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Phase-flip transition in coupled electrochemical cells

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Time delay is introduced in the coupling between a pair of electrochemical cells. As coupling parameters are varied, the anodic current in the two cells oscillate in synchrony in regimes of periodic as well as chaotic dynamics. When the time delay is varied a phase-flip transition is observed: the relative phase between the synchronized oscillations changes abruptly by π. This is accompanied by an experimentally measurable discontinuous change in the frequency of the synchronized oscillators.

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I. INTRODUCTION

Extensive studies on coupled nonlinear dynamical systems have established that, depending on the strength of the coupling, a variety of regimes of synchronization (such as complete, phase, lag, and amplitude synchronization) can be observed [1–12]. The nature of the mutual coupling, on the other hand, can give rise to other domains of synchronization. For example, antiphase synchronization can be generated for repulsive coupling and also with time-delayed coupling [13–18].

Time-delayed coupled oscillators have been investigated recently in a variety of model systems such as coupled Fitzhugh-Nagumo neurons, predator-prey ecological models, limit cycle oscillators (the Landau-Stuart system), and coupled chaotic Rössler oscillators [19,20]. A general phenomenon that has been observed is that when the time delay is varied, the synchrony between the oscillators undergoes a phase flip, namely, the relative phase between the oscillators, $\Delta\phi$ changes by π [20]. This transition has been seen in a circuit experiment [19] as well as in a system of time-delay coupled semiconductor lasers [21] (although the precise form of the coupling there is somewhat different).

In this work, we present experimental evidence for the phase-flip transition in an electrochemical system. Using a pair of mutually coupled electrochemical cells we observe this abrupt change in relative phase in regimes of periodic as well as chaotic dynamics. This latter observation supports earlier numerical studies that have pointed to the existence of the phenomenon in arbitrary dynamical regimes [20]; furthermore, the ubiquity of the phase flip in such systems suggests that time delay can be a powerful control parameter in practical applications.

In Sec. II, we describe the experimental setup that was employed. Our main results are presented in Sec. III, and the paper concludes with a discussion and summary in Sec. IV.

II. EXPERIMENTAL SETUP

The experimental setup configured to study the phase-flip bifurcation consists of a pair of electrochemical cells coupled bidirectionally as shown in Fig. 1. Each cell contains an electrolyte solution wherein three electrodes are immersed. The working electrode, the anode, is an iron disk (Aldrich Iron rod, 99.98% purity, shrouded by epoxy, with a diameter of 6.3 mm). The counterelectrode, the cathode, is a graphite rod, also with diameter 6.3 mm and the reference electrode is the standard saturated calomel electrode (SCE). The present experimental configuration involves anodes facing downward, as in previous work [22]. The electrolyte solution we use is a mixture of H_2SO_4 1.0 M, K_2SO_4 0.4 M, and KCl 71.54 mM, and the cell volume is 150 ml. The temperature is maintained at 298 K.

Experiments are carried out potentiostatically. Each cell is controlled by a potentiostat that adjusts the anodic voltage V_i, $i=1,2$ across the individual anode-cathode electrode

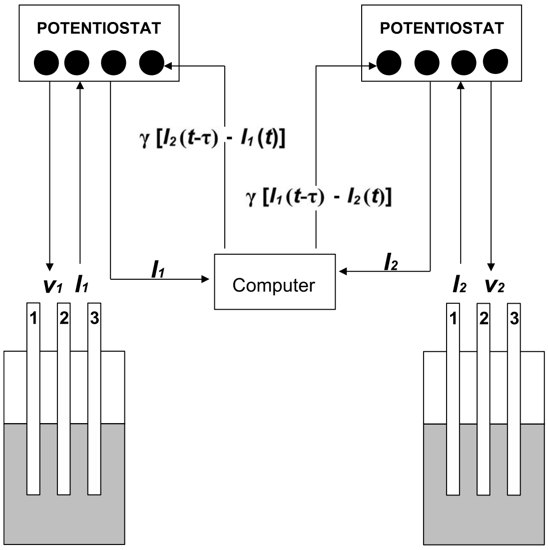

FIG. 1. Schematic of the experiment: two electrochemical cells with three electrodes labeled 1 (reference), 2 (anode), and 3 (cathode) are coupled electronically via a computer. Voltages $V_1=V_2$ are maintained in the cells and corresponding currents I_1 and I_2 are registered. The coupling implemented is bidirectional with equal time delays which are superimposed simultaneously on anodic voltages V_1 and V_2.

pairs, to maintain constant potential difference between an anode and its reference electrode [22,23]. In the present experiments, the anodic voltage was the bifurcation parameter since it determines the autonomous dynamics of the uncoupled cells. We use bipotentiostats PINE Model AFRDE5. Measurements of the two anodic currents I_1 and I_2 are simultaneously made.

Initially, using one of the electrochemical cells, the voltages giving the desired autonomous dynamics in I are determined via the cyclic voltammogram technique [11,23,24]. For the present case, we find that in the vicinity of $V_i = 640$ mV the current I_i is (simply) periodic and around $V_i = 1220$ mV the dynamics is chaotic. Characterization and analysis of the dynamics were carried out using standard diagnostic methods such as the Fourier transform, return maps, and attractor reconstruction [11,22]. The I_1 and I_2 time series are recorded using a data acquisition card installed in the computer. Thereafter, using the recorded data, the appropriate bidirectional time-delayed coupling is obtained as outlined in Fig. 1. These coupling terms are superimposed simultaneously on anodic voltages V_1 and V_2. The autonomous values of V_1 and V_2 are specified to be equal; the observed currents, I_1 and I_2, have slightly different amplitudes due to the level (usually small) of internal mismatch in the experimental setup. This is typical in such electrochemical experiments [24,25].

The specific experiments are performed with the following protocol: both cells are brought into a regime of amplitude synchrony by coupling them diffusively with zero τ, namely, without time delay, and using an appropriate value for the coupling constant γ. In the present experiments we found that $\gamma = -0.04$ mV/mA was sufficient to synchronize the electrochemical oscillators in the periodic region, while for chaotic dynamics the coupling needed was significantly higher, $\gamma = -0.12$ mV/mA. Once the oscillators are synchronized, time delay is introduced in the coupling via the computer that is used to control the experiment and can be varied as needed. We have observed the phase flip for both periodic and chaotic dynamics as described in Sec. III.

III. EXPERIMENTAL RESULTS

A. Phase flip in the periodic regime

For the anodic voltage $V_1 = V_2 = 640$ mV, the autonomous uncoupled current oscillations are periodic. We first couple the cells with zero time delay and achieve synchrony. We then gradually increment τ, and for every value of the time delay for each of currents I_1 and I_2, we compute the frequency Ω_i and phase ϕ_i for each oscillator using the analytical signal analysis through the Hilbert transform [9].

To illustrate the phase flip, we show in Fig. 2(a) the time series of I_1 and I_2 for the two electrochemical oscillators in one particular experiment. The cells are coupled with zero time delay initially, and at time $t = 3$ s, the delay is abruptly increased to 88 ms. At time $t = 12$ s, the delay is again abruptly set to zero, with the coupling $\gamma = -0.04$ mV/mA being constant throughout.

As can be clearly seen, for $\tau = 0$ ms, the oscillators are synchronized in phase, while for $\tau = 88$ ms, the two oscillators are out of phase. The variation in-phase difference with τ is shown in Fig. 2(b) and the frequencies of the oscillators in Fig. 2(c), indicating that the transition occurs just above $\tau = 48$ ms.

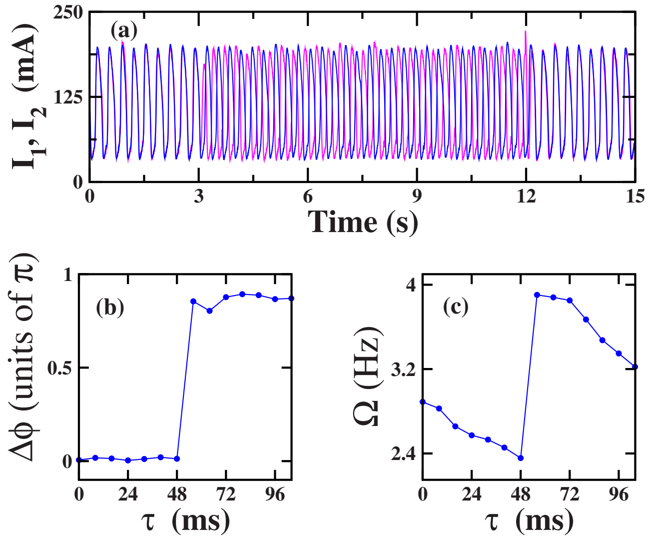

FIG. 2. (Color online) The phase flip in the regime of periodic dynamics. (a) The time series of the two electrochemical oscillators, I_1 and I_2, superimposed. Two regions of in-phase synchronization ($\tau = 0$ ms) and one domain of out-of-phase synchronization ($\tau = 88$ ms) are observed. (b) The phase difference, $\Delta\phi$, as a function of the delay, with τ showing the critical value of τ at which the transition occurs. (c) The frequency of the oscillators, Ω, plotted as function of the time delay, τ, increases abruptly at the critical value of τ.

An important feature of the phase-flip transition is the simultaneous jump in the common frequency of the synchronized oscillators, Ω. As in earlier experiments and in simulations, the frequency for in-phase motion is always lower than that of the out-of-phase dynamics [19].

B. Case of chaotic dynamics

In the second set of experiments the anodic voltage for the two electrochemical cells was fixed at $V_1 = V_2 = 1220$ mV. At this value the autonomous uncoupled dynamics in each cell is chaotic. Upon coupling them with $\gamma = -0.12$ mV/mA and zero time delay they synchronize, retaining chaotic dynamics.

As for the periodic case, we show an illustrative result in Fig. 3(a). For the first 5 s, the time delay of the coupled oscillators is kept at zero. The delay is abruptly increased to $\tau = 112$ ms and then the phase difference changes to π. At $t = 15$ s, the delay is reset to zero, and the dynamics returns to being in phase.

It should be pointed out that judging the phase and frequency in the chaotic regime is not a straightforward matter. Figure 3(b) shows the experimentally measured value of $\Delta\phi$ as a function of the delay, τ; the phases and the frequencies were computed using the procedure suggested by Pikovsky *et al.* [9]. As shown in Fig. 3(c), the frequency Ω of the oscillators abruptly increases as the oscillations switch from

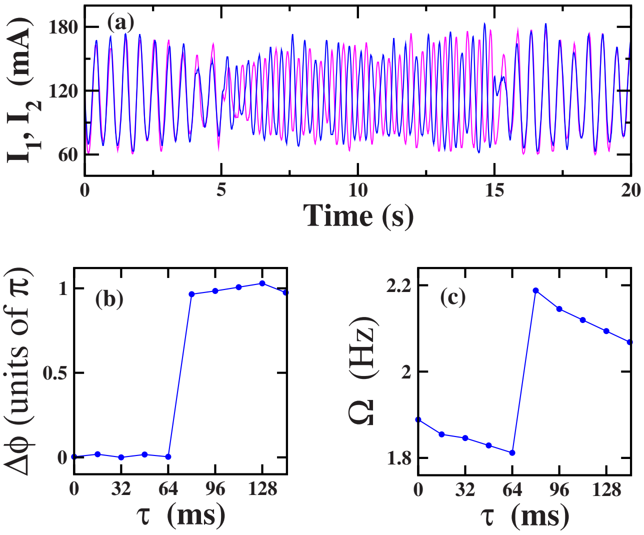

FIG. 3. (Color online) The phase flip in the regime of chaotic dynamics. (a) The time series of I_1 and I_2 superimposed. For $\tau = 0$ ms, two regions of in-phase synchronization are observed, whereas the domain of out-of-phase synchronization is observed for $\tau = 112$ ms. (b) The jump of the phase difference $\Delta\phi$ as a function of τ. (c) The frequency Ω of the oscillators changes abruptly as a function of the time delay.

the in-phase to the out-of-phase synchronization, with the critical value for the transition being around $\tau = 64$ ms.

C. Discussion

In the present experiments the coupling needed to synchronize the oscillators in the periodic regime is smaller than that when the dynamics is chaotic. The required coupling naturally depends on factors intrinsic to the experimental system which here involves a complex set of coupled reactions. When the autonomous dynamics has a positive Lyapunov exponent, the coupling needs to be "stronger" in order to attain complete synchronization.

Similarly, the delay at which the flip transition occurs in the chaotic regime is lower than that in the periodic regime: this is related to the fact that the frequency of periodic oscillations is greater than the dominant frequencies for chaotic dynamics. Further, the phase change at the flip is close to (but not always equal to) π. This is an experimental limitation coming from intrinsic noise and system drift; similarly, complete synchrony of the kind observed in numerical simulations is also difficult to see here.

Finally, given the nature of the phase change, we investigated the possibility that the system dynamics would show hysteresis. A large number of experiments were carried out where the delay was varied in a cyclic manner. However, we found no clear evidence of hysteresis: the transition always occurred at the same value of τ to within experimental noise.

IV. SUMMARY AND CONCLUSIONS

The anodic current in an electrochemical cell provides a record of the complex dissolution and passivation processes as well as all the other electrochemical reactions that take place on the surface of the electrode. Variation in the anodic voltage modifies these elementary reaction rates, resulting in measurable changes in the dynamical states [26]. Given the level of control that is possible, the system of coupled electrochemical cells is therefore ideally suited for the present study.

We have presented the experimental evidence for the phase-flip transition in the regime of synchronized *chaotic* dynamics. Our observations are consistent with earlier simulations that have indicated that such a transition should be observable in coupled chaotic systems [20], and although not shown here, in-phase and out-of-phase regions alternate as the time delay is monotonically varied [19].

The observation of the phase flip in this system—that effectively probes a series of complex coupled reactions—suggests that this is a generic effect that should be realizable in other experimental systems that incorporate time delay. For instance, in larger electrochemical reactors, delay in the coupling would be natural due to the time it takes for the migration of ions. We have mimicked this in the smaller cells by the "manual" introduction of delay: our main motivation was to test the robustness of the flip in a system which has inherent problems of noise and drift and where the noise itself may be stationary. This is an important issue in studying systems such as the ecological food-web model [19] or the coupled semiconductor laser systems [21] experimentally. The abrupt change in phase and the accompanying increase in frequency are both hallmarks of this transition and both features can be of considerable use in practical applications.

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