverage electrocatalysis performed under far-from-equilibrium conditions consists in exploiting the distinct product selectivity of two coexisting stationary states (bistability) in an electrochemical mechanism involving parallel reaction channels. A common example for a mechanism of the latter type is the anodic oxidation of methanol where CO, formic acid, formaldehyde and methylformiate, $HCOOCH_3$, are known to be formed. From dynamical systems theory it is known that bistability involves stationary states which are drastically distinct as to the rates of individual reaction steps. Either steady state may literally turn on a distinct portion of the overall mechanism leading to different product ratios. Moreover, according to theory, a mere perturbation in some variable without changing any parameter suffices to switch the system from one dominant product to the other.

However, non-stationary conditions in electrochemical systems may be advantageous not only in a kinetic, but also in a thermodynamic context. A number of studies reported considerable efficiency increases in nonlinear chemical combustion and nonlinear biochemical systems due to a forced periodic or autonomously periodic conduct [254, 255, 198, 256, 257, 197]. While in linear systems the flux J (reaction velocity) is proportional to the driving force $-\Delta G$ without phase delay, in nonlinear systems a periodic variation of the driving force will lead to a phase-delayed response of the flux, which can in principle exhibit any phase angle usually depending on the forcing frequency ω. Depending on the phase lag an increase or decrease in the time-average of the total dissipation $D = \langle -\Delta G\,J \rangle = \langle P_{in} \rangle - \langle P_{out} \rangle$ may be observed which corresponds to the difference between the input power and the output power. A straight-forward way to modulate the driving force is the modulation of an input parameter such as concentration etc.

Following this line of arguments, one can put forward a twofold argument as to efficiency increases in electrochemical systems under autonomous or driven oscillatory conditions, in particular with respect to continuous electrochemical energy conversion system (fuel-cells).

The first argument refers to dissipation reductions in reaction steps not associated with charge-transfer. Consider a multi-step overall half-cell reaction from A to B with

some intermediate X

$$A \overset{non-ct}{\rightarrow} X \tag{10.1}$$

$$X + z\,e^- \overset{ct}{\rightleftharpoons} B \tag{10.2}$$

where step 10.1 denotes a nonelectrochemical pathway, whereas step 10.2 is a simple faradaic process with - for the sake of simplicity - a free enthalpy efficiency $\eta_G = \frac{-zF\Delta E_{cell}}{\Delta G_{XB}} = 1$ [258]. Furthermore, step 10.1 is to involve multiple chemical steps allowing for oscillatory rates for some parameters (purely chemical oscillator). The educt A and product B are nonessential species and hence can always be kept constant by means of a large reservoir implying a constant overall free enthapy ΔG_{AB}. Under stationary conditions, the total power loss amounts to $D = P_{in} - P_{out} = -\Delta G_{AB}\,J_{AB} + \Delta G_{XB}\,J_{XB} = -\Delta G_{AX}\,J_{AX}$, i.e. involves the chemical dissipation of the nonelectrochemical steps, with J denoting the respective reaction rate. Under nonstationary conditions, however, e.g. for a zero-average modulation of X associated with zero-average modulations of all individual reaction rates due to autonomous oscillations in the pathway from A to X, a constant phase-lag between ΔG_{AX} and J_{AX} arises with ΔG_{AB} still being constant. For appropriate phase angles the time-average of the chemical power loss $D = \langle -\Delta G_{AX}\,J_{AX} \rangle$ can be reduced compared to its stationary value, allowing for an increase in the average electrical work per unit time available in the electrical cirucit $P_{out} = \langle -\Delta G_{XB}\,J_{XB} \rangle = \langle \Delta E_{cell}\,I \rangle$. Put more illustratively, the oscillatory conditions lead to a large rate of production of X when the associated chemical free enthalpy is small and vice versa (cf. [254]).

A second argument refers to the electrical power loss in an energy conversion system (fuel cell) or, equivalently, in electrolysis. In the former case the electrical outer cell voltage E_{cell} drawn at finite current is given by $E_{cell} = E_r - \eta(I_F) - I_{tot}R_i$, while the outer voltage required for electrolysis reads $U_{ex} = E_r + \eta(I_F) + I_{tot}R_i$ where E_r denotes the reversible voltage of the electrochemical step, $\eta(I_F)$ the overpotential losses as a function of the faradaic current I_F, and $I_{tot}R_i$ the inner ohmic voltage losses. Note that the equivalent cell circuit given in Fig. 2-2 underlies this consideration. Obviously, for both cases the the total power loss under stationary conditions reads $D = I_F\,\eta(I_F) + I_{tot}^2 R_i$. Usually in simple electrochemical systems both terms increase the overall power loss. Now consider an electrochemical HNDR oscillator at a potential (see black dot in Fig. 9-22) where it exhibits an impedance behavior similar to that shown in Fig. 8-7 and Fig. 9-21 where the total impedanc is negative over a wide range of ω. In order to avoid capacitive contributions, one can drive the oscillator at exactly the frequency $\omega_0 > 0$ for which the impedance spectrum crosses the negative real axis, i.e. the total impedance Z_{tot} is real and negative and reads $Z_{tot} = R_i + \frac{|Z_F|^2}{\mathrm{Re}\,Z_F}$ with Z_F denoting the differential charge-transfer resistance $Z_F = |Z_F|\,e^{i\varphi} = \Delta\eta(t)\,/\Delta I_F(t) = \Delta\eta_0 e^{i\omega t}\,/\Delta I_{F0}\,e^{i(\omega t - \varphi)}$.

This in turn implies that $\mathrm{Re}\, Z_F$ is negative and large compared to R_i. In the linear regime, one can show that the average total change of dissipation under periodic forcing with frequency ω is generally given by

$$\langle \Delta D \rangle = \frac{1}{2}\, \Delta\eta_0^2 \left(R_i \left[\frac{1}{|Z_{cap}(\omega)|} + \frac{\mathrm{Im}\, Z_F(\omega)}{|Z_F(\omega)|^2} \right]^2 + R_i \left[\frac{\mathrm{Re}\, Z_F(\omega)}{|Z_F(\omega)|^2} \right]^2 + \frac{\mathrm{Re}\, Z_F(\omega)}{|Z_F(\omega)|^2} \right)$$

$$= \frac{1}{2}\, \Delta\eta_0^2 \left(R_i \left[\omega\, C_{dl} - \mathrm{Im}\, Y_F(\omega) \right]^2 + R_i \,\mathrm{Re}^2\, Y_F(\omega) + \mathrm{Re}\, Y_F(\omega) \right)$$

with Z_{cap} denoting the capacitive impedance, Y_F the faradaic admittance and C_{dl} the double layer capacity. When capacitive contributions are negligible due to small C_{dl} this relation reduces to

$$\langle \Delta D \rangle = \frac{1}{2}\, \Delta\eta_0^2 \left(\frac{R_i + \mathrm{Re}\, Z_F(\omega)}{|Z_F(\omega)|^2} \right) = \frac{1}{2}\, \Delta\eta_0^2 \left(\frac{R_i}{|Z_F(\omega)|^2} + \mathrm{Re}\, Y_F(\omega) \right) \; .$$

When the capacitive contributions of Z_F and C_{dl} just cancel, as it is the case at ω_0, one obtains

$$\langle \Delta D \rangle = \frac{1}{2}\, \Delta\eta_0^2 \left(R_i \left[\frac{\mathrm{Re}\, Z_F(\omega_0)}{|Z_F(\omega_0)|^2} \right]^2 + \frac{\mathrm{Re}\, Z_F(\omega_0)}{|Z_F(\omega_0)|^2} \right)$$

which is negative for $0 > \mathrm{Re}\, Z_F > -\frac{|Z_F|^2}{R_i}$. At a Hopf bifurcation where $\mathrm{Re}\, Z_F = -R_i$ with the capacitive contributions cancelling each other the relation reads

$$\langle \Delta D \rangle = -\frac{1}{2}\, \Delta\eta_0^2 \, \frac{R_i}{|Z_F(\omega_0)|^2}\, \mathrm{Im}^2\, Z_F(\omega_0) < 0.$$

This implies that a net increase of the average electrical work per unit time can be achieved not only by periodic forcing, but can also result from autonomous oscillatory behavior. In other words, it is the nonlinear chemistry involved which allows the decoupling of forces and fluxes, gives rise to the above impedance behavior and, in turn, increases the efficiency.

Some of the outlined possible applications remain quite speculative at present. Yet, alongside with a detailed mechanistic understanding they might encourage electrochemists to tackle advanced approaches to application of Nonlinear Dynamics in the future.