Modulation of the Oscillation Period for an Electrochemical Oscillation in an "H_2O_2-Acid-Pt Electrode" System by Deposition of a Small Amount of Metal Atoms

Shuji Nakanishi, Hayato Hommura, Yoshiharu Mukouyama, Toshihiko Matsuda, and Yoshihiro Nakato*
Department of Chemistry, Graduate School of Engineering Science, and Research Center for Photoenergetics of Organic Materials, Osaka University, Toyonaka, Osaka 560-8531

(Received June 8, 1998; CL-980435)

The oscillation period of a current oscillation in reduction reaction of H_2O_2 on a Pt electrode in an acidic solution becomes shorter with time by addition of a small amount of Cu^{2+}, $AuCl_4^-$ or Ru^{3+} ions to the solution, whereas the period becomes longer by addition of Ag^+ ions. The difference is explained by assuming deposition of dispersed metal atoms during the oscillation together with a difference in the H_2O_2-reduction mechanism among the metals.

Chemical and electrochemical oscillations are attractive phenomena from a view-point of dynamic self-organization of molecular systems. In chemical oscillations, reactions proceed in an in-phase mode and therefore the oscillations sometimes show beautiful spatiotemporal patterns such as growing vortexes. In this respect, it is of much interest to investigate the dependence and influence of electrochemical oscillations on microscopic morphological structure of the electrode surface.

Electrochemical oscillations have been reported for various systems as summarized in recent reviews.[1-3] We have recently[4-7] found that three oscillations of different types, named oscillation A, B, and C, are observed in reduction reaction of H_2O_2 on Pt electrodes in acidic solutions, depending on the electrode potential and the kind of anions in the solution. The "H_2O_2-acid-Pt electrode" system has various advantages for oscillation studies, e.g., the electrode is stable during oscillation and the oscillating reactions include only a small number of simple reactions, which makes the oscillation analysis very easy. In fact, the fundamental mechanism of oscillation A has been revealed by mathematical simulation.[8,9] In the present paper, we report that the period of oscillation A is modulated in different ways by addition of a small amount of metal ions such as Cu^{2+}, Ag^+, $AuCl_4^-$ and Ru^{3+} to the solution. This phenomena is interesting from the above-mentioned point of view of investigating the interactions between the oscillations and microscopic structure of the electrode surface.

Electrochemical measurements were done using a polycrystalline Pt (99.97%) disc of 1.0 mm in diameter (0.79 mm^2 in area) as the working electrode. A 10×10 mm^2 Pt plate was used as the counter electrode and a saturated calomel electrode (SCE) used as the reference electrode. The Pt disc electrode was polished with diamond slurry and immersed in 97% H_2SO_4 for one day. Just before measurements, cyclic potential scans were repeated between -0.25 and +1.25 V *vs.* SCE in 0.3 M H_2SO_4 (M = mol/dm^3) for a few minutes. Aqueous electrolytes were prepared using special grade chemicals and water purified from deionised water with a Milli-Q water purification system. Current oscillations were recorded digitally at 1 kHz with a Mac ADIOS II/16 (GW Instruments) and a personal computer.

Figure 1 shows current density *vs.* time curves for oscillation A at a constant potential of -0.31 V *vs.* SCE before and after addition of 1.6×10^{-6} M $AgNO_3$. With no addition of Ag^+ ions, the oscillation continues steadily without any changes in waveform and period for more than 1 h (Figure 1a). When Ag^+ ions are added, the oscillation period becomes longer with time (Figures 1b, c and d) except that the oscillation period shows a disorder at the initial stage (Figure 1b), and finally the oscillation stops (disappears) in about 82 s. Figure 2 shows results of similar experiments for addition of 1.6×10^{-6} M $CuSO_4$. Contrary to the case of Ag^+ ions, the oscillation period becomes shorter with time (Figures 2a, b and c), except that it becomes longer again just before the oscillation stops (Figure 2d, which is for about 2 s before the oscillation stops). The oscillation period in the absence of metal ions varied from experiment to experiment in a range of 0.2 to 0.9 s even with the same electrode (*cf.* Figures 1a and 2a). Figure 3 plots the oscillation period as a function of time in the presence of Ag^+ and Cu^{2+}. Addition of $AuCl_4^-$ and Ru^{3+} gives nearly the same results as the addition of Cu^{2+}.

Cyclic voltammograms have shown that Cu and Ag metals are deposited on Pt for an under-potential deposition condition at about 0.40 to 0.45 V *vs.* SCE, in agreement with the literature.[10] The standard redox potential for Au deposition from $AuCl_4^-$ is 0.76 V *vs.* SCE.[11] These potentials are more positive than the potentials at which oscillation A is observed (-0.29 to -0.32 V *vs.* SCE), indicating that the deposition of metals occurs during the oscillation in case where the solution contains corresponding ions. In fact, the deposition of Au metal during the oscillation was confirmed by XPS analysis of the electrode surface. The deposition of metals was also confirmed by decreases in the peak height of two cathodic and anodic current peaks

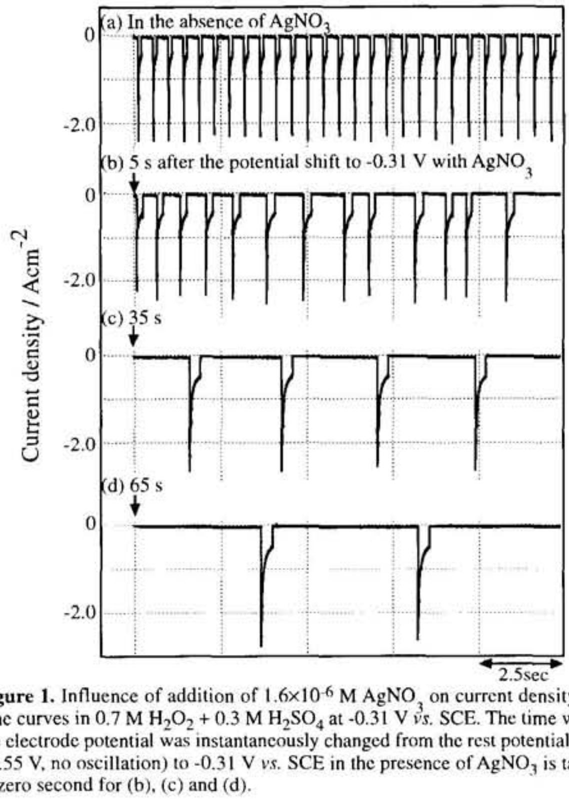

Figure 1. Influence of addition of 1.6×10^{-6} M $AgNO_3$ on current density *vs.* time curves in 0.7 M H_2O_2 + 0.3 M H_2SO_4 at -0.31 V *vs.* SCE. The time when the electrode potential was instantaneously changed from the rest potential (*ca.* +0.55 V, no oscillation) to -0.31 V *vs.* SCE in the presence of $AgNO_3$ is taken to zero second for (b), (c) and (d).

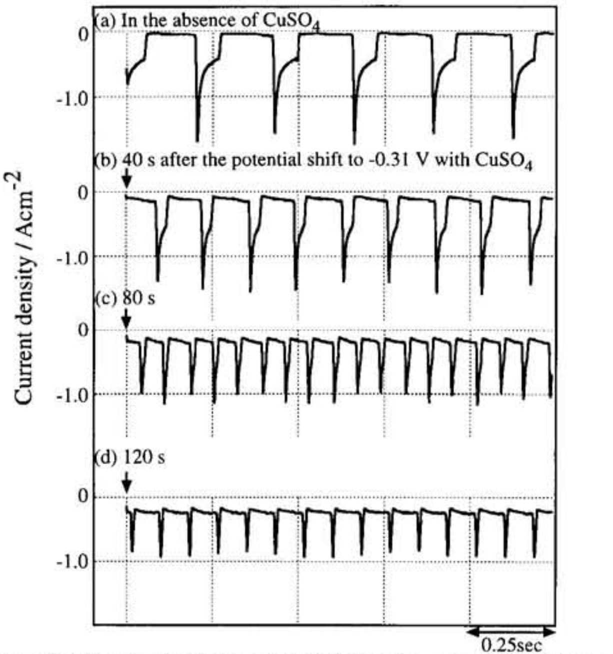

Figure 2. Influence of addition of 1.6×10^{-6} M $CuSO_4$ on current density *vs.* time curves in 0.7 M H_2O_2 + 0.3 M H_2SO_4 at -0.31 V *vs.* SCE. The times for (b), (c) and (d) are measured in the same way as in Figure 1.

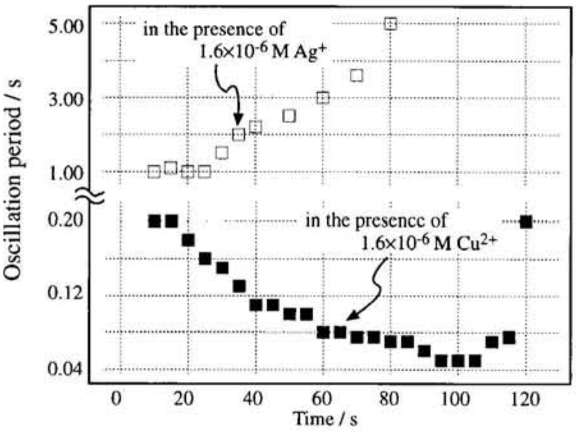

Figure 3. Oscillation period as a fuction of time in the presence of metal ions. The time in the abscissa is measured in the same way as in Figures 1 and 2.

in 0.0 to -0.2 V *vs.* SCE corresponding to formation and detachment of adsorbed hydrogen atoms called upd-H on polycrystalline Pt electrodes.[12] Rough estimation of the amount of deposited metal (Au) by the XPS and electrochemical measurements has shown that it is about 0.3 in surface coverage just after the oscillation stopped.

Now let us consider why the oscillation period becomes longer for the deposition of Ag and shorter for the deposition of Cu, Au and Ru. Figures 1 and 2 show that the change of the oscillation period is caused mainly by the change in the duration time of the low-current state (t_{low}). According to our previous work,[5,8,9] the H_2O_2 reduction in the low-current state is almost completely suppressed by formation of adsorbed hydrogen atoms (upd-H) of a nearly full coverage. However, a small H_2O_2-reduction current still flows even in the low-current state through a small part of naked Pt sites not covered with upd-H. Besides, the current density (j) in the low-current state increases slightly with time (between two high-current states) due to an increase in the H_2O_2 concentration at the electrode surface by diffusion (Figures 1 and 2). A sudden increase in j (or a sudden transition from the low-current state to the high-current state) occurs when the j in the low-current state reaches a critical value (j_c). Thus, if the deposition of a metal, e.g., Ag, on Pt decreases the j, it takes a longer time for the j to reach j_c, i.e., the t_{low} becomes longer.

It is reported[13] that the H_2O_2 reduction on Ag proceeds via bridge-type adsorption of H_2O_2 on two adjacent Ag atoms, whereas that on Au proceeds via end-on-type adsorption of H_2O_2 on an Au atom. Thus, if Ag is deposited monoatomically in a dispersed form, not forming any aggregates nor islands, no bridge-type adsorption of H_2O_2 is possible and hence the H_2O_2 reduction on the deposited Ag does not occur. This implies that the deposition of Ag atoms in such a manner leads to a decrease in j in the low-current state and hence an increase in the t_{low}. On the other hand, for the deposition of Au, the H_2O_2 reduction occurs even for monoatomically deposited atoms because the end-on-type adsorption is possible for such adsorption. Thus, the deposition of Au leads to an increase in j in the low-current state (note that the H_2O_2 reduction on Au occurs continuously with time whereas that on Pt occurs intermittently due to the oscillation) and hence leads to a decrease in the t_{low}. The above arguments are in harmony with the experimental results that the current density (j) in the low-current state increases with time on a long-time scale for deposition of Au as seen from Figures 2b, c and d, whereas the j for the deposition of Ag hardly increases as seen from Figures 1b, c and d.

The present results show that the modification of the Pt surface with other metals on an atomic scale modulates the oscillation period significantly. This is of much interest from the view-point of investigating the interaction of electrochemical oscillations and microscopic surface structure, as mentioned in the introductory part. Detailed studies by use of single crystal Pt electrodes are now in progress.

This work was partly supported by Grant-in-Aid for Scientific Research on Priority Area of "Electrochemistry of Ordered Interfaces" (No. 09237105) from the Ministry of Education, Science, Sports and Culture, Japan.

References

1 J. L. Hudson and T. T. Tsotsis, *Chem. Eng. Sci.*, **49**, 1493 (1994).
2 T. Z. Fahidy and Z. H. Gu, "Modern Aspects of Electrochemistry Vol. 27," ed by R. E. White, J. O'M. Bockris, and R. E. Conway, Plenum, New York (1995), p. 383.
3 M. T. M. Koper, "Advances in Chemical Physics, Vol. 92," ed by I. Prigogine and S. A. Rice, John Wiley & Sons, New York (1996), p. 161.
4 H. Hommura, Y. Mukouyama, T. Matsuda, S. Yae, and Y. Nakato, *Chem. Lett.*, **1996**, 391
5 T. Matsuda, H. Hommura, Y. Mukouyama, S. Yae, and Y. Nakato, *J. Electrochem. Soc.*, **144**, 1988 (1997).
6 Y. Mukouyama, H. Hommura, T. Matsuda, S. Yae, and Y. Nakato, *Chem. Lett.*, **1996**, 463
7 T. Matsuda, Y. Mukouyama, H. Hommura, S. Yae, and Y. Nakato, *J. Electrochem. Soc.*, **144**, 2997 (1997).
8 Y. Nakato, *Denki Kagaku*, **66**, 234 (1998).
9 H. Hommura, Y. Mukouyama, S. Nakanishi, T. Nishimura, and Y. Nakato, *J. Phys. Chem. B*, to be published.
10 D. M. Kolb, M. Przasnyski, and H. Gerischer, *J. Electroanal. Chem.*, **54**, 25 (1974).
11 Chemical Handbook (Kagaku Binran), 4th Ed., Basic Part II, The Chemical Society of Japan, Maruzen, Tokyo (1993), P.II-466.
12 R. J. Nichols and A. Bewick, *J. Electroanal. Chem.*, **243**, 445 (1988).
13 K. Jüttner, *Electrochim. Acta*, **29**, 1597 (1984).