Chaos in Activator-Inhibitor Systems

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Introduction

Chaotic behaviour has been observed in a large number of systems, including many chemical reactions. The aim of the present study is to systematically determine the mechanistic basis of chaos in chemical oscillators. The starting point are minimal oscillators containing exactly one positive feedback loop (autocatalysis, the species on which are referred to as activators) and one negative loop containing at least one additional species (referred to as inhibitor).

Results

Minimal activator-inhibitor systems have been extended using one additional species causing exactly one additional feedback loop. There are a total of 8 possibilities, namely positive or negative 2-loops consisting of the additional species and the activator or inhibitor, as well as four 3-loops with different directions and signs containing all three species. The type of feedback loops can readily be seen in the Jacobian matrix. All such combinations exhibited period doubling and chaos, hereby the systems can be classified into 2 groups depending on where the chaotic region is located in the 2-parameter bifurcation diagrams. The numerical results can be rationalized in terms of Shil’nikov orbits and the codimension-2 points from which these emerge (Takens-Bogdanov- resp. Guckenheimer-Gavrilov points). Application to realistic systems is pointed out using the oxidase-peroxidase oscillator.
Nonautocatalytic Oscillators and Olfactory Response


Introduction

In olfactory cilia, intracellular calcium oscillations have been observed which are not based on any autocatalysis such as calcium-induced calcium release (CICR), but seem to be based on direct negative regulation of cyclic nucleotide-gated channels [1,2].

Results

Using stoichiometric network analysis [3] we clarified the conditions under which nonautocatalytic oscillations can arise in (bio)chemical reaction networks. The results were applied to oscillations in cilia in a model including opening of Ca channels by cAMP, active Ca pumps and blocking of channels by Ca/calmodulin. Then a numerical 4-variable model was developed which is in quantitative agreement with experiment, both with respect to oscillations and to fast adaptation of the olfactory response. The resulting system is refractory (adaptation) without exhibiting excitability, and compared to an earlier system (CO oxidation on Pt), which can show excitability without a refractory zone [4].

References


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**Are Enzymes Molecular Machines?**

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**Introduction**

Enzymes are single-molecule protein catalysts. In the classical Michaelis-Menten view of an enzyme, enzymic action is localized in its active center, while the rest of the protein merely plays a role of a support. Modern experimental evidence suggests that catalytic turnover cycles of an enzyme may include slow functional conformational motions involving the whole protein. Such ordered internal motions, initiated by ligand binding, are not aimed to perform mechanical work, as in molecular motors. Instead, their function consists in transporting a substrate to an active center inside a molecule or in gradually approaching a molecular configuration favorable for a chemical catalytic conversion event.

Single-molecule experiments based on fluorescence correlation spectroscopy (FCS) provide a unique opportunity to monitor catalytic turnover cycles of individual enzyme molecules. Because of their complexity, such experiments have so far been performed only for several different enzymes. Applying special statistical analysis, we have earlier shown that functional conformational motions are present in the enzyme horseradish peroxidase.  

If enzymes operate as cyclic molecular machines and are allosterically activated or inhibited by their own products, a population of enzyme molecules in a micrometer-size fluid reactor can undergo a spontaneous transition to a coherent regime where turnover cycles of individual enzymes are strongly correlated (see and references therein).

**Results**

Re-examining statistical data of well-known single-molecule FCS experiments for the enzyme cholesterol oxidase, we have found that functional conformational motions were also involved in a turnover cycle of this enzyme and have constructed a theoretical model of its single-molecule dynamics. Fully stochastic numerical simulations and mean-field modeling of chemical reactions in extended spatial arrays of allosterically interacting enzymes are furthermore performed. They reveal that synchronization of single turnover cycles can spontaneously in such molecular arrays and various wave patterns of coherent enzymic activity can be observed.

**References**

Corrosion Onset as a Nonequilibrium Critical Phenomenon

L. Organ*, J. L. Hudson*, A. S. Mikhailov

Introduction

Corrosion in stainless steels develops abruptly, as temperature, salt concentration or applied potential are increased. Its onset is accompanied by the formation of metastable pits, i.e., microscopic corrosion seeds of a size of a micrometer that remain active for about a second and then undergo passivation. Each pit leads to a small spike in the total electric current. The traditional view on corrosion onset is that it proceeds through stabilization of individual pits.

About ten years ago, we have suggested\(^1\) that the principal role in the sudden corrosion onset is rather played by interactions between metastable pits, when each pits enhances the probability of appearance of a next pit on the surface. In the first phenomenological model\(^1\), spatial effects were neglected and only temporal memory of the stochastic pitting process was taken into account. The predictions of this model were consistent with the results of statistical analysis of the experimental data series for the electric current\(^2\). Subsequently, a more realistic model of corrosion onset, taking into account release and diffusion of aggressive species in a pit and weakening of the protective oxide layers in its neighbourhood, has been proposed and experiments on corrosion in spatially coupled electrode arrays were performed\(^3\).

Results

Detailed numerical simulations have been performed using the stochastic spatially extended model. They have revealed that, because of a positive feedback in this system, the corrosion onset effectively represents an autocatalytic explosion in the number of metastable pits\(^4,5\). Thus, it can be viewed as a nonequilibrium cooperative critical phenomenon. The transition to the regime of high pitting activity proceeds through propagation of the fronts, similar to the waves of spreading infection. The stabilization of pits occurs only at a later stage, when the whole surface is highly active. These theoretical predictions were tested and confirmed\(^4\) in specially designed optical microscopy experiments that were carried in our Department in a close contact between the experimental and the theoretical groups. The gained new understanding of corrosion onset in stainless steels opens a way for better control and suppression of corrosion processes.

References


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Imaging Metastable Pitting Corrosion on Stainless Steel

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Introduction
Stainless Steel is protected against corrosion by means of an oxide layer naturally forming in the presence of humidity and oxygen. But this protection may break down locally, especially when exposed to protons and chloride ions. This gives rise to the appearance of individual microscopic metastable pits which are sites having an extent of up to a few micrometers where the surface erodes locally. However, after a few seconds the oxide layer inside the pit rebuilds and the corrosion stops\(^1\). This metastable pitting process is regarded as the onset of pitting corrosion, which can lead to severe damage of the material.

In recent years there has been growing evidence that the metastable pits have spatial and temporal influence on each other, which might be mediated through the release of aggressive ions. These ions weaken the protective oxide layer and thus enhance the nucleation rate of metastable pits. Based on those assumptions a stochastic reaction-diffusion model was developed under the guidance of A. Mikhailov and J. Hudson\(^2\) (see Poster PC 3). An autocatalytic reproduction of pitting sites with front-like spreading was found in their numerical simulations\(^3\). Those results stimulated us to adopt Ellipsometry for Surface Imaging (EMSI) to the liquid/solid interface and thus to try to observe metastable pitting corrosion \textit{in situ}.

Results
We succeeded to directly visualize different aspects of the corrosion process by applying two complementary imaging methods simultaneously. While EMSI was used to detect the weakening and rebuilding of the protective oxide layer, contrast enhanced optical microscopy enabled us to follow the formation and spatial distribution of individual pits\(^4\). Recently we found an expanding region of a weakened oxide layer accompanied by a succeeding front like spreading of the pit nucleation zone and an exponential growth of the number of pitting sites. Thus, the existence of propagating fronts during metastable pitting corrosion of stainless steel could clearly be proven. The results corroborate our belief that the transition to higher corrosion rates can be explained by an autocatalytic reproduction of individual metastable pits.

References
Quantitative measurement of the deformation of ultra-thin platinum foils during adsorption and reaction of CO and O\textsubscript{2}

C. Punckt, P. Sanchez Bodega, J. Wolff, H. H. Rotermund

Introduction

An ultrathin Pt-foil with a thickness of 300 nm and 4 mm diameter has a heat capacity of only 10 µJ/K. Thus, even small amounts of heat deposited within the very thin metal foil cause a significant temperature increase. This effect was used for the microcalorimetric determination of heats of adsorption of different gases on Ni and Pt single crystal surfaces\textsuperscript{1,2}. During the adsorption of, for example, CO and O\textsubscript{2} on Pt(110) heat in the order of 200 kJ/mole is released into the metal. If the rim of a Pt(110) single crystal foil is mounted on a substrate, then a temperature difference between the substrate and the foil induced by adsorption and reaction of CO and O\textsubscript{2} can cause thermoelastic stress. This under certain conditions leads to even macroscopic deformations of the metal foil\textsuperscript{3}. It should be possible to measure the amount of heat which is released during the adsorption and/or reaction of CO and O\textsubscript{2} on a catalytic Pt(110)-foil, following the deformation of the foil quantitatively by means of interferometry. Therefore an imaging Michelson-interferometer was set up in order to detect small deformations of the ultrathin Pt catalyst down to 10-20 nm. The catalytic foil was placed in an UHV-chamber equipped with LEED and Ar\textsuperscript{+}-sputtering for sample analysis and preparation. The partial pressures of CO and O\textsubscript{2} could be controlled by the computer.

Results

The profile of the Pt(110) foil could be measured with an accuracy of about 10 nm. Adsorption of CO and O\textsubscript{2} causes a clear mechanical response of the Pt-foil. Depending on sample temperature and partial pressures of the reactants fronts and pulses of deformation were found. The system could be calibrated by using continuous and chopped laser light. A change of the optical properties of the catalytic surface in the presence of adsorbates causes difficulties which will be avoided in a future setup.

References


Combining microstructures and local addressability in a surface chemical reaction

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Introduction

The interplay of spontaneous pattern formation and heterogeneities or geometrical boundaries in nonlinear systems is a topic of intense research in many different fields ranging from catalysis to biology\textsuperscript{1-4}. Pattern-forming reaction-diffusion systems show a wealth of intrinsic spatiotemporal patterns. However, by using microstructured systems (i. e. systems with obstacles, slits, gratings, channels, labyrints etc.) it is possible to analyze the individual components of the dynamics in detail both in experiment and theory. We use microlithography to create fixed inert, no-flux, insulating boundaries on a Pt(110) single crystal and observe the evolution of pulse patterns within the remaining reactive structures under excitable conditions during the catalytic oxidation of CO. Additionally, local addressing of surface activity by means of a focussed laser beam allows for controlled initiation of single reaction waves in the experiment and also permits direct control of reaction waves that propagate on the microstructured sample.

Results

Under the condition of low excitability reaction-pulses do not appear in the experiment naturally (i. e. they do not nucleate at system-intrinsic defects) but are none the less still stable. “Artificial” pulses were generated by focussing laser light at defined locations on the microstructured sample thus establishing sufficiently strong temperature heterogeneities for puls nucleation. The propagation of these pulses was followed, and we found that due to interaction with the geometry of the applied microstructures pulses lost or gained stability. Pulses that had lost stability could be “rescued” by short shots with the laser, complete surface domains could be switched from stable to unstable puls propagation, and some microstructures showed frequency filtering properties. The experimental findings were accompanied by numerical studies with a well established three-variable model\textsuperscript{5} in the group of I. G. Kevrekidis at Princeton University.

References

Hydroxide Adsorption at Ag(hkl) Electrodes using Cyclic Voltammetry, in Situ Second Harmonic Generation, and ex Situ Electron Diffraction


Introduction
The adsorption of hydroxide on the (111), (110), and (100) faces of silver electrodes from mixed NaOH/NaF solution is investigated using cyclic voltammetry, in situ second harmonic generation (SHG) and ex situ electron diffraction. The comparison of the information obtained from each technique allows us to develop a detailed picture of the structures and electronic effects at the three low index Ag(hkl)/alkaline electrolyte interfaces.

Results
Cyclic voltammograms for the three low index silver planes in alkaline electrolytes are compared for the first time. They show two pairs of anodic and cathodic peaks in the potential interval below the equilibrium Ag/Ag₂O potential and are attributed to the specific adsorption of hydroxide ions followed by submonolayer oxide formation. The differences in the cyclic voltammograms for the (111), (110), and (100) planes are ascribed to different (i) work functions, (ii) surface atomic densities, and (iii) corrugation potentials for these surfaces. Ex situ low energy electron diffraction (LEED) and reflection high energy electron diffraction (RHEED) show that disordered adlayers are formed on Ag(111) and Ag(100). This is in contrast to Ag(110), where OH⁻ is found to be adsorbed at potentials negative of the potential of zero charge, forming small antiphase domains of c(2 x 6) symmetry. Further adsorption leads to longer-range order and the removal of antiphase domain boundaries and is associated with a current peak in the cyclic voltammogram (CV). A c(2 x 2) pattern gradually replaces the c(2 x 6) pattern as the potential, and the OH coverage, is increased. At the beginning of the second current wave, another symmetry change takes place which is accompanied by a sharp change in the LEED pattern from a c(2 x 2) pattern to a (1 x 1) pattern with strong background, indicating a disordered adlayer. However, RHEED results show that some patches of c(2 x 2) structure remain on the surface. This later effect holds also for the (100) face. The isotropic (for the (111), (110), and (100) planes) and anisotropic (for the (110) and (111) planes) contributions to the SHG intensity were calculated by fitting the experimental data and are discussed in terms of their dependence on the charge density at the interface, on hydroxide adsorption, and on submonolayer oxide formation.

References
Tip-Enhanced Raman Spectroscopy

B. Pettinger, K.F. Domke, J. Steidtner, D. Zhang

Introduction

Tip-enhanced Raman spectroscopy (TERS) is a versatile analytical tool for the detection and identification of (sub)monolayer adsorbates at single crystalline surfaces. The combinatory technique of Raman spectroscopy and scanning tunneling microscopy (STM) is based on near-field processes associated with localized surface plasmons, which are excited in the cavity between gold STM tip (in tunneling contact) and substrate. Only the adsorbates located underneath the tip apex experience the locally confined enhanced electromagnetic field and give rise to intense characteristic Raman bands.

Results

Intensive studies on the tip etching process have brought about a reproducible, rapid and easy to handle routine to produce sharp Au STM tips with a smooth surface, which are essential for the required field enhancement and localization. Typically, scanning electron microscope (SEM) images show tip radii of approximately 20-30 nm.\(^1\) In comparison to band intensities from normal Raman scattering, a more than \(10^6\)-fold enhancement is observed for TERS. Very intense scattering has been observed for malachite green isothiocyanate at Au(110), Au(111) and Pt(110) samples. For this resonant dye, about 200 molecules underneath the tip are sufficient to be ‘seen’ by TERS. The huge enhancement also permits to obtain TER signals from molecules which are not in optical resonance with the exciting laser line, such as CN\(^-\) at Au(111), thiophenole at Au(110) and Pt(110) or mercaptopyridine adsorbed at Au(111).\(^2,4\) In addition, TERS has been employed to investigate the four DNA bases and their adsorption geometry at a Au(111) surface. The spectral differences for coadsorbed adenine-thymine base pairs indicate orientational changes at the surface due to molecular interactions (e.g. H-bonding). By monitoring the ClO\(_4\)^- stretch vibration, the dependence of the TER band intensities on the distance between tip and metal substrate has been determined. For a tip radius of 20 nm, the initial TER signal drops to \(1/e^2\) within 10 nm retraction of the tip. This illustrates the very local nature of TERS. It is thus a very sensitive vibrational spectroscopy with spatial resolution in the nanometer regime, which yields both chemical and topographic information on the state of the surface (K.F. Domke, J. Steidtner, D. Zhang).

References