

Rotating and Standing Electrochemical Waves Observed for Electrocatalytic Reduction of Hydrogen Peroxide on Pt-Ring Electrode

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Introduction

Self-organized spatiotemporal patterns are observed in variety of non-linear chemical reactions, such as Belousov-Zhabotinsky reaction and surface catalytic reactions. These systems show some common non-linear spatial waves, like propagating, standing, and stationary waves (Turing patterns). Electrochemical reactions with non-linear kinetics also show dynamic spatiotemporal patterns on electrode surfaces. Since the first observation of spatiotemporal patterns in electrochemical system by Lev, et al, a lot of experimental and theoretical studies had been performed.

We have studied electrochemical oscillations during electrochemical reduction of hydrogen peroxide (H_2O_2) on Pt electrodes and found a variety of oscillations named oscillation A-F. Through the studies, a lot of novel features of electrochemical oscillations and electrochemical reactions themselves, such as autocatalytic mechanism of adsorbed negative species on the adsorption of peroxides, the importance of the inhomogeneity of the electrode surfaces for the appearance of oscillations, have been elucidated. In the present paper, dynamic spatiotemporal patterns in oscillation A, which is induced by suppression effect of under potentially deposited hydrogen (upd-H) on H_2O_2 dissociative adsorption, are observed at the first time. Especially, the effect of the applied potential on the observed patterns is investigated in detail.

Experiment

A schematic illustration of the experimental setup is shown in Fig. 1. Polycrystalline Pt ring was used as working electrode. The outer and inner diameters were 19 and 15 mm, respectively. A Ag/AgCl electrode was used as a reference electrode (RE), and a Au was used as a counter electrode (CE). 10 gold wires were placed sufficiently close to the working electrode to measure the local potential of the electrolyte, provides a direct measure of the local current density, i.e., spatiotemporal patterns.

Results

Figure 2(a) shows a current density (j) vs. potential (U) curve in $0.4 \text{ M H}_2\text{O}_2 + 0.3 \text{ M H}_2\text{SO}_4$ under a potential-controlled condition in case the RE was put on the same height of the CE. It can be seen that a spontaneous current oscillation (oscillation A) appears at around -0.35 V . Figure 2(b) shows a time course of oscillation A. The wave shape of the oscillation is independent of the U . Figure 3 shows a position (x) vs. time (t) plot of the local double layer potential (ϕ_{DL}) obtained at the same time as Fig. 2(b), in which the largest measure potential value is shown in black and the smallest one in white. It can be seen that the current flows synchronously at whole the electrode and the trend is independent of the U .

As pointed out by Krischer, et al. the observed

spatiotemporal patterns are drastically changed when the RE was located close to the WE. As shown in Fig. 3, the wave shape of the oscillation strongly depended on the U in this case, and symmetry breaking of the spatiotemporal patterns was observed (Fig 4). When the U was set in -0.28 V , which is near the positive limit of the potential region of oscillation A, standing wave was observed, in which positions π and 2π become nodes of the oscillation. On the other hand, when the potential was set in more negative potentials, rotating wave was seen (Fig. 4(b)), in which the active part rotates on the ring electrode. We are going to show other experimental results in detail together with the results of mathematical calculation.

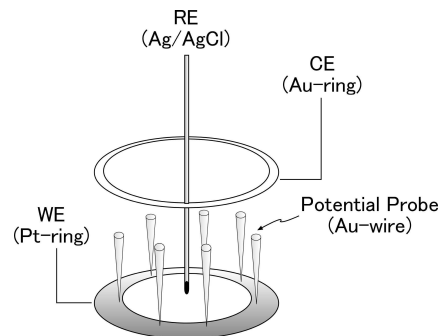


Fig. 1 Schematic illustration of experimental setup.

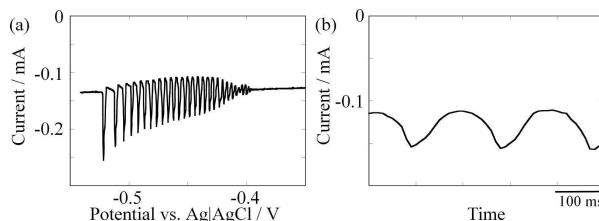


Fig. 2 (a) j vs. U and (b) j vs. t at -0.42 V in $0.4 \text{ M H}_2\text{O}_2 + 0.3 \text{ M H}_2\text{SO}_4$,

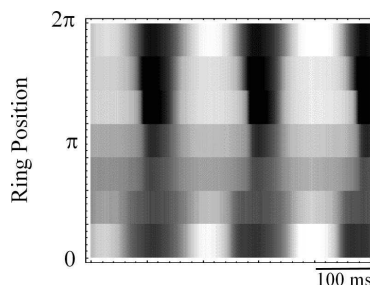


Fig. 3 x vs. t of the local double layer potential (ϕ_{DL}) obtained at the same time as Fig. 2(b). White and black colors mean low-current and high-current density, respectively.

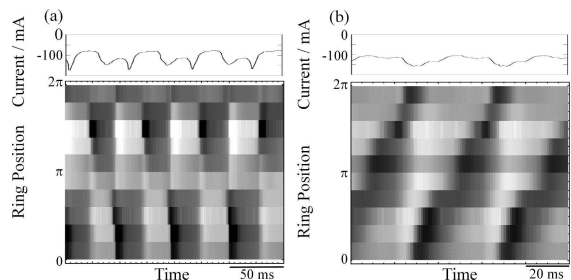


Fig. 4 j vs. t (top) and x vs. t of the ϕ_{DL} (bottom) obtained in (a) positive and (b) negative potential limit of oscillation A. Standing and rotating wave can be seen in (a) and (b), respectively.