Synchronization of non-phase-coherent chaotic electrochemical oscillations

István Z. Kiss, Qing Lv, and John L. Hudson

Department of Chemical Engineering, 102 Engineers’ Way, University of Virginia, Charlottesville, Virginia 22904-4741, USA

(Received 25 October 2004; published 11 March 2005)

Experiments on phase and generalized synchronization of two coupled, nonidentical chaotic electrochemical oscillations are presented. We adapt measures of characterizing synchronization of a non-phase-coherent chaotic behavior and compare its properties and physicochemical mechanism to those of a phase-coherent behavior. Phase synchronization sets in along with the onset of generalized synchronization for the non-phase-coherent oscillations in contrast to phase-coherent oscillations in which the phase synchronization usually occurs at a weaker coupling strength.

DOI: 10.1103/PhysRevE.71.035201 PACS number(s): 05.45.Xt, 82.40.Np

Synchronization of coupled chaotically oscillating systems has received considerable recent interest [1]. Most studies are done with phase-coherent oscillations in which phase and amplitude are easily defined and in which the variance of changes are not due to drift but due to a dynamic process. In the parameter range considered in this paper the electrodissolution undergoes complex chaotic behavior for which standard methods of phase definitions fail. Phases of the oscillations are calculated with a method based on trajectory curvature [10], and a measure of phase synchronization [9] is obtained as a function of the coupling strength. Generalized synchronization is quantified with a test of functional relationship between the two coupled systems using an algorithm based on a method of false neighbors [20]. The coupling strength at which phase and generalized synchronization occurs is determined and compared to results obtained with the coherent chaotic electrodissolution of nickel [7].

A standard three-compartment electrochemical cell consisting of two iron working electrodes (1-mm diameter each with 2-mm spacing), a Hg/Hg$_2$SO$_4$/K$_2$SO$_4$ reference electrode, and a Pt mesh counter-electrode was used. (A schematic of the experimental setup can be found in Ref. [7] ). The applied potential ($V$) of both electrodes was held at the same value. The electrodes were connected to the potentiostat through two individual parallel resistors ($R_{im}$) and through one series collective resistor ($R_{coll}$) which furnishes a global coupling of strength $\varepsilon=R_{coll}/R_{tot}$, where $R_{tot}=R_{coll}+R_{im}/2$ is kept constant. For $\varepsilon=0$, the external resistance furnishes no additional coupling; for $\varepsilon=1$, maximal external coupling is achieved [7].

Both relatively slow and fast cycles are seen in the current time series and the reconstructed attractor shows no obvious center of rotation as shown in Figs. 1(a) and 1(b), respectively. The phase [$\phi(t)$] can be defined using the derivative of the Hilbert transform $H(t)$ of the current $i(t)$

$$\phi(t) = \arctan \frac{dH(t)/dt}{di(t)/dt}.$$  

(1)

Osipov et al. have previously proposed the use of a two-dimensional phase space based on derivative component coordinates [10]. Although there is no unique center of rotation in the phase space using the Hilbert transform [21] [Fig. 1(c)], a unique center is found using the derivative of both coordinates [Fig. 1(d)]; thus Eq. (1) can be used for the definition of phase. The extent of phase coherence can also be seen in the return times of the time series data. While for the phase-coherent chaos of Ni electrodissolution the oscillations have similar return times (±10%) [see Fig. 2(a)], for the non-phase-coherent chaos of iron dissolution [see Fig. 2(b)] oscillations with very small and large periods occur. It is also seen in the figure that this behavior is stationary; the large changes are not due to drift but due to a dynamic process.
The current of electrode 1 vs electrode 2 of the maximum in the cyclic phase difference distribution vored phase difference and no significant inherent coupling synchronization. Using the Hilbert transform, fluctuations from a straight line occur due to the strong non-phase-coherent feature of the chaotic oscillations. Attractor using time-delay coordinates.

We have also confirmed the stationarity of oscillations with a wavelet-based method [22]; the wavelet analysis shows only small fluctuations in characteristic frequencies but no long-term drift.

Without added coupling ($\epsilon=0$) the two-electrode results are shown in Fig. 3. The current of electrode 1 vs electrode 2 [Fig. 3(a)] does not show any obvious correlation. Phases are obtained with Eq. (1) and phase differences defined as $\Delta \phi(t) = \phi_1(t) - \phi_2(t)$. The magnitude of phase differences tends to increase with time [see Fig. 3(b)]; however, large fluctuations from a straight line occur due to the strong non-phase-coherent feature of the chaotic oscillations. (These fluctuations are much smaller for the phase-coherent chaotic Ni electrode dissolution [7].) The histogram of the cyclic phase differences ($\Delta \phi \mod 2\pi$) [Fig. 3(c)] is flat, indicating no favored phase difference and no significant inherent coupling at $\epsilon=0$ through the electrolyte. A synchronization index $\sigma$ can be used to quantitatively characterize the extent of phase synchronization [9]; the value of $\sigma$ expresses the sharpness of the maximum in the cyclic phase difference distribution and is obtained as

$$\sigma = \frac{S_{\text{max}} - S}{S_{\text{max}}}.$$  

where $S$ is the Shannon entropy of the cyclic phase difference distribution ($S= - \Sigma_{i=1}^M p_i \ln p_i$, $M$ is the number of bins in the histogram of cyclic phase differences in Fig. 3(c), $p_i$ is the fraction of data points in the $i$th bin, and $S_{\text{max}}$ is the maximum entropy (flat distribution). $\sigma$ takes on values from 0 to 1 as the distribution changes from flat to a delta function. For $\epsilon=0$ in Fig. 3(c), $\sigma=0.008$.

Generalized synchronization can be characterized with a quantity that expresses a continuous functional relationship between the attractors of the two systems [5]. Continuity was difficult to prove (even for two identical systems); however, a robust algorithm based on false nearest neighbors has been proposed to characterize functional relationships between signals [20]. The method was developed to determine optimal embedding dimension and time delay. Nevertheless, as we shall see below, it provides an efficient way to characterize generalized synchronization as well. At any time $t'$ the phase points of electrode one and two are $x_1(t')$ and $x_2(t')$. The nearest neighbors of these two points, $x_1(t_1)$ and $x_2(t_2)$, respectively, are determined (with the software package OPENTSTOOL [23]). Functional relationships are assumed to exist if both $|x_2(t')-x_2(t_1)|<\delta$ and $|x_1(t')-x_1(t_2)|<\delta$ are fulfilled, where $\delta=0.7$ mA. The reconstruction of the attractors was done using the method of time delays with the current $[i(t)]$ signal of the electrodes; reconstruction parameters (time delay, $\tau=0.015$ s and embedding dimension, $m=4$) were determined in such a way to avoid false neighbors [20]. The functional relationship between the electrodes is characterized by the fraction of phase points $P$ that passes the false neighbor test. An example is shown in Figs. 3(d) and 3(e). The large distances between the phase points at $t'$ (circles) and at $t_1$ and $t_2$ triangles, respectively, show that there is no functional relationship between the two phase points at $t=t'$. The analysis of the whole time series at $\epsilon=0$ gives $P$...
ences are almost zero. The synchronization index has a large
solution of coupling strength were carried out with nickel electrodis-
solution of the coupling strength in Figs. 5

FIG. 4. Two non-phase-coherent chaotic systems with added
coupling ($\varepsilon=0.6$, $V=-0.300$ V). (a) Current of electrode 2 vs elec-
trode 1. (b) Phase difference vs time. (c) Histogram of cyclic phase
difference ($\Delta\phi$ mod $2\pi$ modulated into $[-\pi, \pi]$). (d) and (e) Recon-
structed attractors of the electrodes using time-delay coordinates.
The circles represent phase points at an arbitrary time; triangles
represent nearest-neighbor image points.

$=0.004$, i.e., only a small fraction (0.4%) of the phase points
passes the false neighbor test.

Now we consider the addition of fairly strong coupling
($\varepsilon=0.6$, Fig. 4). With this added coupling there is a remark-
able change in the synchronization properties of the oscillations. Although identical synchronization (corresponding to the
diagonal line) in the $i_1(t)$ vs $i_2(t)$ plot [Fig. 4(a)] is not
present, there is correlation between the currents of the elec-
trodes. The phase differences [Fig. 4(b)] are nearly constant
with some phase slips (these are related to sharp peaks in
time series for which state space reconstruction is inaccu-
rate). The histogram of cyclic phase differences [Fig. 4(c)] has a
maximum near zero; antiphase oscillations are practi-
cally not observed, i.e., the probabilities at $-\pi$ and $\pi$ differ-
ences are almost zero. The synchronization index has a large
value $\sigma=0.412$; our previous studies showed that phase syn-
chronization is established when $\sigma>0.1-0.2$ [7]. Thus, we
see that the phases of the oscillations are correlated and at
$\varepsilon=0.6$ phase synchronization has set in.

The phase points of the attractors shown in Figs. 4(d) and
4(e) pass the nearest-neighbor test. Note that the correspond-
ing phase points (shown in triangles and circles) reside on
different parts of the two attractors; such a mapping is in-
dicative of generalized synchronization. The analysis gave
$P=0.456$ showing that about half of the phase points pass the
false neighbor test.

The synchronization index $\sigma$ and the fraction of data
points that pass the neighbor tests ($P$) are shown as a func-
tion of the coupling strength in Figs. 5(a) and 5(b). The
figures show a similar trend with a large increase in the values
of $\sigma$ and $P$ between $\varepsilon=0.4$ and 0.6. (There is small increase
of these quantities for $\varepsilon<0.4$.) These results imply that
phase and generalized synchronization occur in a parallel
way in the system as the coupling strength is varied.

Similar experiments with two chaotic systems with vary-
ing coupling strength were carried out with nickel electrodissolu-
tion [7]. In this system the chaotic attractor is phase
coherent and phase synchronization was previously shown to
occur at $\varepsilon=0.06$. In Figs. 5(c) and 5(d) $\sigma$ and $P$ are shown as
a function of coupling strength. Phase synchronization sets in
at $\varepsilon=0.06$ at which coupling strength $\sigma$ increases consid-
erably. Generalized synchronization sets in at about $\varepsilon=0.5$ as
shown by the large increase of $P$. Thus, for phase-coherent
chaotic oscillations, phase and generalized synchronization
are distinct processes occurring at weak and strong coupling
strength, respectively.

Depending on the coherence of the chaotic attractor three
types of transitions have been proposed—from unsynchro-
nized to both phase and generalized synchronized states [10].
For phase-coherent attractors the zero Lyapunov exponent
(LE) is associated with the phase dynamics and phase syn-
chronization occurs at weak coupling shortly after the zero
LE becomes negative and generalized synchronization oc-
curs at the strong correlation of amplitudes at large coupling;
apparently, the transition seen in Ni electrodissolution be-
longs to this category. For chaotic attractors with intermedi-
ate phase diffusion the transition takes place via an interior
crisis. For strongly non-phase-coherent attractors phase syn-
chronization is a manifestation of generalized synchronization
and phase synchronization occurs only after one of the
positive LE passes to negative values, i.e., transition to gen-
eralized synchronization. In this case phase locking is pos-
sible only with strong correlations of the amplitudes. Iron
electrodissolution was shown to fall into this category; the
measures for phase and generalized synchronization fol-
lowed the same trend of variations.

Although detailed differential equation models of chaotic
nickel and iron oscillations are not available, the general mechanism for the development of oscillations is known. Chaotic nickel dissolution with a phase coherent attractor can develop through period-doubling bifurcations and the system can be modeled with three variables: potential, and NiO and NiOH surface coverages [24]. However, to capture the basic dynamical features of iron dissolution at least four variables are required [25]; one of them is a slowly varying salt layer thickness. It is likely that this slow variable contributes to the large phase incoherent character of the oscillations.

Two main routes to phase and generalized synchronization have been confirmed in laboratory experiments with electrochemical systems. Depending on the phase-coherent features, phase and generalized synchronization can be independent or highly correlated processes. The robustness of the analysis method applied here can be useful for characterizing other physical, chemical, and biological systems that are composed of oscillations with different degrees of coherence. For example, in an analysis of rat electroencephalographic signals [26] measures of phase and generalized synchronization exhibited similar trends that imply underlying non-phase-coherent dynamics.

This work was supported by the National Science Foundation (Contract No. CTS-0317762).