New Electrochemical Oscillation appeared in $\text{H}_2\text{O}_2$- $\text{H}_2\text{SO}_4$-Pt system by addition of Na$_2$SO$_4$ and K$_2$SO$_4$

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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 $\text{H}_2\text{O}_2$ reduction at Pt electrodes in acidic solutions ($\text{H}_2\text{O}_2$ + 2H$^+$ + 2e$^- \rightarrow 2\text{H}_2\text{O}$) 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 F-, 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 $\text{H}_2\text{O}_2$-$\text{H}_2\text{SO}_4$-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 $\text{H}_2\text{O}_2$-$\text{H}_2\text{SO}_4$-Pt electrochemical system.

RESULTS and DISCUSSION

Figure 1 shows current ($I$) – potential ($E$) curves for a Pt-disc electrode in 0.10 M $\text{H}_2\text{SO}_4$ + 0.25 M $\text{H}_2\text{O}_2$ with or without Na$_2$SO$_4$, measured under potential controlled and current controlled conditions. The $\text{H}_2\text{O}_2$-reduction current started to flow at around 0.8 V. In the absence of Na$_2$SO$_4$, 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 $\text{H}_2\text{O}_2$ 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$_2$SO$_4$ 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$_2$SO$_4$ or higher, the $\text{H}_2\text{O}_2$ 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$_2$SO$_4$. At 0.30 M Na$_2$SO$_4$, 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$_2$SO$_4$. 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 $\text{H}_2\text{SO}_4$ solutions irrespectively of the addition of the salts.

The H$^+$ at the electrode surface was consumed by the $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}_2$-$\text{H}_2\text{SO}_4$-Pt system when Na$_2$SO$_4$ or K$_2$SO$_4$ was added to the solution. The oscillation appeared due to the presence of Na$^+$ and K$^+$.

REFERENCES


This work is partially supported by the Research Institute for Science and Technology of Tokyo Denki University under Grants Q12E-02.