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Period Doubling and Chaos of Spontaneous Oscillatory Phenomena on Iron

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Summary. A new self-oscillating system introducing spontaneous oscillatory phenomena on iron in a sulfuric acid solution of hydrogen peroxide is discussed. This phenomenon can be explained by a continuous oscillation between the active and passive state of iron. Unlike other published systems that only show one-peak oscillations, the potential of iron shows highly complex dynamics: depending on the concentration of hydrogen peroxide and sulfuric acid, a period doubling and non-periodic oscillations in a self-oscillating system were observed for the first time. The reactions were analyzed by methods based on chaos theory and could finally be identified as an example of deterministic chaos.

Keywords. Oscillation; Iron; Chaos; Period doubling.

Introduction

Spontaneous oscillations in the electrode potential of certain metals are examples of pattern forming processes. These self-oscillating phenomena are caused by the rhythmic creation and decomposition of an oxide or saline layer on the metal surface. Self-oscillatory phenomena have so far been observed with iron, nickel, mercury, and cobalt. Only recently, we have reported that this phenomenon can also be observed with copper [1]. With iron, self-oscillations have been discovered in nitric acid [2], potassium chromate solution [3], and hydrogen peroxide [4]. Here, we report on spontaneous fluctuations in the electrode potential of iron hydrogen peroxide in presence of sulfuric acid.

Over the last twenty years, the focus of interest has shifted increasingly away from periodic oscillations and more towards aperiodic phenomena. In this context, the theory of chaos has established itself as a new branch of science. One of its central statements concerns the transition of a system from an ordered into a chaotic state; this may proceed either spontaneously (intermittency) or *via* cycles of period doubling, the so-called *Feigenbaum* route. An analogous behaviour has also been observed in electrochemical systems: in the context of anodic dissolution of nickel under galvanostatic conditions, *Lev et al.* have discovered period doubling and chaotic oscillations in the electrochemical potential [5]. *Basset* and *Hudson* have observed similar patterns by measuring the corrosion current of the anodic

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polarization of copper in hydrochloric acid under potentiostatic conditions [6]. On the other hand, as far as spontaneously occurring oscillations in the electrochemical potential are concerned, only one-peak oscillations are known to date. This paper deals with a method for the production of complex self-oscillations in the electrochemical potential of a new system: iron in a solution of hydrogen peroxide and sulfuric acid.

Results and Discussion

Spontaneous oscillatory phenomena on iron are caused by cyclic passivation and activation of the metal surface. This results in the periodic build-up and decomposition of an oxide layer. In order to generate these oscillations, the potential of iron must be brought close to its passivation potential E_p. This can be achieved either by anodic polarization or by a suitable oxidizing agent in the electrolyte. Moreover, the electrolyte needs to contain a corrosively acting component which causes the redissolution of the oxide layer. In contrast to previously described systems in which periodic self-oscillations occur, the potential of iron in a sulfuric acid solution of hydrogen peroxide reveals far more complex dynamics.

Figure 1 depicts the behaviour of the potential of iron *vs*. time in a motionless sulfuric acid solution of hydrogen peroxide ($c(H_2SO_4) = 0.13\,mol \cdot dm^{-3}$). After an initial transient time the potential values oscillate periodically between a peak value of 0.53 V and a minimum of 0.2 V, which is characteristic for a one-peak oscillation. The corresponding attractor, reconstructed by the time-delay method [7], represents a closed orbit in the two-dimensional phase space (Fig. 2). The fluctuations in the potential are accompanied by an intense development of gas which can be observed every time a potential minimum is reached.

A change in the composition of the electrolyte leads to a change in the dynamics of the oscillation: Fig. 3 shows the potential values of an iron electrode in a sulfuric acid solution of hydrogen peroxide ($c(H_2SO_4) = 0.13\,mol \cdot dm^{-3}$). A relatively short transient time is followed by uniform oscillation of two periodically alternating peak values (0.5 and 0.39 V) and two minima (0.2 and 0.28 V). The time course of the iron potential has adopted the characteristics of a two-peak oscillation. The reconstructed attractor of this oscillation shows two distinctly

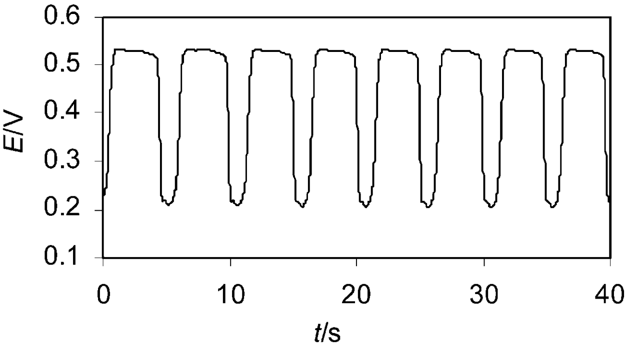

Fig. 1. Spontaneous one-peak oscillation in the potential of iron in a sulfuric acid solution of hydrogen peroxide; $c(H_2SO_4) = 0.13\,mol \cdot dm^{-3}$, $c(H_2O_2) = 0.81\,mol \cdot dm^{-3}$, ambient temperature

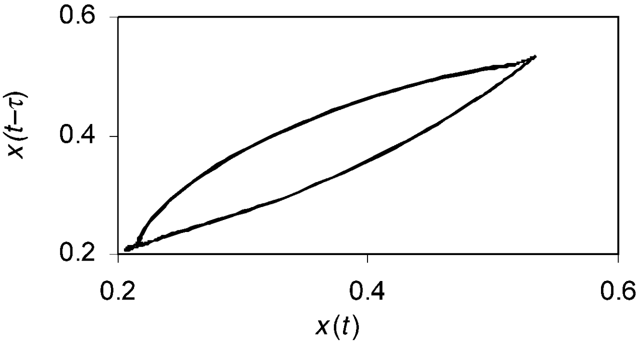

Fig. 2. Application of the time-delay method to the data of Fig. 1; $\tau = 0.06$ s

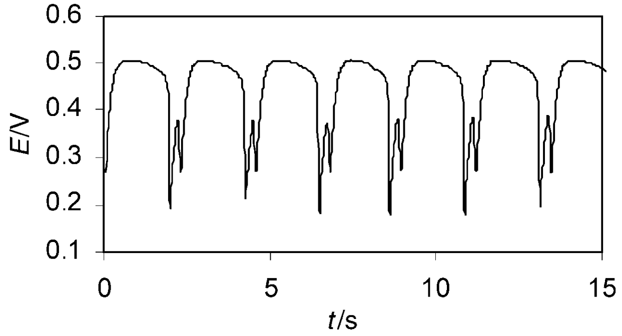

Fig. 3. Spontaneous two-peak oscillation in the potential of iron in a sulfuric acid solution of hydrogen peroxide; $c(H_2SO_4) = 0.13\,mol \cdot dm^{-3}$, $c(H_2O_2) = 1.16\,mol \cdot dm^{-3}$, ambient temperature

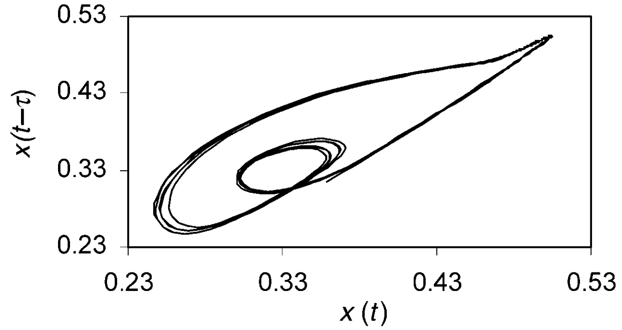

Fig. 4. Application of the time-delay method to the data of Fig. 3; $\tau = 0.04$ s

separated orbits in the phase space (Fig. 4). Two-peak oscillations can also be obtained from solutions of the following composition: $c(H_2SO_4) = 0.13\,mol \cdot dm^{-3}$, $c(H_2O_2) = 1.28\,mol \cdot dm^{-3}$; $c(H_2SO_4) = 0.11\,mol \cdot dm^{-3}$, $c(H_2O_2) = 1.05\,mol \cdot dm^{-3}$; and $c(H_2SO_4) = 0.14\,mol \cdot dm^{-3}$, $c(H_2O_2) = 1.4\,mol \cdot dm^{-3}$.

As shown in Fig. 5, a suitable change in the composition of the electrolyte may lead to period doubling. The recurrent period in this sulfuric acid solution of hydrogen peroxide ($c(H_2SO_4) = 0.15\,mol \cdot dm^{-3}$, $c(H_2O_2) = 1.51\,mol \cdot dm^{-3}$) now consists of four different peaks (four-peak oscillation), from which four separate

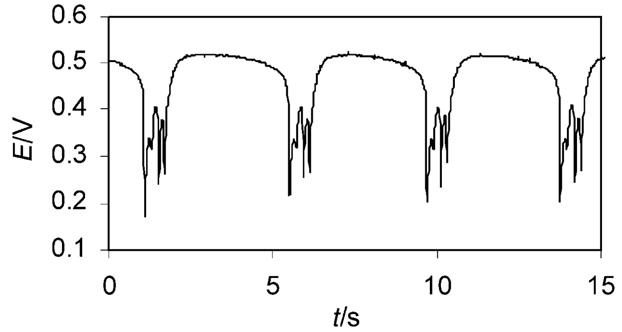

Fig. 5. Spontaneous four-peak oscillation in the potential of iron in a sulfuric acid solution of hydrogen peroxide; $c(H_2SO_4) = 0.15\,mol \cdot dm^{-3}$, $c(H_2O_2) = 1.51\,mol \cdot dm^{-3}$, ambient temperature

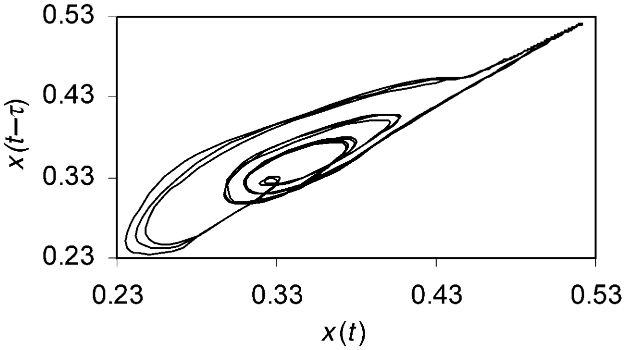

Fig. 6. Application of the time-delay method to the data of Fig. 5; $\tau = 0.02\,s$

orbits result in the phase space (Fig. 6). Four-peak oscillations have also been obtained from solutions of the following composition: $c(H_2SO_4) = 0.145\,mol \cdot dm^{-3}$, $c(H_2O_2) = 1.45\,mol \cdot dm^{-3}$ and $c(H_2SO_4) = 0.13\,mol \cdot dm^{-3}$, $c(H_2O_2) = 1.28\,mol \cdot dm^{-3}$. Moreover, we have also observed the phenomenon of an eight-peak oscillation.

Under specific conditions in the concentration of the electrolyte, *e.g.* $c(H_2SO_4) = 0.165\,mol \cdot dm^{-3}$ and $c(H_2O_2) = 1.51\,mol \cdot dm^{-3}$, exceptional dynamics of the oscillation are observed (Fig. 7). In contrast to the experiments described above, no order in the periodicity can be observed. Apparently, the potential values oscillate randomly between 0.05 and 0.52 V. In order to determine if this is based on a stochastic process or on chaotic behaviour, an analysis of the data was performed.

The frequencies corresponding to the harmonic oscillations are identified in a power spectrum, and their contribution to the total attraction is calculated [8]. Whereas periodic time series exhibit only a small number of sharp pulses, random and chaotic time series are characterized by a wide-range spectrum. The use of the power spectrum thus allows to distinguish between periodic and aperiodic behaviour. Figure 8 depicts a relatively wide-ranging power spectrum obtained from the experimental data in Fig. 7. With this information at hand, the presence of aperiodic dynamics can be deduced.

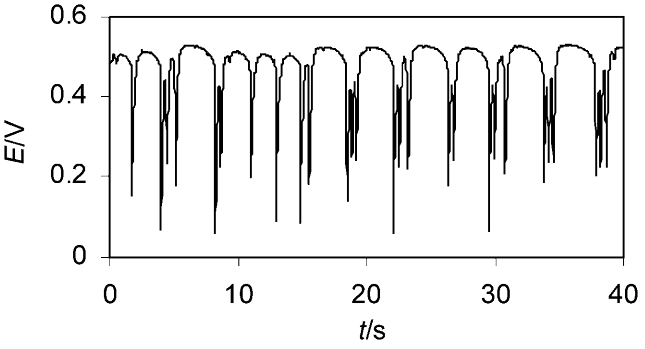

Fig. 7. Chaotic oscillation in the potential of iron in a sulfuric acid solution of hydrogen peroxide; $c(H_2SO_4) = 0.165\,\mathrm{mol \cdot dm^{-3}}$, $c(H_2O_2) = 1.51\,\mathrm{mol \cdot dm^{-3}}$, ambient temperature

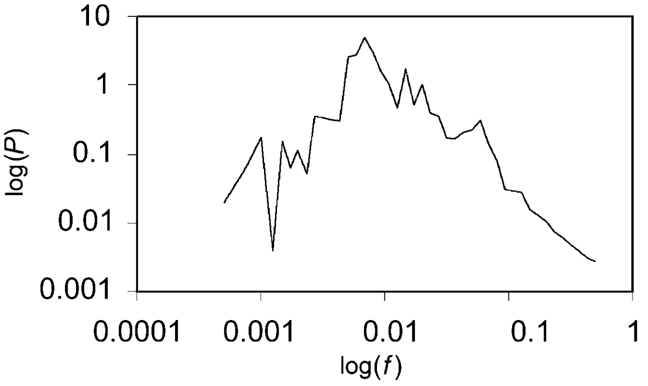

Fig. 8. Power spectrum derived from the experimental data of Fig. 7; *P*: spectral density function, *f*: frequency

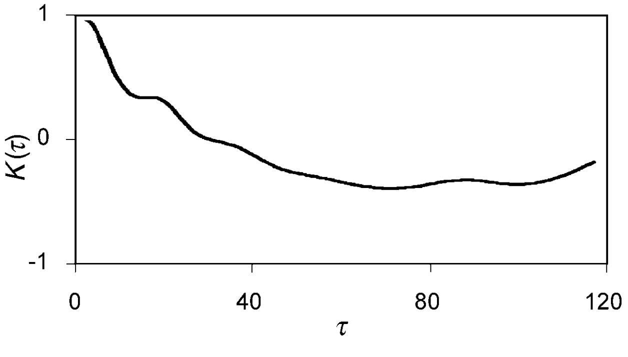

Fig. 9. Autocorrelation function *K* from the time series of Fig. 7

Figure 9 shows the autocorrelation function from the time series of Fig. 7. The correlation function provides a means of determining to what extent separate values depend on their neighbouring points. Accordingly, stochastic data exhibit no correlation, and, with no delay-factors, the function abruptly intersects the zero line. The autocorrelation function of the experimental data in Fig. 9 intersects the

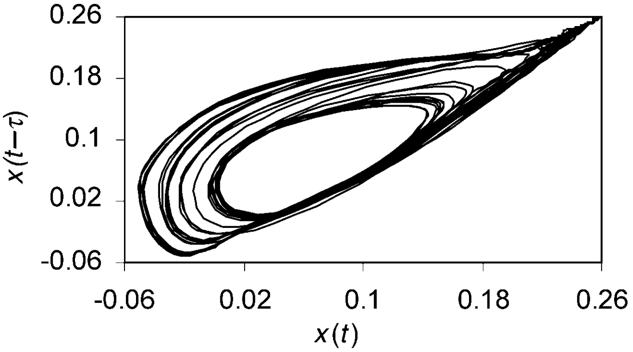

Fig. 10. Application of the time-delay method to the data of Fig. 7; $\tau = 0.06\,\mathrm{s}$

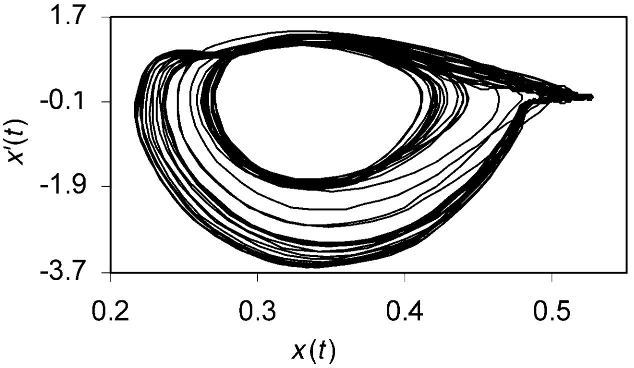

Fig. 11. Application of the differentiation method to the data of Fig. 7

zero line relatively late and therefore proves the non-statistical nature of the experimental values.

With the aid of the time-delay-method and the differentiation method [7], two-dimensional attractors have been reconstructed (Figs. 10, 11). In both diagrams, the values are located on specific orbits in a limited area of the phase space. Again, this shows the existence of a determined chaotic movement rather than a stochastic set of data.

In order to describe the expansion in space of the chaotic attractor, the behaviour of the correlation dimension D with a growing embedding dimension n was investigated (Fig. 12). Whereas the correlation dimension for stochastic data increases linearly with the embedding dimension ($D \geq 5$), Fig. 12 shows – typically for chaotic sets of data – that the values of D experience a saturation with increasing n. Extrapolation to $n = 0$ results in a value of 1.178 for D.

Cause and mechanism of the oscillations

The fluctuations in the potential can be interpreted as an alternating passivation and activation of the iron electrode. To begin with, the active iron dissolves as follows:

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e}^{-} \tag{1}$$

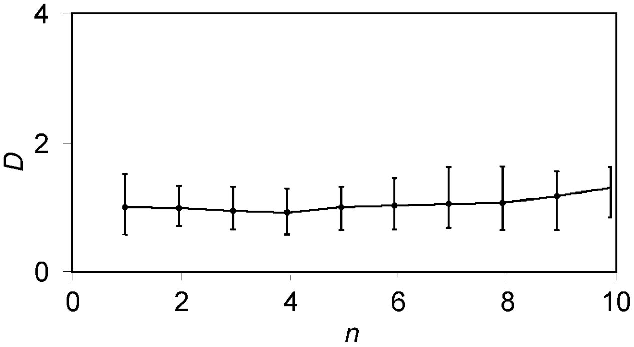

Fig. 12. Mapping of the correlation dimension D *vs*. embedding dimension n for the time series of Fig. 7

The cathodic partial reaction is the reduction of hydrogen peroxide in an acidic environment:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{2}$$

This oxidizing reaction leads to an increase in positivity of the iron potential. Its potential establishes itself at a value which at first lies below the passivation potential E_p. The reduction of the hydrogen peroxide is accompanied by a dissipation of the hydrogen ions, which leads to a *pH* increase in the phase-boundary area of the electrode. This effect is intensified even more by a displacement of the hydrogen ions caused by the accelerated dissolution of iron (Eq. (1)). Consequently, the *pH*-dependent passivation potential E_P ($E_P = 0.58 - 0.059 \cdot pH$ [10]) drops too until the potential of the formation of γ-iron(III) oxide is reached [11].

$$2Fe + 3H_2O \rightarrow \gamma\text{-}Fe_2O_3 + 6H^+ + 6e^- \tag{3}$$

The passivation is accompanied by an increase in the potential of iron. Since the oxide layer is conductive, yet impermeable for ions or particles, it inhibits the active dissolution of iron according to Eq. (1). At the same time, the formation of the covering layer inhibits itself, since no more water molecules are able to reach the iron surface. Moreover, because the electron-producing oxidation of iron is prevented, the reduction of hydrogen peroxide according to Eq. (2) comes to a standstill. Consequently, no more hydrogen ions are being consumed or displaced. Thus, the concentration gradient between the phase-boundary area and the core of the electrolyte is compensated, and the protective layer slowly dissolves:

$$\gamma\text{-}Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O \tag{4}$$

The iron electrode has now reached the active state again. Therefore, the potential drops to a lower value, and the cycle is passed through again.

The intense development of gas observed on the iron electrode is caused by the liberation of oxygen in the decomposition of hydrogen peroxide:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{5}$$

This decomposition is catalyzed by the active iron surface in accordance with the *Haber-Weiss* mechanism [12].

Outlook

Currently we are investigating to what extent a variation of the electrolytic solution, *e.g.* by the addition of chloride ions, has an effect on the potential values of iron in a sulfuric solution of hydrogen peroxide. In this context, the chloride ion is of particular significance, since its corrosive effect has a considerable impact on the dynamics of the oscillation. Furthermore, we have succeeded to create potential waves on long rods of iron which, owing to locally occurring currents, propagate along the entire rod in analogy to the behaviour of rods of copper in a hydrochloric acid solution of hydrogen peroxide reported recently [1]. Another amazing phenomenon arises from the galvanic coupling of self-oscillating electrodes: batteries creating an alternating current are obtained. We are currently carrying out further investigations in this field.

Experimental

An iron rod (purity: 98%; supplier: Goodfellow) with a diameter of 3.2 mm was used as the working electrode. For all measurements, the electrode was immersed into the respective electrolyte solution over a length of 1.2 cm. Whereas one-, two- and four-peak oscillations were easy to reproduce, determined chaotic movements occurred less often. The potential on the iron electrode was registered by a computer aided detection system. A silver/silver chloride electrode was used as the reference electrode, and all potential values stated refer to the standard hydrogen electrode. The recording frequency was 100 Hz. For data logging, the 12 bit A/D converter ADG 12 and the accompanying ELV-Graphs software for the ADG 12 (both supplied by ELV-GmbH, Postfach, D-26787 Leer, Germany) were used.

The experimental data in this work were analyzed with the aid of the following software: Chaos Data Analyzer, IBM PC Version 1.0, 1992 (contact: *J. C. Sprott*, University of Wisconsin, Madison, WI-53706, USA) and Benoit 1.3, TruSoft Int'l Inc. (Contact: www.trusoft-international.com).

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