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An Electrochemically Induced Oscillatory Instability

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We report current oscillations during the potentiostatic oxidation of iodide in aqueous solution. The oscillations become visible as columns of descending liquid with periodic structure colored by iodine (or iodine−starch complex). They can be attributed to a periodically varying flow of solution in front of the electrode due to a density gradient. The instability is explained using a qualitative model with a threshold function for the onset of the flow.

Introduction

Self-organized oscillatory and spatio-temporal concentration patterns in liquids may result from instabilities caused by a physical, or a chemical mechanism, or a combination of both. In physics, pattern formation in hydrodynamic systems which have a rather high extension in space are commonly found.[1] These patterns can be the result of an unstable density gradient. Such an unstable density gradient can be caused, e.g., by temperature,[2] chemical concentrations,[3] or a nonhomogeneous distribution of microorganisms[4−6] leading to surprisingly similar patterns. Additionally, systems with stable density gradients are also able to exhibit pattern formation due to double-diffusion effects.[7,8] A well-known example is the observation of so-called “salt fingers” in a system consisting of a salt solution with a stable density gradient but an unstable temperature gradient.[7]

In chemical and biochemical reaction systems, oscillations and concentration patterns in unstirred solutions are known to result from reaction kinetic instabilities.[9,10] These instabilities arise most commonly from feedback loops in the system, e.g., involving autocatalysis or substrate inhibition. Several oscillatory electrocatalytic reactions are known but the formation of self-organized spatial patterns can be hindered, e.g., by the application of stirring (as during the reduction of hydrogen peroxide[11]); gas bubble formation (as during the oxidation of formic acid[12]); or the deposition of some intermediate (as during the reduction of hydrogen in the presence of copper ions,[13] and during the reduction of indium(III) in the presence of SCN^- [14]).

Often the physical and chemical nature of the instability cannot be separated easily. For instance, chemical or biochemical reactions which lead to the production of a layer of liquid with higher density above a liquid layer with lower density are able to create plumes and spatio-temporal patterns.[15−17] Typical examples for such reaction systems are those which work via catalysis, with the catalyst being located above some volume of the reactants. An important implementation are electrochemical setups, where an electrode which produces a product is hung into the solutions of the reactants. In a particular electrochemical system with an electrode which is extended in space, pattern formation due to Rayleigh-Bénard instabilities was observed.[18] Electrochemical systems are frequently studied, since they are of importance in many industrial production processes.

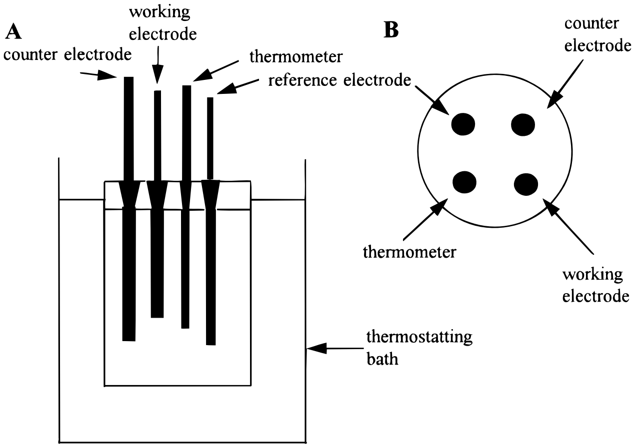

Figure 1. Electrochemical setup.

We study the electrochemical oxidation of iodide and report oscillations in the production of iodine under certain conditions. We are able to correlate the oscillatory behavior and the shape of the descending liquid containing the products. A qualitative model is used to explain the observations.

Experimental Section

The reaction solution contains potassium iodide in deionized water. For better visualization, soluble starch (Merck) is added to a final concentration of 500 mg/L. The cylindric reactor (content 500 mL, height 10 cm) is filled to the top (no free surface) and is thermostated for at least 1 h (20 °C) and left undisturbed for at least 30 min to rule out liquid movement prior to the experiment. The working electrode is positioned horizontally into the solution from above. The active area is a platinum disk (∅ 0.2 cm) surrounded by cylindric Teflon coating (∅ 1.1 cm, see Figure 3). The current is measured at a constant potential (+500 mV vs SCE) versus a platinum counter electrode (Figure 1).

Results

An experiment is started with a potential jump from zero to +500 mV. Figure 2 shows the recording of the current as a function of time for a 20 mM iodide solution. Following the sharp increase after the potential is applied the current drops first to a level of approximately 60 μA, and thereafter slowly

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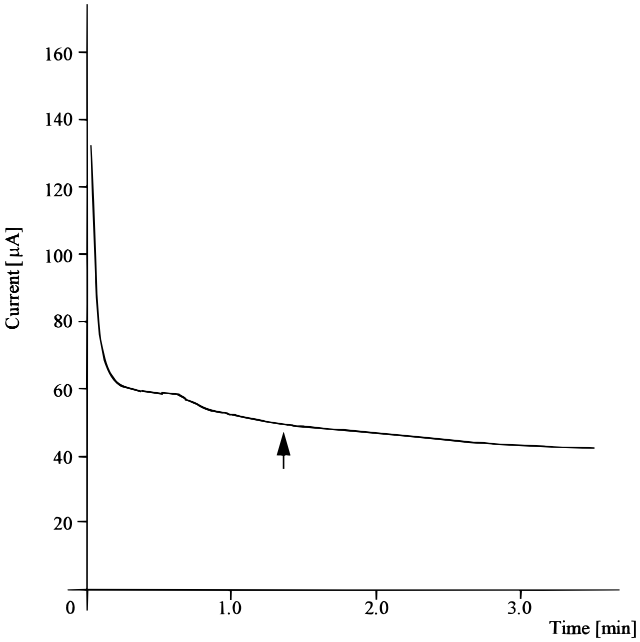

Figure 2. Chronoamperometry of a 20 mM solution of iodide for a potential of +500 mV (vs SCE).

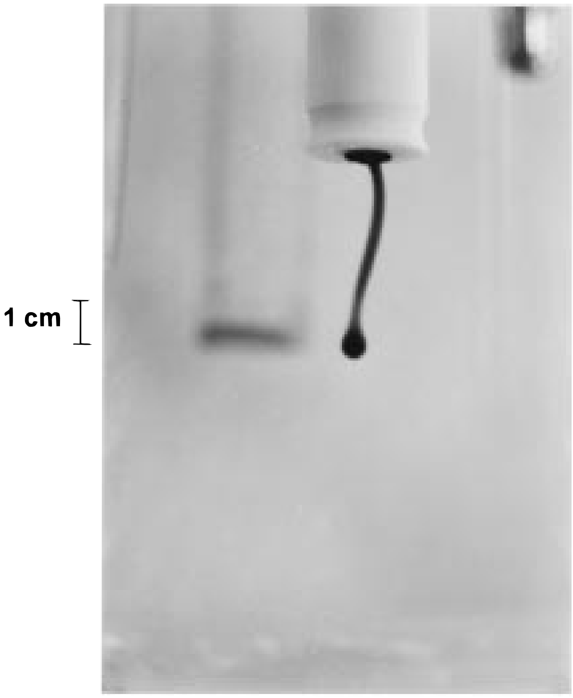

Figure 3. Picture of the solution of the experiment in Figure 2 taken at the time indicated by the arrow.

decreases further. In the long run the current remains on a level higher than 40 μA. During this potentiostatic experiment the production of iodine at the working electrode becomes visible due to the formation of blue iodine−starch complex. Immediately after the start of the reaction a disk of blue iodine−starch complex appears at the electrode. Shortly thereafter, the complex starts to sink forming a liquid column. At the time indicated by the arrow in Figure 2 a picture was taken (Figure 3). It can be seen that the column has a droplike tip and otherwise an even diameter. In the course of the experiment the length of this column increases. The column could be maintained until the experiment was stopped.

In another experiment the same potential is applied to a 200 mM solution of iodide and the current recorded (Figure 4). Following the strong initial increase the current again drops to approximately 60 μA. This time, however, it then starts to increase strongly and in an oscillatory mode reaches a mean level of approximately 400 μA. The oscillation has a nearly constant frequency ($\approx$0.1 s^{-1}), the amplitude is slowly modulated. The oscillation is maintained during the rest of the experiment (which lasted 10 min). As described for the above experiment the formation of blue iodine−starch complex at the electrode is observed after the start of the experiment. Shortly thereafter, the complex starts to sink again forming a column of blue complex. Parallel to the recorded current oscillations the oscillatory formation of bulges of product at the electrode is observed. Whenever the current increases during an oscillation a bulge of blue complex detaches from the electrode and sinks together with the column at a steady velocity. Whenever the current decreases during the oscillations, the diameter of the column at the electrode is substantially smaller. Figure 5a shows a picture taken at the current minimum indicated by the arrow in Figure 4. Figure 5b was taken at a current maximum during the oscillation in another experiment under the same conditions. A new node is about to detach from the electrode.

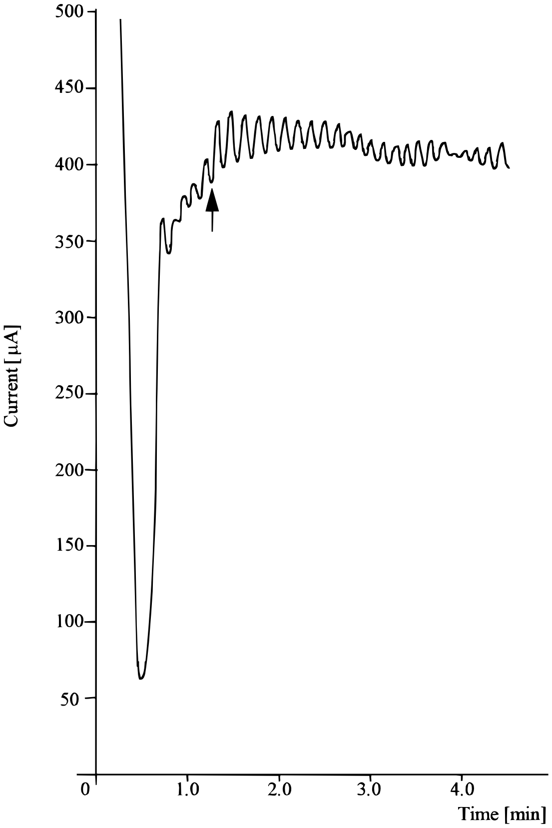

Figure 4. Chronoamperometry of a 200 mM solution of iodide for a potential of +500 mV.

The oscillatory behavior is reproducible, and the frequency varies only slightly. The modulations of the amplitude differ in each case and we also observed periodic oscillations with nearly constant amplitude. Figure 4 is a typical result. The experiments were repeated without addition of starch and the results were equivalent, namely, an approach to a constant nonzero level of the current for low concentration of iodide and high-level current oscillations for high iodide concentration. Even in these cases the columns are visible (due to the color of iodine in water). As before, during the current oscillations nodes are formed in the columns.

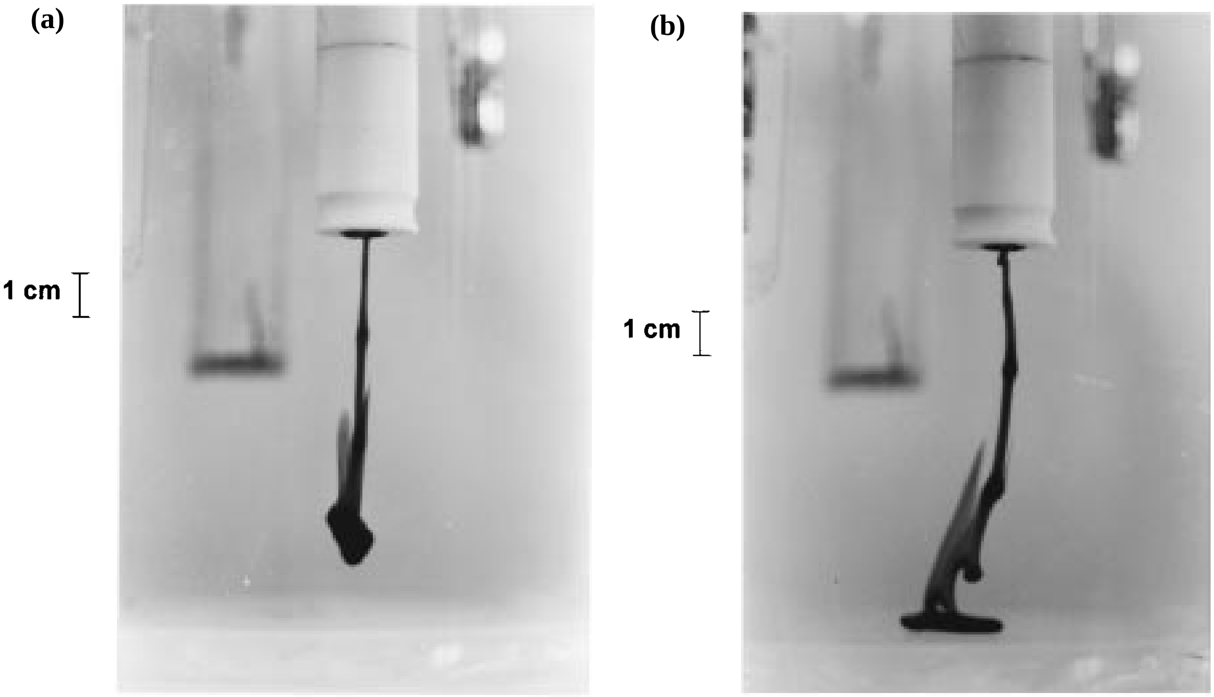

Figure 5. (a) Picture of the solution of the experiment in Figure 4 taken at the time indicated by the arrow. (b) Picture of the solution (conditions as in Figure 4) taken at a current maximum of the oscillation. The iodine flow has already reached the ground of the reactor (bottom of the figure).

Cyclic voltammograms were recorded with a 100 mM solution of iodide in the potential range between +100 and +700 mV at scan rates of 20 and 5 mV/s, respectively. At a scan rate of 20 mV/s, the oxidative branch of the voltammogram shows an abnormally high peak current as compared to the reaction−diffusion case (in the absence of any convection). At a scan rate of 5 mV/s, again the oxidation of iodide shows an abnormally high peak current. On the reductive branch of the voltammogram oscillations of the current are visible in the potential range where oxidation of iodide occurs (from +650 to +400 mV).

In the experiments the products sink at a velocity in the range of some centimeters per minute. Both the steady state and the oscillatory flowing column reach the bottom of the vessel (about 4 cm below the surface of the electrode) without being significantly disturbed. This indicates a purely laminar hydrodynamic flow below the onset of the hydrodynamic oscillatory instability. This leads us to assume that the cause of the oscillatory instability is located near the electrode.

An oscillatory instability with a 200 mM iodide solution was also recorded with a gold electrode as working electrode (other conditions as in Figure 4). As with the platinum electrode the amplitude of the oscillations first increases as a function of the applied potential and then saturates. With glassy carbon as electrode material adsorption processes interfere with the oxidation of iodide and consequently neither a convection-enhanced steady state nor an oscillation is observed.

Oscillatory current behavior was also recorded during the potentiostatic reduction of 7 mM *p*-benzoquinone in 100 mM acetate buffer, pH 5.0 at 19° C.[19] In contrast to the anodic oxidation of iodide these oscillations are strongly irregular, yet they maintain a constant mean level of current. At concentrations above 10 mM benzoquinone, a stable enhanced steady state was found. In these cases products and plume formation are only visible at high concentrations where no oscillations occur.

To develop an understanding of the source of the observed instability we developed a simple qualitative model of the system. The basis of this model is the fact that the substrate (iodide) has a larger diffusion coefficient than the product (iodine or iodine/iodide complexes, respectively). Due to this difference a volume of higher density develops in the vicinity of the working electrode. If the density of this volume reaches a critical value the onset of a convective flow can be assumed. Specifically, we divide the solution into three compartments which are treated as spatially homogeneous. One compartment models the volume in front of the working electrode where substrate is consumed and product is formed. A second compartment models the space beneath the first one, where no reaction takes place. The third compartment represents the bulk volume with an assumed constant concentration of substrate and no product. The model then consists of four coupled differential equations for the evolution of the concentration of substrate (X) and product (Y) in the compartments:

$$\begin{aligned}
\dot{X}_1 &= -2kX_1 + l(X_0 - X_1) + D_x(X_0 + X_2 - 2X_1)\\
\dot{Y}_1 &= kX_1 + l(Y_0 - Y_1) + D_y(Y_0 + Y_2 - 2Y_1)\\
\dot{X}_2 &= l(X_1 - X_2) + D_x(X_0 + X_1 - 2X_2)\\
\dot{Y}_2 &= l(Y_1 - Y_2) + D_y(Y_0 + Y_1 - 2Y_2) \qquad (1)
\end{aligned}$$

where k is the rate of the electrochemical reaction, D_x and D_y are the respective diffusion coefficients, and l is defined as

$$l = v(X_2 + 2Y_2 - X_0 - 2Y_0 - b + |X_2 + 2Y_2 - X_0 - 2Y_0 - b|)$$

X_1 and Y_1 are the respective concentrations in the reaction compartment. X_2 and Y_2 are the respective concentrations in the compartment below where only diffusion takes place. X_0 and Y_0 are the constant concentrations of substrate and product in the bulk solution. The nonlinearity introduced by the piecewise linear function l represents the onset of convection in a phenomenological way.

$$(X_2 + 2Y_2 - X_0 - 2Y_0)$$

is the difference in density between the second compartment and the bulk solution. Beyond a critical value b of this difference convection sets in. Parameter v represents the slope of the rate of convection. A (downward) convective flow is assumed to be followed by a flow of bulk solution to the first compartment (the space in front of the electrode). In the diffusion-limited case (as in the experiment) the concentration of the electroactive species is considered zero at the electrode. Assuming a linear concentration gradient in the immediate neighborhood of the electrode, the current is proportional to $\Delta X = X_1 - X_{\text{electrode}} = X_1$.

Investigating the model (with $D_x > D_y$) we find that similar to the experiment in Figure 2 for certain sets of parameters the concentration X_1 drops to a finite steady-state value associated with a steady convective flow (Figure 6a). If the bulk concentration of substrate (X_0) is increased X_1 drops to a higher level associated with a stronger convective flow. In this case the former steady state has become unstable in a Hopf bifurcation resulting in periodic oscillations of X_1 (Figure 6b).

Discussion

The potentiostatic oxidation of iodide in aqueous solution leads to current oscillations under certain conditions. A prerequisite for these oscillations is the onset of a convective flow of liquid in front of the working electrode. In the present system the convection is visible due to the color of the product of the oxidation. In experiments with a constant nonzero steady state the convective flow forms a column of approximately even thickness (Figure 3). The origin of the convective flow can be explained as follows. Iodine and the iodide−iodine complexes have a lower diffusibility compared to iodide. Due to this difference iodide diffuses (comparatively) quickly to the anode while the products diffuse away from it (comparatively) slowly. Therefore, products accumulate and the density of the solution in front of the anode increases after the start of the reaction. As a consequence at some point a plume detaches. This convective instability is due to an unstable density gradient.

Superimposed on this first instability a second, oscillatory instability is observed at higher concentrations of iodide in the bulk solution. During oscillatory current behavior bulges of product are formed and detach from the electrode shaping a product column with distinct patterning (Figure 5a). There is a close correspondence between recorded current and the visible patterning of the convective flow. From these observations it is evident that the oscillatory instability originates at the electrode and is not a hydrodynamic instability of the flowing product column.

On the basis of these features of the experimental system we have proposed a qualitative model to illustrate a possible mechanism for the occurrence of the observed oscillatory instability. The model strongly simplifies the contributions from reaction and diffusion. The electrochemical oxidation of iodide does not appear to contain steps which are known to create dynamic instabilities (like autocatalysis or feedback inhibition). Furthermore, since the potentiostatic experiments reach a nonzero steady state or mean value of the current, respectively, and the cyclic voltammogram confirms the contribution of factors other than reaction and diffusion, we include convection as an important component of the model. Since the contribution from diffusion is generally approximated by linear equations and we are primarily interested in focusing on the crucial nonlinearity for the oscillations we reduce the spatially extended model (partial differential equation) to a finite set of ordinary differential equations.

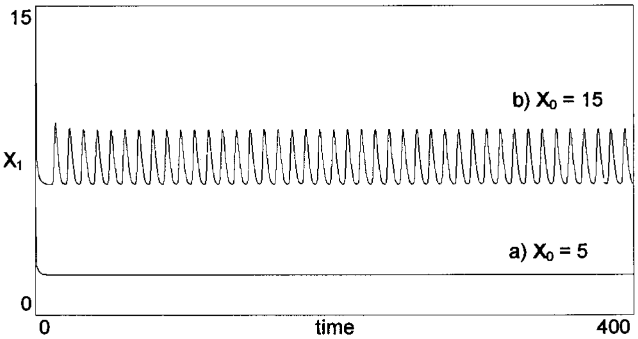

Figure 6. Simulations of the model eq 1 with $D_x = 0.3$, $D_y = 0.1$, $k_1 = 0.3$, $v = 0.15$, $b = 5$. (a) $X_0 = 5$, $Y_0 = 0$, (b) $X_0 = 15$, $Y_0 = 0$. Initial conditions: $X_1 = X_2 = X_0$ and $Y_1 = Y_2 = 0$. description.

With this model (eq 1) we are able to simulate the transition from steady state to oscillatory behavior as a function of the initial concentration of electroactive substrate. In the absence of convection or with constant convective contribution the model is not capable of generating oscillations. Therefore, in the model, the introduction of the piecewise linear threshold function is the necessary nonlinear prerequisite for the dynamic instability. The piecewise linear function can be replaced by an appropriate continuous nonlinear function without loss of the model's capability to generate oscillatory solutions.

The ratio of the diffusion coefficients $D_{\text{iodide}}/D_{\text{triiodide}}$ is approximately 2 (see ref 20), but it is known that in the presence of excess iodine the fast and reversible formation of short polyiodine chains (due to the cooperativity of ion-induced dipole interaction) will increase this ratio.[21,22] For the diffusion coefficients a ratio of 3 was assumed in the simulations of Figure 6, although in the model the oscillatory instability is also found with ratios less than 2. We have simulated a two-dimensional reaction−diffusion system with localized kinetics as in the experiment and with diffusion coefficients $D_{\text{iodide}} = 1.2 \times 10^{-5}$ cm^2/s and $D_{\text{iodine}} = 2.0 \times 10^{-5}$ cm^2/s.[20] Such a system reproduces both the geometry of product formation and the temporal scales of the experiment before the onset of convection. Thus a realistic set of equations to describe the experiment quantitatively can now be worked out.

The exact nature of the threshold in the experiment is unknown. However, there is some evidence that the products of the reaction (the iodine−iodide complexes) can be retained at the positively charged electrode by electrostatic attraction and/or adsorption. Since iodine−iodide complexes easily form growing chains of iodine−iodide with increasing iodine concentration (i.e., I_3^-, I_5^-, I_7^-, etc.[21,22]), the electrostatic attraction per molecule remains the same while the density of the product layer increases until the electrostatic attraction (the threshold) is overcome and convection sets in.

Spatial pattern formation caused by destabilizing concentration gradients was described for instance by Gambale and Gliozzi.[23] A related phenomenon was also observed in an electrochemical system where the patterns were shown to be due to an extended array of convective cells.[18] In our system, in contrast, the diameter of the electrode is too small to allow pattern formation orthogonal to the gradient. Interestingly, Nakabayashi et al. recorded strongly damped oscillations both in galvanostatic and potentiostatic experinents.[18]

The model does not contain specific assumptions about the iodine-iodide system. It would thus be possible that this general core mechanism is applicable to other experimental systems as well. One important factor for the search of further oscillatory systems of the type presented is that a product is formed which has a smaller diffusion coefficient than the substrate. In addition, oscillatory solutions are equally simple to find in modified models with different reaction kinetic assumptions (e.g., the formation of a reversible complex between substrate and product). Indeed, we have observed oscillatory convective behavior during the potentiostatic reduction of *p*-benzoquinone which appears to be related to the present system.[19] Also, the model explicitly predicts that oscillatory solutions occur likewise if the substrate diffuses slower than the product and the setup is turned upside down (e.g., if the working electrode is placed at the bottom of the solution). The result in this case would be an upward convective flow of liquid with lesser density.

An oscillatory instability of buoyant plumes and the corresponding spatio-temporal patterning was observed with helium as an upward streaming fluid.[24,25] To explain this instability a model of the experiment assumes the formation of a toroidal vortex as the result of the (active) injection of helium gas through a burner. Thus pulsating buoyant plumes and the known "puffing" of axisymmetric pool fires is probably caused by a different mechanism than the current oscillations in the present experiment.

To summarize we have described a new oscillatory electrochemical experiment and proposed a simple qualitative model of the system which demonstrates a dynamic instability and subsequent spatio-temporal pattern formation due to the interplay of reaction and diffusion with convection. It will be of interest to gain insight into the physical or physicochemical nature of the proposed threshold function. Alternatively, one could ask whether such a pattern forming process can be obtained in a purely (bio)chemical experiment. For example, can the working electrode in our experiment be replaced by a conventional catalyst or an immobilized enzyme (like horseradish peroxidase in the presence of excess hydrogen peroxide[17])? In any case, the study of such instabilities will be important for the deeper understanding of the pattern forming interplay between reaction, diffusion, and convection.

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