Appearance of a New Oscillation (Named Oscillation C) in H_2O_2- Reduction Reaction on a Pt Electrode in Acidic Solutions by Addition of a Small Amount of Chloride Ions

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A new electrochemical oscillation with a short period of 2 to 10 ms, named oscillation C, appears in H_2O_2-reduction reaction on a Pt electrode in H_2SO_4 solutions when a small amount of chloride ions is added to the solution. It is suggested that oscillation C is caused by competition between H_2O_2 reduction and chloride-ion adsorption, contrary to previously reported oscillations A and B which are caused by competition between H_2O_2 reduction and H^+ reduction.

Electrochemical oscillations have been reported for various systems as summarized in recent reviews,[1-3] including anodic metal dissolution, cathodic metal deposition, oxidation of hydrogen and small organic molecules, and reduction of hydrogen peroxide. The oscillation phenomena are very interesting from a view-point of dynamic self-organization of molecular systems. Moreover, elucidation of the mechanism will give new insights into development of new-type devices as well as understanding of various biological functions.

We reported recently[4-7] that electrochemical oscillations of two types, called oscillation A and B, were observed in H_2O_2-reduction reaction on Pt electrodes in acidic solutions. Oscillation A appears in a potential region just before hydrogen evolution, whereas oscillation B appears in a potential region of hydrogen evolution. In the present paper we report that another new-type oscillation, named oscillation C, is observed in the above "H_2O_2-acid-Pt electrode" system when a small amount of chloride ions is added to the solution. The present "H_2O_2-acid-Pt" system is of much interest because it shows various-type oscillations such as oscillations A, B, and C. Our recent mathematical simulation has shown[8,9] that, for oscillations A and B, a "negative resistance" due to the formation of adsorbed hydrogen atoms (upd-H) plays a key role in their appearance. However, for oscillation C, there is no indication of the presence of such a negative resistance. Thus, mechanistic studies of oscillation C in comparison with oscillations A and B will serve for deep understanding of oscillation phenomena.

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 0.06-μm alumina powder and immersed in 60% HNO_3 for one day to remove contaminations (especially other metals). Just before measurements, cyclic potential scans were repeated between -0.35 and +1.60 V vs. SCE in 0.3 M H_2SO_4 (M = mol/dm^3) for about 30 min. Aqueous electrolytes were prepared using special grade chemicals and water purified from deionised water with a Milli-Q water purification system. Current and potential oscillations were recorded digitally at 1 or 10 kHz with a Mac ADIOS II/16 (GW Instruments).

Figure 1 shows current density (j) vs. potential (U) curves for a Pt-disc electrode in 0.3 M H_2SO_4 + 0.7 M H_2O_2 in the absence and presence of 2.0×10^{-4} M KCl, measured under a current-controlled condition. The oscillation in Figure 1(a), observed in the absence of KCl, is assigned to oscillation B, in which the high- and low-potential states correspond to H_2O_2 reduction and hydrogen evolution, respectively, as reported in a previous paper.[5] Figure 1(a) indicates that steady H_2O_2 reduction starts at about 560 mV vs. SCE and continues until the cathodic current density reaches about 6 mA mm^{-2}. However, when the cathodic current density exceeds the 6 mA mm^{-2}, the electrode potential begins to oscillate, showing that the H_2O_2 reduction and hydrogen evolution occur alternately. Oscillation A does not appear under a current-controlled condition, though it appears under a potential-controlled condition.[5]

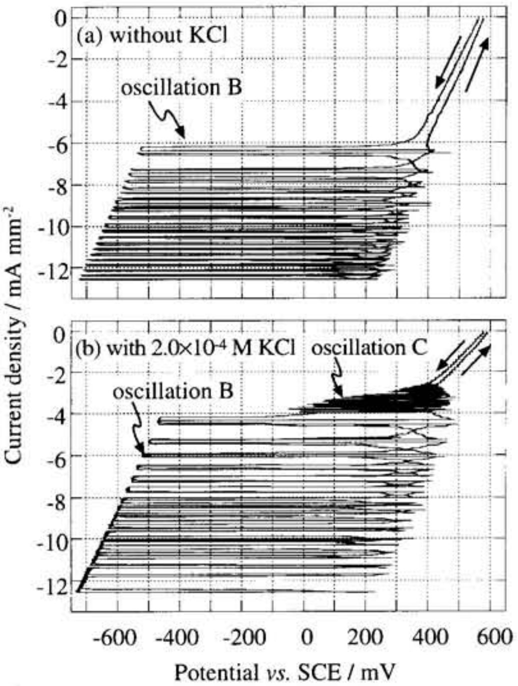

Figure 1. Current density (j) *vs.* potential (U) curves for a Pt-disc electrode, measured under a current-controlled condition, with a scan rate of 0.25 mA mm^{-2} / s. The electrolyte is (a) 0.3 M H_2SO_4 + 0.7 M H_2O_2 and (b) 0.3 M H_2SO_4 + 0.7 M H_2O_2 + 2.0×10^{-4} M KCl.

When 2.0×10^{-4} M KCl was added to the solution, on the other hand, a new potential oscillation, named oscillation C, appeared in a range of the current density lower than that for oscillation B, as seen in Figure 1(b). The amplitude of oscillation C increased with increasing current density contrary to the case of oscillation B. Oscillation C appeared by addition of Cl^-, irrespective of the kind of counter cations. Also, oscillation C appeared in relatively low Cl^- concentrations from 5.0×10^{-6} to 3.0×10^{-2} M, and was the most pronounced when the Cl^- concentration was about 5.0×10^{-3} M in the case of 0.7 M H_2O_2 + 0.3 M H_2SO_4. In too high Cl^- concentrations, not only oscillation C but also oscillation B disappeared. In case where oscillation C was

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pronounced, oscillation C overlapped oscillation B and thus oscillation B became a mixed-mode type oscillation. For the same Cl^- concentration, oscillation C became more pronounced as the H_2O_2 concentration increased. Though oscillation C was observed mainly as the potential oscillations under a current-controlled condition as described above, in solutions of high H_2O_2 concentrations such as 1.2 M H_2O_2 + 0.3 M H_2SO_4 with 1.0×10^{-5} to 1.0×10^{-2} M Cl^- oscillation C appeared as current oscillations, as well, under a potential-controlled condition (Figure 2).

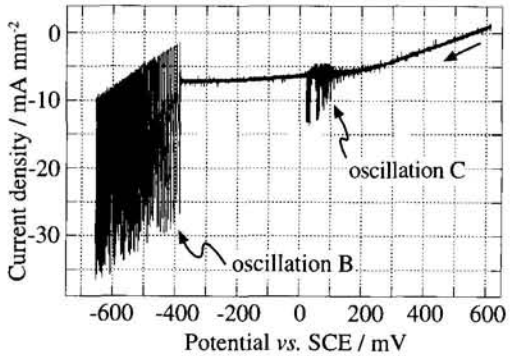

Figure 2. Current density (j) *vs.* potential (U) curve, measured under a potential-controlled condition, with a scan rate of 10 mV / s. The electrolyte is 0.3 M H_2SO_4 + 1.2 M H_2O_2 + 1.0×10^{-3} M KCl.

Figure 3 shows the potential vs. time for oscillation C under a galvanostatic condition at -3.2 mA mm^{-2} in the presence of 2.0×10^{-4} M KCl. When the current density was varied instantaneously from 0 to -3.2 mA mm^{-2} at the time of t = 0 s, the electrode potential suddenly shifted toward the negative but initially remained steady without showing any oscillation. The oscillation started in around t = 0.12 s, followed by a gradual increase in the oscillation amplitude. Figure 3(b) shows the oscillation pattern (waveform) in t ≈ 90 s on an expanded time scale. Oscillation C had a very short oscillation period of ca. 8 ms, in contrast to the period of 0.1 to 1.0 s for oscillations A and B.[5] The shape of oscillation pattern was also quite different from that for oscillations A and B.[5]

The above results strongly suggest that oscillation C is different in nature from oscillations A and B, namely, oscillation C is certainly of a new type. This conclusion becomes much clearer if we consider that the oscillating potential for oscillation C lies in a range from ca. 0.0 V to 0.5 V vs. SCE (see Figure 1(b)) where no hydrogen evolution nor hydrogen-atom adsorption occurs.[5] This implies that oscillation C has no connection with H^+ reduction, though oscillations A and B are caused by competition between H^+ reduction and H_2O_2 reduction.[5] As oscillation C appears only in the presence of Cl^- and also it is reported[10-12] that Cl^- is adsorbed on Pt in potentials more positive than ca. 0.0 V vs. SCE where oscillation C appears, it is most likely that oscillation C is caused by competition between Cl^- adsorption and H_2O_2 reduction. By the way, oscillation B in Figure 1(b) starts at a current density of ca. 4 mA mm^{-2}, somewhat smaller than in Figure 1(a). This may also be attributed to a decrease of the effective area of Pt surface by adsorption of Cl^- ions.

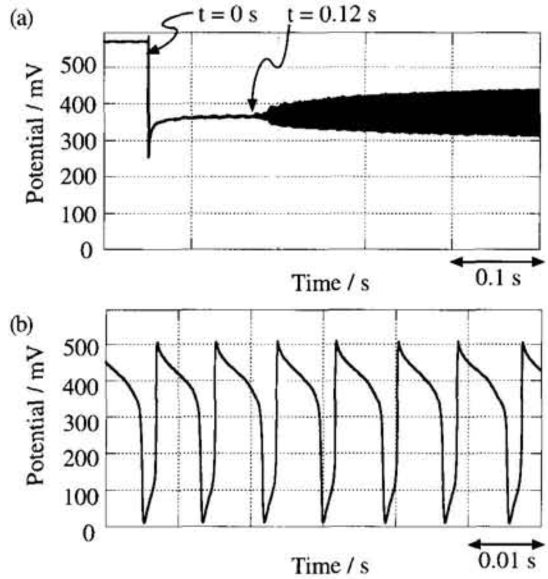

Figure 3. Time courses of oscillation C in 0.3 M H_2SO_4 + 0.7 M H_2O_2 + 2.0×10^{-4} M KCl under a galvanostatic condition at -3.2 mA mm^{-2}. The current density was changed from 0 to -3.2 mA mm^{-2} at t = 0 s for (a). (b) shows the oscillation pattern in t = 90 s.

Detailed mechanism for the appearance of oscillation C is, however, unclear at present. In general, oscillations are caused by the presence of a positive feedback mechanism (or autocatalytic processes). For oscillations A and B, the presence of such a mechanism has been revealed by mathematical simulation.[8,9] For oscillation C, we have not yet been able to find such a mechanism. Further studies are now in progress. It should be emphasized that comparative studies of oscillations of different types such as oscillations A, B, and C will lead to deep understanding of oscillation phenomena as already mentioned in the introductory part.

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