Phase synchronization of nonidentical chaotic electrochemical oscillators

István Z. Kiss and John L. Hudson*

Department of Chemical Engineering, 102 Engineers' Way, University of Virginia, Charlottesville, Virginia 22904-4741, USA. E-mail: hudson@virginia.edu

Received 21st January 2002, Accepted 28th March 2002
First published as an Advance Article on the web 9th May 2002

Experiments on two coupled chaotic electrochemical oscillators with different frequencies are presented. We consider two types of coupling. The first is imposed through a set of external resistors. The second arises from the potential drop in the electrolyte and generally depends on cell geometry and reaction rate. Phase synchronization is observed with the addition of weak coupling of both types. Along with the onset of phase synchronization an increase in the amplitude of the mean current oscillations occurs. Simulations using a coupled form of an electrochemical model support the experimental findings.

1 Introduction

Electrochemical systems exhibit dynamical behavior including bistability, periodicity, quasiperiodicity and chaos1-3 as well as spatiotemporal patterns.4-6 The patterns arise through the interaction of nonlinear reaction and coupling among the reacting sites. Coupling can occur through the potential field and/or transport of chemical species. A large body of numerical and experimental studies indicates the importance of coupling through the potential field.7 Because the potential distribution in the electrolyte depends on the conductivity and the cell geometry (i.e., size of the working electrode, geometrical positions of working, reference and counter electrodes), the strength and the scale of the coupling also are functions of these quantities. Several interesting spatiotemporal phenomena have been observed, e.g., accelerating fronts,7,8 standing and traveling waves,8,9,11 rotating waves,12 spatial period-doublings,13-15 spirals,16-18 and Turing patterns. With increasing the coupling strength in the oscillatory region transitions from unsynchronized periodic behavior through irregular and periodic clusters19 to synchronized oscillations19-22 have been observed. Intermittent and stable clusters in addition to identical synchronization have also been seen in experiments with chaotic oscillators.23-25

In this paper we study the synchronization of two nonidentical chaotic electrochemical oscillators. Although reacting systems are typically composed of a very large number of reaction sites, some of the effects of coupling on overall behavior can be seen even in the simple case of two oscillators. The chosen system is the electrodissolution of Ni in sulfuric acid.31 The oscillators are coupled through a set of serial and parallel resistors.19 We analyze the phases and the frequencies of the individual oscillators and the amplitudes of the mean current, and point out the differences between identical32-34 and phase synchronization. The effect of an important geometrical factor, the size of the electrodes, on the interaction between the electrodes and their synchronization properties is also demonstrated. The experimental findings are supported by numerical studies using a coupled form of an electrochemical model.

2 Experimental

A schematic of the experimental apparatus is shown in Fig. 1.
A standard electrochemical cell consisting of two nickel working electrodes (Aldrich, 99.99%+, 1 mm or 6 mm diameter), a Hg/Hg2SO4/cc. K2SO4 reference electrode and a platinum mesh counter electrode is used in the experiments. The distance between the two working electrodes is about 1 mm. The electrodes are embedded in epoxy and reaction takes place only at the ends. The electrodes are held at the applied potential (V) with a potentiostat (EGGKG PAR 273). Zero resistance ammeters are used to measure the currents of the electrodes and data acquisition is done at 200 Hz. The experiments are carried out in 4.5 M sulfuric acid solution at a temperature of 11 °C.

The two electrodes are connected to the potentiostat through two individual parallel resistors, \( R_{\text{ind}} \) and through one collective series resistor, \( R_{\text{coll}} \) (see Fig. 1). We employ a method of altering the strength of coupling among the electrodes\(^{11}\) while holding all other parameters constant, i.e., the kinetics and the parameters of the individual oscillators are not changed. The total external resistance \( R_{\text{ext}} = R_{\text{coll}} + R_{\text{ind}}/2 \) is held constant while the fraction dedicated to individual currents, as opposed to the total current, is varied. The series (collective) resistor couples the electrodes; the parameter \( \varepsilon = R_{\text{coll}}/R_{\text{ind}} \), the ratio of collective to total resistance, is a measure of coupling (no coupling for \( \varepsilon = 0 \) and maximal coupling for \( \varepsilon = 1 \)).

3 Experimental results

3.1 Two small electrodes

We first consider the dynamics of two electrodes and the effect of coupling imposed through the set of external resistors.

Uncoupled electrodes. The time series of the chaotic current oscillations of the two electrodes without added coupling (\( \varepsilon = 0.0 \)) are shown in Fig. 2a, b. The information dimensions of both of the reconstructed attractors shown in Fig. 2c, d were found to be 2.3 ± 0.1.\(^{15}\)

The structures of the two attractors are very similar; only small differences are noticeable. To characterize the small differences due to surface heterogeneities the frequencies of the oscillators were calculated. The frequency of a time series data corresponding to phase coherent attractor (e.g., shown in Fig. 2c, d) can be accurately calculated from the rate of change of phase. The Hilbert transform of the current

\[
H[i(t)] = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{i(\tau)}{\tau} \, d\tau
\]

is used for the definition of phase\(^{25} \) \( \phi(t) \):

\[
\phi(t) = \arctan \frac{H[i(t)]}{i(t)}
\]

and amplitude \( A(i(t)) \):

\[
A(i(t)) = \sqrt{i(t)^2 + H[i(t)]^2}.
\]

(The notation PV in eqn. 1 implies that the integral should be evaluated in the sense of Cauchy principal value.) We note that the DC component of the current is eliminated for these calculations. Further details of calculation of phases in this specific system are given in a previous paper.\(^{30}\) The frequencies of the oscillators are obtained from a linear fit of \( \phi(t) \) vs. \( t \)

\[
\omega = \frac{1}{2\pi} \frac{d\phi(t)}{dr}.
\]

For the time series in Fig. 2a, b the frequencies are \( \omega_1 = 1.210 \) Hz and \( \omega_2 = 1.196 \) Hz. The phase difference \( \Delta(\phi(t)) = (\phi_1(t) - \phi_2(t)) \) between the oscillators increases almost linearly (Fig. 2e) with \( t \); the deviations from a straight line are due to the chaotic character of the oscillators. The histogram of the cyclic phase differences (\( \Delta(\phi \mod 2\pi) \)) is flat indicating no favored phase difference and no significant coupling at \( \varepsilon = 0 \) through the electrolyte. The amplitudes of the electrodes are also not correlated as is seen in Fig. 2g. The time series of mean current \( \langle i(t) \rangle = \langle i_1(t) + i_2(t) \rangle/2 \) is shown in Fig. 2h. As a result of the lack of synchrony, the mean current shows a more irregular variation than that of the individual currents. The variance of the mean current \( (17 \times 10^{-3} \text{mA}^2) \) is about half of that of the individual currents \( (17 \times 10^{-3} \text{mA}^2) \).

Added coupling, \( \varepsilon > 0 \). Now we consider the addition of weak coupling. Some results obtained at \( \varepsilon = 0.08 \) are presented in Fig. 3. With this added coupling there are only small changes in the dynamics of the individual elements relative to the uncoupled case. The reconstructed attractors (Fig. 3a, b) and their dimensions \( (2.3 \pm 0.1) \) are similar to those seen at \( \varepsilon = 0.0 \).

However, there are substantial changes in the phase dynamics of the two elements and in the mean current. With small coupling both oscillators have the same frequency, \( \omega_1 = \omega_2 = 2.03 \) Hz. The phase differences (Fig. 3c) vary around zero. The histogram of cyclic phase differences (Fig. 3d) has a maximum near zero; antiphase oscillations are not observed, i.e., the probability at \( -\pi \) and \( \pi \) differences are zero. The amplitudes of oscillators (Fig. 3e) are still uncorrelated; however, they do not exhibit as erratic behavior as they do at \( \varepsilon = 0 \). Therefore, although the coupling is not strong enough to synchronize the elements, a weaker form of interaction, phase synchronization,\(^{28}\) has set in. Due to phase synchronization, the dynamics of the mean current (Fig. 3f) are also changed; the oscillations have larger amplitudes \( (15 \times 10^{-3} \text{mA}^2) \) and are now comparable to those of the individual elements \( (18 \times 10^{-3} \text{mA}^2) \).

Phase synchronization occurs at \( \varepsilon = \varepsilon_{PS} \), where \( 0.06 < \varepsilon_{PS} < 0.08 \). The behavior before phase synchronization \( (\varepsilon < \varepsilon_{PS}) \) is characterized by the intermittent temporal variation of phase synchronized regions and phase slips (decrease/increase of \( \Delta(\phi) \)) by \( 2\pi \). The occurrence of phase slips is less frequent closer to phase synchronization. Two measures have been calculated to characterize the extent of phase synchronization: the frequency difference, \( \Delta(o) = |\omega_2 - \omega_1| \) and the phase synchronization index \( \sigma_{1,1} \).\(^{37}\) The value of \( \sigma_{1,1} \) expresses the sharpness of the maximum in the cyclic phase difference distribution and is obtained as

\[
\sigma_{1,1} = (S_{\text{max}} - S)/S_{\text{max}}\]
phase and identical synchronization, we present results in the strongly coupled region. Because the currents are identical, their phase difference is zero (Fig. 5a); the histogram of cyclic phase difference (Fig. 5b) is a delta function having a probability of one for zero phase difference and zero otherwise.

The time dependencies of the amplitudes are also identical (Fig. 5c). Since the time series of the mean current is the same as that of the individual currents, the variances are also equal ($\sigma_2^2 = \sigma_1^2$ mA$^2$). The identical synchronization that occurs with large coupling is a stronger form of synchronization; it is associated with identical phases and amplitudes. In contrast, phase synchronization that occurs with weak coupling requires only bounded phase differences of the two oscillators.

3.2 Two large electrodes

The coupling between the two electrodes can also occur via the potential field in the electrolyte. This coupling depends on cell geometry as well as reaction rate. We explore such effects with the use of two larger electrodes for which the potential drop in the electrolyte is greater than that obtained with the small electrodes. The electrodes have a diameter of 6 mm so that the electrode area is increased by a factor of 36 relative to the electrodes used in the experiments described in the previous section. Oscillations on the larger electrodes occur with smaller external resistance. At $R_{\text{tot}} = 20$ $\Omega$ chaotic oscillations have been found with similar characteristics (time series,
Fig. 6a,b, and attractors, Fig. 6c,d) to those of the smaller electrodes.

The oscillations on the larger electrodes are phase synchronized even without added coupling ($\varepsilon = 0$). The phase difference oscillates around zero (Fig. 6e) and the histogram of cyclic phase differences (Fig. 6f) has a maximum. The phase synchronization index is 0.17. The frequencies of the two oscillators are the same, $o_1 = o_2 = 1.180$ Hz. The two oscillators are not identically synchronized because the amplitudes are not synchronized (Fig. 6g). The time series of the mean current exhibits macroscopic oscillations; the variance of the mean current (7 mA$^2$) is about 80% of the variance of the individual currents (9 mA$^2$). These results are similar to those obtained with the smaller electrodes at weak coupling, $\varepsilon = 0.08$ (Fig. 3).

4 Numerical simulations

Model

We have seen in the experiments that phase synchronization can be effected via coupling through the potential for both the small and large electrodes. To support the experimental findings some numerical simulations have been carried out with a coupled form of a dimensionless electrochemical model.

Several realistic models are available that describe the dynamics of an electrochemical oscillator. In most of the models the potential drop across the double layer is a fast variable with positive feedback; a slow chemical variable is inhibitory. An ODE model for the nickel system has been proposed by Haim et al.; this model has been used successfully in both spatially continuous distributed systems and in discrete systems to interpret spatial patterns during the periodic electrode dissolution of nickel. Although this model does predict chaotic behavior, the region in parameter space in which this chaos occurs is not the same as that presented in the experiments described here. In the experiments with increase in the applied potential, a Hopf bifurcation occurs and shortly thereafter transitions to chaos are seen. In the model, the chaotic behavior is obtained at a higher applied potential, closer to a saddle-loop bifurcation. This difference in distance from the saddle-loop bifurcation is of great importance in the type of experiments being described here, viz., synchronization of oscillators; close to the saddle-loop bifurcation the oscillators have a tendency to exhibit anti-phase oscillations not observed in other regions of parameter space with weak coupling. To avoid this complication, we use here another electrochemical model that does show the chaotic behavior following a Hopf bifurcation and in which no saddle-loop occurs. Electrochemical oscillators have been classified in several studies, although the model used here falls into a different classification than that

Fig. 3  Phase synchronization of two chaotic oscillators with weak coupling ($R_{\text{tot}} = 330$ $\Omega$, $V = 1.280$ V, $\varepsilon = 0.08$). a, b, Reconstructed attractors of the currents of the electrodes. c, Phase difference between the two oscillators vs. time. d, Histogram of cyclic phase difference. e, The amplitude of the current of electrode 2 vs. electrode 1. f, Time series of mean current.
exhibited by the nickel system, it does produce phase coherent chaotic dynamics similar to those of the experiments. (It is a so-called negative differential resistance model although the nickel dissolution is a hidden negative differential resistance system.) Moreover, the model does successfully reproduce the phase synchronization seen in the experiments as we shall see below. The important characteristic of the coupled model is not whether it is based on an NDR or an HNDR oscillator, but rather that it is an activator–inhibitor model coupled through the activator. The model chosen is one proposed by Koper and Gaspard:  

\[
\begin{align*}
    \text{cl}_t &= \frac{V - \epsilon_t}{2R_{\text{tot}}} - 120k(\epsilon_t)u_t + \frac{1}{2R_{\text{tot}}} \frac{\epsilon}{1 - \epsilon} ((\epsilon) - \epsilon_t)
\end{align*}
\]  

Fig. 4 a. The frequency difference of the two chaotic oscillators vs. the coupling strength ($\epsilon$). b. Entropy index ($\sigma_{11}$) as a function of $\epsilon$. c. The variance of one individual current (solid squares) and of the mean current (open circles) vs. $\epsilon$.

Fig. 5 Identical synchronization of two chaotic oscillators at $\epsilon = 1$ ($R_{\text{tot}} = 330 \Omega$, $V = 1.280$ V). a. Phase difference between the two oscillators vs. time. b. Histogram of cyclic phase difference. c. The amplitude of the current of electrode 2 vs. electrode 1. d. Time series of mean current.
$$\frac{du}{dt} = -1.25d^{0.5} k(e) u_l + 2d(w_l - u_l)$$  \hspace{1cm} (7)$$

$$\frac{dw_l}{dt} = 1.6d(2 - 3w_l + u_l)$$  \hspace{1cm} (8)$$

where $e_l$ is the double-layer potential, $u_l$ and $w_l$ are the concentrations of electroactive species in the surface and diffusion layers of the $l$-th electrode ($l = 1, 2$), $d$ characterizes the mass transfer, and $k(e)$ is defined as:

$$k(e) = 2.5\theta^2 + 0.01\exp[0.5(e - 50)],$$  \hspace{1cm} (9)$$

where $\theta$ is the surface coverage of some (inhibiting) chemical species. The value of $\theta$ is approximated by a sigmoidal function:

$$\theta = \begin{cases} 
\exp[-0.5(e - 35)^2] & \text{for } e \leq 35 \\
1 & \text{for } e > 35
\end{cases}.$$  \hspace{1cm} (10)$$

The coupling is through the potential as seen in the last term of the right hand side of eqn. (6); $e = (e_1 + e_2)/2.$ $^{19}$ The parameter $e_i$ represents the dimensionless double layer capacitance and the fact that the values of this parameter on the two electrodes differ is the source for the frequency mismatch. (A similar approach was used in modeling the dynamics of coupled periodic oscillators). $^{19}$ The dimensionless currents of the electrodes are defined as:

$$i_l = \frac{E - e_i}{R_{\text{ind}}}$$  \hspace{1cm} (11)$$

Fig. 6 Two large electrodes (6 mm diameter) in the chaotic region without added coupling ($e = 0.0$, $R_{\text{tot}} = 20 \Omega$, $V = 1.950 V$). a,b. Time series of the currents of the electrodes. c,d. The reconstructed attractors using time-delay coordinates. e. Phase difference between the two oscillators vs. time. f. Histogram of cyclic phase difference. g. The amplitude of the current of electrode 2 vs. electrode 1. h. Time series of mean current.

where $E$ is the summed potential drop on the double layer and the individual resistors

$$E = (1 - e)V + e(e)$$

obtained from the corresponding Kirchhoff equations.

Two uncoupled oscillators

For an appropriate parameter set ($d = 0.11913, R_{tot} = 0.01$) the model exhibits a cascade of period-doubling bifurcations with increasing $V$.

The time series of dimensionless currents and the reconstructed chaotic attractors are shown in Fig. 7. The parameters of the model were optimized for a chaotic region in which the relative frequency difference between the oscillators is about the same as in the experiments (0.5–1%). The parameters were chosen so that the frequencies of the oscillators are $\omega_1 = 0.4737$ and $\omega_2 = 0.4766$. The linearly increasing phase difference (Fig. 7e), the flat cyclic phase difference distribution (Fig. 7f), and the uncorrelated amplitudes (Fig. 7g) all show the lack of synchronization between the electrodes. The mean current is more complex than the individual currents and has a smaller amplitude; the variance of the oscillations (var($i$) = 38) is about half of those of the individual currents (var $i_1 = 75$, var $i_2 = 80$) in accordance with the experiments.

Two coupled oscillators

Now we consider the addition of coupling to the electrodes. The frequencies, the frequency differences, synchronization indices and the variances of the currents are shown in Fig. 8 as a function of the coupling strength.

With increasing the coupling strength the frequencies of the oscillators become equal at $e_{PS} = 2.5 \times 10^{-4}$ (Fig. 8a,b) and the frequency difference remains zero for all $e > e_{PS}$. The frequencies show a maximum with increasing coupling strength; the chaotic oscillations are faster at intermediate coupling strengths and are slower at low or high coupling strengths. The small change of individual frequencies implies a small change of individual dynamics with $e$. The phase synchronization index (Fig. 8c) jumps to about 0.25 at $e = e_{PS}$ indicating phase synchronization. Further increase in $e$ results in a maximum at $e = 2.5 \times 10^{-3}$ and a minimum at $e = 9 \times 10^{-3}$.

Fig. 7 Numerical simulations. Two chaotic oscillators at $\varepsilon = 0.0$, $V = 36.7395$, and $c_{1,2} = 1 \pm 4 \times 10^{-3}$. a,b. Time series of the currents of the electrodes. c,d. The reconstructed attractors using time-delay coordinates. e. Phase difference between the two oscillators vs. time. f. Histogram of cyclic phase difference. g. The amplitude of the current of electrode 2 vs. electrode 1. h. Time series of mean current.
Identical synchronization occurs at $\varepsilon \geq 7 \times 10^{-3}$; here $\sigma_{1,1} = 1$. The variances of the individual currents are larger for intermediate coupling strengths and smaller for low and high strengths (Fig. 8d). The variance of the mean current starts increasing at the onset of phase synchronization and reaches the values of the individual variances at identical synchronization ($\varepsilon = 7 \times 10^{-3}$).

For further comparison with experiments we present two results of simulations, only one of which was seen in the experiments. The first simulations were carried out at a coupling strength of $\varepsilon = 2.5 \times 10^{-4}$, just above the onset of phase synchronization; the second were done at $\varepsilon = 2.5 \times 10^{-2}$, closer to identical synchronization around the minimum of the phase synchronization index. At the onset of phase synchronization (Fig. 9) the histogram of cyclic phase difference has a maximum and is bounded (Fig. 9b), however, the average phase difference is non-zero; the maxima and minima of current oscillations of one electrode always occur earlier than those of the other.

With increasing $\varepsilon$ the phase difference decreases and becomes no longer noticeable at $\varepsilon = 2.5 \times 10^{-2}$ (see Fig. 10).

The attractors (Fig. 10a,b) are larger than those at $\varepsilon = 0$ indicating a change of dynamics. The phase synchronized oscillators have zero phase difference (see Fig. 10c,d) and are not identically synchronized (Fig. 10e). The variance of the oscillations of the mean current ($\text{var}(\langle i \rangle) = 64$) is about 80% of the individual oscillators ($\text{var} i = 73$). At this larger coupling strength the dynamics are similar to those found in the phase synchronized region of the experiments.

### 5 Discussion

Phase synchronization sets in with the addition of a small coupling to nonidentical electrochemical chaotic oscillators. Phase synchronization is weaker than identical synchronization. In identical synchronization both the phases and the amplitudes of all oscillators are identical but in phase synchronization only a bounded phase difference is necessary and there is no restriction on the amplitudes. Along with the onset of phase synchronization an increase of the amplitude of the mean current oscillation is observed. We have shown that phase synchronization of even two reacting sites significantly increases the amplitude of the mean current oscillations and decreases the complexity of the signal. The mean or overall rate of reaction is commonly the important quantity of interest. Recent experiments indicate that this effect is even larger with a population of oscillators.\textsuperscript{42}
For most electrochemical systems spontaneous oscillations are not caused by purely kinetic nonlinearities but rather a potential drop through the electrolyte and/or on an external resistance is also required. In the first system studied here, i.e., that with the small electrodes, the potential drop through the electrolyte was much smaller than that through the external resistors and thus without added coupling the interaction between the electrodes was weak. Phase synchronization was induced by the addition of coupling through a potential drop on a common resistor. In the experiments with two larger electrodes the coupling is due to the potential drop through the electrolyte. The changes in the complexity and amplitude of the mean signal are caused by the addition of coupling, whether that coupling is through external resistors or through the electrolyte.

The decrease in complexity of the mean signal with increase in electrode size is in contrast to the more common case in which an increase in size produces an increase in complexity of the dynamics as has been seen in both experiments and simulations. However, the present experiments were carried out under conditions in which an increase in system size resulted in an increase in coupling strength. In general, an increase in electrode size can change the coupling strength because of changes in potential field, change the local reaction dynamics through a change in double layer potential drop, or change the relationship between the coupling length scale and the size of the reaction surface. Thus changes in system size can make overall dynamics either more or less complex depending on the specific conditions.

Numerical simulations using oscillators coupled through the potential drop reproduced the occurrence of phase synchronization and the associated increase of the mean current oscillations. The model used in the simulations reproduces the dynamics of many electrochemical oscillators and thus the effects seen here are likely to occur in other electrochemical systems.

The potential drop has two roles in the dynamics. It is a necessary component for the occurrence of local oscillations in most cases and it can lead to coherent dynamics even of nonidentical reaction sites and thus to observable macroscopic oscillations.

Acknowledgement
This work was supported by the National Science Foundation (CTS-0000483) and the Office of Naval Research (N00014-01-1-0603). We thank Yumei Zhai for helping with the experiments.

References

Fig. 10 Numerical simulations. Phase synchronized chaotic dynamics at $r = 2.5 \times 10^{-2}$. a, b. The reconstructed attractors using time-delay coordinates of the currents of the electrodes. c. Phase difference between the two oscillators vs. time. d. Histogram of cyclic phase difference. e. The amplitude of the current of electrode 2 vs. electrode 1. f. Time series of mean current.