

From Excitatory to Inhibitory Connections in Networks of Discrete Electrochemical Oscillators

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A network of two coupled electrochemical oscillators is investigated theoretically and experimentally. It is shown that, if the network is controlled potentiostatically with a point reference electrode, the evolution of the system depends both on the uncompensated and solution resistances. As a result, the action of the connections between the two oscillators can be tuned to be either excitatory or inhibitory by changing the relative position of the working, counter, and point reference electrodes. The change of the connection's action induces different in-phase or out-of-phase stable synchronized states. The numerical predictions are qualitatively reproduced experimentally.

1. Introduction

It has been long ago since a phenomenological resemblance between electrophysiological and electrochemical oscillators was suggested.^{1,2} Despite the kinetic analogies between these two classes of nonlinear systems,^{2–6} networks of the former seem to exhibit wealthier types of dynamics than the latter. This might be partially due to the fact that connections between individual neural oscillators can be either excitatory or inhibitory, localized or not, and the action's type can be determined both from the transmitter and the receptor.⁷

In networks of identical oscillatory electrochemical systems, controlled by an appropriate instrumentation, it is intuitively expected that coupling would facilitate activation because the most profound mean of communication is linear and electric and tends to decrease (in absolute values) the electrode's double layer potential and hence activate the oscillator. Nevertheless, as it was shown in a previous work,^{8,9} if the coupling is between nonidentical electrodes, communication can impede, instead of facilitating the activation. Such an altering of the network's response can be achieved, though, only by changing completely the architecture of the assembly.

For convenience, throughout this paper, we will borrow some terms from the field of neurophysiological networks. Hence, an electrode will be called *electrochemical oscillator* and may or may not exhibit periodic activity. An electrochemical oscillator may have a broad dynamic behavior ranging from steady state to chaotic dynamics, and oscillatory activity can be achieved either by changing the parameter's values or due to appropriate coupling. The mean of coupling between electrochemical oscillators will be called *connection*. The

connection might be either electrical (e.g., currents flowing through an electrolytic solution due to potential differences), via diffusion (e.g., molecular fluxes due to concentration gradients), or even chemical. The connection will be called *excitatory* if the averaged action of one oscillator to another is to decrease (in absolute values) the other oscillator's double layer potential and thus facilitate its activity; it is called *inhibitory* if it increases its double layer potential and thus impedes the activity.

In the present article, we investigate a procedure to alter the connections from excitatory to inhibitory in networks of *identical* discrete electrochemical oscillators, without changing the architecture of the network itself. We will consider a network of two point working electrodes controlled potentiostatically with the use of a point reference electrode. It will be shown that the type of connections and, as a consequence, the network dynamics depend both on the uncompensated and the solution resistance of the electrochemical cell. Thus, the type of connections can be altered by changing the ratio of these resistances (e.g., by moving the point reference electrode along the symmetry axis) without changing the position or the nature of the working electrodes. The resulting equations will be investigated numerically for both weak and strong coupling and for uniform and nonuniform frequencies of the individual oscillators. Finally, the theoretical results will be compared qualitatively with experimental observations.

2. Modified Potentiostatic Circuit

For a system consisting of two identical working electrodes controlled potentiostatically, we consider the following main assumptions:

1. The size of each electrode is very small, and the distribution of the system variables on their surface is assumed homogeneous. From the geometric point of view, they are considered as points.

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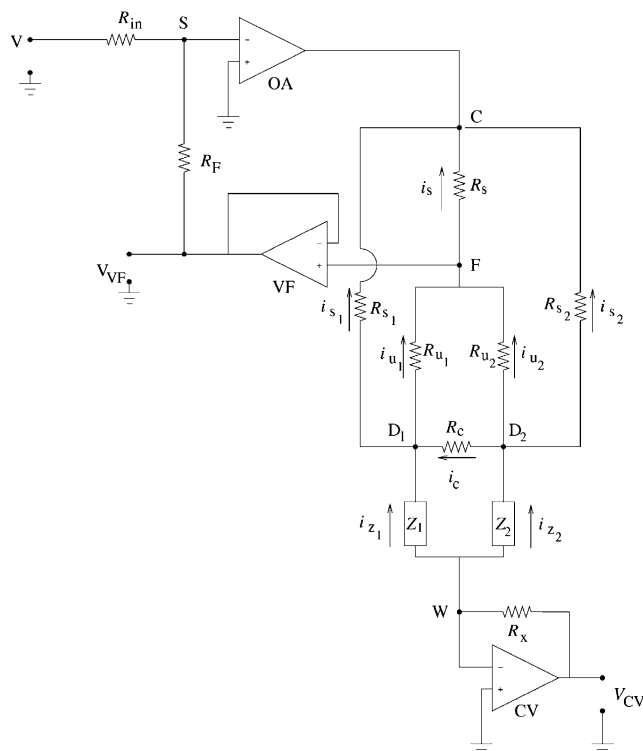


Figure 1. Modified potentiostatic circuit. The two working electrodes located between W and D_k are coupled through the resistance R_c . Current can flow also from the solution resistances R_{sk} .

2. The size of the reference electrode is very small, and it is considered as a point. This assumption may be achieved experimentally by using a Haber-Luggin capillary.

3. The reference electrode is located on the axis of symmetry and at some distance from the working electrodes. Thus, the two working and reference electrode lie on the vertexes of an isosceles triangle.

4. No current flows through the reference electrode toward the potentiostatic circuit.

5. The counter electrode is large and located far from the working and reference electrodes. The overpotential at the counter is ignored.

6. The current flowing from each working electrode toward the counter consists of three components: (a) The current flowing from the working electrode through the uncompensated resistance (between working and reference) and a solution resistance (between reference and counter). (b) The current flowing from one working electrode toward the other due the difference of the surface potentials. (c) The current flowing from the working electrode toward the counter electrode through a solution resistance without passing through the corresponding uncompensated resistance. This current component has to be included due to the position of the reference (assumption 3).

Under the above assumptions, the system can be described by the equivalent circuit of Figure 1. Each working electrode or oscillator, Z_k , $k = 1$ or 2 , is located between points W and F. The point W represents the metal side of these electrodes and D_k a point just outside the double layer. A point reference electrode and a counter electrode are located at F and C, respectively. Due to the current-to-voltage converter (CV), the point W is grounded

$$V_W = 0 \quad (1)$$

Additionally, due to the main operational amplifier (OA), the potential at the reference electrode is equal to minus the applied potential

$$V_F = -V \quad (2)$$

Finally, due to the Voltage Follower (VF), no current is drawn from the reference electrode.

The two working electrodes are located at some distance from each other and can instantaneously attain different potential values, V_{Dk} , due to a phase difference; thus, they can communicate through currents flowing along the resistance R_c . Furthermore, because the reference is a point, it does not represent an equipotential line located at some distance from the surface of the working electrodes, and thus, currents flowing through Z_k flow both from R_c , the uncompensated resistance R_{uk} , and the resistance R_{sk} . The presence of this resistance is a natural addition, because it is not possible to expect a total current flow through the point F in such a spatially extended system (assumption 6).

At point F, we have due to Kirchhoff's current law

$$i_s = \sum_{m=1}^2 i_{u_m} \quad (3)$$

or equivalently

$$V_F - V_C = R_s \sum_{m=1}^2 \frac{V_{D_m} - V_F}{R_{u_m}} \quad (4)$$

Additionally, due to Kirchhoff's voltage law, we have

$$(V_{D_k} - V_C) = (V_F - V_C) + (V_{D_k} - V_F) \quad (5)$$

At point D_k , $k = 1, 2$, we have

$$i_{z_k} = i_{u_k} + i_{s_k} + (-1)^k i_c \quad (6)$$

or equivalently

$$i_{z_k} = \frac{V_{D_k} - V_F}{R_{u_k}} + \frac{V_{D_k} - V_C}{R_{s_k}} + \sum_{m=1}^2 (-1)^{m+k} \frac{V_{D_m}}{R_c} \quad (7)$$

Combining eqs 4 and 5 with eq 7, we obtain

$$i_{z_k} = \frac{V_{D_k} - V_F}{R_{u_k}} + \frac{V_{D_k} - V_F}{R_{s_k}} + \frac{R_s}{R_{s_k}} \sum_{m=1}^2 \frac{V_{D_m} - V_F}{R_{u_m}} + \sum_{m=1}^2 (-1)^{m+k} \frac{V_{D_m}}{R_c} \quad (8)$$

If we assume that the element Z_k consists of an nonlinear resistance (due to the faradaic processes) and a capacitance in parallel,¹⁰ then

$$i_{z_k} = i_{e_k}(U_k, c_k) + C_k \frac{dU_k}{dt} \quad (9)$$

where C_k is the capacitance of the double layer and $U_k = (V_W - V_{D_k})$ is the potential drop at the double layer. The total faradaic current, i_{e_k} , depends on the kinetics of the electrode reactions and is a function of the double layer potential and concentration

c_k just outside the double layer. Combining eqs 8 and 9 and using also eqs 1 and 2, we obtain, for $k = 1$ or 2

$$C_k \frac{dU_k}{dt} = \frac{V - U_k}{R_{u_k}} - i_{e_k}(U_k, c_k) + \frac{V - U_k}{R_{s_k}} + \frac{R_s}{R_{s_k}} \sum_{m=1}^2 \frac{V - U_m}{R_{u_m}} - \sum_{m=1}^2 (-1)^{m+k} \frac{U_m}{R_c} \quad (10)$$

For the concentration, c_k , of the electroactive species, we assume variations only along the axis of symmetry and a linear concentration profile in the diffusion layer of length δ_k . Under these assumptions, we obtain^{11,12}

$$\frac{dc_k}{dt} = \frac{2D_k}{\delta_k^2} (c_{k,b} - c_k) - \frac{2}{\delta_k F A_k} \frac{V - U_k}{R_{u_k}} + \frac{2}{\delta_k F A_k} i_{q_k}(U_k, c_k) \quad (11)$$

where D_k is the diffusion coefficient, A_k is the electrode area, $c_{k,b}$ is the bulk concentration, F is the Faraday constant, and i_{q_k} is the faradaic current due to the electrochemical process where these species are participating. Here, for simplicity, we assumed also that the migration flux for the electroactive species is equal to the potential drop on the corresponding uncompensated resistance and that the number of electrons is $n = 1$. From eqs 10 and 11, we observe that in the present formulation the coupling is linear and only in the electric variable.

We assume that the two oscillators are identical, i.e., $\delta_k = \delta_m = \delta$, $C_k = C_m = C$, $A_k = A_m = A$, $D_k = D_m = D$, and $c_{k,b} = c_{m,b} = c_b$. In dimensionless variables, eqs 10 and 11 are written

$$\epsilon \frac{du_k}{d\tau} = \frac{v - u_k}{r_{u_k}} - I_{e_k}(u_k, x_k) + G_k(\mathbf{u}, \mathbf{p}_k) \quad (12)$$

$$\frac{dx_k}{d\tau} = (1 - x_k) - \frac{v - u_k}{r_{u_k}} + I_{q_k}(u_k, x_k) \quad (13)$$

where $u_k = FU_k/RT$ (similarly for v), $x_k = c_k/c_b$, $\epsilon = 2CRT/F^2 A c_b \delta$, $r_{u_k} = F^2 D c_b A R_{u_k} / \delta RT$ (similarly for all the resistances), $\tau = 2Dt/\delta^2$, and $I_{e_k} = \delta i_{e_k}/c_b DFA$ (similarly for I_{q_k}). The vectors $\mathbf{p}_k = (v, r_s, r_c, r_{s_k}, r_{u_1}, r_{u_2})$ and $\mathbf{u} = (u_1, u_2)$ represent the systems' parameters and electric variables, respectively. The coupling function G_k is given by, for $k = 1$ or 2

$$G_k(\mathbf{u}, \mathbf{p}_k) = \frac{v - u_k}{r_{s_k}} + \frac{r_s}{r_{s_k}} \sum_{m=1}^2 \frac{v - u_m}{r_{u_m}} - \sum_{m=1}^2 (-1)^{m+k} \frac{u_m}{r_c} \quad (14)$$

For $r_{s_k}, r_c \rightarrow \infty$, eq 12 becomes

$$\epsilon \frac{du_k}{d\tau} = \frac{v - u_k}{r_{u_k}} - I_{e_k}(u_k, x_k) \quad (15)$$

and, thus, represents an uncoupled electrode.¹¹ On the other hand, for $r_{s_k} \rightarrow \infty$ but finite r_c , eq 12 becomes

$$\epsilon \frac{du_k}{d\tau} = \frac{v - u_k}{r_{u_k}} - I_{e_k}(u_k, x_k) - \sum_{m=1}^2 (-1)^{m+k} \frac{u_m}{r_c} \quad (16)$$

and, thus, represents the case of an equipotential line reference electrode, instead of a point reference electrode. In this case,

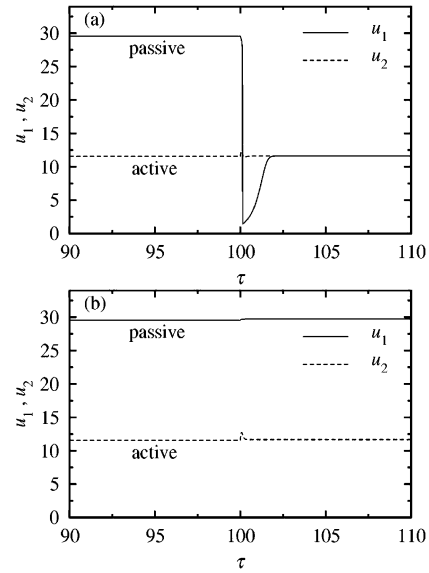


Figure 2. Coupling of two oscillators in the bistable regime. (a) Excitatory coupling leading to the activation of the passive oscillator, $r_s = 40$. (b) Inhibitory coupling leading to further passivation of the passive oscillator, $r_s = 120$. Coupling is effective for $\tau \geq 100$.

the current flowing through r_{s_k} is infinitesimally small and the electrodes are coupled via currents flowing through the resistance r_c .

For the remainder of the article and for the sake of simplicity, we further assume that the total faradaic current, I_{e_k} , is described by an N-type current vs voltage relationship and I_{q_k} is a fraction of the total faradaic current

$$I_{e_k} = x_k(a_1 u_k + a_2 u_k^2 + a_3 u_k^3) \quad (17)$$

$$I_{q_k} = \alpha I_{e_k}, \quad \alpha < 1 \quad (18)$$

The considerations above might seem very simplistic, but the results presented in the next sections are expected to be qualitatively the same as far as the $\dot{u}_k = 0$ nullcline is a nonmonotonic function and its intersection(s) with the $\dot{x}_k = 0$ nullcline correspond to one or three hyperbolic fixed points, in the oscillatory and bistable case, respectively.

Finally, we set $\epsilon = 1 \times 10^{-3}$, $a_1 = 1.125$, $a_2 = -0.075$, $a_3 = 0.00125$, and $\alpha = 0.1$.

3. Coupling in the Bistable Regime

At the first stage of the numerical investigation of eqs 12 and 13, we deal with the case where both oscillators lie in a bistable regime. This is achieved by setting $r_{u_k} = 20$ and $v = 29.7$. For these parameter values, each oscillator has three steady states, two being stable and one unstable. For the stable steady states, we designate the one corresponding to high values of u_k, x_k as passive and the one corresponding to low u_k, x_k as active.

For $\tau = 0$, the initial conditions of the oscillators are set in a way such that oscillator $k = 1$ is on the passive state and oscillator $k = 2$ on the active. Also, the coupling term G_k is turned off. Obviously both oscillators remain on their corresponding states because these are stable and there is no coupling present (see Figure 2 for $\tau < 100$). For $\tau \geq 100$, coupling is turned on. As can be seen in Figure 2, the time evolution of the coupled system depends on the value of r_s for fixed values of the rest of the resistances $r_c = 1 \times 10^3$ and $r_{s_k} = 5r_c$. Thus, for $r_s = 40$, Figure 2a, once the coupling is effective, the passive

oscillator is rapidly excited and reaches the active steady state. This behavior is designated as *excitatory coupling*.

By preserving the values of all parameters and altering only the value of r_s , the response of the system is drastically changed. As can be seen in Figure 2b for $r_s = 120$ when the coupling is turned on for $\tau \geq 100$, the passive oscillator not only is not activated but is further passivated due to its connection with the active one (notice the small increase of u_1). We designate this behavior as *inhibitory coupling*, since activation of a passive oscillator is impeded by the connection.

4. Coupling in the Oscillatory Regime

4.1. Weak Coupling. In the case where the resistances r_{sk} and r_c are very large (but not infinite) in comparison to r_{uk} and r_s , the connection between the two oscillators can be considered as weak. Under this condition, the evolution of the phase difference, χ , between the two oscillators is governed by^{7,13,14}

$$\dot{\chi} = \mu[H_2(-\chi) - H_1(\chi)] = -\mu H(\chi) \quad (19)$$

where μ describes the weakness of the connection. The connecting functions $H_k(\chi)$ are given by

$$H_k(\chi) = \frac{1}{T} \int_0^T \mathbf{Q}_k(\tau) \cdot \mathbf{G}_k(\gamma(\tau + \chi)) d\tau \quad (20)$$

where $\gamma(\tau)$ is the periodic orbit of the uncoupled oscillator, \mathbf{G}_k is the coupling function, and T is the period. In the present study

$$\mathbf{G}_k = \begin{pmatrix} G_k(\mathbf{u}, \mathbf{p}_k) \\ 0 \end{pmatrix} \quad (21)$$

The vector $\mathbf{Q}_k(\tau) = (Q_k^{(1)}, Q_k^{(2)})$ is the solution of the equation adjoint to the linearized equation of the uncoupled system around the periodic orbit

$$\dot{\mathbf{Q}}_k = -D\mathbf{F}_k(\gamma(\tau))^T \mathbf{Q}_k(\tau) \quad (22)$$

subjected to the normalization condition

$$\frac{1}{T} \int_0^T \mathbf{Q}_k(\tau) \cdot \mathbf{F}_k(\tau) d\tau = 1 \quad (23)$$

where \mathbf{F}_k is the right-hand side vector function of eqs 12 and 13 for $\mathbf{G}_k = 0$ and $D\mathbf{F}_k^T$ is the transposed of the Jacobian calculated on the uncoupled periodic orbit. Apparently, steady states of eq 19 with $\partial H/\partial \chi > 0$ correspond to stable synchronized solutions.

In Figure 3, the connection function, $H(\chi)$, together with the steady states are presented, calculated by XPP-AUT¹⁵ with the use of the Williams and Bowtell method,¹⁶ for $r_c = 1 \times 10^3$, $r_{sk} = 5r_c$, $r_{uk} = 10$, and $\nu = 28.95$. As can be seen in Figure 3a, for $r_s = 40$, eq 19 has three steady states. The in-phase synchronized solution, corresponding to $\chi = 0$, as well as the anti-phase solution, corresponding to $\chi = \pi$, are both stable. On the other hand, the two out-of-phase solutions are unstable. When the value of r_s is increased, the situation is reversed. Thus, for $r_s = 60$, Figure 3b, the in-phase and anti-phase solutions are unstable whereas the out-of-phase solutions are stable. We attribute this change of stability to a change of the connections from excitatory to inhibitory.

Two examples of the stable synchronized solution corresponding to excitatory coupling are shown in Figure 4. In the first case, Figure 4a, the initial conditions of the two oscillators are chosen in a way such the initial phase difference on the uncoupled limit cycle is $\chi = 0.23\pi$. For $\tau \geq 100$, the coupling

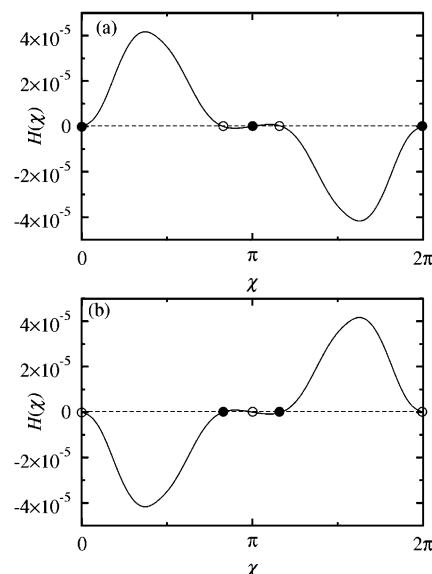


Figure 3. Connecting function, $H(\chi)$, versus the phase difference, χ , for two weakly coupled oscillators. (a) Excitatory coupling for $r_s = 40$ and (b) inhibitory coupling for $r_s = 60$. Filled and open circles designate stable and unstable synchronized solutions, respectively.

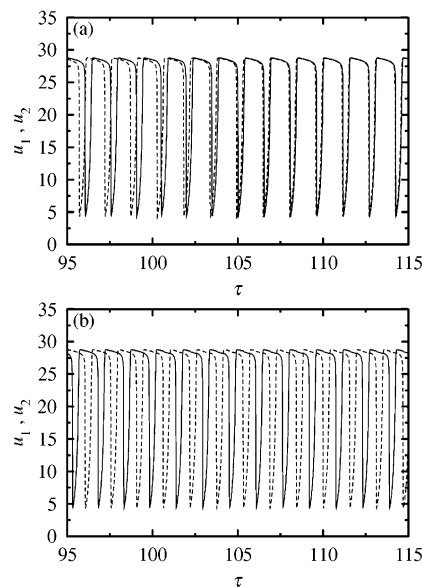


Figure 4. Synchronized behavior for weak excitatory coupling, $r_s = 40$. (a) In-phase synchronization, $\chi = 0$, and (b) anti-phase synchronization, $\chi = \pi$. Coupling is effective for $\tau \geq 100$.

is made effective. Because the phase difference $\chi = 0.23\pi$ is within the domain of attraction of the in-phase stable solution (see Figure 3a), the two oscillators are rapidly synchronized in phase. If the initial phase difference is within the domain of attraction of the anti-phase stable solution, as in Figure 4b where $\chi = \pi$, once the coupling is effective, the oscillators synchronize anti-phase.

When r_s is increased and the coupling is inhibitory, the only stable solution is out-of-phase synchronization. An example for $r_s = 60$ and initial phase difference $\chi = 0.066\pi$ is shown in Figure 5a. While the oscillators are uncoupled, they oscillate with the initially imposed phase difference, but when the coupling is made effective, for $\tau \geq 100$, they tend to synchronize out-of-phase with a phase difference $\chi = 0.83\pi$.

All of the above results hold if the two oscillators are identical and in the absence of frequency differences. In the presence of

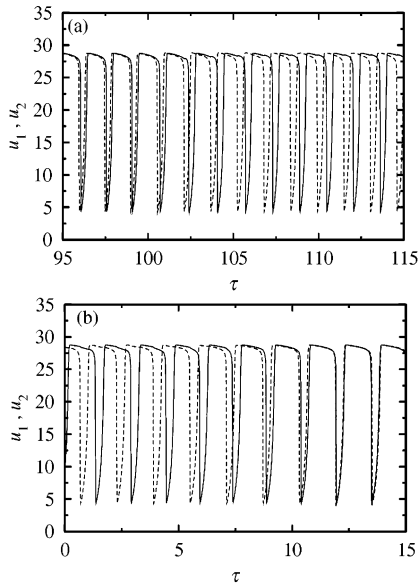


Figure 5. (a) Out-of-phase synchronization for weak inhibitory coupling, $r_s = 60$. Coupling is effective for $\tau \geq 100$. (b) Disappearance of the anti-phase solution in the presence of frequency differences for weak excitatory coupling, $r_s = 40$, $r_c = 1 \times 10^3$, $r_{u1} = 10$, and $r_{u2} = 9.8$.

frequency differences, $\Delta\omega$, between the two oscillators, eq 19 is modified to

$$\dot{\chi} = \mu\Delta\omega - \mu H(\chi) \quad (24)$$

Thus, the steady states of eq 24 are not the points of intersection of the graph of $H(\chi)$ with the x axis but with the line $-\Delta\omega$. Direct inspection of Figure 3a shows that in the presence of frequency differences and in the case of excitatory coupling, the anti-phase solution might disappear and the only stable solution is almost in-phase synchrony. From Figure 3b, it is easily concluded that in the case of inhibitory coupling and in the presence of frequency differences an out-of-phase stable solution always persists (even though shifted to lower or higher χ values) for sufficiently small $\Delta\omega$. An example of the disappearance of the anti-phase solution in the case of excitatory coupling and small frequency differences is shown in Figure 5b. The conditions are identical to those of Figure 4b but a small frequency difference is imposed by setting $r_{u1} \neq r_{u2}$. It can be seen that, even though the initial conditions are set to $\chi = \pi$, the system is synchronized almost in-phase because this is the only stable solution. The persistence of a completely in-phase or almost in-phase solution depends on the value of the relaxation parameter,^{17–19} ϵ , and it will be discussed in a future publication.²⁰

Because there is a transition from excitatory to inhibitory coupling by changing r_s , and the transition is expressed as a reversal of the $H(\chi)$ graph, Figure 3, it is to be expected that there is a critical value of r_s for which $H(\chi) = 0$ for every χ . In this case, even though coupling is present, the oscillators are expected to fire independently, and thus, the response will be *drifting*. It is rather straightforward to find the condition under which a transition is to be expected. From eqs 20 and 21, we have

$$H_k(\chi) = \frac{1}{T} \left[\frac{1}{r_c} - \frac{r_s}{r_{u_m} r_{s_k}} \right] \int_0^T Q_k^{(1)}(\tau) u_m(\tau + \chi) d\tau + \hat{H}_k(\tau) \quad (25)$$

where $\hat{H}_k(\tau)$ includes all χ -independent terms; here $m = 2$ when

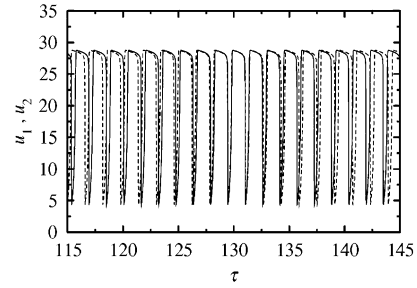


Figure 6. Drifting response for weak excitatory coupling, $r_s = 50$, in the presence of small frequency differences.

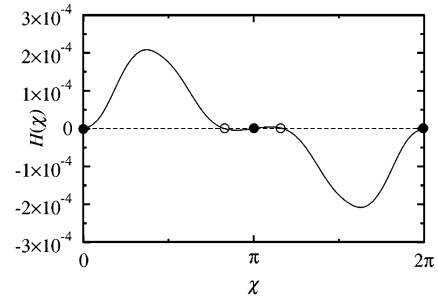


Figure 7. Connecting function in the case $r_{s_k} \rightarrow \infty$. Oscillators are coupled only through the resistance $r_c = 1 \times 10^3$.

$k = 1$ and $m = 1$ when $k = 2$. Thus, the function $H_k(\chi)$ becomes χ -independent if

$$r_s = \frac{r_{u_m} r_{s_k}}{r_c} \quad (26)$$

This is indeed the case, as can be seen in Figure 6. The conditions are set identical to those of Figure 5b except of $r_s = 50$. For this value of r_s , the connecting function is zero for all χ . Because the two oscillators are slightly different, they oscillate independently with a nonconstant phase difference.

Finally, it is worth noticing that when $r_{s_k} \rightarrow \infty$ and the system is described by eqs 16 and 13 then the oscillators are always coupled through excitatory connections. As can be seen in Figure 7, in this case, the in-phase as well as the anti-phase solution are stable whereas the out-of-phase solutions are unstable. This situation holds for any value of r_c . Hence, when the reference electrode is an equipotential line and oscillators are coupled only through r_c , the connections cannot be tuned by changing the position of the reference or the distance between the oscillators. Apparently, in the presence of $\Delta\omega$, the stable anti-phase solution might disappear and the only remaining stable state is (almost) in-phase synchronization.

4.2. Strong Coupling. When r_c and r_{s_k} are not large in comparison to r_{u_k} and r_s , then the analysis of section 4.1 does not hold because the network cannot be described by eq 19. Hence, we turn back to eqs 12 and 13; the function G_k , eq 14, is rewritten

$$G_k(\mathbf{u}, \mathbf{p}_k) = u_m \left(\frac{1}{r_c} - \frac{r_s}{r_{u_m} r_{s_k}} \right) + \hat{G}_k(u_k, \mathbf{p}_k) \quad (27)$$

where $m = 2$ when $k = 1$ and $m = 1$ when $k = 2$.

When the connecting function is written in the split form of eq 27, the first term represents the influence of the dynamical variables of the other oscillator, whereas the second term does

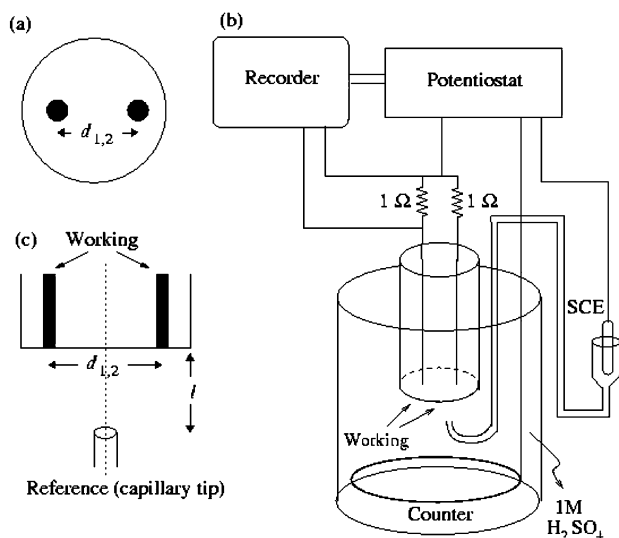


Figure 8. (a) Bottom view of the working electrodes assembly consisting of two electrodes with distance $d_{1,2}$, (b) experimental setup together with the recording system and (c) cross section of the working electrode assembly together with the tip of the reference electrode capillary located at l .

not depend on the dynamical variables of the other oscillator

$$\hat{G}_k(u_k, \mathbf{p}_k) = \frac{v - u_k}{r_{s_k}} + \frac{r_s}{r_{s_k}} \frac{v - u_k}{r_{u_k}} + \frac{r_s v}{r_{s_k} r_{u_m}} - \frac{u_k}{rc} \quad (28)$$

where $m = 2$ when $k = 1$ and $m = 1$ when $k = 2$.

Apparently, the effect of the term \hat{G}_k is to shift the $\dot{u}_k = 0$ nullcline while preserving both its shape and the existence of the limit cycle (for not too small values of r_c and r_{s_k}). The remaining term can be treated as an excitatory or inhibitory connection, depending on the sign of the coefficient, $(1/r_c - r_s/r_{u_m}r_{s_k})$. Under the condition of eq 26, the connecting term vanishes and the oscillators are apparently uncoupled.

In the case of strong coupling, numerical calculations for $r_{u_k} = 10$, $r_c = 1 \times 10^2$, and $r_{s_k} = 5r_c$ reveal that for $r_s < r_{u_m}r_{s_k}/r_c$ the only stable solution is in-phase synchrony, similarly to Figure 4a. Anti-phase synchronization, like the one presented in Figure 4b, could not be observed, even if the initial conditions were set to an exact $\chi = \pi$ phase difference. On the other hand, for $r_s > r_{u_m}r_{s_k}/r_c$, the only stable solution is out-of-phase synchronization, similar to the result presented in Figure 5a. It seems that, in the presence of strong coupling, the connections can be tuned from excitatory to inhibitory, as in the case of weak coupling, but the anti-phase solution either does not exist, or it is unstable even for small values of r_s .

5. Experimental Observations

5.1. Experimental Setup. The configuration of an assembly consisting of two working electrodes is shown in Figure 8. Each electrode was made from pure Fe wires (Nilaco Co., 99.5%) of 1 mm diameter. The electrodes were embedded in photosetting resin (Maruto Instruments Co., Ltd) in a way such the reaction takes place only at the ends of the Fe wires, Figure 8a,c. Prior to each experiment, the electrodes were polished with a series of wet 200–2000 grit silicon carbide sandpaper and then cleaned with distilled water and rinsed with ethanol.

This electrode assembly was used as working electrode in a standard three-electrode arrangement with respect to a SCE reference electrode with a Haber-Luggin capillary, as shown in

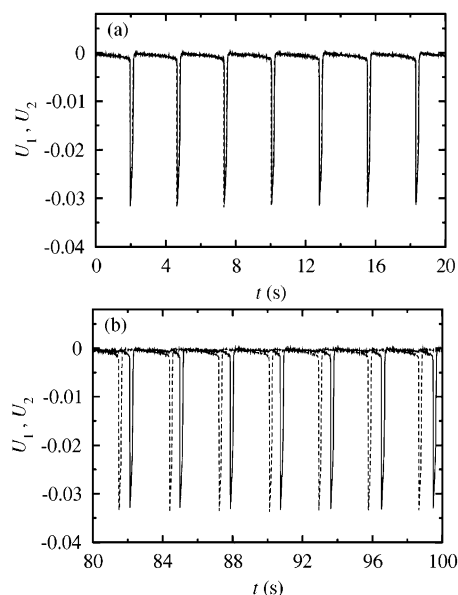


Figure 9. Synchronization of two oscillators for $d_{1,2} = 5$ mm and $V = 282$ mV. (a) In-phase synchronization for $l = 10$ mm (traces overlapped) and (b) out-of-phase synchronization for $l = 2$ mm.

Figure 8b. The tip of the capillary was located in a distance l below the plane of the assembly and its position was adjusted by using an x – y – z stage. The distance of the two working electrodes was $d_{1,2}$. Several values of $d_{1,2}$ were used for the experiments, as it will be described later. The counter electrode was made from a 1 mm diameter copper wire, coiled up to a 3 mm diameter helix and bent to a ring. The plane of the copper ring was parallel to the plane of the assembly and its center was located about 50 mm below it, Figure 8b.

The potential was controlled by a potentiostat (Hokuto Denko, HA-151). The working electrodes were connected to the potentiostat through two small resistors (1Ω) in order to measure the currents of the electrodes independently. The potential drop on each resistor was measured and stored by using a Memory Hicoder 8841 with 4ch analogue unit 8946 (Hioki E. E. Co.), Figure 8b.

The measuring system did not perturb the electrochemical system because its input impedance was higher than $1 \text{ M}\Omega$ and each recording channel was isolated. The total current was also measured by the potentiostat. No significant difference of the system's response was observed when the recording system was absent or present.

The experiments were carried out in a 1 M H_2SO_4 solution, diluted from concentrated sulfuric acid (Wako Pure Chemical Industries Ltd.).

5.2. Synchronization of Oscillations. In the presence of only one working electrode, the system exhibits periodic oscillations of relaxation type over a range of values of the applied potential, V , as was described in previous publications.^{21,22} In the case of an assembly consisting of two oscillators, the system's response depends both on l and $d_{1,2}$.

For large values of l and by keeping $d_{1,2}$ fixed, the two oscillators oscillate homogeneously, with an almost zero phase difference and for any initial conditions tested experimentally. A representative example of the in-phase synchronization is shown in Figure 9a for $l = 10$ mm, $d_{1,2} = 5$ mm, and $V = 282$ mV. In this case, when one oscillator is firing, the other will immediately fire an oscillatory peak; that is, the oscillators *excite* each other. Notice that, in this and all remaining figures, U_k

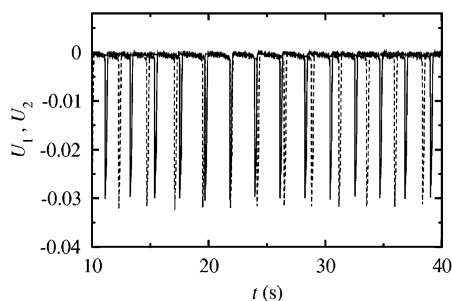


Figure 10. Drifting for $l = 4$ mm, $d_{1,2} = 5$ mm, and $V = 282$ mV.

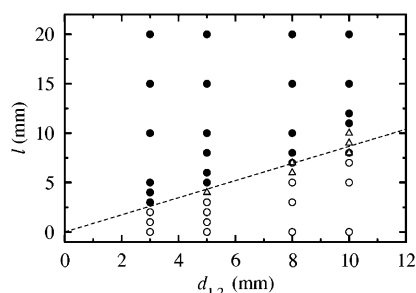


Figure 11. Diagram representing the dependence of the synchronized states as a function of the distance between the two oscillators, $d_{1,2}$ and the distance between the assembly and the reference electrode, l . Open and filled circles represent inhibitory (out-of-phase) and excitatory (in-phase) connections, respectively. Triangles represent drifting response (absence of coupling). The dashed line represents the approximated locus of the critical values of l . $V = 282$ mV.

represents the potential difference measured on the small external resistances.

When the value of l is decreased, while keeping V and $d_{1,2}$ fixed, the response turns from in-phase to out-of-phase synchronization. An example of the out-of-phase synchronization can be seen in Figure 9b for $l = 2$ mm. It has to be noted that, in several measurements, the phase difference during out-of-phase synchrony might change slightly during the course of the measurement due to experimental imperfections, but oscillatory peaks never overlap; that is, the oscillators always *inhibit* each other for small l .

Because a transition from excitation to inhibition is observed by decreasing l , it is to be expected that there is a critical value of l for which drifting will be observed. Under the present values of the system parameters, this transition is observed for $l = 4$ mm. As can be seen in Figure 10, for this value of l , the oscillators oscillate completely independently. Due to a slight frequency difference, peaks may overlap and the effect of coupling is apparently absent.

The critical value of l , for which a transition occurs from excitatory to inhibitory coupling, depends on the value of $d_{1,2}$, whereas all of the rest of the parameters are kept fixed. A graph showing the dependence of the synchronized states on the values of l and $d_{1,2}$ is presented in Figure 11. As can be seen in this figure, for large values of l , the connections are excitatory and the network is synchronized in-phase (filled circles). As l is decreased, the connections become inhibitory and the synchronized state is out-of-phase (open circles). For all $d_{1,2}$ values, there is a critical value of l for which the oscillators are apparently uncoupled and the response is drifting (triangles). The locus of the critical l values can be approximated by the straight dashed line, expressed by the relation: $l = d_{1,2} \sin(60^\circ)$.

6. Discussion

When coupled electrochemical oscillators are under study, it is commonly considered that the total current flowing through the cell consists of mainly two components, one flowing from the working to the reference electrode via the corresponding uncompensated resistance and the other flowing from one working electrode to another via a solution resistance. This formulation of the problem (in the continuous or discrete form) is based on the assumption that a reference electrode is located at some distance from the working electrodes network and defines an equipotential line or plane, depending on the geometry of the system. This procedure was applied in several discrete or continuous cases and in two or three dimensions.^{23–28}

The case of a point reference electrode has been studied also in a number of publications.^{29–33} These papers deal mainly with spatio-temporal patterns on continuous electrode surfaces, and it was shown that the type of pattern depends on the relative position of point reference and possibly the counter electrode. Even though the exact mechanism for the influence of the geometrical arrangement of the electrodes was not clearly presented, it was pointed out that the sign of the coupling function could be altered along the continuous electrode surface as a function of the distance between working and reference electrodes.²⁹

From the experimental point of view, an influence of the distance between working and working-reference electrodes on the synchronization of electrochemical oscillations was presented in the past.^{34,35} In these papers, coupled electrochemical oscillators were studied under a variety of electrode arrangements, and a qualitative explanation of the synchronous states was presented, based on the conclusion that the nature of coupling is mainly electrical. Similarly, it was suggested³⁶ that periodic electrochemical oscillators such as iron disks embedded in the same isolating plane oscillate in-phase under coupling conditions. Nevertheless, detailed studies of large number of discrete periodic nickel or iron oscillators revealed a rich collection of spatiotemporal patterns such as synchronization and clustering.^{37–40}

In the present paper a modified potentiostatic circuit was introduced for the description of a system consisting of two point working electrodes and a point reference electrode. We focus on this system not only because of our interest on coupled discrete electrochemical oscillators but also because in such a discrete case the influence of a point reference electrode is easily visualized. Hence, because of the selected geometry, the total current flowing through the working electrodes cannot be assumed to pass through the point defined by the position of the reference, via the corresponding uncompensated resistances. It was assumed that this current consists of three components, the one flowing through the uncompensated resistance, the second between the two working electrodes (through a coupling resistance), and the third through a solution resistance toward the counter electrode. The current flowing through the coupling resistance introduces a connection which is linear and symmetric, whereas the current flowing through the solution resistance introduces an additional linear connection which is a function of the solution and uncompensated resistances and thus a function of the relative position of working, reference, and counter electrodes.

Because of this specific form of coupling, the type of connections can be tuned by changing the relative values of the resistances involved. This fact was more comprehensively manifested in the case of two oscillators in the bistable regime where, depending on the resistances, the connection could be

either excitatory or inhibitory, the former facilitating activation and the latter impeding activation and driving a passive oscillator toward an even more passive state, Figure 2. This phenomenon is the discrete analogous of the continuous case^{29,33} where activity of a specific portion of a ring electrode induces stronger tendency to passivity on an electrode area on the opposite side. A similar situation holds for two oscillatory electrodes, where depending on the combination of the resistances the coupling can be excitatory or inhibitory. In the case of weak coupling these two cases correspond to stable in-phase and anti-phase, and stable out-of-phase synchronized states, respectively. In the continuous case presented in the literature³³ the analogous situation was expressed as a transition from homogeneous oscillations to a rotating wave. Thus, by changing the values of the resistances, and/or the initial conditions, different stable states could be achieved and the network could be tuned to the desired state.

In a previous work,⁸ it was shown experimentally that the type of connections in electrochemical oscillatory networks is different when the interacting electrodes are of the same nature or different (anode–anode and anode–cathode interaction, respectively). Nevertheless, in that case, the type of connections can be altered by changing the geometry of the network. In contrast, in the present case, the connection can turn from excitatory to inhibitory by varying the position of the reference electrode while preserving the network's geometry.

A comparison between the numerical and experimental results shows a very good qualitative resemblance. When the reference electrode is located far from the network (small r_s) the oscillators synchronize in-phase, Figures 4a and 9a. In the experimental case, the in-phase state is the only stable state, as it was confirmed by changing the initial conditions of the electrodes and performing perturbation experiments; a stable anti-phase state was never observed. This contradiction between experiment and theoretical predictions might be due to two reasons. If the coupling is weak, it was shown in section 4.1 that this is to be expected if there is a small frequency difference between the two oscillators (Figure 5b). Indeed, a small frequency difference is always present in the experimental case, and thus, the anti-phase solution is expected to disappear even when the coupling is weak. If the coupling is strong, then the anti-phase solution does not exist or it is unstable, as it was discussed in section 4.2, and thus, it is not expected to be observed experimentally.

When the reference electrode is located near the network (large r_s), it was predicted that the oscillators synchronize out-of-phase, Figure 5a. This was indeed the state observed experimentally, Figure 9b. Both in the numerical calculations and in the experiment, the oscillators oscillate with a phase difference and peaks never overlap. Inspection of Figures 5a and 9b reveals that while one oscillator is firing a peak the other turns to a more passive state and thus inhibited.

Finally, there is a critical value of the resistances (or distances, in the experimental case) where the oscillators seem effectively uncoupled. In this case, even though coupling is present, the one oscillator does not influence the other, and thus, they oscillate independently (compare Figures 6 and 10). In the case of completely identical oscillators, this would imply a preservation of the initial phase difference throughout the evolution of the network's response, whereas in the presence of small frequency difference, the phase difference between the oscillators would vary nonsystematically.

The exact effect of the connections' tuning on the spatio-temporal evolution of large, and possibly asymmetric, networks is still an open problem. The same holds for networks consisting

of chaotic electrochemical oscillators. It is to be expected that such networks may adjust a given property in many different states (complete, phase, lag, generalized synchronization, etc.)⁴¹ depending upon the coupling configuration. It remains to be seen whether the present formulation can be used in order to alter the synchronized states of chaotic electrochemical oscillators and predict experimental observations.

As a conclusion, it can be stated that when a network of identical discrete electrochemical oscillators is controlled potentiostatically with respect to a point reference electrode, under bistable or periodic oscillatory conditions, then the type of connections between the network elements can be tuned by changing the relative positions of the working, reference, and counter electrodes while preserving the spatial symmetry of the arrangement.

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References and Notes

- (1) Ostwald, W. Z. *Phys. Chem.* **1900**, 35, 333.
- (2) Franck, U. F. *Prog. Biophys. Chem.* **1956**, 6, 171.
- (3) Lillie, R. S. *J. Gen. Physiol.* **1920**, 3, 107.
- (4) Lillie, R. S. *J. Gen. Physiol.* **1925**, 7, 473.
- (5) Okamoto, H.; Tanaka, N.; Naito, M. *Chem. Phys. Lett.* **1995**, 237, 432.
- (6) Amatore, C.; Brown, A. R.; Thouin, L.; Warkocz, J.-S. *C. R. Acad. Sci. Paris IIC* **1998**, 1, 509–515.
- (7) Hoppensteadt, F. C.; Izhikevich, E. M. *Weakly Connected Neural Networks. Applied Mathematical Sciences*; Springer-Verlag: New York, 1997; Vol. 126.
- (8) Karantonis, A.; Miyakita, Y.; Nakabayashi, S. *Phys. Rev. E* **2002**, 65, 046213.
- (9) Miyakita, Y.; Karantonis, A.; Nakabayashi, S. *Chem. Phys. Lett.* **2002**, 362, 461.
- (10) Newman, J. S. *Electrochemical Systems*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1991.
- (11) Koper, M. T. M.; Sluyters, J. H. J. *Electroanal. Chem.* **1993**, 347, 31.
- (12) Karantonis, A.; Shiomi, Y.; Nakabayashi, S. *Int. J. Bifurc. Chaos* **2001**, 11, 1275.
- (13) Kuramoto, Y. *Chemical Oscillators, Waves, and Turbulence*; Springer-Verlag: Berlin, 1984.
- (14) Ermentrout, G. B.; Kopell, N. *J. Math. Biol.* **1991**, 29, 195.
- (15) Ermentrout, G. B. *XPP-AUT: X-Windows Phase-Plane plus Auto*; University of Pittsburgh: Pittsburgh, PA, 2002.
- (16) Williams, T. L.; Bowtell, G. *J. Comput. Neurosci.* **1997**, 4, 47.
- (17) Somers, D.; Kopell, N. *Biol. Cybern.* **1993**, 68, 393.
- (18) Somers, D.; Kopell, N. *Physica D* **1995**, 89, 169.
- (19) Izhikevich, E. M. *SIAM J. Appl. Math.* **2000**, 60, 1789.
- (20) Karantonis, A.; Pagitsas, M.; Miyakita, Y.; Nakabayashi, S. Manuscript in preparation.
- (21) Sazou, D.; Karantonis, A.; Pagitsas, M. *Int. J. Bifurc. Chaos* **1993**, 3, 981.
- (22) Karantonis, A.; Pagitsas, M. *Int. J. Bifurc. Chaos* **1997**, 7, 107.
- (23) Koper, M. T. M.; Sluyters, J. H. *Electrochim. Acta* **1993**, 38, 1535.
- (24) Flätgen, G.; Krischer, K. *J. Chem. Phys.* **1995**, 103, 5428.
- (25) Karantonis, A.; Shiomi, Y.; Nakabayashi, S. *J. Electroanal. Chem.* **2000**, 493, 57.
- (26) Karantonis, A.; Nakabayashi, S. *Electrochim. Acta* **2000**, 46, 745.
- (27) Mazouz, N.; Krischer, K.; Flätgen, G.; Ertl, G. *J. Phys. Chem. B* **1997**, 101, 2403.
- (28) Mazouz, N.; Flätgen, G.; Krischer, K. *Phys. Rev. E* **1997**, 55, 2260.
- (29) Christoph, J.; Otterstedt, R. D.; Eiswirth, M.; Jaeger, N. I.; Hudson, J. L. *J. Chem. Phys.* **1999**, 110, 8614.
- (30) Birzu, A.; Green, B. J.; Otterstedt, R. D.; Jaeger, N. I.; Hudson, J. L. *Phys. Chem. Chem. Phys.* **2000**, 2, 2715.
- (31) Birzu, A.; Green, B. J.; Jaeger, N. I.; Hudson, J. L. *J. Electroanal. Chem.* **2001**, 504, 126.
- (32) Birzu, A.; Green, B. J.; Otterstedt, R. D.; Hudson, J. L.; Jaeger, N. L. *Z. Phys. Chem.* **2002**, 216, 459.

- (33) Jaeger, N. I.; Otterstedt, R. D.; Błrcirzu, A.; Green, B. J.; Hudson, J. L. *Chaos* **2002**, *12*, 231.
- (34) Mukouyama, Y.; Hommura, H.; Matsuda, T.; Yae, S.; Nakato, T. *Chem. Lett.* **1996**, 463.
- (35) Matsuda, T.; Mukouyama, Y.; Hommura, H.; Yae, S.; Nakato, Y. *J. Electrochem. Soc.* **1997**, *144*, 2996.
- (36) Rush, B.; Newman, J. J. *J. Electrochem. Soc.* **1995**, *142*, 3770.
- (37) Fei, Z.; Kelly, R. G.; Hudson, J. L. *J. Phys. Chem.* **1996**, *100*, 18986.
- (38) Fei, Z.; Hudson, J. L. *J. Phys. Chem. B* **1997**, *101*, 10356.
- (39) Fei, Z.; Green, B. J.; Hudson, J. L. *J. Phys. Chem. B* **1999**, *103*, 2178.
- (40) Kiss, I. Z.; Wang, W.; Hudson, J. L. *J. Phys. Chem. B* **1999**, *103*, 11433.
- (41) Boccaletti, S.; Kurths, J.; Osipov, G.; Valladares, D. L.; Zhou, C. *S. Phys. Rep.* **2002**, *366*, 1.