New Electrochemical Oscillations in Reduction Reactions on a Platinum Electrode in Hydrogen Peroxide Containing Sulfuric Acid Solutions

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A new pronounced electrochemical oscillation is found in the potential region of hydrogen evolution on a platinum electrode in a sulfuric acid solution containing high–concentration hydrogen peroxide. A mechanism is discussed, and it is shown that this oscillation is considerably different in origin from that reported in low hydrogen peroxide concentrations.

Elucidation of chemical and electrochemical oscillations will give new insights into dynamically self–organizing ability of molecular systems. A number of electrochemical oscillations are reported for anodic metal dissolution,[1–3] cathodic metal deposition,[1,4] oxidation of hydrogen molecules[1,5,6] and small organic compounds,[1,7] and reduction of hydrogen peroxide.[1,8–19] Of these reactions, the reduction of H_2O_2 is of special interest because the oscillations are observed on a variety of metal electrodes such as Ag,[8] Au[9] and Pt[10,11] and semiconductor electrodes such as Cu_5FeS_4,[12] $CuFeS_2$,[13] CuS,[14] Cu_2S,[15] $CuInSe_2$[16] and GaAs,[17] and show various oscillatory patterns.[10,11] In the present paper, we report new pronounced oscillations found in electrochemical reduction on a Pt electrode in sulfuric acid solutions containing high–concentration H_2O_2.

Measurements were done using a normal three–electrodes system together with a potentiostat/galvanostat, a potential programmer and an X–Y recorder. Polycrystalline Pt wires of 99.97% purity, 0.3 mm in diameter and 5 to 15 mm in length, were used as the working electrode. They were polished with an emery paper, immersed in 97 wt% H_2SO_4 for one day, and rinsed. In some cases, a few cyclic potential scans were performed in 0.5 M H_2SO_4 (1 M = 1 mol dm^{-3}) between -0.25 and 1.0 V *vs.* SCE before measurements of oscillations. There was a tendency that the oscillations were more reproducibly observed by these pretreatments probably due to cleaning of the electrode surface. A saturated calomel electrode (SCE) was used as the reference electrode and a Pt plate as the counter electrode. Aqueous electrolyte solutions were prepared using special grade 30 wt% H_2O_2, 97 wt% H_2SO_4 and water purified from deionised water with a Milli–Q water purification system.

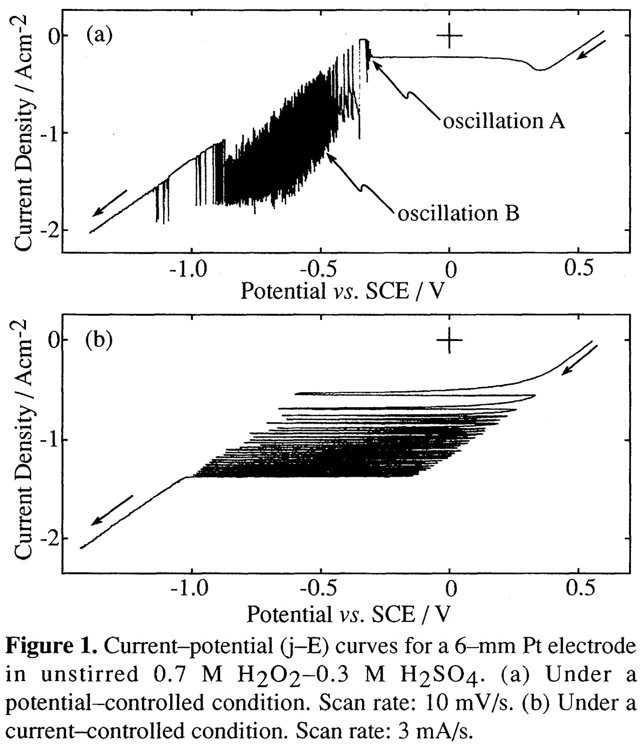

Figure 1. Current–potential (j–E) curves for a 6–mm Pt electrode in unstirred 0.7 M H_2O_2–0.3 M H_2SO_4. (a) Under a potential–controlled condition. Scan rate: 10 mV/s. (b) Under a current–controlled condition. Scan rate: 3 mA/s.

Figure 1(a) shows a current–potential (j–E) curve for a 6–mm long Pt wire electrode in an unstirred 0.70 M H_2O_2–0.30 M H_2SO_4 solution when the potential was scanned toward the negative at a rate of 10 mV/s under a potential–controlled condition. A cathodic current due to the H_2O_2 reduction starts at *ca.* 0.6 V *vs.* SCE and reaches the diffusion-limited current around 0.4 V. The j–E curve shows a differential "negative impedance" in a potential region from -0.30 to -0.33 V, where a current oscillation, hereafter called oscillation A, appears. Oscillation A stops at about -0.32 V, but another much more pronounced oscillation, hereafter called oscillation B, starts at *ca.* -0.35 V and continues down to *ca.* -1.1 V. In the potential region more negative than *ca.* -0.33 V, gas bubble evolution attributable to hydrogen evolution was observed at the electrode surface. When the solution was stirred, the oscillations with nearly the same amplitude and frequency as those in the unstirred solution were observed but only in a narrow potential region from about -0.6 to -1.0 V. Figure 1(b) shows a j–E curve observed when the current was scanned at a rate of 3 mA/s under a current–controlled condition. In this case, oscillations of the electrode potential with a very large amplitude of 0.9 V are observed.

Oscillation A in the present work seems to correspond to the oscillation reported by Hudson *et al.*[10] and Koper *et al.*[11] They

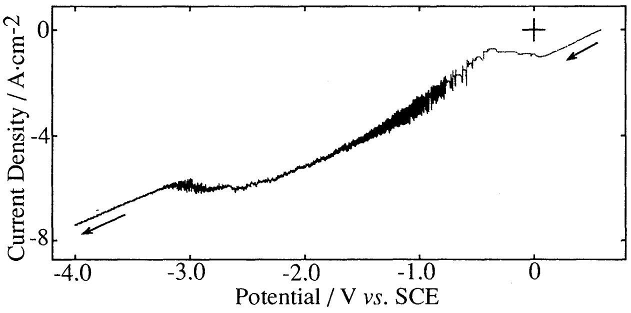

Figure 2. Current–potential (j–E) curve for a 6–mm Pt electrode in unstirred 1.1 M H_2O_2–0.3 M H_2SO_4 under a potential–controlled condition. Scan rate: 10 mV/s.

reported only this type of oscillation because they used, as the electrolyte, H_2SO_4 solutions containing H_2O_2 in relatively low concentrations (0.02–0.23 M), lower than those of H_2SO_4. It is to be noted also that oscillation A in Figure 1, observed in a high H_2O_2 concentration, is a stable and sustained oscillation, though Koper *et al.* reported that the current oscillation in the low H_2O_2 concentrations became stable only when an electric resistance was inserted in the external circuit.

Detailed experiments have shown that oscillation A appears in a wide range of the concentrations of H_2O_2 and H_2SO_4 from 0.02 to 1.00 M, almost irrespective of their ratio, though in many cases as a spike, whereas oscillation B is observed only in the concentration of H_2O_2 considerably higher than that of H_2SO_4 which is in a range of 0.20 to 0.50 M. The importance of the high H_2O_2 concentration in oscillation B is also clearly seen in Figure 2 where oscillation B in 1.10 M H_2O_2 continues down to a very negative potential of -3.2 V.

Some experiments were done in order to search for the origin of oscillation B. First, various metals such as Au, Ag, Cu, Pd, W and Ti were used as the working electrode, but only Pt showed the oscillation. Next, a small amount (3.6×10^{-5} M) of $CuSO_4$ was added to a 0.70 M H_2O_2–0.30 M H_2SO_4 solution. The current oscillation in the Pt electrode, which had been observed till that time, was gradually weakened and finally stopped, probably due to the deposition of a thin Cu layer on the Pt electrode. These results clearly show that the catalytic activity of the Pt electrode plays an important role in oscillation B.

Koper *et al.* noticed that the oscillation (corresponding to oscillation A in the present work) was observed in the potential region of the differential "negative impedance", lying just a little more positive than the potential region of hydrogen evolution, and ascribed the oscillation to the negative impedance caused by the "hydride passivation" of the Pt electrode due to the H^+ reduction.[11] This interpretation implies that the adsorbed H atoms on Pt act as a catalytic poison for the reduction of H_2O_2.

Based on this idea, oscillation B can be explained as follows: Let us consider the j–E curve of Figure 1(b) obtained under the current–controlled condition. On a small current density (j), the electrode potential lies in 0.6 to 0.4 V, much more positive than the equilibrium hydrogen evolution potential, and only the reduction of H_2O_2 occurs with no potential oscillation. When j increases and exceeds the diffusion limited current density for H_2O_2, the surface concentration of H_2O_2 approaches zero, and the reduction of H^+ ions (hydrogen evolution) should start in order to keep the large current density, accompanied by a large potential shift toward the negative. While the hydrogen evolution occurs, the Pt surface is fully covered with the adsorbed H atoms and we can assume that no H_2O_2 reduction occurs due to their poisonous action as suggested by Koper *et al.* Thus, the surface concentration of H_2O_2 increases again with time due to its diffusion. The high surface H_2O_2 concentration and the negative electrode potential, however, induces a strong instability near the electrode surface because the equilibrium potential for the H_2O_2 reduction is highly positive (~1.5 V). Consequently, a sudden change from the H^+ reduction to the H_2O_2 reduction may occur, accompanied in this case by a potential shift toward the positive. Repetition of such processes produces potential oscillations.

It should be pointed out that the adsorbed H atoms in the potential region of oscillation A are on the three– or four–fold symmetry sites of the surface Pt lattice, called upd-H, whereas such sites are completely filled and another type of the adsorbed H atoms (on–top H), leading to the hydrogen evolution, are formed in the potential region of oscillation B.[20,21] This suggests that oscillation B may be considerably different in origin from oscillation A. Though the oscillation patterns of oscillation B are very complex, depending on the electrode potential or the current density, the concentrations of H_2O_2 and H_2SO_4, their ratio, and the size and the shape of the Pt electrode, their detailed analyses as compared with oscillation A will give useful information on the understanding of electrochemical dynamics.

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