

Magnetic field induced hopping among Arnold entrainment tongues of coupled iron electrochemical oscillators

Hiroaki Koyama, Hirofumi Nakao, Hiroshi Y. Yoshikawa, Seiichiro Nakabayashi *

Department of Chemistry, Faculty of Science, Saitama University, Sakura-ku, Shimo-okubo, 225, Saitama 338-8570, Japan

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ABSTRACT

A pair of the electrochemical oscillators was entrained with a short distance between the electrodes. A phase map of the entrainment was obtained as a function of the distance and their intrinsic frequency ratio. Each entrainment zone formed a triangle in shape as predicted by Arnold. Although each oscillation was periodic under decoupled condition, coupling out of the zones evolved aperiodic oscillations. Magnetizing one of the coupled iron electrodes induced pattern hopping among the zones. This magnetic field effect was ascribed to reduction of the oscillation frequency, which was drastically anisotropic depending on the magnetized direction to the reaction surface.

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1. Introduction

Clock pendulums are known to mechanically entrain in their phase, when they are hanged on the same wall. Similar phenomena occur between oscillating chemical [1–5] and electrochemical reactions [6–9], and also in biological systems [10–12]. Among them, self-sustained electrochemical current oscillation has attracted particular interest owing to simplicity of the overall reaction: $M \rightarrow M^{n+} + ne^{-}$, where M and M^{n+} represent metallic and its ionic form of the electrode. The electrodisolution often accompanies current oscillations at a point close to the Flade potential [13,14]. Under more anodic potential than that, non-conductive metal oxide film covers on the entire surface to terminate the oscillation and the electrodisolution. Under appropriate potential close to Hopf bifurcation [15], the dissolution reaction becomes bistable to repeat forming and breaking cycles of the non-conducting surface oxide, which induces the self-sustained current oscillation. The stability of the oxide is determined by two parameters: pH and electrode potential, as shown by the Pourbaix diagram at the steady state [13,14].

Recently, partially synchronized chaos has been found in a few numbers of non-linear electrochemical oscillators, in which some but not all the oscillators are synchronized with each other. Coupling among the oscillators was achieved through resistors inserted between the electrodes and the potential controlling circuit [6,7]. These findings suggest a possible mechanism for generation of a spatiotemporal pattern at a non-linear interface such as a non-linear electrodeposition of Ag–Sb [16], where each finite area at the surface is coupled by spatiotemporal distribution of local current. Likewise, the electrochemical oscillators can be coupled, without

any additional resistor, by electrochemical waves (potential and ion waves) emitted into the electrolyte solution around the electrodes [8,9]. In our studies of coupled iron oscillators and network, they showed instantaneous synchronization due to their relaxation waveform in the oscillating current [8,9]. The coupled oscillators with the same polarity (anode–anode or cathode–cathode) tend to emit current pulses at the same time as an excitatory coupling, but those with different polarities (anode–cathode) prevent overlapping of current pulses as an inhibitory coupling [8,9].

The excitatory-coupled two self-sustained iron electrochemical oscillators is the simplest example for entrainment between two electrochemical oscillations. Despite their simplicity, no phase map (the so-called Arnold map) [17] for the entrainment with respect to the coupling strength and frequency difference between the two oscillations has yet been reported, which is one of the topics of this report. The second topic is to evaluate the magnetic field effect on the entrainment. Much has been reported for the magnetic field effect on non-oscillating electrochemical reactions [19,20]. Most of them have been caused by modified mass transportation due to magneto-hydrodynamics. However, since iron and iron oxide have relatively large magnetic susceptibility, the magnetic energy charged in electrodes has a chance to shift the thermodynamic stability and affect the oscillation phenomena.

2. Experimental

The oscillator consisted of iron anode and copper cathode dipped in an aqueous solution containing 1 M sulfuric acid and 0.4 M copper sulfate. Potential between the iron and the copper electrodes was applied by a multi-channel potential source, in which each channel was electrically isolated with isolation resistance over 1 GΩ, i.e., each potential for the oscillator was equivalent to be supplied by an independent battery, as schematically

* Corresponding author.

E-mail address: Sei@chem.saitama-u.ac.jp (S. Nakabayashi).

shown in Figure 1a. The working bistable electrode was iron wire with a diameter of 0.8 mm. The iron wire was cut and polished to form a cylindrical shape. The surface of the iron wire was insulated by nail polish except in the expected reacting area, as shown in blue and brown areas in Figure 1b–b and b–c, respectively. The counter electrode was a coiled copper wire, whose reacting area was 100 times larger than that of the iron electrode in order to maintain quasi-polarographic condition for the iron electrode. Quasi-polarographic condition was maintained by a drastic difference in the reaction areas of the iron anode and the coiled copper counter cathode. These electrodes were in contact with an aqueous solution containing high activity of Cu^{2+} to stabilize the potential drop at the copper counter-quasi reference electrode. The distance L between the iron and copper electrodes was 30 mm.

In order to magnetize a single electrode, a small spherical ferrite magnet with a diameter of 5 mm was put on the iron wire, as shown in Figure 1b. The magnetic flux density (B) onto the reaction surface was measured by a Gauss meter (Lake Shore 421).

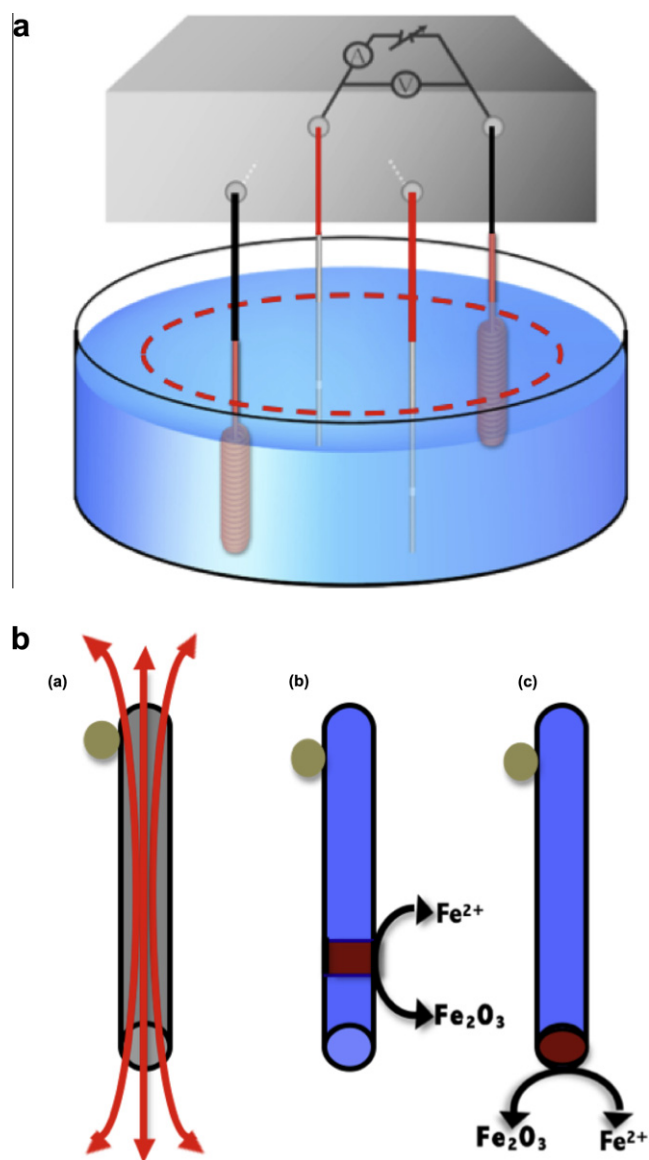


Figure 1. Schematic representation of the experimental setup: (a) magnetic flux density (red lines) of magnetized iron electrode (b–a), reaction occurring at cylindrical side surface (b–b), and that at bottom surface (b–c). A brown sphere attached to the iron electrode in (b) is a ferrite magnetic bead. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results

3.1. Potential dependence on the oscillation of a single oscillator

Under constant applied potential (E), a self-sustained current oscillation appeared in the potential window from 215 to 245 mV. Under $E < 215$ mV, a non-oscillating steady state (SS1) was observed with a constant current of 7.5 mA, owing to the electro-dissolution of iron. For $E > 245$ mV, another steady state (SS2; an excitatory state) appeared, in which the current was almost zero owing to passivation by the iron oxide. Within the oscillatory region ($215 \text{ mV} < E < 245 \text{ mV}$), the current oscillated periodically. The amplitude and the period of the oscillations ($T = 2\pi/\omega$) increased with increasing E and the distance between iron and copper electrodes (L), as shown in Figure 2. With increasing E , the transition from SS1 to a limit cycle oscillation was obtained at $V = 218$ mV, but with decreasing E from the oscillatory region, the transition back to SS1 was observed at $E = 215$ mV.

3.2. Entrainment phase map

While two linearly aligned oscillators were coupled with a short distance between the iron-iron electrodes. A close temporal view of the entrained current pulses is shown in Figure 3. The diagram above this figure is a schematic display of the alignment of oscillators, where the gray and red dots represent the iron and copper electrodes, respectively. Both oscillators emitted the pulses at almost the same time, but a slight time difference was evident. The pulse from the oscillator with a lower intrinsic frequency (i.e., the frequency under decoupled conditions) followed that from a higher frequency. This is the relationship of master and slave oscillators with higher and lower frequencies, respectively. The master oscillator behaves as a pace-making oscillator of the coupled system. Both oscillators were locally coupled by the electrochemical wave between the pair of iron electrodes. The time delay between the rising edges of the pulses is assigned to the induction time for breaking the non-conductive surface oxide at the slave electrode.

The entrainment has been achieved not only with a pair of oscillators having exactly identical intrinsic frequency, but also with a pair having similar but different frequencies. Under the excitatory-coupled conditions, the entrainment allowed a margin in the difference in frequencies. The width of the margin depended on the distance between the coupled iron electrodes, d , as shown in Figure 4. With linearly aligned two oscillators in the entrainment region, where the current pulses are temporally overlapped at every N th time, the pulses were investigated as a function of the intrinsic frequency ratio of the neighboring iron electrodes, $R_f = \omega_1/\omega_2$; ω can be controlled by E and d . Three insets in this figure show the temporal patterns of the synchronization for (1:1) to (1:3).

The (1:1) entrainment was observed around $R_f \sim 1$. The entrainment zone was sharpened with increasing d , with a peak at $R_f = 1$. Almost identical triangular shapes were obtained for (1:2) entrainment around $R_f \sim 2$, and that for (1:3) around $R_f \sim 3$. All the three entrainment zones were similar in their shapes like right triangles with tops at $R_f = 1, 2, 3$ and $d = 15$ mm, over which the synchronization disappeared. With $d < 4$ mm, a lower-order synchronization triangle overlapped with that of a higher order. For example, (1:1) entrainment zone penetrated into that for (1:2). Arnold mathematically predicted that the shape of the entrainment zone for coupled nonlinear oscillators had to be triangular, like a tongue [15,17]. The triangular zones in Figure 4 can be interpreted as ‘Arnold’s tongues’ for the synchronization of the nonlinear electrochemical oscillators. The steeply rising edge and the overlapping are characteristic features of electrochemical synchronization.

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