

Wave instabilities in an excitable electrochemical system

R. D. Otterstedt, N. I. Jaeger, and P. J. Plath

Institut für Angewandte und Physikalische Chemie, Universität Bremen, FB2 Biologie/Chemie, Postfach 330440, D-28334 Bremen, Federal Republic of Germany

J. L. Hudson

Department of Chemical Engineering, Thornton Hall, University of Virginia, Charlottesville, Virginia 22903-2442

(Received 30 October 1997; revised manuscript received 9 June 1998)

Spatiotemporal pattern formation under potentiostatic control in the excitable potential range at the active/passive transition of cobalt in buffered phosphoric acid has been investigated in a ribbon electrode geometry. The propagation of an active area with modulation and wave splitting has been observed, depending on the parameters potential and time of passivation prior to excitation. The modulation and wave splitting are influenced both by the kinetics of repassivation on the electrode surface and by long-range coupling and positive feedback through the electric field. Modulation in the vicinity of the system boundary gives rise to an apparent reflection of the active area at the boundary.

[S1063-651X(98)08610-3]

PACS number(s): 82.20.Mj, 82.45.+z, 47.54.+r

INTRODUCTION

Pulses traveling through chemically reacting excitable media can undergo wave splitting and reflection. In the former, the pulse proceeding in the forward direction sends out a pulse in the reverse direction, resulting in two pulses traveling in opposite directions. In the latter, the pulse, upon reaching the boundary of the reacting region, reverses direction, resulting in a single pulse traveling in the opposite direction.

Sevcíková, Marek, and Müller observed splitting and reversal of waves in a homogeneous reacting mixture, the Belousov-Zhabotinskii reaction, carried out in the presence of an electric field [1]. Both wave splitting and reversal were related to changes in the shapes of the wave front and the refractory tail. Luss and co-workers have investigated nonisothermal oxidation reactions on metal catalysts and observed both wave reflection and back-and-forth front movement [2,3]. They showed the importance of global coupling and of nonuniform catalyst activity on the observed behavior. A model showing the rich variety of patterns to be anticipated on a one-dimensional catalytic surface under an integral constraint, namely, the average temperature of the catalyst, was analyzed by Middy *et al.* [4]. Two recent papers on simulations with reaction-diffusion equations have shed considerable light on the mechanism of wave splitting and reflection in reacting systems. A pulse instability in a model of the excitable CO oxidation on platinum (110) has been described by Bär *et al.* [5]. The instability leads to backfiring in a one-dimensional system and to spiral breakup in two dimensions. Backfiring occurs in this model in some parameter regions when the refractory tail has shrunken due to a delayed inhibitor production. Wave splitting and reflection of pulses at a no-flux boundary have been reported by Petrov, Scott, and Showalter [6] in numerical simulations of a reaction-diffusion model using a significantly higher diffusivity of one reactant than for the other (autocatalytic) variable.

Electrochemical reactions have furnished many examples of patterns in the excitable, oscillatory, and bistable regimes [7–9]. Spatiotemporal pattern formation has been studied in bistable [10,11] and oscillatory [12–15] electrochemical systems and the role of spatial coupling through the electric field in electrochemical systems has been analyzed in a model by Flätgen and Krischer [16] and Mazouz, Flätgen, and Krischer [17].

In this paper we present results of experimental studies of modulation, wave splitting, and reflection in an electrochemical system, namely the dissolution of cobalt in buffered phosphoric acid. The system differs from the homogeneous experimental systems mentioned above and from other reaction-diffusion systems in that the dynamics are heavily influenced by the electric field, which furnishes a long-range coupling. Furthermore, the kinetics of the deposition and dissolution reactions contribute to the features of the dynamics.

Under the conditions of the experiments the system is excitable. After the leading edge passes a location, a porous salt film forms due to the high dissolution rate of cobalt into the solution and the low solubility of different cobalt phosphates. Excitability is reestablished as soon as a passivating oxide film is formed beneath the salt film. This happens, according to an idea proposed to explain oscillations [18], when the *pH*-dependent Flade potential is exceeded due to migration of H^+ ions out of the salt film. The (local) restoration of the passive layer leads to a considerable decrease of the Ohmic potential drop at sites adjacent to the freshly passivated one, which leads to an increase of the potential drop across the double layer. This in turn facilitates the formation of the passive layer on salt film covered areas where the *pH* is high enough; the system becomes excitable again at these areas. Nonlocal coupling affects the propagation of the excited state as well as the repassivation of the surface.

EXPERIMENT

The experiments are done with a cobalt ribbon approximating a one-dimensional geometry. Details of the experi-

mental procedure have been reported [14].

Passivity of the electrode was established by stepping the potential from the rest potential to the potential at which the experiment is to be carried out. It took 3–4 s for passivity to be accomplished depending on the applied voltage. The time for which the system was held passive prior to the experiment has been taken as parameter controlling the excitability of the system since the passive layer continues to grow and does not reach a final thickness within 1 h of polarization. The electrode was then activated at one end by touching the surface with a blank cobalt wire. The potential distribution on the ribbon was measured with 12 auxiliary silver/silver chloride potential probes positioned equidistantly above the electrode surface.

RESULTS

The experiments were carried out in the excitable region at a potential somewhat anodic (more positive) relative to the Flade potential at which a transition from an active to a passive state occurs. Under the conditions of the experiments there is only one single, stable steady state. The electrode is excited at the position 50 mm and the active area (excited state) propagates from this end of the ribbon to the other. Three parameters are important. One is the time at which the electrode is held in the passive state before the experiment is started; the longer this time the greater the thickness of the passive layer and the greater the perturbation required to excite the system. The second parameter is the applied potential. The third parameter is the concentration of phosphate species in the electrolyte. A high concentration increases the rate of repassivation after the active area has traversed the electrode and also decreases the potential drop in the electrolyte; the potential drop across the double layer (the driving force for the reaction) is the difference between the applied potential and the potential drop in the electrolyte.

At $0.25M$, the active area propagates from one end of the ribbon to the other with a slight acceleration until the whole electrode is active. (These results are not shown.) The salt film formation, necessary for the repassivation, is a very slow process in the low solute concentration. After the leading edge of the active area has traversed the electrode, the electrodisolution of the metal continues for about 60 s before the repassivation tail traverses the electrode; the repassivation then occurs very quickly.

At $0.75M$, similar results are obtained with two exceptions. First, the repassivation occurs more quickly at this higher concentration. Thus the leading edge of the activated area traverses the electrode as above and there is a time in which the electrode remains essentially active before the repassivation traverses the electrode. This traverse is fast. Second, the propagation is slightly modulated, i.e., the active area contracts from the back side and then expands in the reverse direction intermittently. The main results presented here were obtained at the solute concentration $1.25M$ with variation of the remaining parameter, the imposed potential.

Figure 1 shows results obtained at an applied potential of 1140 mV, i.e., 15 mV anodic to the Flade potential. The potential as measured by the reference electrodes as a function of space and time is shown in Fig. 1(a) and the total current as a function of time is shown in Fig. 1(b). Note that

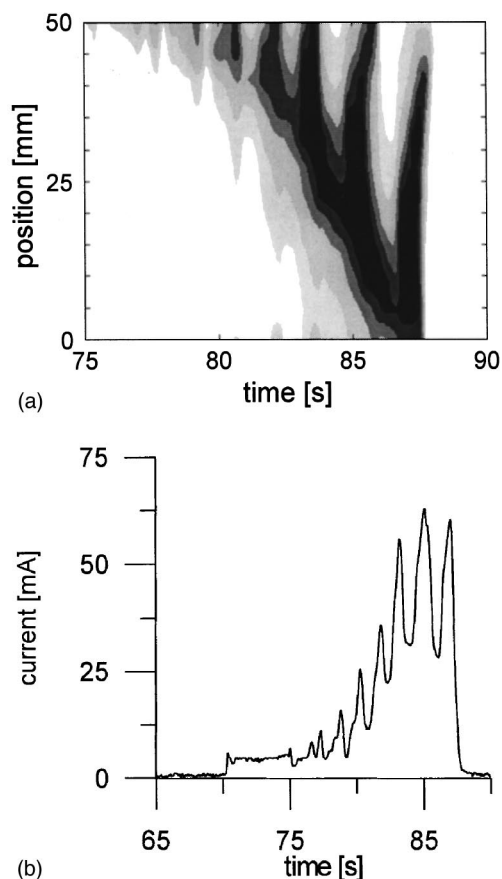
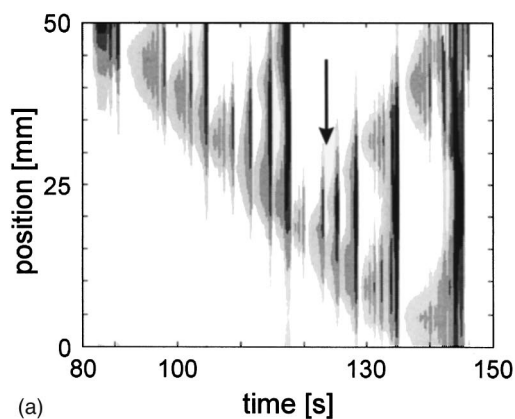


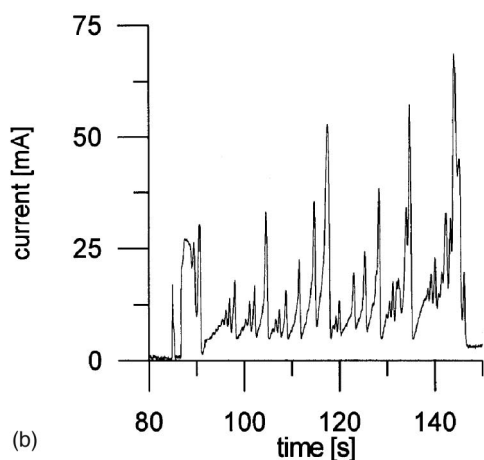
FIG. 1. (a) Modulated activation of the electrode. Projection of five selected equipotential lines onto the space time plane. The area between adjacent equipotential lines is displayed in a gray tone; white denotes total passivity and black denotes highest activity. The pH is 1.4, the concentration of phosphorous is $1.25M$; and there is 60-s passivation at 1140 mV, i.e., 15 mV anodic of the Flade potential, prior to activation with a 0.8-mm^2 cobalt wire. The repassivation occurs uniformly. (b) Integral current-time curve corresponding to (a).

the repassivation occurs more quickly than at lower concentrations; this can be seen in both Figs. 1(a) and 1(b). The repassivation still occurs too slowly to produce a narrow active area traversing the electrode. Most important for the present discussion is the appearance of modulation of the active area under these conditions, i.e., the increase and decrease in size of the active area. The oscillations in the current vs time trace [Fig. 1(b)] reflect the modulation of the active area.

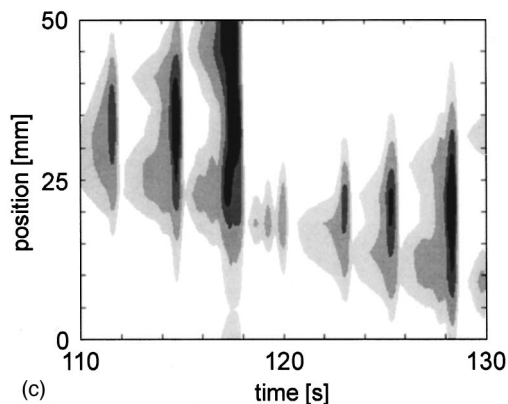
The results obtained by changing the applied potential to 1160 mV, which is 35 mV anodic with respect to the Flade potential, are shown in Fig. 2. The time the leading edge needs to traverse the electrode is about 3 times longer compared to Fig. 1. Since the frequency of modulation is similar in the two cases, more modulation events can be seen in Fig. 2(a) than in Fig. 1(a). This is reflected in the current-time curve [Fig. 2(b)]. The speed of the active area traveling in the reverse direction is somewhat greater than that of the forward moving leading edge. Note that the trailing edge associated with most modulation events does not reach the point at which the active area was initiated. The splitting of the active area occurs at about $t = 121$ s (arrow). After the



(a)



(b)



(c)

FIG. 2. (a) Activation of the electrode with wave splitting. The pH is 1.4, the concentration of phosphorous is $1.25M$, and there is 60-s passivation at 1160 mV, i.e., 35 mV anodic with respect to the Flade potential, prior to activation with a 0.8-mm^2 cobalt wire. (b) Integral current-time curve corresponding to (a). (c) Blowup of Fig. 2(a) is shown in Fig. 2(c), in which the splitting can be clearly seen (arrow).

splitting at $t=121$ s, the oppositely moving active areas reach their respective ends at approximately the same time, the entire electrode is active for a short time, and a rapid repassivation occurs at approximately $t=145$ s. A blowup of Fig. 2(a) is shown in Fig. 2(c), in which the splitting can be clearly seen (arrow).

The experiment for which the results are given in Fig. 3 was done at a potential intermediate between those of Figs. 1 and 2, i.e., at 1150 mV. Both the time the leading edge needs to traverse the electrode and the number of modulation

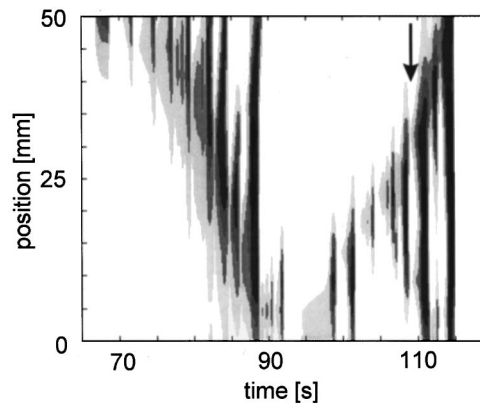


FIG. 3. Activation of the electrode with modulation and reflection at the end of the ribbon. The pH is 1.4, the concentration of phosphorous is $1.25M$, and there is 60-s passivation at 1150 mV, i.e., 25 mV anodic with respect to the Flade potential, prior to activation with a 0.8-mm^2 cobalt wire.

events are between those of Figs. 1 and 2. Moreover, an apparent reflection of the active area at the boundary occurs, as can be seen in Fig. 3. The active area now travels in the opposite direction and undergoes splitting again at $t=108$ s (arrow). It is likely that this apparent reflection also occurs under the conditions of Fig. 2, but it was not observed in our experiments.

DISCUSSION

Consider first the experiments done at low electrolyte concentration. In this case the repassivation rate was very low for two reasons. First, the area of active electrodisolution was very large and for a transient period occupied the entire electrode. When the active area is large, the total current is high and the potential drop in the electrolyte is large. This results in a decreased potential drop across the double layer, a lower rate of metal dissolution, and thus a delayed formation of the repassivated region. Second, the repassivation is slow because the formation of the salt film is slow at the low phosphate concentration.

As the electrolyte concentration is increased the rate of repassivation increases. Activation and passivation rates seem to be of the same order at the concentration $1.25M$, which prevents the active area from spreading over the whole ribbon before repassivation starts. Once repassivation has started at the beginning of the ribbon, it spreads quickly into the area behind the leading edge, which thereby is slowed down. When the repassivation edge reaches the freshly activated area behind the leading edge (excited state), i.e., areas in which the salt film and/or the pH in the salt film and the potential are not apt to induce passivity, the decrease in the current stops. Once the current decrease is stopped, every increase of the current due to the propagation of the leading edge is positively fed back by the field. Since the freshly passivated area behind the leading edge is more easily activated (due to its thinness in comparison to the passive area in front of the leading edge), the active area expands in the reverse direction and modulation is observed. It seems that the repassivation is not fast enough to stop the increase in the current before the edge traveling in the reverse direc-

tion reaches the beginning of the ribbon; thus every modulation event covers the whole ribbon up to the leading edge.

As the potential is increased at the same electrolyte concentration (Fig. 2 relative to Fig. 1) the higher potential effects a higher repassivation rate. As a consequence, modulation events are now confined to a smaller portion of the system length. Splitting of the active area apparently occurs if the repassivation time is shorter than the time that the backward moving edge of the active area needs to reach the end of the system. As soon as passivity is reestablished, the current drops sharply. This current drop in turn causes the electrode potential in nearby locations to increase, which accelerates the spreading of the newly formed passive layer. The remaining active areas, i.e., the formerly leading edges, which are now small areas with low currents, do not collapse because the lacking salt film renders passivation impossible so that the splitting of the active area is accomplished, i.e., the two still excited regions will start to expand in both directions into the freshly formed passive layer. Sometimes, when modulation is great, the tails of the two split areas meet

and the entire surface is momentarily active and then repassivation occurs almost uniformly (Fig. 2 at $t = 145$ s).

The apparent reflection (Fig. 3) can be explained in the same manner. In this case, splitting takes place near the edge of the electrode. The forward propagating area reaches the boundary of the electrode very quickly, so that only the backward propagating area remains.

CONCLUSION

The long-range coupling and the kinetics of the activation and passivation processes combine to produce wave splitting and an apparent reflection in an electrochemical system.

ACKNOWLEDGMENTS

Financial support by the Deutsche Forschungsgemeinschaft (Grant No. JA-346-16-1), NATO (Grant No. 950057), and the National Science Foundation is gratefully acknowledged.

-
- [1] H. Sevcíková, M. Marek, and S. C. Müller, *Science* **257**, 951 (1992).
- [2] M. D. Graham, S. L. Lane, and D. Luss, *J. Phys. Chem.* **97**, 7564 (1993).
- [3] M. A. Liauw, M. Somani, J. Annamatai, and D. Luss, *AIChE J.* **43**, 1519 (1997).
- [4] U. Middy, M. Sheintuch, M. Graham, and D. Luss, *Physica D* **63**, 393 (1993).
- [5] M. Bär, M. Hildebrand, M. Eiswirth, M. Falcke, H. Engel, and M. Neufeld, *Chaos* **4**, 499 (1994).
- [6] V. Petrov, S. K. Scott, and K. Showalter, *Philos. Trans. R. Soc. London, Ser. A* **347**, 631 (1994).
- [7] H. L. Heathcote, *J. Soc. Chem. Ind.* **26**, 899 (1907).
- [8] R. S. Lillie, *Science* **67**, 593 (1928).
- [9] K. Yamagiwa, *Jpn. J. Med.* **1**, 439 (1948).
- [10] G. Flätgen and K. Krischer, *Phys. Rev. E* **51**, 3997 (1995).
- [11] R. D. Otterstedt, P. J. Plath, N. I. Jaeger, J. C. Sayer, and J. L. Hudson, *Chem. Eng. Sci.* **51**, 1747 (1996).
- [12] J. L. Hudson, J. Tabora, K. Krischer, and I. G. Kevrekidis, *Phys. Lett. A* **179**, 355 (1993).
- [13] J. C. Sayer and J. L. Hudson, *Ind. Eng. Chem. Res.* **34**, 3246 (1995).
- [14] R. D. Otterstedt, P. J. Plath, N. I. Jaeger, and J. L. Hudson, *Phys. Rev. E* **54**, 3744 (1996).
- [15] O. Lev, M. Sheintuch, L. M. Pismen, and H. Yarnitzky, *Nature (London)* **336**, 458 (1988).
- [16] G. Flätgen and K. Krischer, *J. Chem. Phys.* **103**, 5428 (1995).
- [17] N. Mazouz, G. Flätgen, and K. Krischer, *Phys. Rev. E* **55**, 2260 (1997).
- [18] U. F. Franck and R. FitzHugh, *Z. Elektrochem.* **65**, 156 (1961).