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Suppressing spatiotemporal disorder via local perturbations in an electrochemical cell

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We report experimental results depicting suppression of complex spatiotemporal dynamics under the influence of local periodic stimulations. In an experimental electrochemical system, applying a continuous forcing signal to one of the sites in an array of eight coupled oscillators, the naturally complex behavior of the remaining seven electrodes can be converted to periodic responses. The oscillations remain periodic as long as the forcing is active and revert back to exhibiting chaotic dynamics after the control is switched off. These results can also be interpreted as experimental realization of ''phase-synchronization'' induced via local driving in an extended system. A possible relevance to the experimentally observed calcium wave patterns is pointed out.

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Coupling of nonlinear oscillatory units is a simple way to create spatiotemporal chaos. The response of such spatiotemporally hyperchaotic systems depends on the nature of coupling and dynamical evolution of the local oscillator. Appropriate tuning of system parameters can yield dynamics that are strongly disordered (maximally chaotic) with a rapid decay of correlations both in space and time. Taming of complex dynamical behavior typical of distributed dynamical systems can be achieved using feedback [1–5] or external forcing techniques [6,7]. Numerical results involving parametric resonance [7] indicate the suppression of natural turbulent dynamics in the presence of strong global forcing via stabilization of coherent structures (spirals, Turing patterns, etc.). Experimental confirmation of these simulations was reported for the light sensitive Belousov-Zhabotinsky (BZ) reaction [8]. In both cases, the external forcing had to be implemented globally in order for induction, propagation, and subsequent maintenance of long-range ordered patterns.

Recently, it was reported [9,10] that high-dimensional chaotic dynamics typical of spatiotemporal systems could be converted to a well-defined ordered state without having to perturb the entire system. These simulations were carried out on spatially extended systems comprising of diffusively coupled periodic oscillators in the limit where the dynamics could be computed via integration of corresponding partial differential equations. Sinusoidal forcing function of the type $A\sin(\omega t)$ was superimposed on the evolution equation of one of the oscillators (via modulation of a control parameter or as an additive term). If the amplitude (A) of the perturbation exceeds a certain threshold and the forcing frequency is appropriate (the intrinsic frequency of an isolated oscillator is a good starting point) the prevalent spatiotemporal complexity is replaced by an ordered state. This stabilized coherent state is comprised of periodic pulse trains propagating from the point of stimulation to the end of the chain [9,10]. Subsequent to the induction of global order, the local dynamics of each of the oscillators is rendered periodic. To summarize, recent numerical simulations indicate successful suppression of complex spatiotemporal dynamics in the presence of local periodic perturbations.

In this paper, we report experimental confirmation of the numerical results suggesting that inception of global order via local nonvanishing perturbations is possible. The system chosen for implementation of this local forcing strategy is a three-electrode electrochemical cell. This electrochemical system has been used to study the potentiostatic electrodissolution of iron in a sulfuric acid buffer [11] under ambient temperature (295–300 K) conditions. The anode of the cell is an array of eight iron electrodes shrouded by epoxy. Electrolyte solution is a mixture of 1 M H_2SO_4 and 1 M Na_2SO_4. Anodic potential is measured relative to a $Hg/Hg_2SO_4/K_2SO_4$ reference electrode, while cathode is a cylindrical platinum mesh encircling the array. Experiments were performed in an impinging jet cell as shown in Fig. 1. The diameter of the jet is 5 mm and the distance from the jet to the electrode surface is 6 mm. Each electrode is made from pure iron wire of a diameter 0.5 mm. Distance between the electrodes is 0.05 mm and they are embedded in epoxy in a straight line configuration as shown in Fig. 1. Thus, the length of the eight-electrode configuration is 4.95 mm. The reference electrode is located next to the jet, that is, 6 mm from the plane of the working electrode and 4 mm from the axis; the separation is in a direction normal to the orientation of the eight working electrodes. Corrosion (electrodissolu-

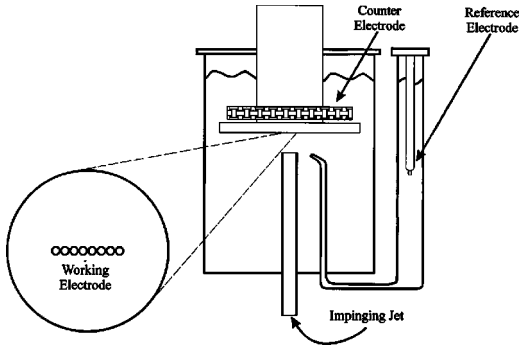

FIG. 1. Experimental setup used to observe and subsequently control the spatiotemporal complexity observed during potentiostatic dissolution of iron in sulfuric acid.

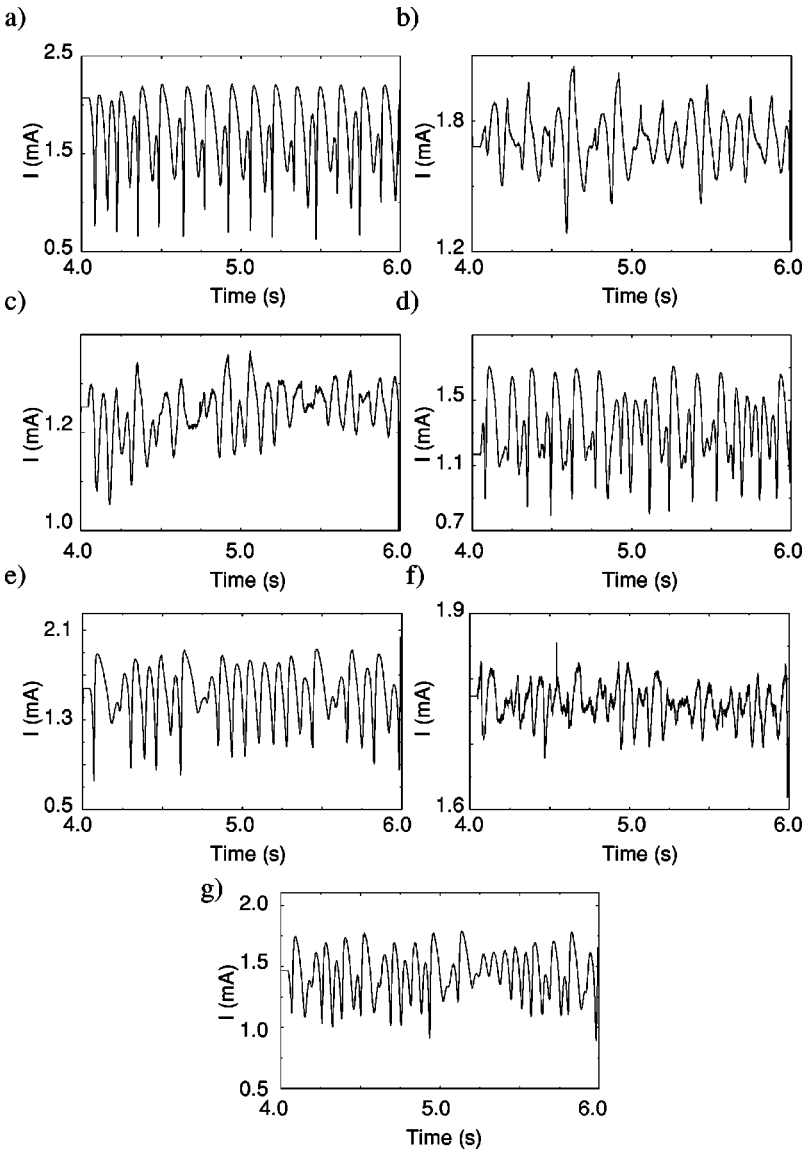

FIG. 2. The time series of the eight electrode array configuration in the absence of control. (a)–(g) correspond to electrodes 2–8, respectively.

tion) takes place only on the ends. Electrodes and the epoxy are sanded to a flat plane before each experiment with 180 grit silicon carbide sandpaper. The surface is then washed with deionized water and dried with compressed air.

Electrochemical reaction is controlled by a bipotentiostat (Pine Model AFRDE 4) and a wave form generator (HP 33120). Electrodes in the array are linked to the anode jacks of the bipotentiostat through the zero-resistance ammeters (ZRA). The ZRA circuit consists of an operational amplifier and associated feedback circuitry such that the individual currents of the electrodes in the array can be measured without altering their polarization potentials. To mimic the periodic forcing implemented in the numerical simulations [9,10] one of the electrodes is forced sinusoidally in the galvanostatic mode while the seven response electrodes are held at one potential. Data were recorded using a 32-channel data acquisition card (Keithley DAS-180HC2) installed in a pentium PC. The eight outputs from the ZRA box are measured and recorded at the sampling rate of 2000 Hz.

Figures 2(a)–2(g) show a section of the time series for the seven response electrodes in the uncontrolled case where no forcing is imposed. The other electrode (#1), which subsequently is forced (sinusoidally) in the galvanostatic mode is held at zero current. Note that there are variations among the currents of the seven electrodes. Time series of unforced chaotic oscillators in other geometries, a 61-hexagonal array and a ring of 29 electrodes, are discussed in [11] and [12], respectively. In all cases, including the eight-electrode configuration being considered here, the spatially extended system is heterogeneous, i.e., there are slight variations among the electrodes and in the spacings. In our experiments, there are additional variations not seen in the ring geometry due to the assymetric flow field. Coupling among the electrodes is due to several factors including diffusion, convection, and migration. Thus, both local and long-range [13,14] components of coupling dictate the system dynamics.

The appropriate perturbation frequency ω to implement the control was obtained from examining the Fourier spectra of the natural dynamics and was calculated to be $\omega = 25$ Hz. Some results obtained with a forcing frequency of 25 Hz and an amplitude of 7.5 mA applied to electrode #1 are shown in Fig. 3. Figure 3(a) is the forced electrode. Fig-

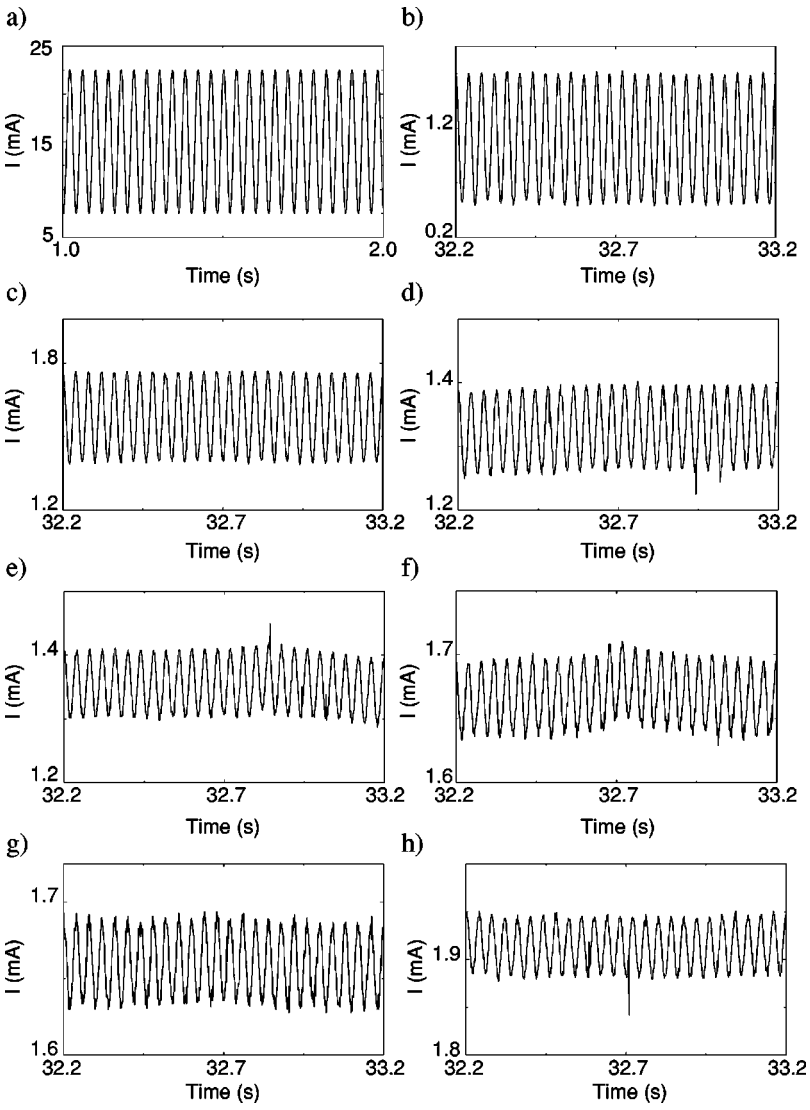

FIG. 3. The time series of the eight electrode array configuration subjected to local periodic stimulus. (a)–(h) correspond to electrodes 1–8, respectively.

ures 3(b)–3(h) show the dynamics for the remaining electrodes after transients have died out. The chaotic dynamics have been converted to period-one oscillations for all the electrodes. The forcing signal is able to maintain control and suppress the spatiotemporal complexity. Similar to numerical observations, the control emanates from the forcing electrode and spreads down the array. However, instead of a smooth propagation of order observed in simulations, experimental results are as shown in Fig. 4. The forcing signal was initiated at time ($t=6$ s). Almost instantly, the second and third electrode start exhibiting periodic dynamics. The fourth electrode joins in after a little delay. After an elapsed time of about 20 s, the fifth electrode joins in and almost immediately electrodes six, seven, and eight start to exhibit periodic dynamics as shown in Figs. 3(b)–3(h). It should be pointed out that although the forced dynamics are in different amplitude ranges, the frequency of the period-one oscillations is identical for all the response electrodes and to that of the forcing signal ($\omega=25$ Hz). This is similar to phase synchronization of coupled oscillators as defined by Fujigaki, Nishi and Shimada [15]. When the forcing was turned off, the electrodes went back to exhibiting chaotic dynamics.

The experiments were repeated several times under these conditions. In most cases, the observed response was as described above, i.e., all electrodes were brought to a periodic state. Occasionally, however, only the electrodes (one to four) nearest the forcing electrode became periodic. It ap-

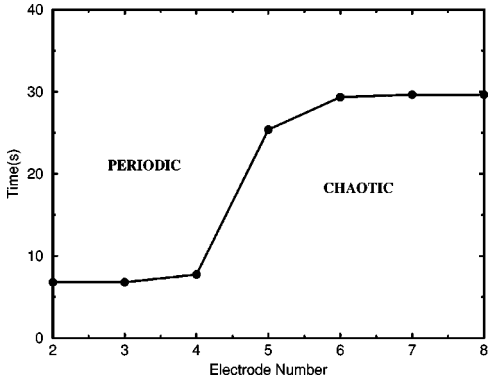

FIG. 4. Propagation of the control signal down the array. Control was initiated at time$=6$ *s* and complete suppression of spatiotemporal chaos is attained at time$=30$ s. This time lag between the third and the fourth electrode was observed consistently.

pears that the coupling is sometimes not strong enough to overcome fluctuations induced by system inhomogeneities and drift.

It was observed that control of the observed spatiotemporal complexity is sensitive to the parameters of the forcing signal. The propagation of the periodic state was only observed for a narrow frequency range. The forcing frequency was varied over the range between 5–120 Hz. Some degree of periodic response was observed only in the range between 20–30 Hz outside that range, the dynamics remained chaotic for all forcing amplitudes. Between 20 and 30 Hz, the response depended on forcing amplitude. The following dependency on forcing amplitude was obtained at a forcing frequency of 25 Hz: (1) 0.5 mA, the adjacent electrode becomes periodic, (2) 2.5 mA, the two nearest electrodes become periodic, (3) 5.0 mA, usually three electrodes become periodic, (4) 7.5 mA, up to all seven electrodes exhibit periodic dynamics, (5) 10.0 mA, usually, three electrodes become periodic and sometimes more.

At frequencies greater and less than 25 Hz (but still in the range between 20–30 Hz) the effect of forcing became weaker as the distance from 25 Hz became greater. Thus, for example, at a frequency of 27 Hz, a greater forcing amplitude is required to have the same effect compared to a frequency of 25 Hz.

We also tried these experiments with electrodes in a ring configuration. The ring consisted of 29 electrodes of individual diameters 0.5 mm, separated by less than 0.05 mm. Thus, the electrode size and separation distance were the same as in the eight-electrode configuration discussed above. Chaotic behavior on this ring has been discussed in a previous paper [12]. When a single electrode was forced as above, the chaos was suppressed on the 3–4 electrodes on either side of the forced electrode. The remaining electrodes (20–22) remained in a chaotic state. The suppression of the chaos occurred quickly as was seen in the suppression of the first three in the experiment with eight electrodes. However, even after a long time, no additional propagation of periodic behavior was seen. Thus, the propagation of control appears to be less in the larger system than in the smaller. The chaotic dynamics of the distant oscillators is propagated back to the neighbors of the forced element.

This control of spatiotemporal chaos is complicated due to the existence of numerous unstable spatial modes, but, is more important too, because of its possible applications in plasma, laser devices, and chemical systems where both spatial and temporal dependencies need to be considered. These results could also be considered as an experimental verification of phase synchronization [15], where the coupled oscillators are synchronized with each other in phase, but are different in amplitudes and location in state space. Finally, as pointed out by Baier *et al.* [9], this paper is of interest in an information-theoretic context in biology. Local temporal information of biological relevance could be encoded in a meaningfully ordered spatial pattern that creates corresponding temporal signals at distinct sites. Furthermore, pattern formation inside a cell could act as a biologically relevant encoding mechanism to transfer extracellular signals to targeted sites of biochemical action. Experimental evidence of such an encoding mechanism in biological cells was found by Camacho and Lechlieter [16]. They reported experimental formation of a regular spatial calcium wave pattern following a local receptor activation by applying an external concentration level of bombesin to *Xenopus* oocytes. Similar to our experimental observations, their results indicate that transduction of information is possible for only finite ranges of receptor activation. This implies that the extended system acts as a nonlinear frequency filter such that only a range of temporal signals get translated to an ordered spatial pattern. Finally, in their experiments, brief receptor activations do not spread over the whole cell but are destroyed in the vicinity of the point of activation. This is consistent with our observations.

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