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Controlled pulse reversal on a ring electrode

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Abstract

Oscillatory rotating activation pulses on a Pt ring electrode during formic acid oxidation were externally perturbed via a trigger electrode at one location of the ring. While usual phase resetting was obtained for small perturbation amplitudes, stronger perturbations resulted in reversal of the direction of pulse motion when applied behind the pulse over a wide phase interval. The results are in agreement with simulations carried out with a reaction–migration model and can be rationalized in terms of short-range positive and long-range negative coupling. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In an excitable medium the excitation is usually confined to a small region of space propagating with a certain velocity. The return to the initial state of the element of an excitable medium and a diffusional flow to a neighboring element of the medium result in the propagation of a travelling pulse [1]. Rotating pulses have been observed in a variety of systems, namely in heterogeneous catalysis [2–4], electrochemical systems [5–7] and even in in-vitro heart tissue [8,9]. In early 20th century, Lillie [5] reported pulse pattern in transmission of activation of passive metals and it was considered as a model of the protoplasmic or nervous type of transmission. Recently, Lev et al. [6] reported a travelling pulse of current density in the electro-dissolution of nickel wires in acidic media. More recently, we observed a spatiotemporal travelling pulse on the Pt ring electrode in the electrocatalytic oxidation of HCOOH [7]. González et al. [8,9] theoretically and experimentally showed resetting and annihilating waves in a ring of cardiac tissue.

The direction of motion of the resulting pulses usually depends in a non-trivial way on the initial conditions and/or inhomogeneities of the medium and thus often results more from ‘chance’ than from deliberate experimental control. In the normal heart, the control of travelling waves, such as pulse advancement and double pulse reversal, may be effective in the therapy of tachycardia of cardiac tissue [8,9]. On the other hand, to control activity (or tolerant passivation) of the electrode by external electrical stimulus might be effective in running a fuel cell without suffering deactivation of the whole electrode.

Here we present experiments and computer simulations of an electrochemical system where the direction of a pulse can be reversed at will using an external perturbation.

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2. Experimental

The experiments were carried out with a Pt ring as working electrode (WE) with inner diameter of 34.5 mm and outer diameter of 40.5 mm, thus exhibiting a geometric area of 7 cm^2. A Hg/Hg$_2$SO$_4$ reference electrode was placed at the center of the ring and a counter electrode from platinized Pt located well above (40 mm) the other electrodes. Eleven reference electrodes were distributed at about 0.3 mm distance from the WE in order to monitor the local potential, while at the 12th position a Pt wire (ca. 1 mm from the WE) served as an external trigger.

All solutions were prepared with ultrapure water (Millipore Milli-Q water, 18 MΩ cm) and were kept at room temperature. Before each experiment, the Pt ring WE was chemically cleaned in H$_2$SO$_4$:30% H$_2$O$_2$ (1:1) and a preliminary voltammetric curve between −600 and +600 mV (vs. Hg/Hg$_2$SO$_4$) was recorded in 0.5 M H$_2$SO$_4$ to confirm the absence of any residual surface impurities. The electrolyte was 0.1 M HCOONa/ 0.033 M H$_2$SO$_4$ (pH = 2.85), to which 10^{-3} M Bi(ClO$_4$)$_3$ was added, which leads to a substantial increase of the electrocatalytic activity of Pt towards direct formic acid oxidation. Prior to each cyclic voltammetry (CV) measurement, the initial WE potential was kept at open circuit potential of −320 mV in order to establish the same bismuth coverage of the Pt electrode. After each experiment, the WE was treated in conc. HClO$_4$ (Merck, suprapur) to completely remove residual bismuth adatoms.

An in-house-built potentiostat (Electronic Lab, Fritz-Haber-Institut der MPG) was used for all CV and chronoamperometry (CA) experiments and the data were transferred to an IBM compatible PC controlled by a GPIB interface.

3. Results and discussion

On the anodic scan during the cyclic voltammogram of the Pt ring electrode in formic acid solution, potentiostatic current oscillations were obtained in a potential range from about +90 to +250 mV. Due to the proximity of the RE to the WE, no in-phase oscillations were possible; rather, anti-phase spatiotemporal oscillations developed in the form of standing waves or rotating pulses [7,10].

A rotating pulse was subject to a pulse-shaped perturbation of usually ca. 200 ms duration. For small trigger amplitudes (⩽1.0 V), no pulse reversal was obtained, rather the pulse rearranged in the same direction with its phase advanced or retarded compared to what it would have had without the perturbation. An example is shown in Fig. 1. Thus, the response resembled the well-

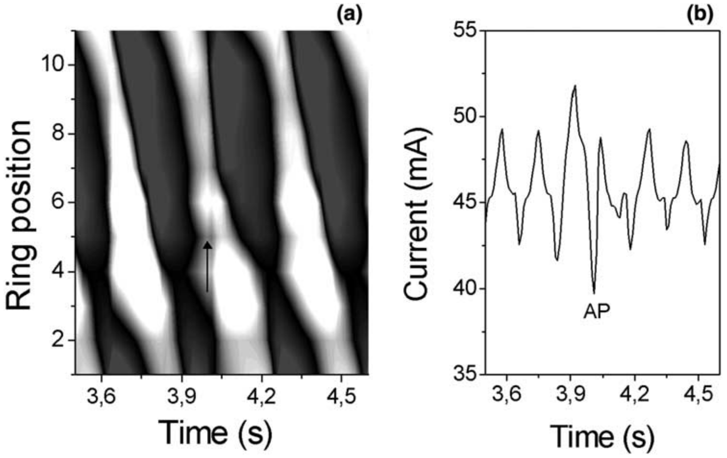

Fig. 1. Phase resetting of a rotating pulse due to a locally activating perturbation of +1 V and 200 ms applied at position 12. (a) is spatiotemporal contour plot and (b) is temporal current oscillation with function of time (black: active state, white: passive state).

known phase resetting behavior of limit cycles for small perturbations (see [11,12]). Phase resetting refers to a change of phase that is induced by a stimulus (here pulse perturbation) and it can be induced in many biological systems by appropriately chosen stimuli. For example, the rhythm of the human heart is normally set by a specialized region of the atria called the sinus node. However, in some hearts there are extra beats that can interfere with the normal sinus rhythm. Sometimes these extra beats can reset the rhythm.

The situation changed significantly for higher perturbation amplitudes ($\geqslant 2$ V). Regarding the pulse as an active (high-current) zone on an otherwise passive (low-current) electrode, a perturbation in front of the pulse led to pulse advancement, whereas perturbing behind it resulted in reverse of direction. This is shown in Fig. 2, where a clockwise travelling pulse and an anticlockwise direction induced by two subsequent perturbations. On the ideal electrode the total current I (Fig. 1b resp. 2c) would be constant during pulse rotation. However due to inhomogeneities of the ring electrode, I exhibits characteristic oscillations which repeat every period. For a given electrode the location of the pulse on the ring could thus be assessed indirectly without necessity of real-time spatiotemporal measurements. Note that the pulse orientation was also visible from the integral current (see Fig. 2c), i.e., at least some inhomogeneities were asymmetric. For phase shifts around (perturbation right on the pulse), the pulse appeared stationary for some time before starting to move again, as shown in Fig. 3 (‘critical slowing down’).

Computer simulations were carried out using a reaction–migration system with the double-layer potential $\varphi(x,t)$ as a fast variable and a chemical species $c(x,t)$ as a slow variable.

$$C_{\mathrm{dl}}\partial_t\varphi = -i_{\mathrm{reac}}(\varphi,c) + \frac{U-\varphi}{R} + \kappa\int_0^{2\pi} H(|x-x'|)[\varphi(x')-\varphi(x)]\,\mathrm{d}x' \quad (1)$$

$$\partial_t c = \epsilon(-i_{\mathrm{reac}}(\varphi,c) + 1 - c),\quad \text{where } i_{\mathrm{reac}}(\varphi,c) = ck(\varphi). \quad (2)$$

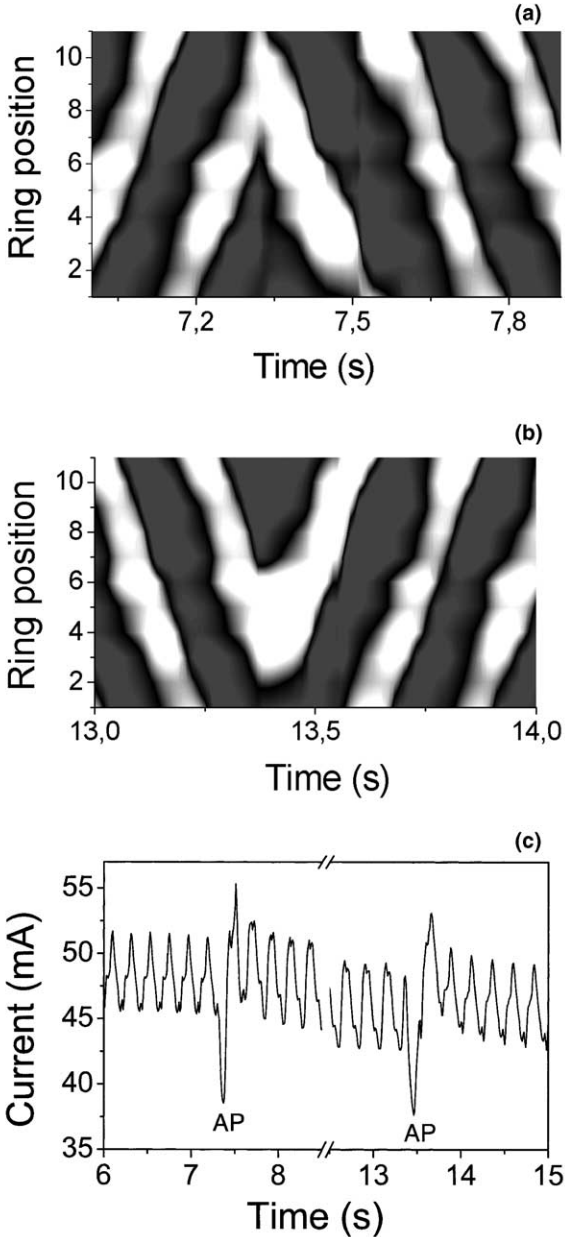

Fig. 2. Double reversal of a rotating pulse due to a locally activating perturbation of +2 V and 200 ms applied at position 12. (a) and (b) show the spatiotempral pattern and (c) is the corresponding current oscillations.

Here, C_{dl} denotes the double layer capacity, i_{reac} the local faradaic current density, $\kappa(\phi(x,t))$ the faradaic reaction rate, U the outer applied potential, R the total resistance, and κ the conductivity

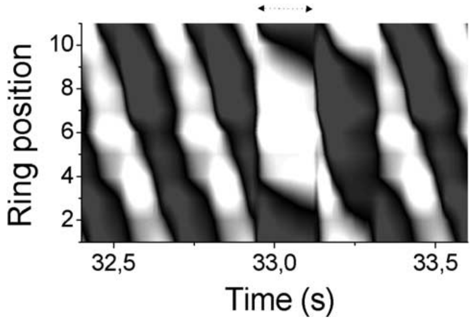

Fig. 3. Critical slowing down of a rotating pulse due to a locally activating perturbation of +1 V and 200 ms applied at position 12.

of the electrolyte. At the heart of the spatial integral coupling lies the spatial coupling function $H(|x - x'|)$ which represents the coupling between two points x and x' along the WE. Due to the symmetry of the electrode geometry, H is simply a function of the distance $x - x'$ between two points. Spatial coupling along the WE occurs via ion migration in the electric field and is described by a coupling function $H(x, x')$ which couples every location of the electrode to every other one. For the geometry in question (ring as WE with RE in the center), H falls off with distance and becomes negative on the opposing side of the ring (for details of the derivation of H from potential theory and its exact shape see [13–15]).

Fig. 4 reproduces computer simulations of pulse advancement (a) and pulse reversal (b) occurring when the perturbation was applied at different phases. As in experiment, the perturbation has to exceed a threshold so that reversal can occur. The above phenomena can be rationalized in terms of the non-local nature of migration coupling. The activating trigger acts most strongly locally, but also non-locally everywhere on the electrode, the perturbation strength at other places being determined by the coupling function $H(x, x')$, which effect in particular causes passivation on the opposite side. For small perturbation amplitudes, the local activation predominates leading to standard phase resetting. At higher amplitudes the remote passivation also becomes important. Consequently a perturbation behind a pulse will cause the local current to increase behind, but decrease in front of the pulse. This is exactly opposite to the natural (unperturbed) current gradients on both sides of the pulse, i.e., it must change its direction of motion. The described behavior is expected in general for systems that combine short-range activation with long-range inhibition coupling.

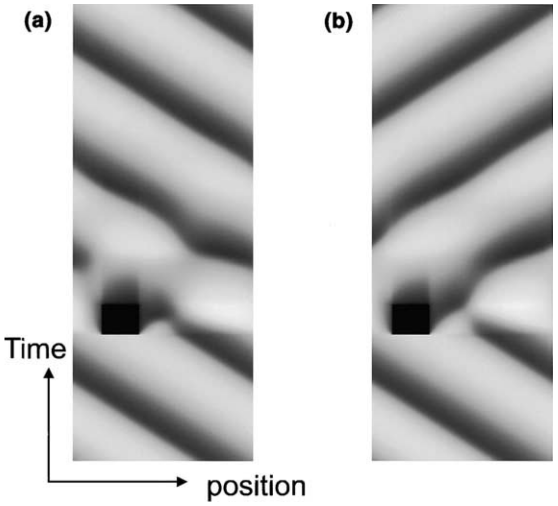

Fig. 4. Theoretical simulation of controlled pulse pattern. (a) Pulse advancement and (b) pulse reversal.

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References

[1] A.S. Mikhailov, Foundations of Synergetics I, Springer, Berlin, 1994.
[2] S.L. Lane, D. Luss, Phys. Rev. Lett. 70 (1993) 830.
[3] J. Christoph, M. Eiswirth, N. Hartmann, R. Imbihl, I. Kevrekidis, M. Bär, Phys. Rev. Lett. 82 (1999) 1586.
[4] S.Y. Yamanoto, C.M. Surko, M.B. Maple, R.K. Pina, Phys. Rev. Lett. 74 (1995) 4071.
[5] R.S. Lillie, Science 48 (1918) 51.
[6] O. Lev, M. Sheintuch, L.M. Pismen, C. Yarnitzlay, Nature 336 (1988) 488.
[7] J. Lee, J. Christoph, P. Strasser, M. Eiswirth, G. Ertl, J. Chem. Phys. 115 (2001) 1485.

[8] H. González, Y. Nagai, G. Bub, L. Glass, A. Shrier, Prog. Theor. Phys. Suppl. 139 (2000) 83.
[9] Y. Nagai, H. González, A. Shrier, L. Glass, Phys. Rev. Lett. 84 (2000) 4248.
[10] P. Strasser, J. Christoph, W.-F. Lin, M. Eiswirth, J.L. Hudson, J. Phys. Chem. A 104 (2000) 1854.
[11] A.T. Winfree, The Geometry of Biological Time, Springer, New York, 1980.
[12] D. Kaplan, L. Glass, Understanding Nonlinear Dynamics, Springer, Berlin, 1995.
[13] J. Christoph, R.D. Otterstedt, M. Eiswirth, N.I. Jaeger, J.L. Hudson, J. Chem. Phys. 110 (1999) 8614.
[14] J. Christoph, P. Strasser, M. Eiswirth, G. Ertl, Science 284 (1999) 291.
[15] J. Christoph, Ph.D. Thesis, Freie Universität Berlin, 1999.