The emergence of synchrony behavior in weakly coupled electrochemical oscillators via a 'metallic plate'

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ABSTRACT

We have made an effort to investigate thoroughly the coupled behavior of a spatio-temporal system of two limit cycle electrochemical oscillators (Fe/H_2SO_4) in the absence and presence of a metallic plate (using copper and platinum). The oscillators exchange information via the common electrolyte solution and the magnitude of information exchange varies with the distance (d) between the oscillators, i.e. the lesser the d the more will be the coupling strength and vice-versa. The presence of metallic plate between the working electrodes (Fe) enhances the magnitude of potential distribution in the solution which leads to the increase in entrainment area, i.e. the product of distance between the oscillators d and their parameter mismatch. To explain the experimental findings numerically, the pulse coupling mechanism based on the delta function (Kronecker) has been introduced.

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1. Introduction

Synchronization has been a subject of great interest among the researchers for centuries since Christiaan Huygens found empathy between the oscillating pendulums. Although this phenomenon is investigated extensively in the numerous fields such as biology [1–3], chemistry [4–7], physics [8–10], and engineering [11,12], the researchers are still curious to understand the emergence of coherent behavior even in a system of two oscillators. This is due to the fact that in the natural systems there could exist multiple ways to exchange the information other than the conventional diffusive coupling. The recent studies and the literature from the last decades also reveal that the scientific community tries to explore the alternate schemes on the name of nonscalar coupling (conservative coupling) [13], nonlinear coupling (complex interactions using specified trajectories) [14,15], dynamic coupling (i.e. coupling via a dynamic environment) [16,17], differential coupling (wherein an oscillator gets affected by the rate of change of the other oscillator's state variables, i.e. fast/slow, rather than by the instantaneous magnitude of its state variables) [18], asymmetric coupling (that means different coupling constants) [19,20] etc. Analogously, we have explored a novel scenario wherein the correlation between two non-electrically coupled electrochemical oscillators gets enhanced (i.e. unsynchronized/weakly-synchronized behavior to weakly-synchronized/phase synchronized behavior) with the insertion of a metal (copper, platinum) piece (2 dimensional, like a plate) between them.

In the present work, the coupled behavior of two electrochemical oscillators has been studied systematically by changing the distance (d) between them for both the cases, i.e. with and without metallic plate. It has been observed that the presence of a metallic plate enhances the entrainment area (the product of distance between the oscillators d and their parameter mismatch). For this study, two metals, copper and platinum, have been used. Since both the metals yield similar behavior, only the results with copper plate have been presented. This consistency of both the metals also verify that the metallic character is the only reason behind the emergence of presented phenomenon and not the metallic plate bipolarity wherein copper plate could participate in the redox reactions under high voltage conditions [21]. In addition, the magnitude of potential distribution in the solution (which is in millivolts range) with and without metallic plate also suggests that the emergence of synchrony in weakly interacted electrochemical cells is only the consequence of the enhancement in coupling strength, i.e. enhancement in the magnitude of potential spikes. To explain these experimental findings, the pulse coupling mechanism based on the delta function (Kronecker) has been introduced by considering that the emergence of synchrony behavior in the weakly coupled electrochemical oscillators via a metallic plate is a consequence of increasing coupling strength. The shown numerical results are found to be in a good agreement with the experimental findings. To the best of our knowledge, this coupling scheme has not been explored, so far.

The paper is organized as follows: the experimental setup employed in the present work has been discussed in Sect. 2 whereas Sect. 3 incorporates the experimental findings and discussions. Furthermore, the pulse coupling mechanism model along with the numerical results is discussed in Sect. 4. Finally, the paper is concluded in Sect. 5.

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2. Experimental setup

Fig. 1 represents the schematic diagram of the experimental setup that has been employed to study the metallic plate effect on the weakly coupled behavior of a pair of electrochemical oscillators (i.e. Fe|0.7 M H_2SO_4) exhibiting limit cycle dynamics. The iron electrodes of diameter 1 mm (Nilaco Co., 99.5%) have been used wherein only the bottom surfaces were allowed to act as the reacting surface area and the rest of the electrodes' surfaces (i.e the cylindrical sides) were coated by resin. All the experiments on limit cycle oscillators were carried out in a mixture of 0.7 M sulfuric acid (H_2SO_4) and 0.4 M copper sulfate ($CuSO_4$). Before each experiment, the bottoms of the electrodes' surfaces were polished by a series of wet sandpapers of grid sizes 600, 1200, and 2000 and after this mechanical polishing, the electrodes were rinsed by Milli-Q water. The counter electrodes were coiled copper electrodes (Nilaco Co., 99.9%, 1 mm diameter), whose reacting surface areas were 100 times larger than that of the iron working electrode so that the polarographic conditions could be fulfilled. In the two-electrode systems shown in Fig. 1, Fe electrodes act as the anode whereas the Cu electrodes behave as the cathodes. In each of this system, a distance of 25 mm was maintained between Fe (working) electrode and Cu (counter as well as reference) electrode. Moreover, the positions of the reaction surface areas of both the working electrodes (Fe) were aligned at the same height.

In the study of coupled behavior of these two systems (as schematic shown in Fig. 1), the copper plate (Nilaco Co., 99.9%) was employed as a metallic plate because it is quite stable in the strong acidic conditions. The dimensions of the copper plate was 3 mm × d mm × 16 mm where d is the distance between the Fe (working) electrodes of the two systems. Before each experiment, the copper plate was carefully polished and rinsed. The copper plate was placed in the solution below the reacting surface area (3 mm) in a manner that the plates' edges should only be aligned with the edges of the working electrodes (Fe). This is important because the presence of a part of the metallic plate just below the reacting surface area hinders the mass transfer in the diffusion layer and induces the feedback effect [22]. A potentiostat (HA-151, Hokuto-Denko) was used to apply the potentials to both the electrochemical cells wherein each supply was electrically isolated by pulse isolation trans (Denkeiseiki F1). A digital recorder (8841 Memory Hicorder, Hioki) was used to record the current signals from the potentiostat. Moreover, Fig. 2(a) shows the side view of the experimental setup to study the metallic plate effect in a pair of nonidentical limit cycle oscillators interacting via a common electrolyte solution wherein the applied potentials, i.e. E_1 and E_2, are the controlled parameters. The autonomous behavior of these two limit cycle oscillators corresponding to their applied potentials, are given in Fig. 2(b) and (c).

Furthermore, the platinum plate (of dimensions 3 mm × d mm × 16 mm) has also been used (results not shown) to ensure that the metallic nature of the copper plate is the only reason behind the emergence of presented phenomenon (i.e. not the metallic plate bipolarity wherein

Fig. 2. The subplot (a) represents the schematic side view of the experimental setup used to study the coupled behavior of two electrochemical cells (exhibiting limit cycle dynamics) in the absence and presence of a metallic plate. The subplots (b) and (c) represent the uncoupled time-series ($d = \infty$) of Osc1 (red) and Osc2 (blue), respectively, i.e. autonomous dynamics of two cells (the current oscillations I_i at the Fe electrodes of diameter 1 mm). Here T_i represents the intrinsic time-periods, i.e. the time intervals wherein oscillators exhibit both active and passive states, and T'_i corresponds to the time interval wherein the oscillators stay in the passive states ($i = 1,2$).

copper plate could participate in the redox reactions under high voltage conditions [21]). In addition to this, the potential distribution at the vicinity of the copper plate has also been measured. For this, a platinum wire was used as a probe to measure the potential distribution in the solution along the vicinity of copper plate surface (experimental setup given in Fig. 5(a)). Here, the potential was recorded with respect to the SCE (saturated calomel electrode), located far from the Fe-Cu system (i.e > 10 mm).

3. Experimental results and discussion

In the present work, the metallic plate effect has been demonstrated by the emergence of synchrony behavior in the weakly interacting electrochemical systems. This effect has been shown in Fig. 3 wherein by inserting a copper plate, the irregular and uncorrelated dynamics of the weakly coupled limit cycle oscillators becomes regular and coherent. This coherent mode depicts the master–slave relationship, i.e. the lag synchrony behavior wherein the oscillator having lower intrinsic frequency ($\frac{1}{T_2}$ of Osc2, Fig. 2(a)) follows the oscillator having higher intrinsic frequency ($\frac{1}{T_1}$ of Osc1, Fig. 2(b)). This time lag between master and slave decreases with the increase in coupling strength (1/d) and decrease in parameter mismatch ($|E_1-E_2|$). Furthermore, the master–slave behavior could be understood in terms of an increase in the total flux across the diffusion layer of one cell (say target cell) by the pulse signal of H^+ ions
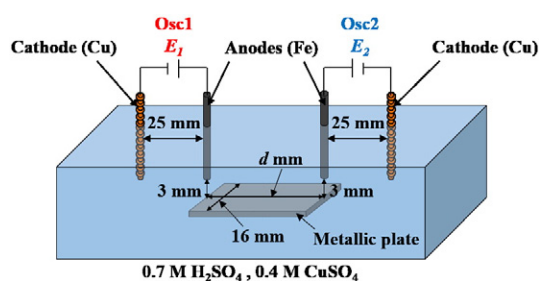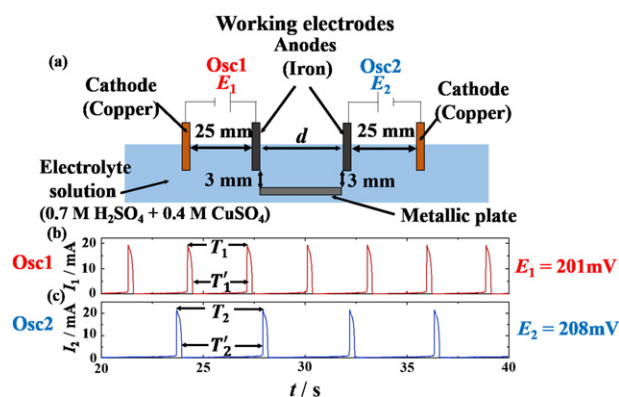

Fig. 1. The schematic diagram of the experimental setup used to study the metallic plate effect on the non-electrically coupled behavior of two electrochemical oscillators (exhibiting limit cycle dynamics) interacting via a common electrolyte solution. The employed electrochemical oscillator is a system of two electrodes wherein Fe acts as an anode (working electrode) and Cu acts as a cathode (counter as well as reference electrode).
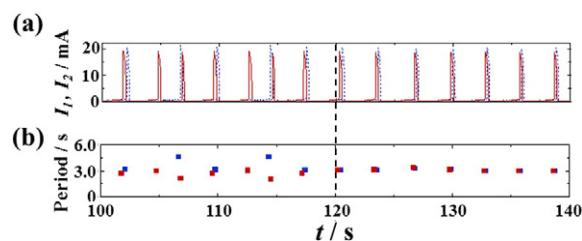

Fig. 3. The time-series in subplot (a) depict the dynamical transition in the weakly coupled limit cycle electrochemical oscillators, Osc1 ($E_1 = 201$ mV, red) and Osc2 ($E_2 = 208$ mV, blue) having frequency mismatch $\frac{T_2}{T_1} = 1.44$, separated at $d = 4.5$ mm, with the insertion of a copper plate of length 4.5 mm (at $t = 120$ s), i.e. no-synchrony to lag synchrony behavior, where the subplot (b) shows this transition by the alteration of their time-periods.