A Model for Oscillating Hydrogen Liberation at $CuInSe_2$ in Presence of H_2O_2

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Abstract

It is shown that hydrogen evolution can be obtained far from equilibrium as an oscillating mechanism during the electrochemical reduction of hydrogen peroxide at copper-containing semiconductor electrodes. Periodic hydrogen evolution was experimentally verified by in-situ Differential Electrochemical Mass Spectroscopy (DEMS). We report a working mechanistic model accounting for the most relevant features of the experimental system. Some of the novel possibilities for electrocatalysis arising from far from equilibrium nonlinear processes in presence of autocatalysis are discussed.

Introduction

The classical hydrogen evolution reaction has been called the „archetype“ for the study of electrochemical reactions, since it involves simple versions of features which are met in nearly all of them[1]. It is indeed a reaction which comes very close to the condition of thermodynamic reversibility, as supported by ample experimental evidence.

On the other hand it is also well known, that far from equilibrium mechanisms involving , for example, oscillations, all-or-non reactions or chaos, are relatively frequent in electrochemistry and physical chemistry. In biology, in fact, nonlinear and synergetic mechanisms are known to play a key role. The electrocatalytic advantage of many biological systems has frequently been emphasized. In the case of biological hydrogen evolution, for example, which is typically accomplished by (Ni, Fe)-hydrogenases, it is known that in some cases iron alone in (Fe)-hydrogenase can efficiently catalyze hydrogen evolution indicating the presence of a nonlinear mechanism. It is therefore interesting to include nonlinear electrocatalytic mechanisms into the search for improved catalysis with less noble electrode materials. Some aspects of far from equilibrium electrocatalysis have been published by our group before[2,3]. In the present work a mechanism of periodic hydrogen evolution is presented.

Electrochemical systems with oscillatory behavior have been known for a long time, especially those connected with anodic dissolution and passivation processes[4]. Cathodic oscillations are less often observed (e.g. in the cathodic reduction of organic substances[5]). Several papers report the oscillations during the reduction of hydrogen peroxide[6,7]. Due to the complicated behavior of chemical and physical processes at surfaces the theoretical understanding of most of the reported electrochemical oscillations is not satisfactory. However, it is well known that a necessary precondition for nonlinear electrochemical phenomena (bistability, oscillations, chaos) is the existence of a negative differential resistance in the voltammogram in a certain potential interval (i.e. a negative slope in the current-potential curve)[8].

A very interesting general model utilizing the coupling of a negative differential resistance with a diffusional delay process was presented a year ago by Koper and Sluyters[9]. In this model only two ordinary differential equations, one for the current balance, another for the mass balance of

the electrochemically reacting substance, are sufficient to qualitatively describe a wide variety of electrochemical oscillations.

Cathodic oscillations of several copper containing electrodes (e.g. copper sulfides and copper iron sulfides) in hydrogen peroxide solutions have been reported[6]. It was also demonstrated that semiconductor properties of the electrode material are not a necessary precondition for oscillations. Very recently several types of oscillations (ordinary, mixed mode and chaotic) were investigated at copper-indium-diselenide ($CuInSe_2$) cathodes in acid as well as basic solutions containing hydrogen peroxide.[10]

Experimental

P-type CuInSe2 single crystals were grown at the Hahn-Meitner-Institut by the method of Chemical Vapour Transport (CVT). Material properties as well as the procedure of electrode preparation will be described elsewhere[11]. As the electrochemical behaviour for polished p-$CuInSe_2$ electrodes (geometrical surface area A = 0.12 cm^2) in the dark was found to be similar in many respects to that of etched electrodes under illumination (photoinduced oscillations), the experiments described in this paper were performed at polished electrodes in the dark. Experiments with etched electrodes where illumination represents an additional control parameter for the oscillatory behaviour will be presented in a forthcoming paper[12]. The DEMS-setup consisted of an electrochemical cell (three electrode configuration with Ag/AgCl as reference and Pt as counter electrode) which was connected via a membrane inlet system with the computer controlled mass spectroscopic equipment (Fa. Balzers)[13]. The DEMS-experiments were performed in 0.5 M H_2SO_4 (Merck) with 0.8 M H_2O_2 (Merck perhydrol®

30%, suprapur). A potentiostate/galvanostate (Heka, Model PG 284) was used for potential or current control respectively. In the figures all potentials are given with respect to the normal hydrogen electrode (NHE).

Results

When a polished p-type $CuInSe_2$ single crystal is polarized in a H_2O_2 containing electrolyte (0.5 M H_2SO_4), temporary or sustained electrochemical oscillations are observed.[6,10] They appear both under potentiostatic and galvanostatic conditions. It was found that the oscillations are coupled with a periodic release of hydrogen. This is demonstrated with the experiments described in Figs.1 and 2. In Fig. 1 simultaneously to the current-potential scan the hydrogen mass signal was recorded via Differential Electrochemical Mass Spectroscopy (DEMS)[14]. In the forward scan the H_2-mass signal increases for $U < -0.5$ V/NHE showing that H^+-reduction takes place in this potential region. In the back scan pronounced potential oscillations occur for a current density of $-5\ mA/cm^2 < j < -3\ mA/cm^2$ with the negative turning points of the oscillations clearly extending into the "H_2-region". (For clarity the H_2-mass signal is only shown for the forward scan).

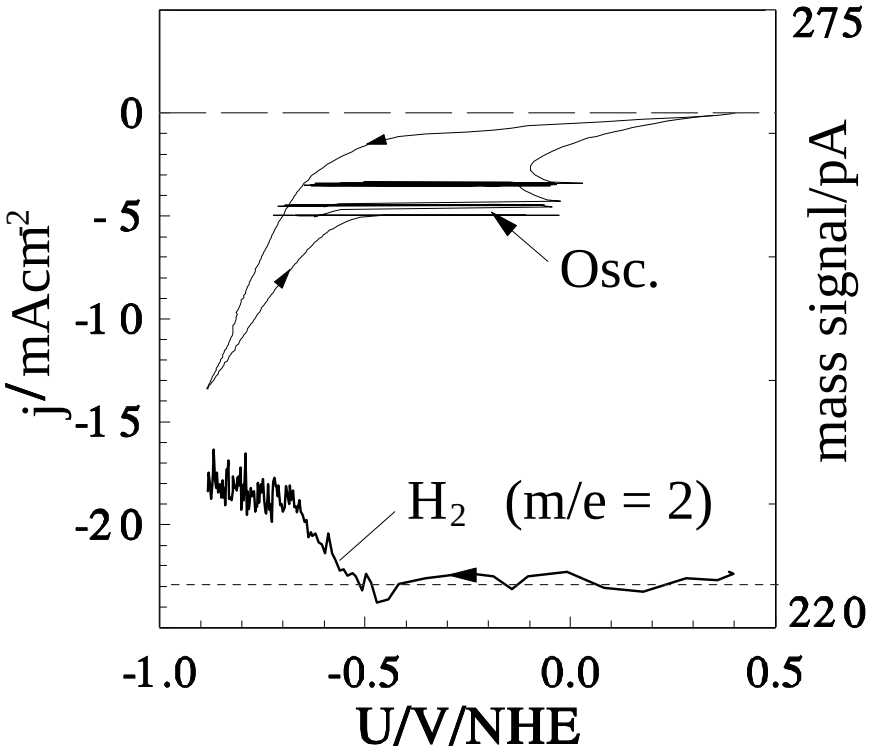

Fig. 1: Galvanostatic current-potential scan (scanrate: 10 µA/s) in the dark with simultaneously recorded hydrogen mass signal (m/e = 2). Pronounced potential oscillations in the backward scan in the region -5 mA/cm^2 < j < -3 mA/cm^2. For clarity the H_2-mass signal is only shown for the forward scan. (p-$CuInSe_2$ with polished surface / 0.5 M H_2SO_4 /0.8 M H_2O_2)

Fig. 2 shows the corresponding time series for a constant current density j= -3.5 mA/cm^2. Although the signal-to-noise-ratio is not very good it is clearly seen that the hydrogen mass signal oscillates in phase with the potential and the H_2-mass signal is reaching its maximum at the negative turning points of the electrode potential. This experiment indicates that the process of H^+-reduction is of crucial importance for the oscillation mechanism.

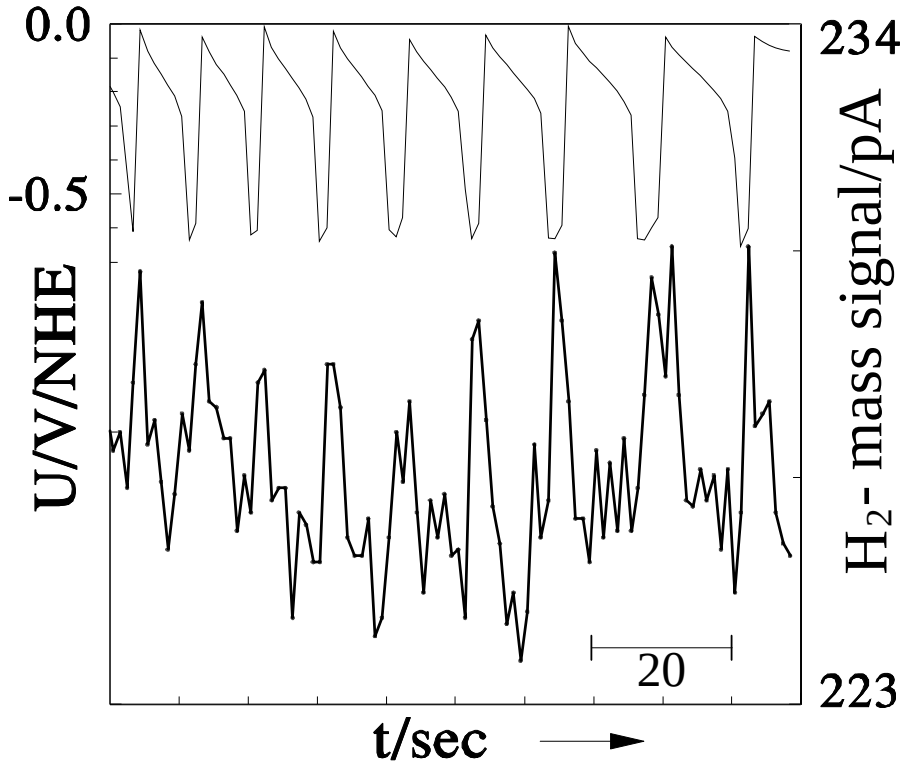

Fig. 2: Potential oscillations and corresponding H_2-mass signal versus time for a constant current density j = - 3.5 mA/cm^2 under the same conditions as in Fig.1.

We consider this as sufficient experimental evidence for a far from equilibrium periodic hydrogen evolution reaction for which the following model is suggested.

The Model

The simple but realistic model of Koper and Sluyters[9] for general electrochemical oscillations contains two differential equations:

$$C_d \frac{dU}{dt} = \frac{U_0 - U}{A \cdot R_s} - n \cdot F \cdot k(U) \cdot c$$
$$\frac{h}{2} \cdot \frac{dc}{dt} = -k(U) \cdot c + \frac{D}{h} \cdot (c_b - c) \qquad (1)$$

where U_0 is the circuit potential, U the actual electrode potential, C_d the double layer capacitance, R_s a serial ohmic resistance, A the electrode surface area, n the number of electrons transferred in one effective reaction step, F the Faraday constant, k(U) the potential dependent effective rate constant and c the concentration (in mole per unit volume) of the electroactive species at the electrode surface. The effective thickness of the diffusion layer is denoted by h, c_b is the concentration in the bulk of the solution, and D the diffusion coefficient. The first equation simply describes the conservation of current; and the second one accounts for the balance between the consumption of the electroactive species in the electrode reaction on the one hand and the diffusion of this species trough the diffusion layer towards the surface on the other hand. Here, all the adsorption and reaction kinetics is described by the effective rate constant k(U). For the example of the potential dependent adsorption of an ion which catalyzes the reaction of the electroactive species Koper and Sluyters showed the existence of a negative resistance and the possibility of sustained oscillations.[9]

The aim of this paper is to derive an expression for k(U), which contains the most relevant aspects of the oscillating hydrogen evolution in combination with H_2O_2 reduction. Firstly, we

have to take into account the processes of H_2O_2 reduction and decomposition at the electrode surface (M denotes here a free active surface site which is expected to be copper):

(i) the direct reduction of H_2O_2:

$$M + H_2O_2 + 2H^+ + 2e^- \rightarrow M + 2H_2O$$

(ii) the catalytic decomposition of hydrogen peroxide and oxygen evolution:

$$H_2O_2 + M \rightarrow H_2O + ½\ O_2 + M$$

(iii) the reduction of the dissolved oxygen (the reaction scheme is adopted from Tributsch (1975)[6]):

$$M + O_2 \rightarrow M\text{-}O_2 \quad \text{(rate determining step)}$$

$$M\text{-}O_2 + e^- \rightarrow M\text{-}O_2^-$$

$$M\text{-}O_2^- + M + H_2O \rightarrow M + HO_2^- + M\text{-}OH$$

$$M\text{-}OH + e^- \rightarrow M + OH^-$$

(iv) Secondly, the experimental results indicate the necessity to account for the hydrogen evolution: from the Volmer-Heyrowsky scheme (for the preference of this model at copper-containing electrodes see[15]) in acidic media follows:

$$M + H^+ + e^- \rightarrow M\text{-}H$$

$$M\text{-}H + H^+ + e^- \rightarrow M + H_2$$

(v) Finally, we postulate a recombination reaction of adsorbed hydrogen and hydroxyl radicals:

$$M\text{-}OH + M\text{-}H \rightarrow 2M + H_2O$$

All these processes play together a crucial role in enabling the cathodic oscillations:

- the direct reduction of hydrogen peroxide is able to maintain the relatively high current density and to introduce the diffusional time delay necessary for the so called relaxation oscillations (according to the second equation in (1));
- the hydrogen evolution reaction leads to adsorbed hydrogen, which acts as an inhibitor for the hydrogen peroxide reduction due to the decrease of free surface area;
- however, as a consequence of the Volmer-Heyrowsky mechanism of hydrogen evolution, the surface coverage of adsorbed hydrogen is changing only slightly in a wide potential range. Therefore it is necessary to take into account the competitive adsorption of OH radicals during the oxygen reduction, which can be of stronger potential dependence, and the recombination reaction with adsorbed hydrogen leading in an indirect way to a strong potential dependence of hydrogen coverage. This latter reaction step (v), in combination with (iv), not only guarantees the strong potential effect on the hydrogen coverage, but also introduces an additional instability (autocatalytic generation of free surface area) in the reaction network.

If we consider M-OH and M-H as the only relevant adsorbed species responsible for the oscillations and assume that the concentration of dissolved oxygen near the electrode surface (resulting from reaction (ii)) is always constant at the saturation concentration, then we obtain the following subset of differential equations describing the coverage kinetics:

$$\frac{dx}{dt} = k_1(U)\cdot(1-x-y) - k_2(U)\cdot x - k_3\cdot x\cdot y$$
$$\frac{dy}{dt} = k_4\cdot(1-x-y) - k_5(U)\cdot y - k_3\cdot x\cdot y \qquad (2)$$

with the Butler - Volmer equation

$$k_i(U) = k_{i,0}\cdot\exp(-\frac{\alpha FU}{RT}) \;;\quad U<0$$

Here, x(t,U) and y(t,U) denote the coverages of M-H and M-OH normalized to one, respectively. Accordingly, k_1 and k_2 are the rate constants of the Volmer-Heyrowsky scheme, k_3 is the recombination rate constant, k_4 the rate constant of the first reaction in (iii) depending on the oxygen concentration, and k_5 the rate constant for the last reaction in (iii). Further we assumed that the individual transfer coefficients α of the reactions are equal to each other. Together with the equations (1) we obtain a system of four differential equations coupled by the rate constant k(U) which is responsible for the direct hydrogen peroxide reduction (i):

$$k(t,U) = k_0 \cdot \exp(-\frac{\alpha nF}{RT} U) \cdot (1 - x(t,U) - y(t,U)) \qquad (3)$$

If we consider, for the sake of mathematical simplicity, that the recombination rate constant k_3 (which certainly is very large) will go to infinity, then the coverages x and y will become quasistationary, i.e. the equations (2) can be equated to zero. This system of two algebraic equations can now be solved independently leading to the potential dependence of the quasistationary coverages:

$$k(U) = k_0 \cdot \exp(-\frac{\alpha nF}{RT} U) \cdot (1 - x(U) - y(U))$$

with (4)

$$(x(U) + y(U)) = \left\{ \begin{array}{ll} \dfrac{k_1(U) - k_4}{k_1(U) + k_2(U) - k_4} & \text{for} \quad k_1(U) - k_4 \le 0 \\ \dfrac{k_1(U) - k_4}{k_1(U) - k_5(U) - k_4} & \text{for} \quad k_1(U) - k_4 > 0 \end{array} \right\}$$

(If k_3 is sufficiently large to maintain the quasistationarity but finite, the function x(U) + y(U) will become a smooth curve, see Fig. 3 for several numerical values of k_3.)

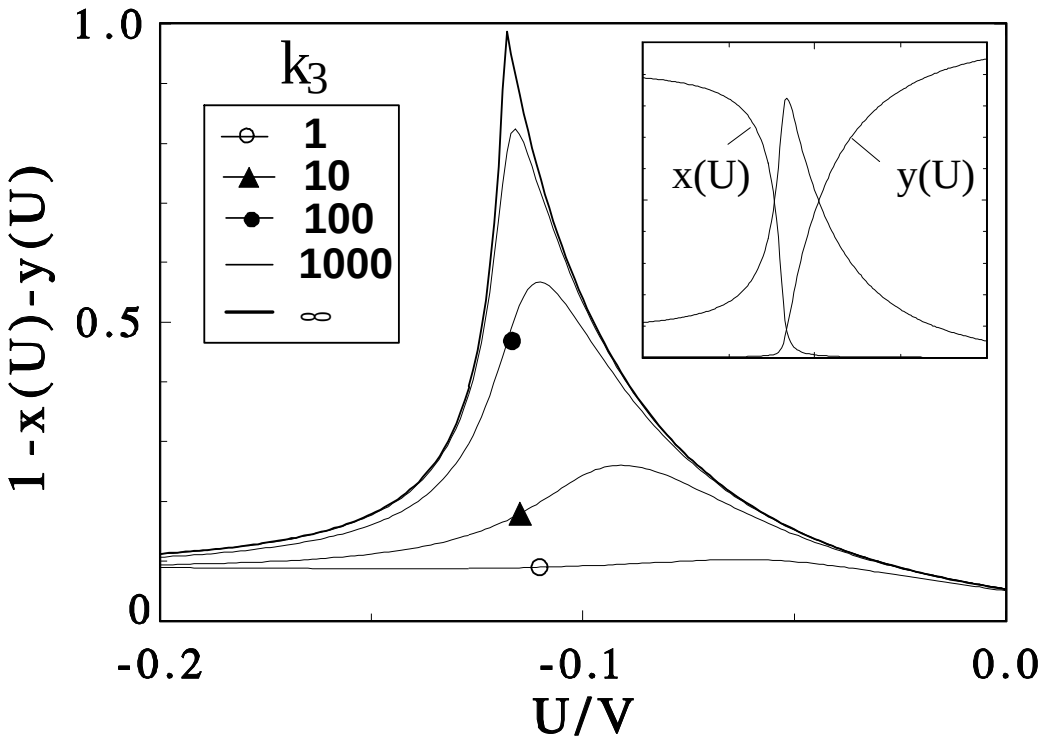

Fig. 3: Quasistationary potential dependence of the free surface 1 - x(U) - y(U) for different values of the rate constant k_3 in eq.(2). Other values used for calculation: $k_{1,0} = 1.0$, $k_{2,0} = 0.1$, $k_4 = 10$, $k_{5,0} = 0.5$, $\alpha = 0.5$. Inset: potential dependence of the individual coverages x and y for $k_3 = 1000$.

In this way we returned to the system (1), with all nonlinear kinetics (i)-(v) now concentrated in one effective rate constant k(U). This system can be solved numerically. It leads, under quite reasonable assumptions concerning the magnitude of parameters, to limit-cycle oscillations. These oscillations are, at least qualitatively, able to describe the experimentally observed ones (see the comparison in Fig. 4).

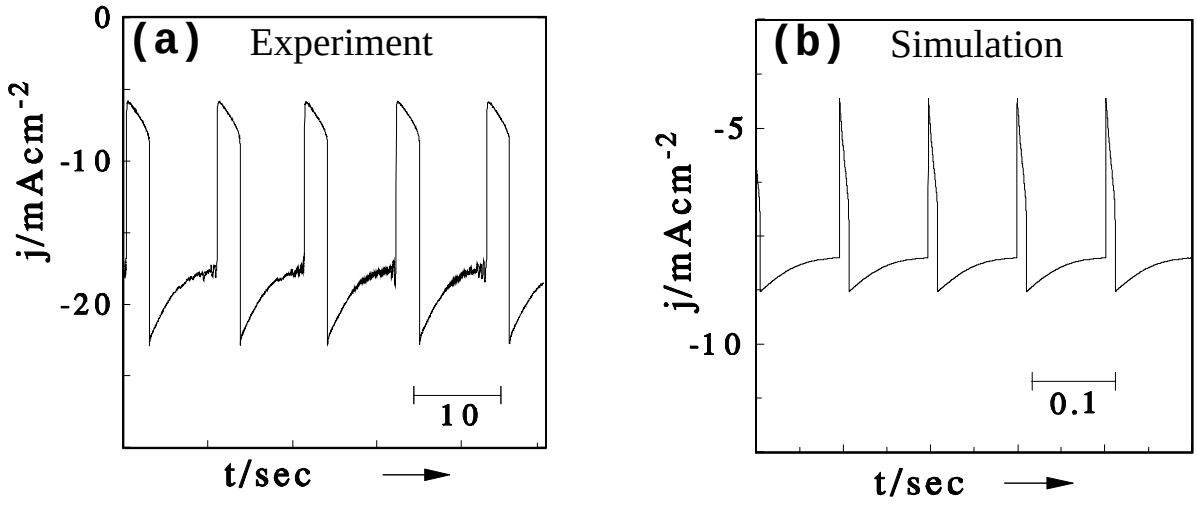

Fig. 4: Comparison between experimental and simulated potentiostatic oscillation characteristics.
(a) Experiment: p-$CuInSe_2$ / 0.5 M KCl / 0.4 M H_2O_2, pH = 9. U = - 0.55 V/NHE, R_S = 200 Ω
Polished electrode in the dark.
(b) Simulation: same values of the rate constants as in Fig. 2, and $k_s = \infty$, R_S = 200 Ω, c_b = 1 M, D = 10^{-5} cm^2/s, h = 0.012 cm, k_f = 0.17, C_d = 44 μF, A = 0.12 cm^2.

It should be noted, that the small oscillations in the experimental curve just before the sharp upjump of the current density are significant[16] and indicate the possibility of the transition to chaos through a homoclinic orbit. However, this is beyond the capabilites of our simplified two-variable model and subject to further investigations of the complete model.

Discussion

We were able to derive a relatively simple mechanistic model describing the observed relaxation oscillations during the H_2-evolution in presence of H_2O_2-reduction at $CuInSe_2$-cathodes under quite realistic assumptions. Necessary elements of the model are, beyond the

capacitive positive feedback according to the Koper-Sluyters model, the hydrogen evolution reaction as well as the recombination of adsorbed hydrogen with adsorbed hydroxyl radicals. We found that the interaction between the hydrogen peroxide reduction on the one side and the hydrogen evolution on the other is a necessary condition to reproduce the observed oscillations in the numerical model simulations. A major inaccuracy is the predicted time domain of oscillations. It may be explained by the assumption of infinitely fast synchronization of the oscillation processes parallel to the surface in the model. In reality, the propagation velocity of the reaction front will be definitely finite.

Several additional refinements of the model seem to be possible and necessary to describe more quantitatively the observed variety of oscillatory pattern: First, the full system of the four differential equations (1) and (2) should be analyzed numerically. Furthermore, the knowledge of the H_2O_2 / O_2 - reduction is very incomplete and the mechanistic steps (i)-(iii) probably have to be replaced by a better founded kinetics. But fortunately, the capability for oscillations (i.e. the negative resistance) of the presented model is very insensitive to the specific H_2O_2 / O_2 - reduction kinetics, provided any adsorbed reactive oxygen or hydroxyl species occur[11]. In this respect the hydrogen evolution reaction plays the dominating role in sustaining the oscillations. H_2O_2 could, theoretically, be replaced by another O_2-donor and by another electron acceptor.

Certainly, at this point of model refinement, the semiconductor properties of the electrode material must also be taken into account. This is especially necessary to describe photoinduced oscillations and an unexpected inverted photoeffect found in the investigated nonlinear system[10,12,17].

Another direction for the extension of the theoretical model is the consideration of a second delay process to describe the equally observed[10] chaotic and mixed-mode oscillations in the

system. This can be done by a more accurate description of the diffusion process[18], or by introducing a reversible surface reaction leading to an inactive oxidized species[19].

As outlined in other publications[2,3], new opportunities may be opened for electrocatalysis through nonlinear mechanisms of synergetic nature. (The term „synergetic“ is used to underline the co-operative behavior of nonlinear systems caused by the slaving principle of Haken.) In a situation far from equilibrium order may be built up at the expense of total entropy production. Such a local order, if it affects the molecular structure of the interface, may open new perspectives for electrocatalysis. For this reason model systems of electrochemical oscillations should receive special attention with respect to catalysis and interfacial stability[20].

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