

New Electrochemical Oscillation appeared in H_2O_2 - H_2SO_4 -Pt system by addition of Na_2SO_4 and K_2SO_4

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INTRODUCTION

Chemical and electrochemical oscillations have been studied extensively because they are attractive phenomena from the viewpoint of dynamic self-organization of molecular systems.

We have reported that the H_2O_2 reduction at Pt electrodes in acidic solutions ($\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$) shows various types of oscillations, named oscillations A, B, C, D, E, F and G. Oscillation A is observed in the potential region of formation of under-potential deposited H (upd-H), whereas oscillation B is observed in the region of hydrogen evolution reaction (HER) (see. Figure 1a) [1]. Oscillations C and D are observed when a small amount of Cl^- or Br^- is added to the solutions. The adsorption and desorption of the anions on Pt surface causes oscillations C and D [2]. When a single-crystal Pt(111) or Pt(100) electrodes are used, oscillation E is observed in the potential region more positive than that of the formation of upd-H and oscillations F and G are observed in the presence of Br^- .

We also have reported that oscillation B disappears whereas oscillation E is enhanced by the addition of I^- , which adsorbs on the Pt surface strongly. We furthermore have reported the effect of metal ions, such as Ag^+ and Cu^{2+} . The period of oscillation A can be modified by the electrodeposition of the metal ions on the Pt surface.

Recently, we have studied the effect of Na^+ and K^+ on the H_2O_2 - H_2SO_4 -Pt electrochemical system and found a new oscillation, named oscillation H. In this presentation, we will report the conditions for the appearance of the new oscillation and discuss the mechanism of the oscillation. It is a unique feature that such a large number of kinds of oscillations, i.e., eight kinds of oscillations, are observed in the H_2O_2 - H_2SO_4 -Pt electrochemical system.

RESULTS and DISCUSSION

Figure 1 shows current (I) – potential (E) curves for a Pt-disc electrode in 0.10 M H_2SO_4 + 0.25 M H_2O_2 with or without Na_2SO_4 , measured under potential controlled and current controlled conditions. The H_2O_2 -reduction current started to flow at around 0.8 V. In the absence of Na_2SO_4 , the reduction current was constant in the potential region between ca. 0.5 and -0.1 V under potential controlled conditions. A negative differential resistance (NDR) appeared at around -0.1 V because the formation of upd-H suppressed the H_2O_2 reduction. Because of the NDR, oscillation A appeared as a current oscillation. Oscillation B appeared as a current oscillation, and also as a potential oscillation under current controlled conditions.

As the Na_2SO_4 concentration increased, the I - E curves changed drastically. Oscillations A and B disappeared and the HER current decreased (in absolute value) under potential controlled conditions because of the presence of Na^+ [3]. At 0.20 M Na_2SO_4 or higher, the H_2O_2 reduction current fluctuated under potential controlled conditions in the potential region between ca. 0.5 and -0.1 V, where the reduction current was constant without Na_2SO_4 . At 0.30 M Na_2SO_4 , the new oscillation, named oscillation H,

appeared as a potential oscillation, as shown in Figure 1h. The range of oscillation H was between ca, 0.2 and 0.5 V. Accordingly, oscillation H is not attributed to the NDR caused by the formation of upd-H.

Almost similar behavior was observed by the addition of K_2SO_4 . The appearance of oscillation H can be attributed to the presence of the cations, Na^+ and K^+ , because SO_4^{2-} and HSO_4^- anions were present in the H_2SO_4 solutions irrespectively of the addition of the salts.

The H^+ at the electrode surface was consumed by the H_2O_2 reduction. The transport of H^+ to the electrode surface decreased due to the cations, because the presence of the cations diminished the electromigration transport of H^+ [3]. Therefore, the local pH at the electrode surface during the H_2O_2 reduction increased more in the presence of the salts than without the salts. We, then, can postulate that the appearance of oscillation H is attributed to the increase in the local pH.

CONCLUSION

We have found a new potential oscillation in H_2O_2 - H_2SO_4 -Pt system when Na_2SO_4 or K_2SO_4 was added to the solution. The oscillation appeared due to the presence of Na^+ and K^+ .

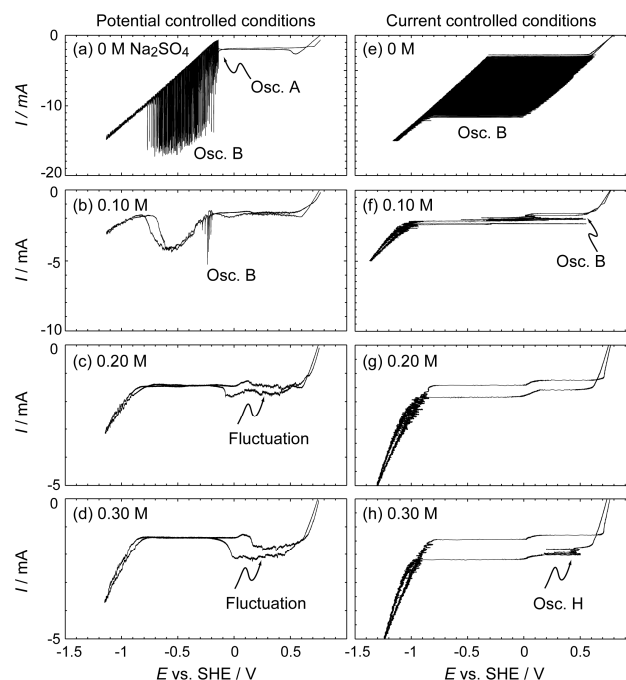


Figure 1. The I – E curves for a Pt-disc electrode in 0.10 M H_2SO_4 + 0.25 M H_2O_2 + x M Na_2SO_4 where x is varied from 0 to 0.30 M, measured under (left) potential controlled and (right) current controlled conditions at scan rates of 0.01 V s^{-1} and 0.01 mA s^{-1} , respectively

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