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Experimental observation of different types of chaotic synchronization in an electrochemical cell

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Chaotic synchronization for a pair of electrochemical oscillators is studied experimentally. The underlying bidirectional coupling between the two oscillators is achieved by immersing the two anodes in a common electrolytic solution. The horizontal distance between these two electrodes determines the strength of the coupling constant. On monotonically decreasing the distance between the two anodes, different domains of chaotic synchronization, namely, no, phase, lag, and complete synchronization, are identified. Furthermore, dynamics from the different transition intervals are also characterized.

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The importance of synchronization lies in its omnipresent nature and its relevance to numerous physical [1–3], chemical [4], physiological [5], and ecological processes [6]. The first reported endeavors involving synchronization are attributed to Huygens in the 17th century using pendulum clocks. These experiments were designed to study the locking of rhythms for swinging pendulums in the presence of weak coupling. More recently, a small subset of the synchronization phenomena in nonlinear systems, namely, chaotic synchronization, has gathered notoriety in the scientific community. Chaotic synchronization sounds a little contradictory on the surface since the sensitive dependence to the initial conditions, leading to divergence of the nearby trajectories (signature of chaotic dynamics), seems instinctively incompatible with the convergence effect, deemed indispensable for the attainment of synchronization. Chaotic synchronization, although studied earlier by Yamada and Fujisaka [7,8] and by Afraimovich *et al.* [9], was brought to the foreground by the works of Pecora and Carroll [10,11]. Thereafter, this concept of chaotic synchronization has evolved and has been extended to tackle more sophisticated problems both theoretically and experimentally [1–4,6,12]. Recent books [13–15] and an excellent review article [16] document the advances made and the current challenges that constitute the state of the art in this multidisciplinary field.

Electrochemical oscillators have proved to be a fertile playground for nonlinear dynamicists in general and chaoticians in particular. Both regular and irregular (chaotic) oscillations have been observed and analyzed in diverse electrochemical processes, including both anodic and cathodic reactions under potentiostatic and galvanostatic conditions [17,18]. A plethora of distinct dynamical behavior such as spontaneous oscillations, period doubling, mixed mode dynamics, multistability, and existence of deterministic chaos have been reported. It was realized, by the group of Hudson and collaborators that coupled electrochemical oscillators could serve as an excellent experimental paradigm to explore, identify, and characterize diverse synchronization phenomena [19,20]. Using experiments with two or more electrochemical oscillators, coupled through external resistors, they have successfully studied the phenomenon of chaotic synchronization. Moreover, they have also studied collective behavior exhibited by a population of such oscillators [22].

In this Rapid Communication, we report experimental results involving the synchronization of non-identical (parameter mismatch) chaotic oscillators subjected to a bidirectional coupling. Transport of chemical species is the most natural way that coupling emerges between these chaotic (electrochemical) oscillators. In contrast to previous works [19–21], the coupling strength in our experiments is a function of the mutual distance between the two oscillators. Moreover, in the present work, we systematically varied the coupling constant. This enabled us to identify the different domains of synchronization, including the experimental detection of lag synchronization in a chemical system, for a pair of nonidentical oscillators. The main motivation for these experiments was to verify the theoretical framework presented in the seminal work of Rosenblum and co-workers [23]. The authors in this paper, using numerical simulations, reported a transition sequence starting from a no-synchronization state and ending at a lag-synchronization state. Lag synchronization [24] is defined as a synchronous regime for which the states of the two oscillators are nearly identical but there exists a constant time lag between the two dynamics. This implies that in lag synchronization one finds correlated amplitudes and a constant phase shift. In our experiments, by varying extremely carefully the horizontal distance between the two anodes, we were able to identify each one of these different synchronization regions. This included the detection of the elusive lag-synchronization domain. These results provide experimental evidence for the entire transition sequence involving conversions from a state of no synchronization → phase synchronization → lag synchronization → complete synchronization.

A typical electrochemical cell consists of three electrodes, namely, the anode, the cathode, and the reference, immersed in an electrolytic solution. In the case of potentiostatic experiments the potential (anodic voltage V) between the anode and the reference electrode is maintained constant. This anodic voltage acts as the control or bifurcation parameter for the system dynamics. Consequently, the current between the anode and the cathode (anodic current I) is the system observable that normally changes its dynamical properties as the control parameter (V) is varied. However, in order to study synchronization of two chaotic oscillators, we modified the standard electrochemical cell by adding an extra anode. The experiments were carried out potentiostatically with anodes that were made of iron (Aldrich 99.98% purity) disks with a diameter of 6.3 mm, shrouded by epoxy. This was designed to ensure that the anodic reactions (dissolution) were restricted to the surface of the anode exposed to the electrolytic solution. The cathode was a 6.3 mm graphite bar

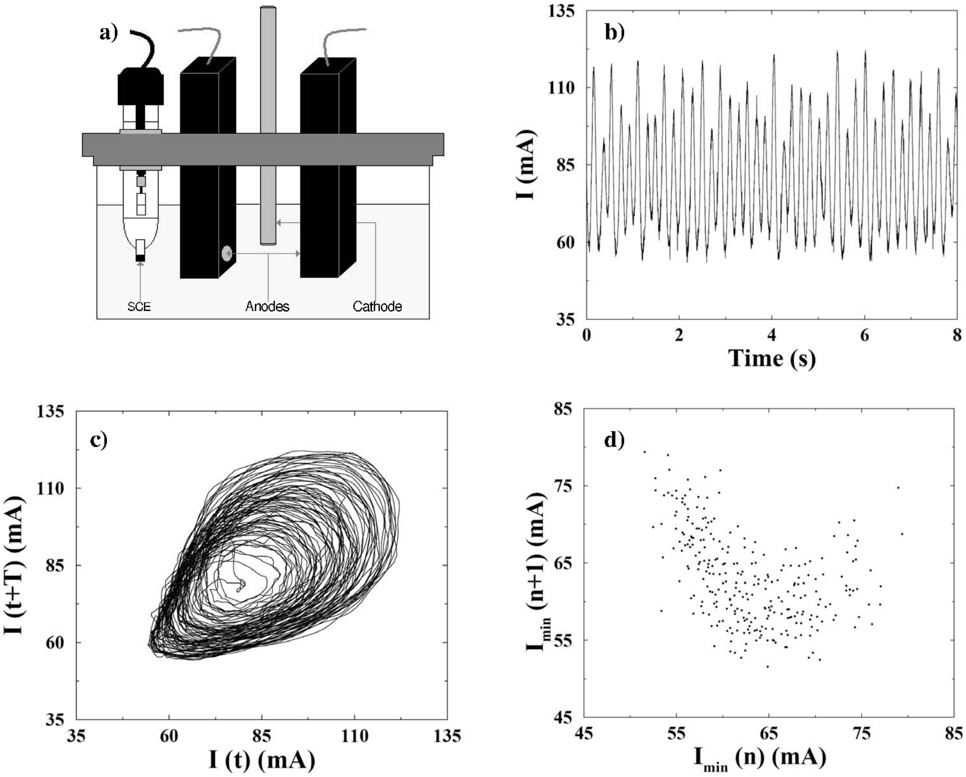

FIG. 1. (a) The schematic of the electrochemical cell configured to study chaotic synchronization. The two anodes were positioned facing each other so that the horizontal distance between them determines the coupling strength. The cathode was placed, equidistant to both the anodes, at a distance of 1 cm out from the line connecting the two anodes. (b) The chaotic time series of anodic current (I) observed for the anodic voltage at 750 mV. (c) The reconstructed chaotic attractor obtained from the time series of (b) using the delay technique. (d) The unimodal return map, calculated using successive minimas, from the chaotic time series of (b).

and the reference was a saturated calomel electrode. The electrolyte solution was a mixture of 1.0M sulfuric acid, 0.4M potassium sulfate, and 53.66 mM potassium chloride. A volume of approximately 300 ml was maintained in the cell. Figure 1(a) shows the four-electrode electrochemical cell configured to study chaotic synchronization. The anodes (iron disks) were immersed in the solution facing each other [see Fig. 1(a)] such that the horizontal distance between them determines the strength of their mutual (bidirectional) coupling. A bipotentiostat (Pine Model AFRDE5) was used to control the two anodic potentials (V_1, V_2) individually and measure the two anodic currents (I_1, I_2) simultaneously.

Before embarking upon the synchronization experiments, appropriate chaotic dynamics needed to be located. This was accomplished using the standard cyclic voltammogram technique. Different dynamical responses of the anodic current I were observed as the scan parameter anodic voltage V was varied between 0 and 1200 mV. Repeated scans revealed the existence of suitable chaotic dynamics in the parameter domain between 730 and 850 mV. Figure 1(b) shows a typical chaotic time series, used for synchronization experiments, of the anodic current (I) observed in the electrochemical cell. Figure 1(c) shows the reconstructed chaotic attractor and finally in Fig. 1(d) the corresponding return map with a characteristic unimodal shape is presented.

Experiments were carried out to identify the different domains of synchronization exhibited by a pair of nonidentical chaotic oscillators subjected to bidirectional coupling. Apart from the inevitable inherent differences between the two electrodes (anodes), a small parameter mismatch (different anodic voltages) was intentionally introduced between the two anodes. However, it was ensured that the chaotic nature of the underlying attractors was preserved. This parameter mismatch is considered indispensable for the observation of the elusive bidirectional lag synchronization [23,25], one of the synchronization domains of interest. The observed synchronization phenomena in our experiments were acutely sensitive to the mutual coupling (relative distance) between the two anodes. Therefore a compasslike device was employed to carefully vary, in small steps, the relative distance between the two anodes.

For extremely weak coupling, corresponding to a large horizontal separation between the two anodes, the two chaotic attractors oscillate independently. Figure 2(a) depicts the chaotic evolution of the two anodic currents. The absence of any interdependence between the two time series becomes more evident if one generates the I_2 vs I_1 plot shown in Fig. 2(b). The resultant attractor of Fig. 2(b) is structureless, indicating that the coupled system is located in the domain of no synchronization. As the mutual distance between the two anodes is monotonically decreased, the coupled dynamics exhibit phase synchronization. This phase-synchronization effect, evident from the time series of Fig. 2(c), is characterized by the absence of correlation in the amplitude domain and the prevalence of synchrony in the frequency domain. The corresponding attractor for the coupled system is shown in Fig. 2(d). It reveals a closed curve typical for phase-locked dynamics.

Augmenting the coupling strength (decreasing the mutual distance) further reveals the emergence of lag synchronization in the system dynamics. This lag domain proved rather evasive to find and extremely difficult to maintain since it was highly sensitive to the experimental noise. A systematic scan of the coupling constant and the parameter mismatch in conjunction with an attentive analysis of the time series [23,25] was required for the reliable detection of lag synchronization. Figure 2(e) shows the time series of the anodic

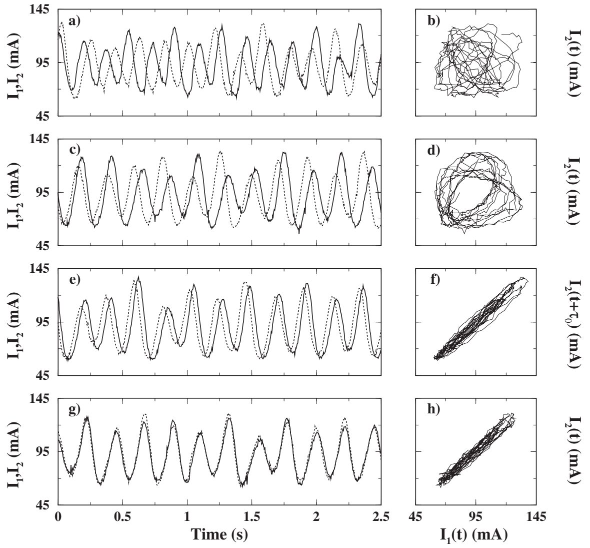

FIG. 2. Different synchronization phenomena recorded as the coupling strength is increased (mutual distance was decreased) monotonically. A small parameter mismatch was introduced intentionally by choosing the two anodic voltages to be 750 and 755 mV, respectively. (a) Two superimposed chaotic time series of the anodic currents $[I_1(t),I_2(t)]$ when the mutual distance between the two anodes is 5 cm. (b) $I_2(t)$ vs $I_1(t)$ plot for the time series of (a). For this coupling strength the dynamics are located in the domain of no synchronization. (c) Two superimposed chaotic time series of the anodic currents $[I_1(t),I_2(t)]$ when the mutual distance between the two anodes is 3.5 cm. (d) $I_2(t)$ vs $I_1(t)$ plot for the time series of (c). For this coupling strength the dynamics are located in the domain of phase synchronization. (e) Two superimposed chaotic time series of the anodic currents $[I_1(t),I_2(t)]$ when the mutual distance between the two anodes is 2.4 cm. (f) $I_2(t+\tau_0)$ vs $I_1(t)$ plot for the time series of (e). For this coupling strength the dynamics are located in the domain of lag synchronization. (g) Two superimposed chaotic time series of the anodic currents $[I_1(t),I_2(t)]$ when the mutual distance between the two anodes is 1.35 cm. (h) $I_2(t)$ vs $I_1(t)$ plot for the time series of (g). For this coupling strength the dynamics are located in the domain of complete synchronization.

currents exhibiting bidirectional lag synchronization. The constant time lag τ_0 observed is an intrinsic property of the bidirectionally coupled system and depends mainly on the coupling strength and the parameter mismatch. The $I_2(t+\tau_0)$ vs $I_1(t)$ plot, presented in Fig. 2(f), reveals that the resultant attractor is sputtered (falls) along the identity line, indicating the emergence of bidirectional lag synchronization. This lag synchronization, when located, was robust in our experiments and at times persisted for about 250 oscillations.

Finally, when the two anodes are placed in close proximity, the chaotic dynamics enter the domain of complete synchronization. This is evident upon visual inspection of the superimposed anodic current time series presented in Fig. 2(g). Consequently, the $I_2(t)$ vs $I_1(t)$ curve falls along the line of identity as shown in Fig. 2(h).

To quantify the experimental observations involving the different regimes of synchronization, a similarity function [23,25] between the chaotic time series for the two coupled oscillators was calculated. This similarity function computes a time-averaged difference between the two anodic currents (I_1,I_2) taken with the time shift τ and is defined as

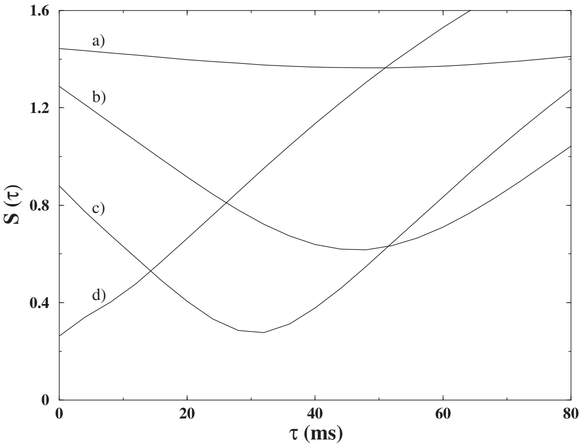

FIG. 3. Similarity functions $[S(\tau)]$ calculated using the experimental time series of anodic currents. The curves labeled *a*, *b*, *c*, and *d* correspond to the domains of no, phase, lag, and complete synchronization, respectively.

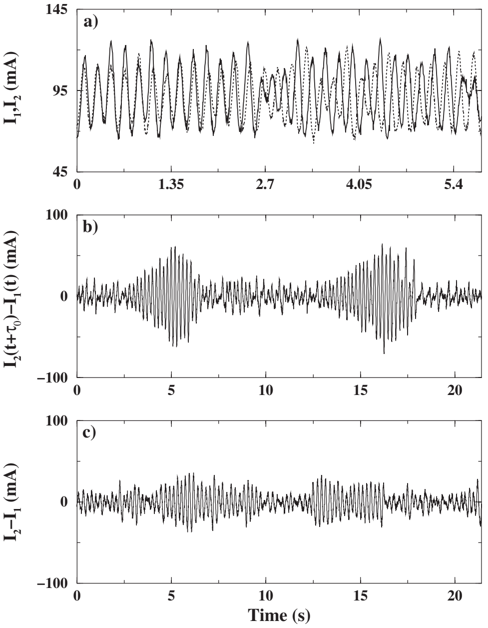

FIG. 4. Dynamics from the transition intervals separating the different domains of synchronization in the coupled system. (a) Section of the superimposed time series for the two anodic currents $[I_1(t),I_2(t)]$ showing the coexistence of phase- (between 0 and 2.7 s) and no-synchronization (between 2.7 and 5.8 s) domains. The longer version of this time series (not shown) indicates that for this coupling strength (mutual distance=4.4 cm), the chaotic dynamics of the two anodes exhibit intermittent phase synchronization. (b) Time series indicates that for this coupling strength (mutual distance=3.1 cm), the chaotic dynamics of the two anodes exhibit intermittent lag synchronization. (c) Time series indicates that for this coupling strength (mutual distance=2.1 cm), the chaotic dynamics of the two anodes exhibit intermittent amplitude synchronization.

$$S^2(\tau) = \frac{\langle [I_2(t+\tau) - I_1(t)]^2 \rangle}{[\langle I_1^2(t) \rangle \langle I_2^2(t) \rangle]^{1/2}}. \tag{1}$$

Figure 3 shows the similarity functions calculated using the anodic current timeseries for different coupling strengths. The curve labeled a corresponds to the experiment when the two oscillators are placed far apart and consequently find themselves in the regime of no synchronization. For this scenario, the similarity function $S(\tau)$ almost does not depend on τ [23] (signals are independent) and has an average value of $\approx \sqrt{2}$.

Upon decreasing the distance between the anodes, phase synchronization was observed as depicted by the curve labeled b. The minimum in this curve reveals the emergence of some characteristic time shift between the two anodic currents. Further augmentation of the coupling strength led to the emergence of lag synchronization as illustrated by the similarity curve labeled c. $S(\tau) \rightarrow 0$ in this curve for an appropriate lag time τ. This τ coincides with the lag time observed (τ_0) in the corresponding time series of Fig. 2(e). Finally, the similarity function labeled d reveals a monotonically increasing curve [$S(\tau) \approx 0$ for $\tau = 0$], a behavior characteristic of oscillators exhibiting complete synchronization. The reason that $S(\tau)$ fails to reach zero for $\tau = 0$ might be the significant levels of internal noise prevalent in our electrochemical cell. This internal noise in conjunction with the parameter mismatch and system drift preclude the attainment of better amplitude synchronization.

Apart from identifying the distinct domains of synchronization, the dynamics in the transition intervals were also analyzed. First, the coupling strength was chosen such that the coupled system is located between the domains of no and phase synchronization. The time series in Fig. 4(a) shows that the coupled dynamics for this mutual distance (4.4 cm) exhibits a mixture of nonsynchronized and phase-synchronized chaotic behavior. However, unfortunately, in our experiments, the emergence of periodic phase synchronization or scaling laws for the intermittent phase slips [26] could not be verified. Second, the coupling strength was chosen such that the system is located between the domains of phase and lag synchronizations. The time series $[I_2(t+\tau_0) - I_1(t)]$ vs t in Fig. 4(b) indicates that the coupled system exhibits intermittent lag synchronization. Finally, the system is placed between the domains of lag and complete synchronization. Consequently, the observed dynamical behavior corresponds to the intermittent amplitude synchronization as shown in Fig. 4(c). Our experimental results compare well with the numerically computed bifurcation diagrams [23,27] reported previously.

In conclusion, our results provide experimental evidence of the entire conversion route between the domain of no synchronization and the domain of complete synchronization for a pair of coupled nonidentical chaotic oscillators. This includes the detection of the evasive lag synchronization. The fact that we were able to verify the existence of this synchronization sequence despite the presence of intrinsic noise and system drift gives credence to the belief that these phenomena are generic in nature and therefore could be conceived in other real systems.

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