Synchronous Current Oscillations in Electrochemical Reduction Reactions on Two Platinum Electrodes in Sulfuric Acid Solution Containing Hydrogen Peroxide

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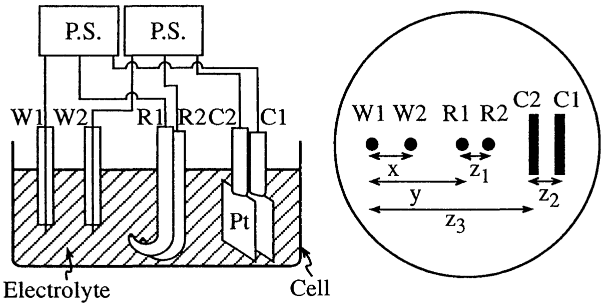
(Received February 21, 1996)

Synchronous oscillations are found for reduction currents on two independently potential–controlled Pt electrodes in 0.7 M H_2O_2–0.3 M H_2SO_4. It is shown that electrical interaction between the two oscillating electrochemical systems through the electrolyte solution is responsible for the synchronization.

The coupling of two or more chemical oscillations occurring at different locations, called entrainment, is very interesting from a point of view of communication of signals in chemical and biological systems. A considerable number of experimental studies have been made on the coupling of oscillating chemical reactions in homogeneous solutions,[1,2] at gas/solid interfaces[3,4] and in electrochemical systems,[5-11] and heat transport, mass transport (transport of reaction intermediates or products) and electrical interaction are pointed out as possible mechanisms for the coupling. However, detailed mechanisms still remain quite obscure. Very recently Nakabayashi *et al.* studied synchronous current oscillations in anodic dissolution reactions of two iron electrodes in a sulfuric acid solution, and explained them as being caused by the propagation of a concentration wave of H^+ ions (chemical wave) between the two iron electrodes.[11] In the present paper, we report that synchronous current oscillations, found in reduction reactions on two Pt electrodes in a H_2O_2–H_2SO_4 aqueous solution, are caused by electrical interaction between the oscillating systems.

Figure 1 shows schematically an experimental set-up used for the measurements of the coupling of the electrochemical oscillations. It consists of two sets of electrochemical systems, each composed of the working electrode (a 99.97% pure Pt wire, 0.3 mm in diameter and 5 mm in length), the counter electrode (a Pt plate, 5x5 mm^2 in area) and the reference electrode (a saturated calomel electrode, SCE) together with a commercial potentiostat and a potential programmer. The two sets of the electrochemical systems are independent of each other except that all the electrodes are immersed in the common electrolyte solution. In most experiments, the electrodes were arranged on a straight line in the electrochemical cell as shown in Figure 1(b); the positions of the two counter electrodes (C1 and C2) and one of the working electrodes (W1) were kept fixed, whereas the positions of the other working electrode (W2) and the two SCE's (R1 and R2) were allowed to move along the straight line so as to be able to change the strength of the coupling between the two oscillating systems. A 0.7 M H_2O_2–0.3 M H_2SO_4 (1 M = 1 mol dm^{-3}) aqueous solution was used as the electrolyte, and prepared by special grade chemicals and water purified from deionized water with a Milli-Q water purification system. The solution resistance between the working and the reference electrodes 10 mm apart was about 15 Ω, as measured with a Hokuto-Denko HI–203 IR Compensation Instrument.



(a) side view (b) top view of the cell

Figure 1. Schematic illustrations of an experimental set-up. P.S.: potentiostat, W1 and W2: working electrodes (Pt wires), R1 and R2: reference electrodes (SCE's), C1 and C2: counter electrodes (Pt plates). Electrolyte: 0.7 M H_2O_2–0.3 M H_2SO_4 aq. The distances x and y were varied, while the distances z_1, z_2 and z_3 were fixed (z_1=5 mm, z_2=5 mm, and z_3=50 mm unless otherwise noted).

We have reported in our previous paper[12] that, when a Pt electrode is under a potentiostatic condition in 0.7 M H_2O_2–0.3 M H_2SO_4, oscillations in the reduction current are observed in potential regions from -0.30 to -0.32 V *vs.* SCE (oscillation A) and from -0.35 to *ca.* -1.1 V (oscillation B). In the experimental set-up of Figure 1, such oscillations occur on the two working electrodes W1 and W2. Figure 2 shows some examples of the oscillations observed in the potential region of oscillation B. The oscillation period and pattern changed with time in a rather complex manner. However, in general, in cases where W1 and W2 were placed far apart from each other or W2 and R1 were placed close to each other, independent oscillations with no correlation in

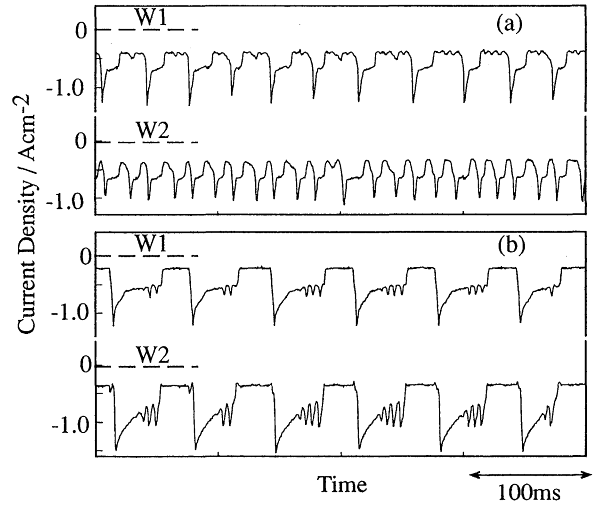


Figure 2. Currents *vs.* time for the two working electrodes W1 and W2. (a) W1: -0.4 V *vs.* SCE, W2: -0.4 V *vs.* SCE, x=20 mm and y=25 mm, and (b) W1: -0.4 V *vs.* SCE, W2: -0.5 V *vs.* SCE, x=20 mm and y=50 mm.

the oscillation period and pattern, such as shown in Figure 2(a), were observed, whereas, in the other cases, the synchronous oscillations, having the same period and pattern, such as shown in Figure 2(b), were observed.

Detailed experiments were done in order to get information on the critical distance (x) between W1 and W2 to which the synchronous oscillations, indicative of the presence of the coupling, were observed. The obtained results are summarized in Table 1. It is seen that the critical distance, x, is strongly dependent on the distance, y, between W1 and R1 (cf. Figure 1(b)), or, in other words, the synchronous oscillations do occur even when x is large if y is large enough. The change of y under the potentiostatic condition should change the spatial distribution of the electric potential (ϕ^S) in the electrolyte solution, which arises from the ohmic drop due to the current flow. Therefore, the result of Table 1 clearly shows that the synchronous oscillations in the present work are caused mainly by electrical interaction between the two oscillating systems. It may be pointed out also that this result can never be explained by the mechanism of mass transport (transport of reaction intermediates or products) because the mass transport is not affected by the change of y.

Table 1. The x and y values in which the synchronous oscillations are observed [a]

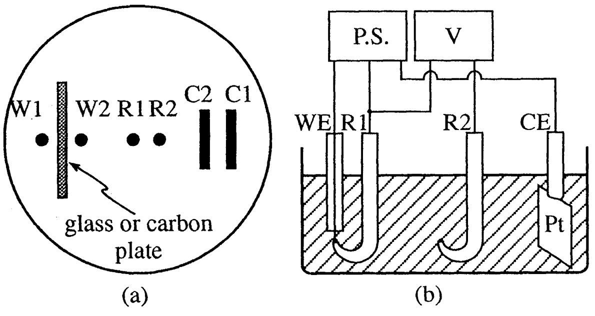
x/mm	5	10	20	30	45[b]
y/mm	>10	>20	>30	>40	>60

[a] This table means that, when x is, say, 5 mm, the synchronous oscillations are observed if y is larger than 10 mm.

[b] Only in this case, z_3 was made 70 mm.

Further experiments were done in order to get supports for the above conclusion. First, we inserted an insulating glass plate between W1 and W2, as illustrated in Figure 3(a). The synchronous oscillation, observed till that time, suddenly stopped by this procedure, and changed to the independent oscillations. On the other hand, when a conductive carbon plate of the same size as the glass plate was inserted instead of the glass plate, the synchronous oscillations did not stop and continued in the same way as before. These results indicate also that certain electrical interaction plays an important role in the coupling of the oscillating systems.

As mentioned above, the results of Table 1 suggest that the spatial distribution of the potential, ϕ^S, in the electrolyte, arising from the ohmic drop due to the current flow, is responsible for the electrical interaction between the two oscillating systems. We thus measured it by using an experimental set-up shown in Figure 3(b). The ϕ^S value, measured as the potential of R2 against R1, both R1 and R2 being an SCE, oscillated synchronously with the oscillation of the current under the potentiostatic condition, the ϕ^S shifting toward the positive with the increase in the cathodic current. Figure 4 shows the spatial distribution of the current-normalized ϕ^S value (*i.e.*, the peak ϕ^S value divided by the corresponding peak current). The ϕ^S changes rather gradually toward the CE. It is thus reasonable to assume that an overlap of such widely extending distributions of ϕ^S between the two oscillating systems induces their coupling. Further detailed mechanisms are now under study.



(a) (b)

Figure 3. (a) A top view of an electrochemical cell showing the position and the size of a glass or carbon plate, and (b) an experimental set-up for the measurement of ϕ^S. V: voltmeter, WE: working electrode, and CE: counter electrode.

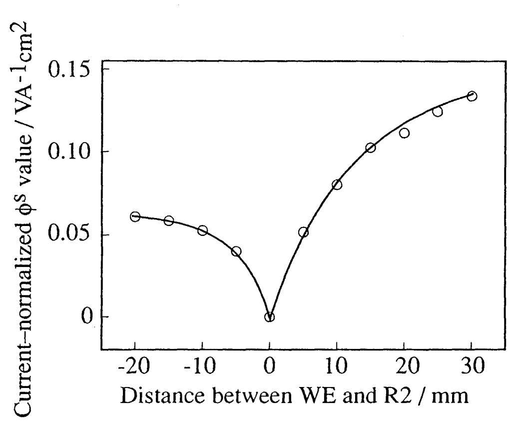


Figure 4. The current-normalized ϕ^S value as a function of the distance between WE and R2, where WE, R2, and CE are arranged on a straight line (*cf.* Figure 3(b)). A negative distance in the abscissa implies that R2 is placed on the opposite side of CE.

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