2 Backgrounds

This thesis deals with problems that involve two fields, nonlinear dynamics and electrochemistry. In this chapter, the backgrounds from both fields necessary to understand the thesis are briefly summarized.

2.1 Activator-inhibitor systems, oscillations and Turing structures

Nonlinear dynamics deals with the temporal evolution of systems that are described by nonlinear rate laws. If the rate laws contain certain dependencies, these systems may exhibit the spontaneous formation of order, such as temporal oscillations or spatial patterns [1, 29, 32, 33]. In many cases, and in particular in the electrochemical systems considered here, the models belong to the class of activator-inhibitor systems, which possess one specific but widespread type of nonlinear dependences. Consider a system whose dynamics is described by two variables u and v. This system is an activator-inhibitor system, if the activator u catalyzes its own production (autocatalysis) and activates the formation of the inhibitor v, while v inhibits the formation of u (Fig. 2.1).
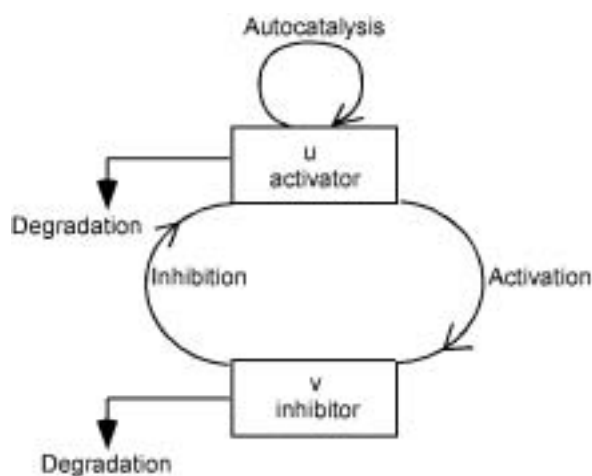

Figure 2.1: Schematic representation of the interactions in an activator-inhibitor system.

Neglecting space for a moment, activator-inhibitor systems can be written in the general form:

$$\frac{du}{dt} = f(u,v),$$ (2.1a)

$$\frac{dv}{dt} = g(u,v),$$ (2.1b)

whereby $\partial f / \partial u > 0$, $\partial f / \partial v < 0$, and $\partial g / \partial u > 0$, $\partial g / \partial v < 0$. The first two inequalities result from the requirement that the activator catalyzes its own production but is consumed by the inhibitor, whereas the last two inequalities take care that the formation of the inhibitor is stimulated by the activator but not by the inhibitor itself (i.e., it is not produced autocatalytically). Detailed studies on activator-inhibitor systems can be found in the book by J. D. Murray [34].

If the characteristic time of the activator is much shorter than the one of the inhibitor, activator-inhibitor systems exhibit oscillations. This can be seen easiest if we consider a specific activator system:

$$\frac{du}{dt} = -u^3 + (a+1)u^2 - au - v + b,$$ (2.2a)

$$\frac{dv}{dt} = cu - dv,$$ (2.2b)

where $0 < a < 1$, b, c and d are constants, whereby c and d are positive. The null clines of f(u, v) and g(u, v) are the set of points (u, v) in the u, v plane that satisfy f(u, v) = 0 or g(u, v) = 0, respectively (Fig. 2.2).

When crossing a null cline, the corresponding function (f or g) changes sign. Furthermore, the intersection of the two null clines is a stationary state, S. With this in mind, we can illustrate why an activator-inhibitor system possesses oscillatory solutions if typical changes of the activator occur on a shorter time scale than those of the inhibitor. Consider the situation depicted in Fig. 2.2. Suppose, the system is in the steady state and a small fluctuation occurs such that it increases u slightly. For this state, f > 0 and g > 0. If f >> g (i.e., the characteristic time of a change of u is much larger than one of v), u will further increase rapidly, until it reaches the f null cline. Once on the f null cline, v slowly increases, the

system thereby staying on the *f* null cline, until we come to the maximum of *f*, where a further small increase of *v* takes the system to values where *f* < 0. Again, since changes in *f* are much faster than those of *g*, *u* will decrease rapidly, until the system again reaches a branch on the *f* null cline that is, this time, the branch at low values of *u*. On this branch, *g* < 0, and hence *v* decreases, until the minimum of the *f* null cline is reached. A further decrease of *v* brings the system again in a region in which *f* > 0, and thus a fast change of *u* drives the system back to the outer branch of the *f* null cline where the scenario repeats: *v* again increases, until the maximum of the null cline is reached, and the system again undergoes a transition to the low *u* branch of the *f* null cline and so on. The system is oscillatory. In much the same way, it can be shown that the system will rest on the stationary state S if typical changes of *v* are faster than those of *u*.
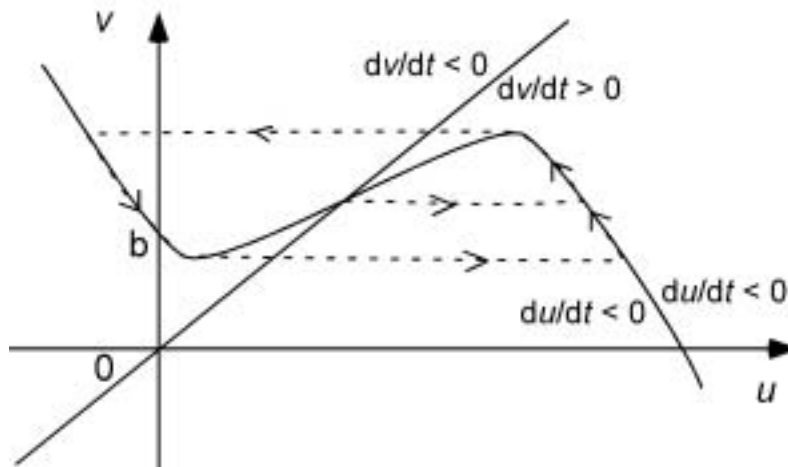

Figure 2.2: *Null clines for the above model in Eq. (2.2) with b in a certain value range (the solid straight line is the v null cline, the polynomial solid curve the u null cline, their intersection is the steady state of the system). The steady state can be unstable upon perturbation, and limit cycle periodic solutions are possible (dashed line).*

Thus, we can summarize that an activator-inhibitor system with a fast activator dynamics possesses oscillatory solutions, whereas oscillations do not exist if the inhibitor dynamics is faster than the activator dynamics. However, also in this case, the system might undergo an instability if it is spatially extended and

further conditions are fulfilled. This fact was first realized by Alan Turing, long before the concept of activator-inhibitor systems described above was developed.

In 1952, Turing proposed a pioneering idea in order to understand morphogenesis [35], "…although it (remark: Turing refers here to the spatially extended system) may originally be quite homogeneous, it may later develop a pattern or structure….". In this article Turing investigates a chemical reaction mechanism, in which two species are involved that we would nowadays classify as an activator-inhibitor mechanism. He demonstrated that this mechanism can generate stationary structures or patterns from a homogeneous initial state if one of the species (the inhibitor) diffuses faster than the other one (the activator). Thus, the graphical representation of an activator-inhibitor system as given in Fig. 2.1 can be extended to that one in Fig. 2.3.
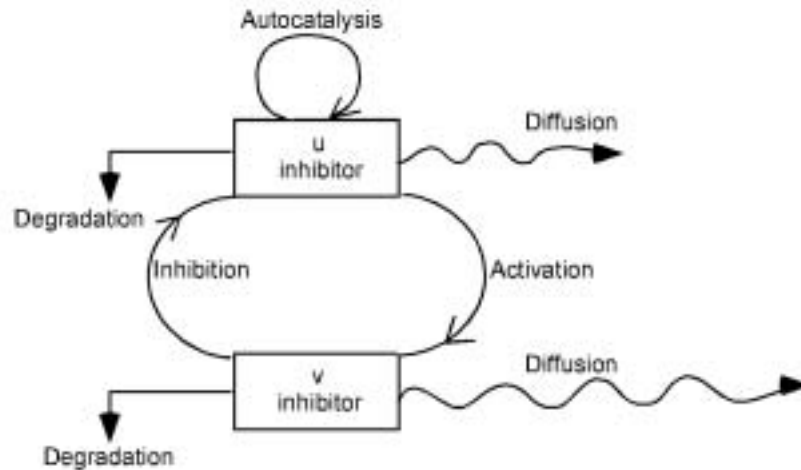
Figure 2.3: *Schematic representation of the interactions in an activator-inhibitor system and a fast diffusing inhibitor.*

The general form of an activator-inhibitor model in a spatially extended domain thus reads:

$$\frac{\partial u}{\partial t} = f(u,v) + D_u \nabla^2 u , \qquad\qquad (2.3a)$$

$$\frac{\partial v}{\partial t} = g(u,v) + D_v \nabla^2 v , \qquad\qquad (2.3b)$$

where u is still the activator ($\partial g / \partial u > 0$) and v the inhibitor ($\partial f / \partial v < 0$). If $D_u \geq D_v$, the system will eventually turn to a uniform steady state. However, if $D_u < D_v$, stationary concentration patterns may eventually form spontaneously. Such patterns are also called Turing structures or Turing patterns.

The mechanism, by which an activator-inhibitor kinetics coupled to diffusion generates Turing structures, is illustrated in Fig. 2.4. In Fig. 2.4a, a local fluctuation of the activator (solid curve) occurs while the system is initially in a homogeneous steady state. Because of the autocatalytic kinetic of u, the small fluctuation initiates the further growth of the activator, which also activates the production of the inhibitor and thus leads to a local increase in the concentration of the inhibitor (Fig. 2.4b). The higher local concentrations of both activator and inhibitor also induce lateral diffusion fluxes (Fig. 2.4c). Since the inhibitor diffuses faster than the activator, it soon reaches regions in which the activator concentration is not yet increased. In this region the high inhibitor concentration keeps the activator concentration low; hence, the slow flux of the activator into this region cannot initiate the autocatalytic formation of u. As a result, a 'spot' of high activator concentration forms that is surrounded by a cloud of increased inhibitor concentration. Thus, the final state shown in Fig. 2.4d remains stationary.

While this picture is a helpful visualization of how Turing structures develop, it lacks one important feature of Turing patterns. A Turing pattern does not consist of an individual 'spot' but of a 'series of spots' which possess a defined distance. This is because a Turing pattern has a defined wavelength. The wavelength is completely defined by the kinetic parameters of the model and independent of the physical dimension of the system [8].
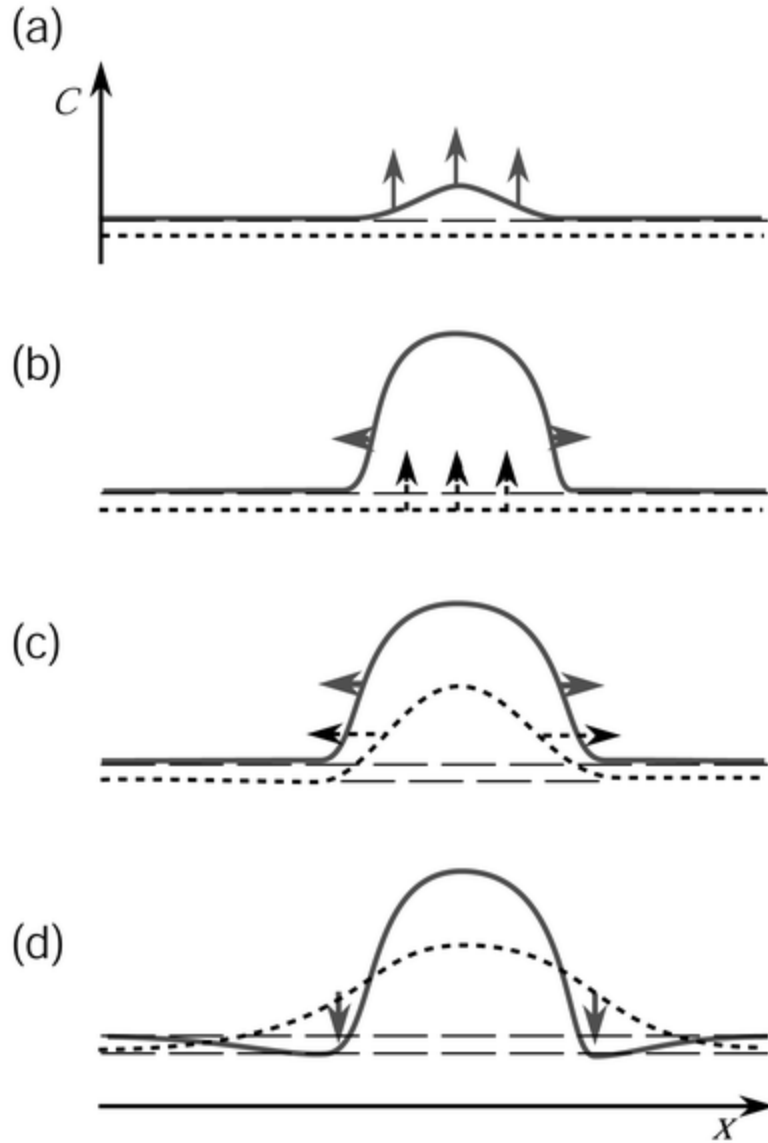
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Figure 2.4: Evolution of a stationary structure in an activator-inhibitor system, in which the inhibitor diffuses faster than the activator. After [36].

2.2 Nonlinear dynamics of electrochemical systems

Electrochemical systems exhibiting instabilities often behave like activator-inhibitor systems [15], whereby the electrode potential is an essential variable. It takes on the role either of the activator or of the inhibitor. In the following we shortly review the basic equation describing the dynamics of the electrode potential in a homogeneous situation, discuss under which conditions the

electrode kinetics supports instabilities and consider the transport processes lateral to the electrode. The interplay of these transport processes and the dynamics of the uniform system determines the type of patterns which form at the electrode/electrolyte interface.

2.2.1 Electrochemical double layer and evolution equation of the electrode potential

In electrochemistry, the interface between the electrode and the electrolyte is decisive for the kinetics of any electrochemical reaction. An important contribution on the nature of the interface goes back to Helmholtz (around 1870) and is known today as the Helmholtz model. Helmholtz regarded the interface between the electrode and the electrolyte as a parallel plate condenser of molecular dimension (also called double layer). Later, this model was continuously refined to fit experimental results. The current picture of the double layer structure and its corresponding potential distribution in front of the electrode are schematically depicted in Fig. 2.5.

In Fig. 2.5a, the metal plate has surface excess charge. In front of the metal, the solvent molecules (water) and fully solvated ions of opposite charge are attracted to the metal surface by electrostatic forces (the fully solvated ions are called non-specifically adsorbed ions). The plane through the center of the non-specifically adsorbed ions and parallel to the metal surface is called the outer Helmholtz plane (OHP). The distance between the OHP and the metal surface is about 0.3 nm, which is the approximate radius of the fully solvated ions. Some ions (e.g., anions, particularly halide ions) may slip off part of their solvation shells and form a chemical bond with the metal surface. Such ions are called specifically adsorbed ions. The plane through the center of these specifically adsorbed ions and parallel to the metal surface is called the inner Helmholtz plane (IHP). Beyond the OHP, some counter charges from the electrolyte are incorporated in the double layer for charge compensation.
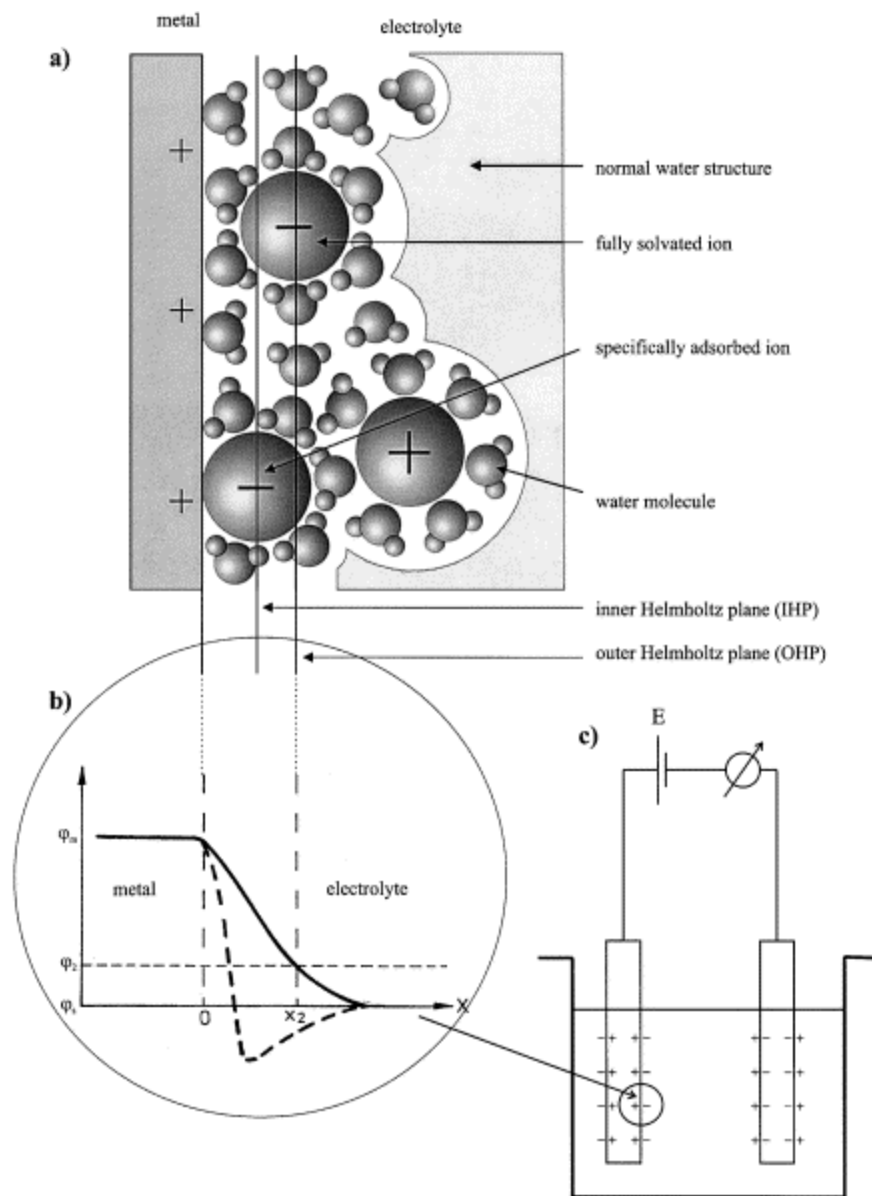
Figure 2.5: (a) Schematic diagram of the metal/electrolyte interface. (b) Potential drop across the interface in the case of non-specific (—) and specific (- - -) ion adsorption. (c) Schematic diagram of a two-electrode electrochemical cell. After Kolb [37].

The potential drop in the double layer in the case of non-specific (solid line) and specific (dashed line) ion adsorption is shown in Fig. 2.5b. ϕ_m, ϕ_s and ϕ_2 are potentials inside the metal, in the electrolyte, and at the OHP x_2, respectively.

The potential drop in the double layer in the case of non-specific ion adsorption is assumed to be linear, while in the case of specific ion adsorption, it decreases (the metal with positive excess surface charge) faster and has an overshooting feature.

In Fig. 2.5c, a two-electrode electrochemical cell is shown. The cell is driven by an external voltage E. Normally, besides these two electrodes (one is the working electrode (WE) and the other one the counter electrode (CE)), a reference electrode (RE), which has a constant potential drop, is employed in an electrochemical experiment in order to have a better control over the potential of the WE, which is in many experiments the quantity of interest.

To mathematically describe the temporal evolution of the potential drop across the double layer during an electrochemical experiment, it is helpful to use an equivalent electric circuit of the electrochemical cell [13, 38, 39]. The electrochemical interface can be modeled by a parallel connection of a capacitor with capacitance C and a general faradaic impedance (Z_{reac}, associated with charge transfer between reactants and the electrode). The electrolyte can be described as an ohmic resistor connected in series to this interfacial circuit. Across both, the interface and the electrolyte between the WE and the RE, there is a constant voltage U (which in an electrochemical experiment is realized by means of a potentiostat). If we denote the potential drop across the double layer by ϕ_{DL}, the potential drop across the electrolyte between the WE and the RE then becomes $IR = U - \phi_{DL}$, where I is the total current and R the electrolyte resistance (Fig. 2.6).

Applying Kirchhoff's law to the equivalent circuit, we obtain the following evolution equation for the double layer potential:

$$C\frac{d\phi_{DL}}{dt} = -j_{reac}(u, \phi_{DL}) + \frac{U - \phi_{DL}}{A\,R} \qquad (2.4)$$

where C is the specific double layer capacitance, j_{reac} the faradaic current density which depends in general on ϕ_{DL} and often also at least on one other variable u

(such as a reactant concentration). The term on the left is the capacitive current density, and the last term on the right represents the migration current density passing through the electrolyte, whereby R is the resistance between the WE and the RE and A the electrode area.
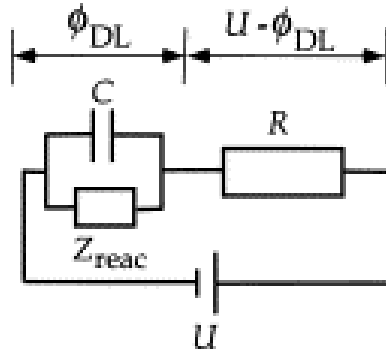

Figure 2.6: Equivalent circuit of an electrochemical cell. (C: capacitance of the double layer, Z_{reac}: faradaic impedance; R: uncompensated electrolyte resistance; U: externally applied voltage; ϕ_{DL}: potential drop across the double layer, in the text also called interfacial potential or double layer potential.) After [15].

2.2.2 NDR and instabilities in electrochemical systems

In electrochemical systems a dynamic instability is in most cases associated with a negative differential resistance (NDR) of the current-potential characteristics, $I_{reac}(\phi_{DL})$ [12, 13]. NDRs leading to an N-shaped current-potential characteristics (N-NDR type system) are quite widespread and may develop owing to three causes [12, 13, 15, 40]: First, an adsorbate (or 'poison') might block surface sites for an electrochemical reaction at high overpotentials. The smaller number of 'free' surface sites then leads to a decrease of the reaction current with increasing overpotential. Second, the reaction might be catalyzed by an adsorbate which desorbs from the electrode with increasing overpotential. Third, for anions which are reduced or cations which are oxidized, electrostatic 'double layer effects' might lead to a smaller concentration of the electroactive species with increasing overpotential.

Fig. 2.7 shows different current-potential characteristics together with the so-called load line, which can be obtained from the total current through the cell and is given by the following relation:

$$I = (U - \phi_{DL}) / R = U / R - \phi_{DL} / R.$$ (2.5)

Note that the load line has a negative slope because of the negative sign in front of the last item in Eq. (2.5).
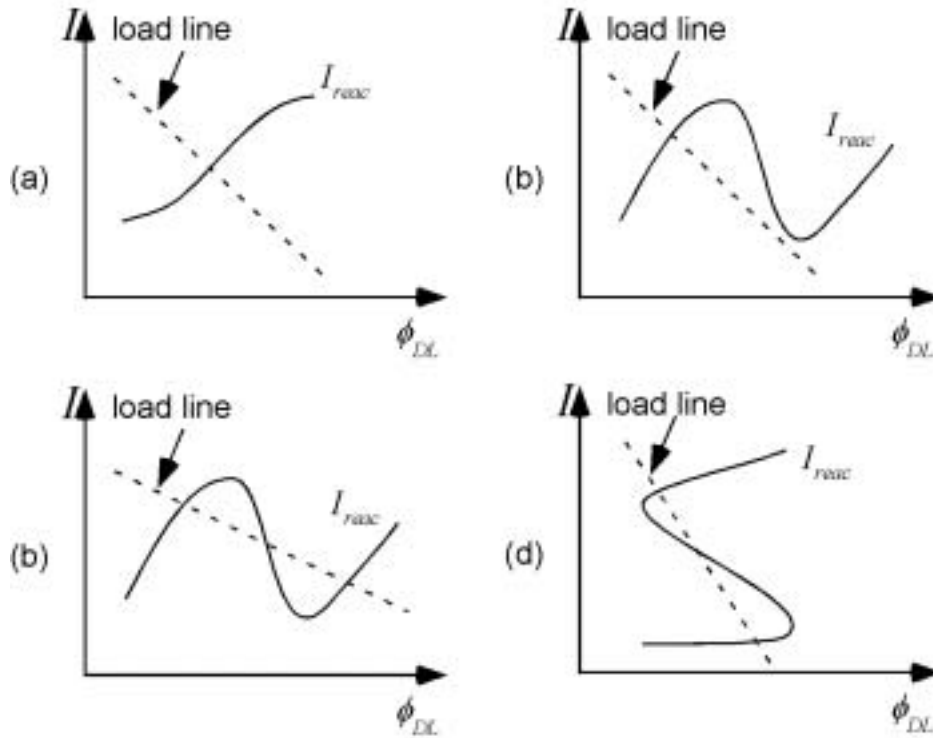

Figure 2.7: Schematic diagram on the principle of the origin of instabilities.

Let us assume that the system's dynamics is described by the evolution equation of ϕ_{DL} alone (Eq. (2.4)), which implies that all quantities, such as the coverage of the electrode surface by an adsorbate or the concentration of a reacting species in the reaction plane, adjust rapidly to a change in ϕ_{DL}. Then, an intersection between the current-potential characteristics and the load line denotes a

stationary state of the system. The stability of this steady state can be analyzed by linear stability analysis. As demonstrated in [12], the stationary state is stable, whenever the current-potential characteristics possesses a positive slope, but may become unstable, if the steady state lies on a branch of $I(\phi_{DL})$ with a negative slope, i.e., when the I - ϕ_{DL} characteristics possesses a negative differential characteristics. This can be illustrated easily: Suppose that the system is in a stationary state and that ϕ_{DL} is slightly perturbed towards more positive values. If the I_{reac} - ϕ_{DL} curve has a positive slope at the stationary state (positive differential resistance), as in Fig. 2.7a, then the slightly larger value of the electrode potential also leads to a larger current, I_{reac}. Since $\phi_{DL} = U$ - IR and U is constant (potentiostatic condition), the potentiostat will take care that ϕ_{DL} decreases again, i.e., the fluctuation is damped and the steady state is stable. According to the same argumentation, one arrives at the conclusion that if the I_{reac} - ϕ_{DL} curve has a negative slope (negative differential resistance (NDR)), the stationary state will be unstable for a sufficiently large electrolyte resistance.

The I_{reac} - ϕ_{DL} curve depicted in Fig. 2.7b possesses the shape of an 'N', whereby the differential resistance of the middle branch is negative. Electrochemical systems with such a characteristics are called N-NDR systems. Still, for the situation shown, the stationary state is stable, since the load line intersects the current-potential curve on a branch with a positive slope.

As illustrated in Fig. 2.7c for a low electrolyte conductivity (manifesting itself in a small slope of the load line), an N-NDR system may possess three steady states at a given set of parameters. The two outer steady states are on positive sloped branches of the I_{reac} - ϕ_{DL} curve and are consequently stable. The middle steady state is in the NDR region and is unstable. The system is thus bistable.

As discussed above, perturbations of ϕ_{DL} from a steady state on the unstable (negative differential resistance) branch are enhanced. Formally, we can interpret this positive feedback as an autocatalysis. Often, in N-NDR systems there is a second variable which varies on a time scale that is slower than the one of the electrode dynamics. Thus, to describe the dynamics of these systems, a second

coupled evolution equation has to be considered to describe the dynamics of these systems completely. If there is a negative feedback between this second variable and ϕ_{DL}, the electrochemical system behaves exactly like an activator-inhibitor system. In the simplest realization of an electrochemical activator-inhibitor system, the system possesses an N-shaped I-ϕ_{DL} characteristics and the transport of the electroactive species is partially mass transport limited. Denoting the concentration of the electroactive species by u, the dynamics of such a system is described by the following two coupled equations [12].

$$C \frac{d\phi_{DL}}{dt} = -\, nFuk(\phi_{DL}) + \frac{U - \phi_{DL}}{A\,R}, \tag{2.6a}$$

$$\frac{du}{dt} = -\frac{2}{\delta} u\, k(\phi_{DL}) + \frac{2D}{\delta^2}\left(u_b - u\right), \tag{2.6b}$$

where δ is the diffusion layer thickness, D the diffusion coefficient of the electroactive species and u_b its bulk concentration. Furthermore, it has been assumed that the reaction current is proportional to u and $k(\phi_{DL})$ has an N-shaped characteristic. The two terms on the left hand side in Eq. (2.6b) describe the consumption of the electroactive species by the reaction current and its replenishment by diffusion, respectively. How the interaction of the electrode potential and the concentration of the electroactive species lead to oscillations is depicted in Fig. 2.8.

The depicted N-shaped I-ϕ_{DL} characteristic corresponds to infinitely fast transport. For slower transport, the concentration of the reactant in front of the electrode decreases, and it decreases the more, the larger the current. At the beginning of an experiment the concentration of the reactant in front of the electrode is equal to the bulk concentration. Now, suppose that initially a potential close to the maximum of the I-ϕ_{DL} characteristics is adjusted, e.g., $\phi_{DL,1}$ in Fig. 2.8. Then the system would attain the state ($\phi_{DL,1}$, I_1). However, the consumption of the reactant would initially be larger than the replenishment by transport; the concentration, and, thus, the current would therefore decrease slowly. Thus, the potential drop through the electrolyte becomes smaller for the lower current, and consequently the potentiostat causes an increase of ϕ_{DL}. If in this way ϕ_{DL} is

driven to values, at which the I/ϕ_{DL} characteristic possesses an NDR, then ϕ_{DL} is 'produced autocatalytically', as discussed above, until it reaches values on the outer branch which again possesses a positive differential resistance. On this branch, the current is, however, much smaller, and the concentration of the electroactive species increases again at this low reaction rate. Accordingly, the current increases slowly, and the potential decreases again. In this way, the system is driven back to the NDR branch, where in turn, the decrease in ϕ_{DL} continues self-enhanced, until a situation similar to our initial situation establishes and the cycle starts anew. The described mechanism is exactly the mechanism that leads to oscillations during periodate reduction, whose spatial pattern formation is further investigated in chapter 6. At this point we conclude that N-NDR systems may behave like activator-inhibitor systems, whereby the electrode potential takes on the role of the activator and a chemical species the role of the inhibitor. Since in most situations the characteristic time associated with temporal changes of the electrode potential is faster than the one associated with those of the concentration (or coverage) of the relevant chemical species, N-NDR systems typically exhibit oscillatory dynamics.
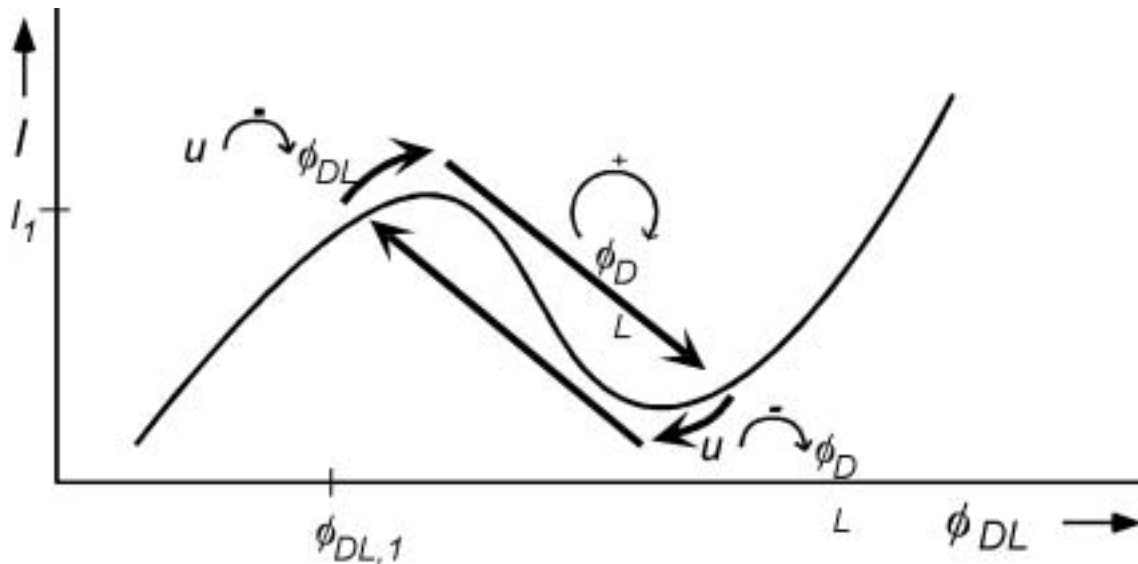

Figure 2.8: Illustration of how oscillations occur in N-NDR systems as a result of the interaction of electrode potential and concentration in the case of the slow transport of the reacting species.

There is another type of electrochemical systems, in which the electrode potential acts like an inhibitor variable and a chemical species takes the role of the activator. The most important class of these systems is associated with an 'S-shaped' current–potential curve, as depicted in Fig. 2.7. In this case, the S necessarily arises due to an autocatalytic mechanism of a chemical species, and, for steady states on the sandwiched 'NDR' branch, the electrode potential acts stabilizing [36, 41]. Since the characteristic time of changes in ϕ_{DL} is shorter than the one of changes in the concentration of a chemical species, it can be deduced that S-NDR systems do not oscillate easily, and in fact, so far no oscillations were observed in S-NDR systems. Nevertheless, also S-NDR systems are predicted to exhibit interesting self-organization phenomena, and these are patterns in space and not in time. This can be anticipated if we look at spatial transport processes lateral to the electrode surface. If we assume that the dynamics of an S-NDR system is captured by two variables, the electrode potential and the concentration of an electroactive species in the reaction plane or the coverage of an adsorbate, then a general local fluctuation will lead to gradients parallel to the electrode in the electrode potential and in the concentration (or coverage). The first gradient causes migration currents to flow parallel to the electrode surface, whereas the second one induces lateral diffusion fluxes (or surface diffusion of adsorbates). Hence, the general spatially extended S-NDR system is governed by the following set of equations:

$$\frac{\partial u}{\partial t} = f(u, \phi_{DL}) + D_u \nabla^2 u \,, \tag{2.7a}$$

$$C \frac{\partial \phi_{DL}}{\partial t} = g(u, \phi_{DL}) + migration\ cross\ currents \,, \tag{2.7b}$$

whereby the functions f and g determine the homogeneous dynamics of the system and have the typical properties of rate equations of activator-inhibitor systems. Since the term defining the lateral migration currents (the migration cross currents) is complicated and would require the discussion of the mathematical description of the potential distribution in the electrolyte, we refrain here from giving an explicit formula.

If we compare this set of equations with the general activator-inhibitor equations in extended systems (Eqs. (2.3)), we see that in Eq. (2.7) the basic difference is the transport process associated with the inhibitor, which is migration instead of diffusion. With the objective to investigate the possibility of the formation of Turing structures in electrochemical systems, Mazouz et al. [28] conducted a theoretical study, in which they showed that the characteristic rate, with which a local perturbation in ϕ_{DL} spreads, is much faster than the one, in which a perturbation of a chemical variable spreads. Furthermore, they showed that owing to this fast transport process of the inhibitor variable, electrochemical systems with an S-shaped current–potential curve may easily undergo a Turing-type instability resulting in a stationary potential and concentration pattern. The experimental verification of this prediction was a major task in this thesis and is discussed in chapters 4 and 5.