

Pacemaker-Driven Spatiotemporal Patterns on an Electrode Array

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Received: May 16, 1997; In Final Form: July 28, 1997[®]

Experiments were carried out with a hexagonal array of 61 iron electrodes in sulfuric acid solution under conditions in which slow active–passive relaxation oscillations occur. The currents of the individual electrodes were measured independently, and therefore the spatiotemporal patterns that occurred were directly determined. The potential of one or more of the electrodes was held at a value below that of the remaining electrodes; the electrodes at lower potential had a higher natural frequency and thus acted as pacemaker centers. Activation waves emanated from these pacemakers; the repassivation waves had the same characteristics as those on an array or single electrode held at a constant potential, e.g., from edge to center in the period-one parameter region. Long-range coupling plays an important role in the dynamics of electrochemical reactions; arrays of electrodes at constant potential behave qualitatively similar to single electrodes of the same total surface area. Both the size of the pacemaker centers (the number of electrodes held at a lower potential) and the difference in frequency between the pacemaker and nonpacemaker electrodes could be varied independently. Since conditions at positions across the reacting surface, the array, can be varied systematically, the array can be used to study the influence of pacemakers or model “defects” on a type of heterogeneous reacting system.

Introduction

Temporal oscillations and spatiotemporal patterns have been observed during a number of electrochemical reactions¹ including the electrodisolution of metals^{2–9} and electrocatalytic reactions.^{10–14} The anodic electrodisolution of iron in acidic solution is an example of the former type. Under potentiostatic conditions autonomous current oscillations can occur.^{15–18} Depending on system parameters, notably applied potential and mass transfer coefficient between the electrolyte and electrode, two general types of oscillations occur. In one region of parameter space high-frequency (10–500 Hz), often chaotic oscillations have been observed.^{19–20} In a second region, near the Flade potential above which the electrode is passive, slow (period of seconds to minutes) relaxation oscillations can occur.²¹ For experiments done under potentiostatic (constant potential) conditions, the current then oscillates between high values, corresponding to an active surface, and low values, corresponding to a passive surface.

The passivation of the electrode is caused by the growth of a surface film and the activation, conversely, by its dissolution. The formation and dissolution of the surface film do not occur uniformly, but rather by the spread of active or passive regions across the electrode surface. The passivation phase of the oscillatory cycle is relatively slow and can under some conditions be seen visually. For example, Pigeau and Kirkpatrick²² investigated periodic relaxation oscillations on a circular electrode. During the passivation phase of the oscillation, a zone with higher reflectance emerges at the outer rim and propagates toward the center; that is, the active region of the electrode surface remains approximately circular and the diameter of this circle decreases during the passivation. After some time there is a activation which is too fast to be characterized by visual methods, and this is followed by another slow passivation. Hudson et al.²³ have extended these studies; the periodic current was measured as a function of time and the surface was observed with the aid of a microscope and a

video camera. A spatiotemporal period-doubling was observed. With changes in the parameter (potential), the spatial symmetry of the oscillatory state broke giving rise to a period-doubled oscillation. This resulted, after further decreases in potential, in a periodic state in which it appeared that half of the electrode underwent activation-passivation during one-half of a cycle and the other half of the surface participated during the next half of the temporal cycle. Similar studies have also been carried out on a ring electrode.²⁴ On the ring, as on the disk, a spatiotemporal period-doubling was seen as the potential was lowered; subsequently, however, more complicated, bifurcations took place with further change in the parameter

In a previous paper²⁵ we reported on patterns during autonomous oscillations with arrays of iron electrodes in sulfuric acid solution; the arrays consisted of a number of small disks which were made from the ends of wires embedded in an insulator. All the electrodes were held at the same constant potential and the current in each of the electrodes was measured independently. High and low current on an individual electrode corresponds to active and passive conditions respectively and waves and moving patterns can be characterized from the time series of current from many sites. Thus the patterns could be determined directly and information not available from visual techniques was obtained. Much faster measurements can be made with the array than with visual methods using standard video cameras. During active-passive oscillations in the iron/sulfuric acid system, the activation is very fast whereas the passivation is slow. Both activation and passivation occur by the motion of a wave front across the electrode surface and both of these, including the fast activation waves, can be measured using the arrays.

An array of electrodes behaves approximately like a larger, single electrode of the same total area; the analogy is not perfect, of course, since there is a current distribution on each single electrode. This similarity exists because much of the coupling in the electrochemical system is through the electrolyte and long-range effects are important. Therefore, the spatiotemporal bifurcations that occur on the single electrode occur also on

[®] Abstract published in *Advance ACS Abstracts*, November 15, 1997.

the array. (Long-range interactions have received considerable attention recently in reaction–diffusion^{27–31} and electrochemical^{12,24,7,26} systems.)

The emphasis of this paper is on nonuniform reacting surfaces. Nonuniformities arise commonly in heterogeneous chemical reactions and even in liquid-phase systems. The rate of reaction at surface defects can differ from the reaction rate at other locations on a surface and the defects can thus influence both spatiotemporal patterns and the overall rate of reaction. In surface reactions the heterogeneity might be a structural defect^{29,31–33} whereas in a liquid-phase reaction, small heterogeneous impurities can play an important role.³⁴ The defects can then act as centers for target patterns or wave trains and can be a site to which a spiral tip is pinned. The arrays of electrodes used in these studies can be used as a model system for the study of nonuniform surfaces because the conditions at each of the electrodes in the arrays need not be identical. For example, one could use electrodes of various sizes or of various compositions. In the present paper we simply hold the potential of one or more of the electrodes at different values and these electrodes, since their rate of reaction is different, act as pacemakers or model “defects”.

Both the size of the of the inhomogeneous region and the difference in frequency between the pacemaker and nonpacemaker regions (in oscillatory media) are important parameters; although these can be varied in simulations,³⁴ they are not so easily controlled in most experiments. However, both can be varied systematically in studies such as those being discussed here, i.e., with arrays of electrodes in electrochemical experiments.

The arrays of electrodes can be conveniently used to study the effect of pacemaker centers on spatiotemporal patterns. The arrays have a second feature (in addition to the direct availability of information on reaction rates at individual sites) which distinguishes them from single electrodes, viz., the individual electrodes need not all be held at the same potential. In this paper we describe experiments carried out with arrays in which the electrodes are broken into two groups; each group of electrodes is held at a constant potential but the two potentials are different. The currents of the individual electrodes are again measured. In the type of oscillation being studied the frequency increases as the parameter, the applied potential, is lowered. Thus the group of electrodes which is held at a lower potential, at which the natural frequency is higher, acts as a pacemaker center. The experiments are done with an array of 61 electrodes; the size of the region acting as a pacemaker is varied from a single electrode to an area of approximately the size of half the total electrode surface. In a second set of experiments the oscillations are forced by imposing a square-wave potential on one group of electrodes.

Experiments

The configuration of the array consisting of 61 electrodes used in the study is shown in Figure 1. Each electrode is made from pure iron wire (Aldrich Chemical Co., Inc. 99.99+%) of diameter 0.5 mm. The distance between the wires is less than 0.05 mm. The electrodes are embedded in epoxy and reaction takes place only on the ends. The electrode array faces downward and the electrolyte is stagnant.

Experiments are carried out in 1 M H₂SO₄ solution. The volume is 300 mL. The reference electrode is a standard Hg/Hg₂SO₄/K₂SO₄ electrode in a capillary, the end of which is below the array and about 5 mm from the surface. The counter electrode is a cylindrical platinum foil in the plane of and encircling the array. The potentials are controlled by a

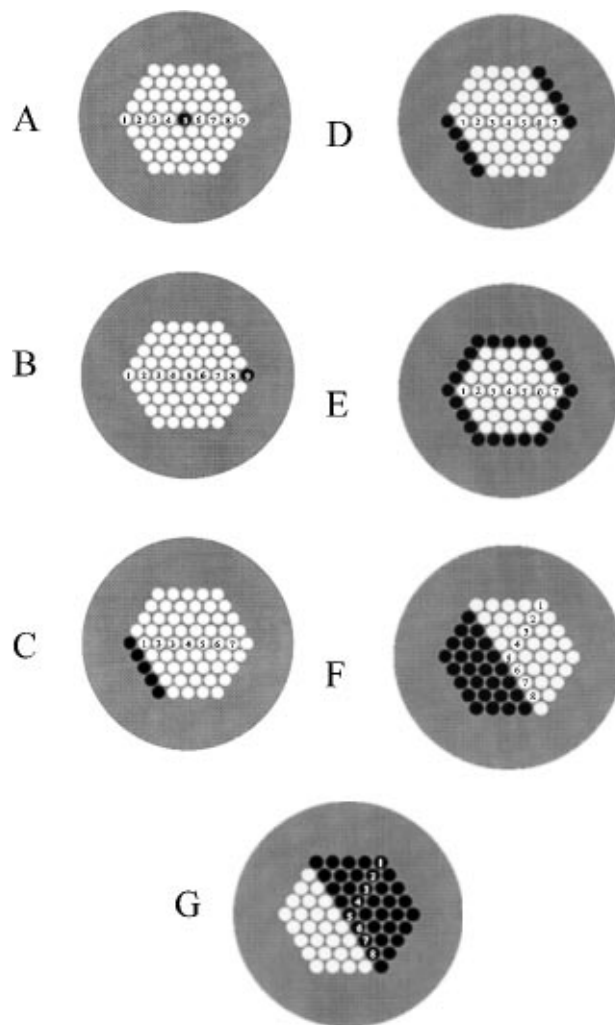


Figure 1. Configurations of electrode array (61 electrodes, diameter = 0.5 mm). The electrodes shaded black are the pacemakers.

bipotentiostat (Pine Model AFED4). Electrodes in the array are divided into two groups which separately link to two working electrode jacks (k1 and k2) of the bipotentiostat through a ZRA box. These two electrode groups can be operated independently.

Configurations of the electrodes in group k1 and group k2 are shown in Figure 1. Black and white indicate the electrodes of group k1 (the pacemakers) and group k2 respectively. A few of the electrodes in the figure are numbered for use in presentation of individual currents.

A pentium PC installed with a 32 channel data acquisition board (Keithley DAS-1800HC2) is used for data sampling. Both the total current and the currents of 29 of the 61 individual electrodes can be measured simultaneously with this arrangement. The sampling frequency of each channel is 2500 Hz.

A function generator (HP 3312A) is used as an external input source of the bipotentiostat. The external input can be imposed on either group k1 or group k2 although in these experiments the forcing is done only with the group k1.

A few preliminary potentiostatic experiments were made in which all the electrodes were at the same potential. In this case the potential was first held at a value in the passive region (−110 mV) and then was swept slowly (0.5 mV/s) in the cathodic direction to the desired value and held there. In the main experiments with pacemakers, a bipotentiostat was used so that the two electrode groups could be held at different potentials; the potential k2 was held at a fixed value and the potential k1

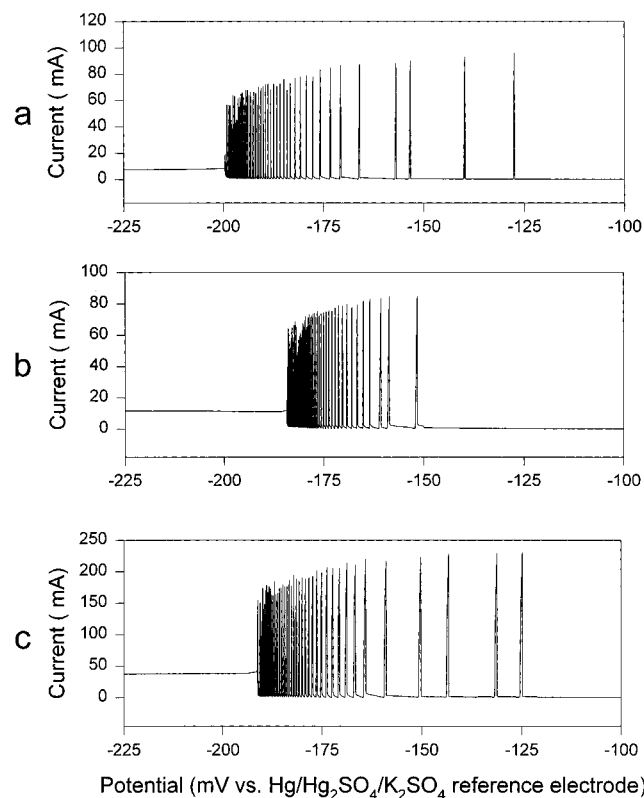


Figure 2. Current vs applied potential, sweep rate in cathodic direction = 0.5 mV/s: (a) 16 (4×4) electrode array, diameter = 0.5 mm; (b) single rod electrode, diameter = 2 mm; (c) 61 electrode array, diameter = 0.5 mm.

was swept from -110 mV in the cathodic direction to the desired potential.

Results

Arrays with Uniform Potential. We begin by describing a few experiments in which all of the electrodes in the array are held at the same potential; for additional details of such experiments, see ref 25. In Figure 2 the current obtained by sweeping the potential in the cathodic direction (positive to negative potential) is shown. In Figure 2a–c the working electrodes are a 4×4 array of 0.5 mm diameter electrodes, a single electrode of area 2.0 mm, and an array of 61 electrodes in the hexagonal pattern shown in Figure 1. the total area of the reaction surface is the same in parts a and b of Figure 2. In all three experiments the potential is decreased at a rate of 0.5 mV/s.

The results of the three experiments are qualitatively similar. At high potentials the electrode is passive and no oscillations occur. As the potential is lowered, slow active–passive relaxation oscillations begin. The frequency of these oscillations increases as the potential is lowered. At still lower potentials, the electrode is in the active state.

We now turn to potentiostatic experiments in which the potentials of all 61 electrodes in the hexagonal array are held at the same constant value. For potentials above approximately -130 mV the electrode is passive, i.e., the current is very low, approximately zero. Results obtained at two somewhat lower potentials (-160 and -185 mV) in the oscillatory range are presented in Figures 3 and 4, respectively. Figure 3 (-160 mV) shows a period-one, slow relaxation oscillation. The total current, i.e., the sum of the current of all 61 electrodes, is shown in Figure 3a. During one period the electrode is passive, there is a fast activation in which the current rises from approximately

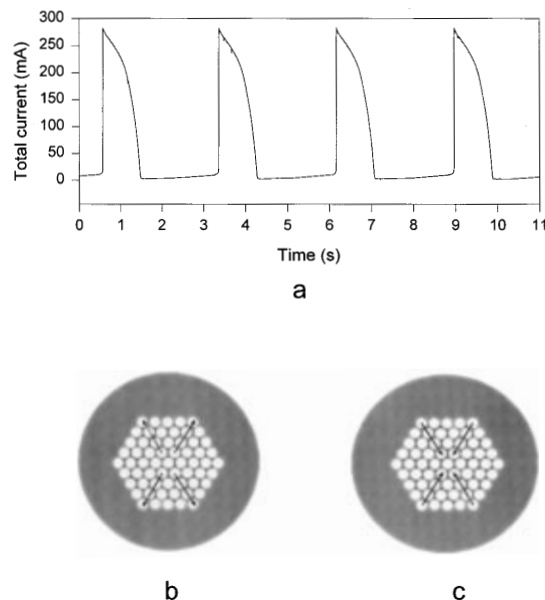


Figure 3. Autonomous oscillations; all electrodes at same potential; $E = -160$ mV (Hg/Hg₂SO₄/K₂SO₄) period-one oscillations: (a) total current; (b) activation; (c) passivation.

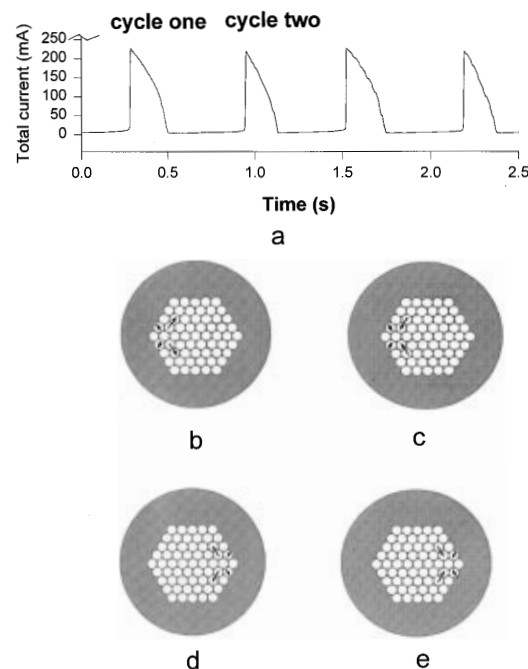


Figure 4. Autonomous oscillations, all electrodes at same potential; $E = -185$ mV (Hg/Hg₂SO₄/K₂SO₄) period-two oscillations: (a) total current; (b) cycle one, activation; (c) cycle one, passivation; (d) cycle two, activation; (e) cycle two, passivation.

zero to approximately 280 mA, and a slower passivation during which the current returns to its passive value. The currents of individual electrodes are also measured; these individual currents are not shown here but shall be shown for other experiments below. The activation and passivation do not occur uniformly, but rather waves move across the array during both activation and passivation processes. The wave directions during the activation and passivation for the oscillations of Figure 3a are shown in Figure 3b and c, respectively. The activation begins at the center of the array and propagates to the outside; the passivation begins at the outer rim and proceeds to the center. The passivation has been measured on a single electrode by visual means and is similar to that seen in Figure 3c for the electrode array.²³ Both the passivation and activation waves

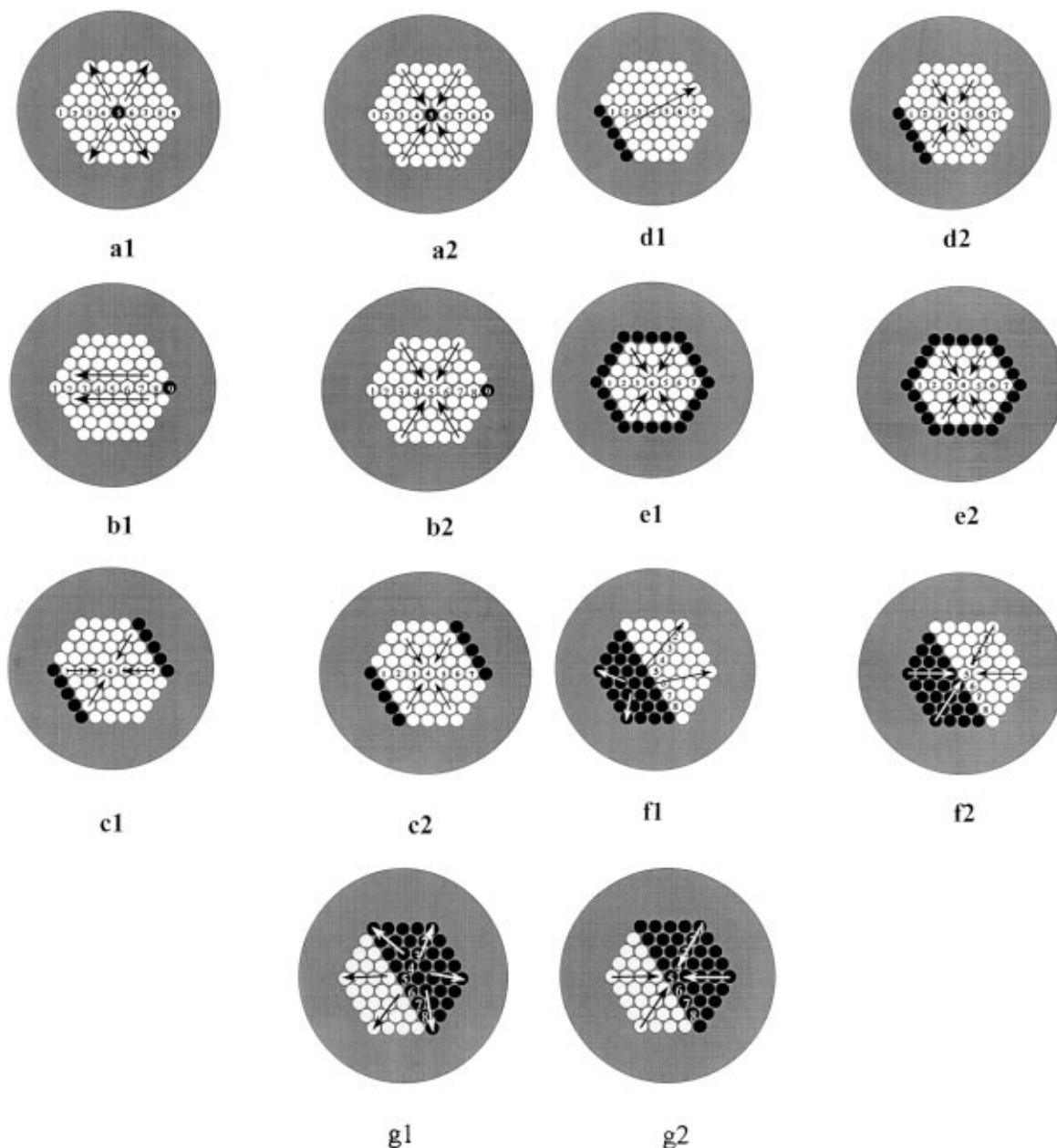


Figure 5. Wave directions in the seven configurations; period-one oscillations; k1 (black) electrodes at low (forcing) potential, k2 (white) at high potential. a₁, b₁, c₁, d₁, e₁, f₁, g₁, activation; a₂, b₂, c₂, d₂, e₂, f₂, g₂, passivation.

accelerate as they propagate. The passivation wave, which is the easiest to characterize because it is slower, accelerates from an initial value of approximately 6 mm/s to a final value of approximately 60 mm/s. The activation waves are much faster; they accelerate from approximately 550 to 650 mm/s as the wave moves from the center to the edge. The period-one relaxation oscillations, as seen in Figure 3, occur in the potential range from -130 to -170 mV. Within this range the frequency of the oscillations increases as the potential is decreased.

As the potential is decreased further, a spatiotemporal period doubling takes place at approximately -170 mV. The total current and the wave patterns on the arrays are shown in Figure 4 for one value of the applied potential, $E = -185$ mV. It can be seen that the frequency of these oscillations is higher than that of Figure 3, following the general trend that frequency increases as the potential is lowered. Furthermore, a period now includes two activation-passivation sequences. As seen in Figure 4b, the first activation begins in the left region of the array, the passivation then is a wave returning to the same location (4c). The next activation begins at a location on the

right side of the array (4d) and the passivation returns to that same location (4e). The next activation starts the cycle again. We show the wave patterns at a potential past that at which the period doubling has taken place. At the period doubling, the center of the activation and passivation waves seen in Figure 3b,c split. The two resulting centers move apart as the potential is lowered, resulting then in the behavior seen in Figure 4b–e.

Below approximately $E = -195$ mV the electrode is in the active (nonoscillating) state.

Arrays with Pacemakers. We now discuss the experiments which were done by holding one group of electrodes at one (constant) potential and the second group at a second (constant) potential. The configurations were shown above in Figure 1. In each case to be discussed, the electrode(s) shaded black was (were) held at the lower of the two potentials and thus at a condition with a higher natural frequency. As we shall see, the higher frequency centers served as sources or pacemakers for the activation waves; the qualitative features of the repassivation on the array, however, were not affected by the pacemakers.

The signals from the pacemaker and nonpacemaker electrodes are denoted by k_1 and k_2 , respectively.

We start with experiments in which the nonpacemaker electrodes are held either at $-160 \text{ mV} < E_{k_2} < -130 \text{ mV}$ (within the period-one oscillation range) or at $-130 \text{ mV} < E_{k_2} < -100 \text{ mV}$ (within the passive range but near the oscillatory region). The pacemaker electrodes are at a lower potential $-210 \text{ mV} < E_{k_1} < E_{k_2}$. The pacemakers always oscillate under the conditions of these experiments; in some cases they are held at a potential which would be active if the entire array were held at that value. However, since the area of the pacemakers is, of course, always less than the area of the entire array and since the behavior of the system is influenced by the conditions of all the electrodes, conditions are such that the pacemakers oscillate. To produce a significant effect of the pacemaker electrodes, the difference in potential between the pacemaker and nonpacemaker electrodes had to be greater than a threshold value. The difference had to be 70 mV or greater in the case of a single pacemaker electrode (configurations A and B); however, the potential difference can be smaller in other configurations in which there are more pacemaker electrodes.

The results of such experiments are shown in Figures 5–8. Wave directions for seven configurations can be seen schematically in Figure 5. The total currents for the pacemaker and nonpacemaker groupings and for selected individual electrodes are presented in Figures 6–8 for three representative experiments.

When the pacemaker electrode is in the center of the array, Figure 5a, the activation and passivation have the same pattern as when the array has a uniform potential, i.e., the passivation begins in the center and the passivation ends there. Compare to Figure 4a,b where the same pattern is seen.

However, when the pacemaker is not in the center, the pattern is altered. Consider, for example, Figure 5b where a single pacemaker (lower potential) electrode is at the outer edge of the array. In this case the activation takes place at the pacemaker electrode, i.e., the activation is a wave which begins at the pacemaker electrode and traverses the array from right to left as shown. The passivation, however, is an axisymmetric wave which ends at the center of the array; the passivation is thus the same as that which occurs with arrays at uniform potentials.

Other examples are given in Figure 5c–g. In each case the activation begins at the pacemaker electrodes. Note, for example, Figure 5e where both the activation and passivation are circular waves progressing toward the center. In this case the activation waves begin at the outer edge of the array because the pacemakers are at the edge. The activation is thus in the opposite direction as that on a uniform array in which the activation waves would be from center to edge. The passivation occurs as always in its normal direction which is radially inward.

Thus in all experiments in which the nonpacemaker electrodes are at a potential which is either in the period one region or in the passive region, the repassivation occurs from the outside to the center of the array, i.e., it occurs in the same manner as the autonomous repassivation in the period one region as seen in Figure 3. The potential of the nonpacemaker electrodes has a major influence on the passivation process, and therefore whether the entire array is in a period one or a period two regime.

The currents on nine individual electrodes for the experiment in which a single electrode (number 9) at the rim of the array acts as the pacemaker are seen in Figure 6b,c. It can be seen that the pacemaker electrode activates first and that this is

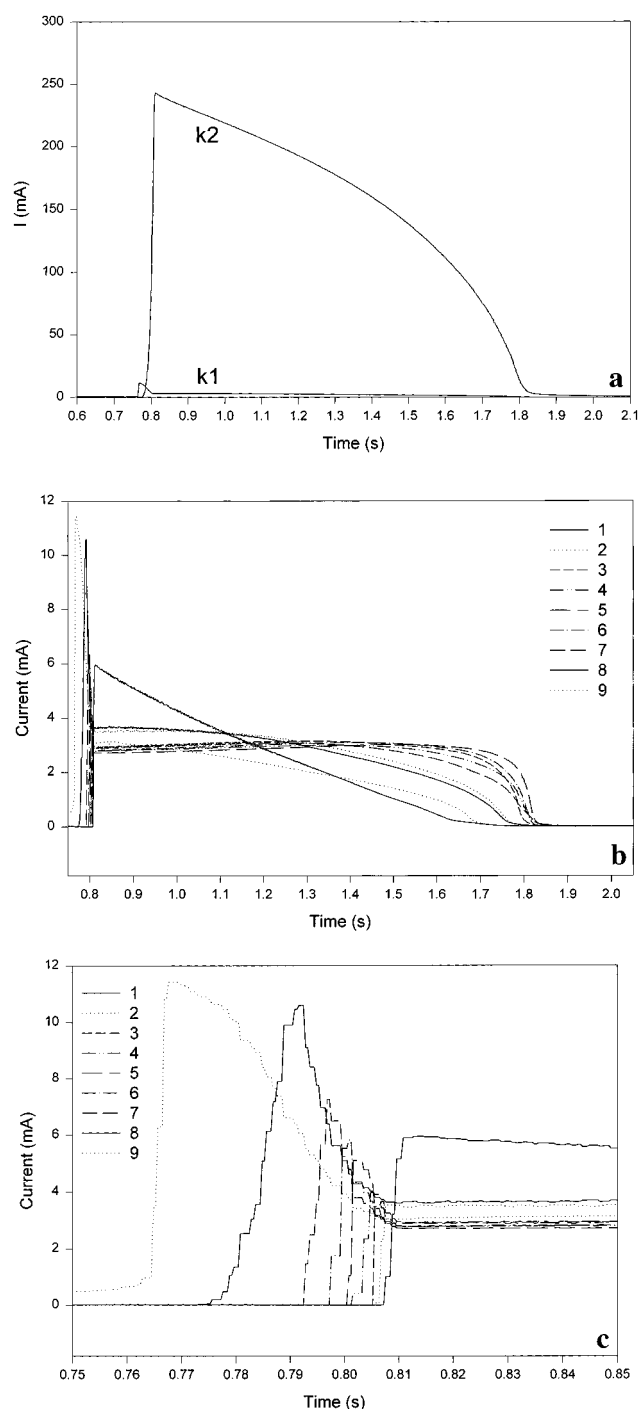


Figure 6. Currents and potentials corresponding to Figure 5, configuration B; a single electrode at the rim of the array acts as a pacemaker; period-one oscillations. k_1 at -195 mV , k_2 at -120 mV ($\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$). (a) Total current of k_1 and k_2 . (b) Currents of individual electrodes. (c) Currents of individual electrodes, activation (expanded scale).

followed by activation of the other electrodes as the activation wave propagates from right to left in the figure; the same result can be seen in a slightly different manner in Figure 6a where the current of the single pacemaker electrode (k_1) leads the total current on the remaining 60 electrodes (k_2).

Other experiments were carried out in which there were larger numbers of pacemaker electrodes (see Figure 1c–g). As examples, we describe two such experiments in which the area of the pacemaker electrodes is approximately the same as that of the nonpacemakers. Figure 7 corresponds to configuration F in which 26 electrodes are held at a lower potential

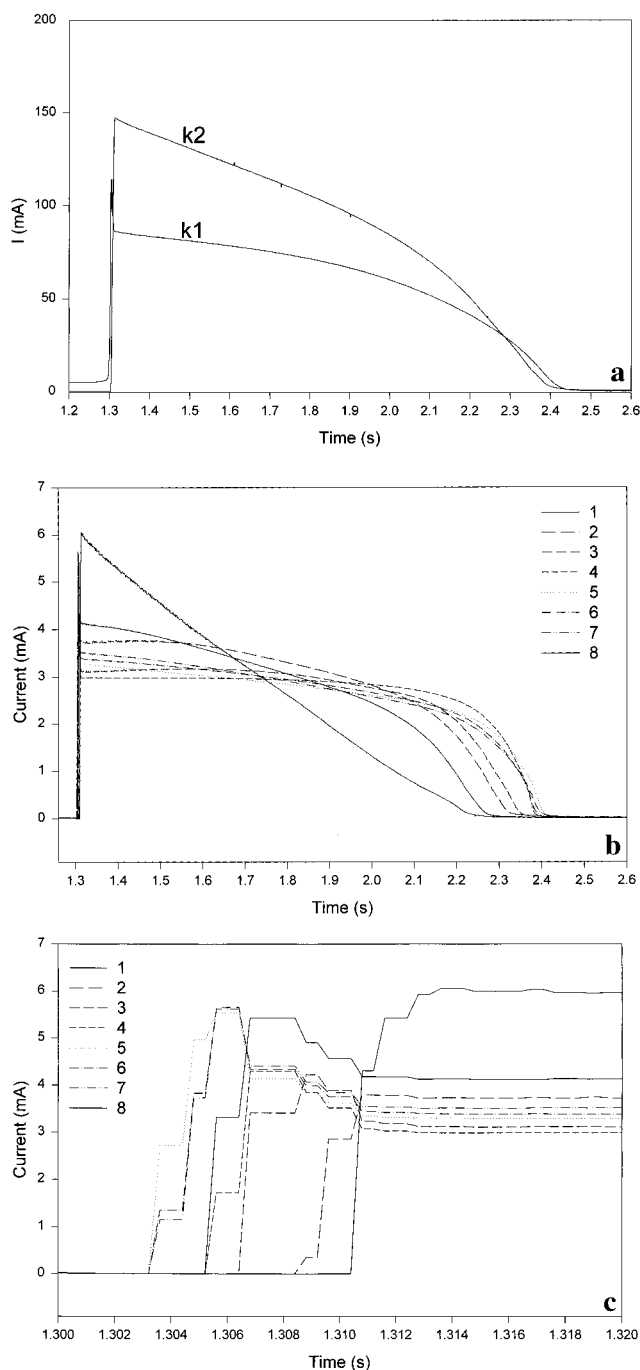


Figure 7. Currents and potentials corresponding to Figure 5, configuration F; 26 pacemaker electrodes; period-one oscillations, k1 at -175 mV, k2 at -120 mV ($\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$). (a) Total currents of k1 and k2. (b) Currents of individual electrodes. (c) Currents of individual electrodes, activation (expanded scale).

(autonomously higher frequency); Figure 8 corresponds to configuration G with 35 autonomously higher frequency electrodes. The 61 hexagonal array cannot be partitioned into two identical halves and thus with these two experiments we bracket the half higher frequency pacemaker/half lower-frequency condition. In Figure 7a it is seen that the total current on the 26 (pacemaker) electrodes leads that of the remaining 35. The individually measured currents (Figure 7b,c) simply show that the activation waves emanate from the 26 pacemakers and the passivation from the edge of the entire array; this was shown schematically in Figure 5f. In Figure 8a it can be seen that when the 35 electrodes are held at a potential at which they have a naturally higher frequency, their total current leads that

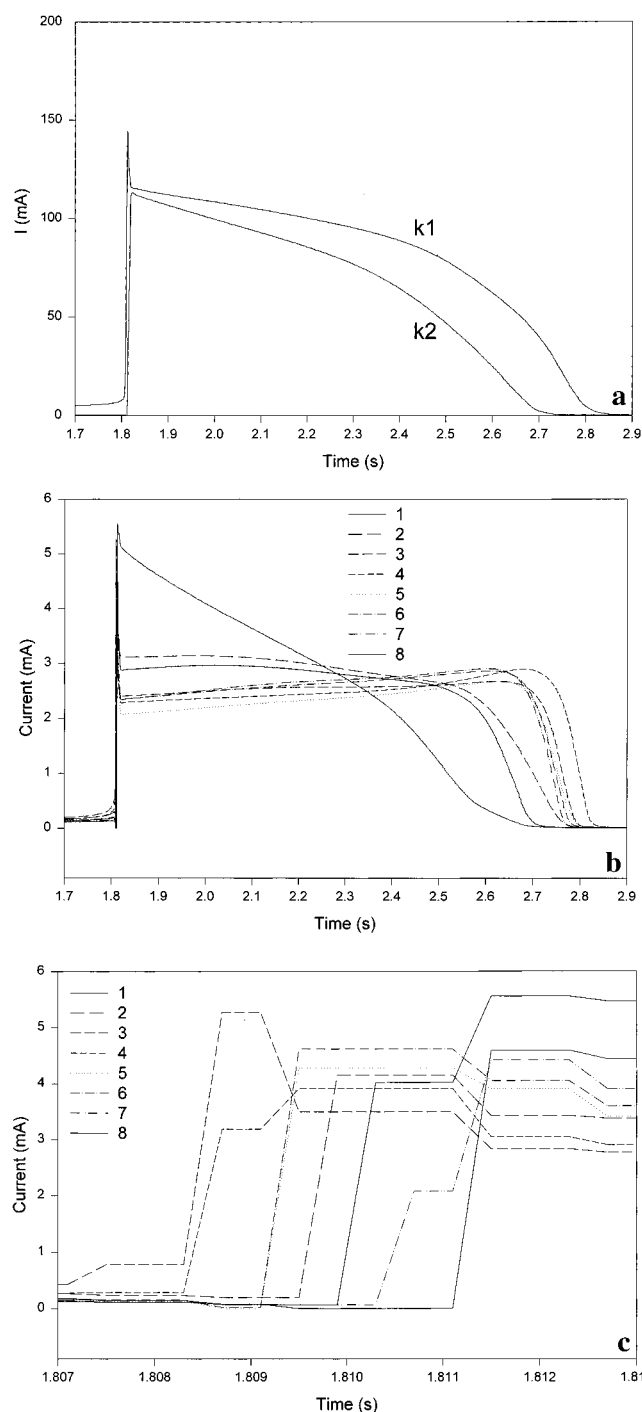


Figure 8. Currents and potentials corresponding to Figure 5, configuration G; 35 pacemaker electrodes; period-one oscillations, k1 at -175 mV, k2 at -100 mV ($\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$). (a) Total currents of k1 and k2. (b) Currents of individual electrodes. (c) Currents of individual electrodes, activation (expanded scale).

of the remaining 26; the activation waves emanate from the 35 electrodes as can be seen in the schematic of Figure 5g and in the individual time series of Figure 8b,c.

We now describe an experiment in which the nonpacemaker electrodes are held at a potential at which period two oscillations naturally occur. A single electrode on the rim of the array (configuration B) is held at a lower potential. Again the activation waves emanate from the pacemaker electrode. The passivation, however, takes place as in the period two state seen above in Figure 4, i.e., the passivation occurs alternatingly to the right and left portions of the array; a schematic of the wave behavior is given in Figure 9.

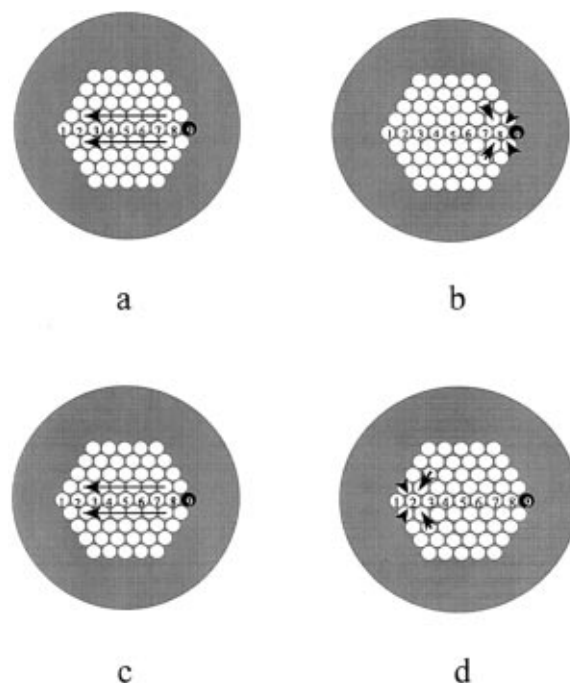


Figure 9. Wave directions, configuration B; period-two oscillations; k1 (black) electrodes at low potential, -200 mV; k2 (white) at high potential, -175 mV ($\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$). Left column, activation; right column, passivation; (a, b) cycle one; (c, d) cycle two.

Forced Oscillations. We carried out a few experiments with forcing, i.e., in which the pacemaker electrode is varied periodically with a square wave form. Only one electrode configuration is considered, viz., that of the single forcing electrode at the rim of the array (configuration B). The results of these experiments can thus be compared to those presented above where the wave patterns are given in Figure 5b for the period one regime and in Figure 9 for the period two oscillation. The difference here is that the single electrode on the rim of the array is not held at a constant potential but rather undergoes a controlled forced periodic oscillation.

We first consider a case in which 60 of the electrodes (k2) are held at -120 mV. (This is in the passive region, close to the period-one region; similar results are obtained when the electrodes are held at a potential in the autonomous period-one region.) The forcing electrode (k1) is cycled between -100 and -200 mV at frequency 0.2 Hz; 0.2 Hz is close to the natural frequency under these conditions. The potentials and the total current of the 60 k2 electrodes are shown in Figure 10. The forcing and response have a 1:1 frequency ratio. Note that there is a significant constant time delay between the drop in potential of k1 and the activation of the electrode and the resulting rise in current. The patterns on the electrode surfaces are the same as those which occur when the k1 pacemaker is held constant, i.e., they are the same as seen above in Figure 5b.

A similar experiment is considered but now the 60 unforced electrodes (k2) are held at a potential of -180 mV at which period-two oscillations occur autonomously. The single forcing electrode k1 is cycled between -150 and -250 mV at frequency 1.11 Hz. The potentials and the resulting current of the 60 electrodes are shown in Figure 11. (Note that the time scales of Figures 10 and 11 are different since at the lower potentials of Figure 11 (-180 mV) the oscillations are faster.) There is again, in Figure 11, a time delay between the drop in potential of k1 and the resulting rise in current of the remaining electrodes. The wave directions are the same as those shown in Figure 9, i.e., the same as in the case in which the pacemaker

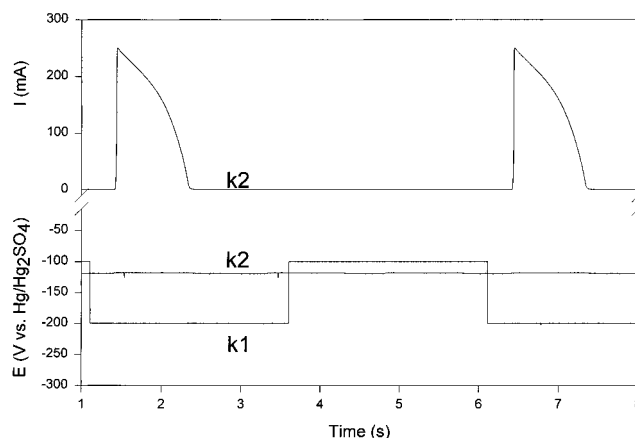


Figure 10. Total current of k2. Forced oscillations, configuration B, k2 at -120 mV; k1 cycled between -100 and -200 mV at frequency 0.2 Hz; 1:1 frequency ratio, k2 to k1. Wave directions shown in Figure 5b.

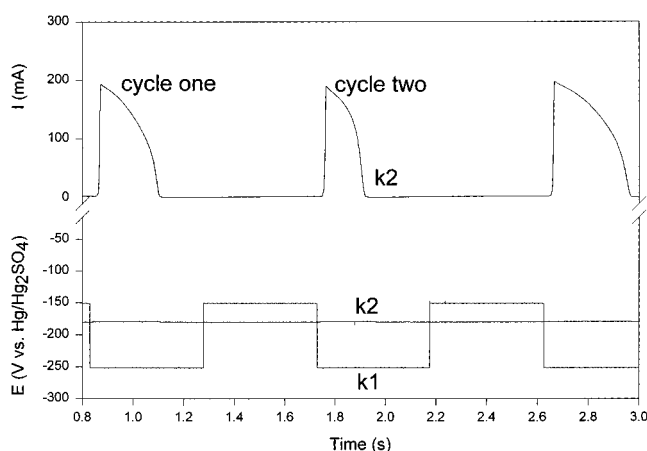


Figure 11. Total current of k2. Forced oscillations, configuration B, k2 at -180 mV in period-two oscillation region; k1 cycled between -150 and -250 mV at frequency 1.11 Hz; 1:2 frequency ratio, k2 to k1. Wave directions shown in Figure 9.

was held at a constant potential. This is a period-two oscillation. There is a 1:2 frequency ratio of k2 to k1.

Finally, we consider an experiment very close to that of Figure 11. The 60 electrodes k2 are again at -180 mV, and the forcing frequency of k1 is still 1.11 Hz. However, k1 is now cycled between -130 and -230 mV. The results are shown in Figure 12. Note that the amplitude of the forcing signal in Figure 12 is the same as that in Figure 11, i.e., the difference between the maximum and minimum is 100 mV. However, in Figure 12 the forcing potentials are slightly more anodic; under the conditions of Figure 12 the forcing is weaker than that of Figure 11. The wave directions which are obtained from the measurements of the individual currents (Figs. 12 b-e) are again as shown in Figure 9. However, there is now a 1:4 frequency ratio of k2 to k1; this can be seen in Figure 12a.

Discussion

The relaxation oscillations being considered here consist of a periodic cycle of activation and passivation of the electrode surface. The cycle, beginning with an active surface, likely consists of the following steps: metal dissolution occurs and iron sulfate forms on the surface, a passive oxide layer grows under the salt layer passivating the surface, and the salt film dissolves leaving the oxide layer.³⁵ The activation, acid dissolution of oxide, follows.

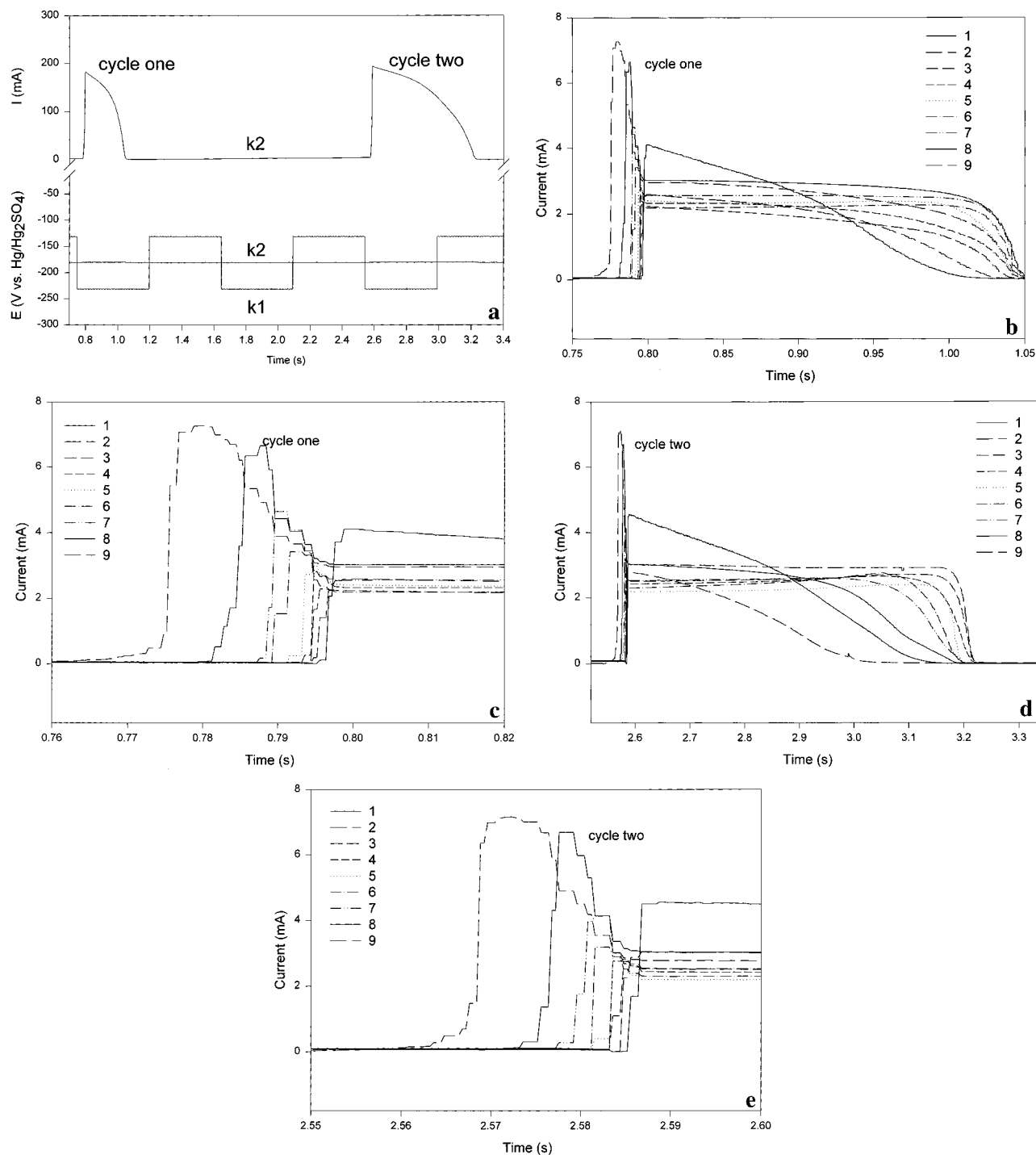


Figure 12. Total current of k_2 . Forced oscillations, configuration B, k_2 at -180 mV in period-two oscillation region; k_1 cycled between -130 and -230 mV at frequency 1.11 Hz; $1:4$ frequency ratio, k_2 to k_1 . Wave directions shown in Figure 9. (a) Total current of k_2 , potentials of k_1 and k_2 . (b) Currents of individual electrodes, cycle one. (c) Currents of individual electrodes, cycle one, activation (expanded scale). (d) Currents of individual electrodes, cycle two. (e) Currents of individual electrodes, cycle two, activation (expanded scale).

During the oscillations the surface is not uniform, but rather waves propagate across the surface in both the activation and passivation stages. We use in these experiments arrays of electrodes where the current through the electrodes can be individually measured; thus the rate of reaction as a function of both position and time is obtained.

An array behaves similarly to a single electrode of the same shape and total area. The analogy is not exact because the current distribution on a single electrode will not be the same as that on a series of electrodes separated by an insulator, even if all the electrodes are at the same potential; for a discussion of primary and secondary current distributions on electrodes

see, for example, Newman.³⁶ Nevertheless, the behavior of the processes described here is strongly influenced by long-range interactions through the electrolyte. Since the long-range interactions are important, the insulating regions between the electrodes do not alter the qualitative behavior of the surface patterns and the oscillations.

We see that in the case of the active-passive relaxation oscillations being investigated here that the activation waves emanate at the high frequency pacemaker sites. The repassivation, however, normally takes place as though there were no pacemaker present but rather is controlled by the conditions of the (larger) nonpacemaker region. Thus if the potential of the

nonpacemaker electrodes is in the parameter region where period-one oscillations take place, the repassivation occurs by the radially inward growth of a passivating region; if the potential is in the period-two region, the repassivation occurs via waves progressing, in an alternating fashion, to sections on either side of the array.

We carried out a few experiments in which the potential of the pacemaker electrodes were forced externally. In all cases seen there was a simple rational ratio (1:1, 1:2, 1:4) of oscillation frequency to forcing frequency and phased-locked, periodic oscillation took place; other types of behavior are certainly possible. As in the autonomous cases, the activation waves emanated from the pacemaker centers while the repassivation occurred as though the array was at a uniform potential. The current of the nonpacemaker electrodes always lagged behind the potential of the pacemakers; the phase lag was shorter at higher forcing frequencies.

The arrays of electrodes used in this study serve as a model heterogeneous reacting system. They have the advantage that the rate of reaction can be measured at each location of a reacting surface although, of course, in the present work we have broken the surface up into 61 discrete segments. In the electrochemical system this does not change the overall behavior or the spatiotemporal patterns on the surface (as compared to a single, larger electrode) because the coupling between reacting sites is largely through the electric field. The emphasis of the present paper is on nonuniform surfaces, i.e., surfaces in which the conditions of the surface vary with position. Since the arrays can be made up of electrodes of various sizes or properties or simply can be held at various potentials, as in the present case, they can be used as model systems for studies of surface "defects". One (or more) of the electrodes in the arrays being studied here can be made to act as a pacemaker or activity center as was seen above. The natural frequency of oscillation depends on the applied potential and the electrode or electrodes at lower potential, and higher frequency, play this role. There is the advantage in these array experiments that the position and strength of the "defect" can be controlled since the number and position of the pacemaker electrodes as well as the frequency ratio between different locations on the array are easily controlled parameters.

Arrays such as those studied in these experiments are likely to be useful not only in the study of the effects of nonuniform surfaces and of nonuniform forcing, but also of feedback control of spatiotemporal patterns.

Acknowledgment. This work was supported in part from grants from the National Science Foundation and from the Chevron Oil Company.

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