Appearance of an Oscillation through the Autocatalytic Mechanism by Control of the Atomic-Level Structure of Electrode Surfaces in Electrochemical H₂O₂ Reduction at Pt **Electrodes**

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The influence of the atomic-level structure of electrode surfaces on electrochemical oscillations has been studied in a system of H_2O_2 reduction on Pt electrodes in acidic solutions. A current oscillation of another type, named oscillation E, has been found to appear for an atomically flat single-crystal Pt(111) electrode, in addition to previously reported oscillations, named oscillations A and B. Oscillation E does not appear for atomically flat Pt(100), Pt(110), polycrystalline Pt, and Pt(111) with atomically nonflat surfaces. Mathematical simulation by use of a model including an autocatalytic effect of adsorbed OH for dissociative adsorption of H_2O_2 , as a possible explanation, has reproduced the appearance of oscillation E, as well as observed correlations between the appearance of oscillation E and the magnitudes of H₂O₂-reduction current and "negative" resistance. It is discussed that an efficient autocatalytic mechanism works at the atomically flat Pt(111) surface, which is responsible for the appearance of oscillation E at this surface.

Introduction

Chemical and electrochemical oscillations are attractive phenomena from a viewpoint of dynamic self-organization of molecular systems. Electrochemical oscillations have been reported for a variety of systems as summarized in recent reviews.^{1–3} Recently low-index single-crystal metal electrodes with well-defined surface structures have been used for mechanistic studies of oscillations.⁴⁻¹⁰ Ertl et al.⁴ reported that the oscillatory patterns for H₂ oxidation on Pt in the presence of Cu²⁺ and halide ions depended on the crystallographic surface structures of Pt electrodes, and explained it to be due to a difference in the binding strength of halogen atoms on different single-crystal surfaces.

We have been studying electrochemical oscillations for H₂O₂ reduction on Pt electrodes in acidic solutions.^{11–16} Interestingly, various oscillations of different types, named oscillations A, B, C, and D, have been found to appear. Oscillation A is observed in a potential region just before hydrogen evolution,^{11,12} whereas oscillation B is observed in a potential region of hydrogen evolution.^{11,12} Oscillations C and D are observed in the presence of a small amount of halide ions such as Cl⁻, Br⁻, and I⁻ in the electrolyte.^{13–15} Moreover, the oscillation period for oscillation A is modulated by adsorption of inert metal atoms, such as Cu, Au, Ag, and Ru, to submonolayer amounts.¹⁶ These results indicate that the oscillations in the "H2O2-acid-Pt electrode" system are sensitive to the atomic-level structures of electrode surfaces.

In the present paper, we report that the atomic-level structures of the electrode surfaces affect not only the adsorption behavior

RE (HE) WE CE Pt disk Platinized P or HClO4 H_2 Cation exchange membrane Electrolyte

 $(0.3 \text{ M} \text{H}_2\text{SO4} \text{ or HClO4} + \text{H}_2\text{O2})$

Figure 1. An electrochemical cell used for measurements of current oscillations: WE, working electrode (single-crystal or polycrystalline Pt disk); CE, counter electrode (Au plate); RE, reference electrode (a hydrogen electrode, composed of platinized Pt, 1.0 M H₂SO₄ or HClO₄, and 1 atm of hydrogen gas).

but also the reaction mechanism, resulting in an appearance of another type of oscillation, named oscillation E, at the crystallographically most-flat Pt(111) surface. The result is important for deeper understanding of the mechanisms of electrochemical reactions themselves as well as the oscillation mechanisms.

Experimental Section

The electrochemical cell used is schematically illustrated in Figure 1. A half-spherical single-crystal or polycrystalline Pt



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disk electrode (about 1-2 mm in diameter), used as the working electrode (WE), was held such that only the flat surface was in contact with the electrolyte by use of its meniscus. The electrolyte was 0.3 M H₂SO₄ or HClO₄ (pH 0.55) with or without H₂O₂ (M = mol/dm³). A gold plate was used as the counter electrode (CE). A hydrogen electrode, composed of a platinized platinum electrode, 1.0 M H₂SO₄ or HClO₄, and highly pure hydrogen gas, was used as the reference electrode (RE). Either 1.0 M H₂SO₄ or HClO₄ in the hydrogen electrode was chosen so that the common acid was used in the WE and RE compartments. The WE and RE compartments were separated with a cation exchange membrane (Nafion 117).

Single-crystal Pt(111), Pt(100), and Pt(110) electrodes with atomically *flat* surfaces were prepared by the method of Clavilier et al.¹⁷ Single-crystal Pt spheres were prepared by heating Pt wires (99.97% in purity) in a hydrogen flame. They were cut in parallel to the Pt(111), Pt(100), and Pt(110) faces, and polished with diamond slurry. They were then annealed in a hydrogen flame for 30 min for Pt(111), and 180 min for Pt-(100) and Pt(110). Just before measurements, all the electrodes were annealed again in a hydrogen flame for 60 s and immediately quenched in Ar-bubbled pure water. Single-crystal Pt(111) electrodes with atomically nonflat surfaces were also used for reference. The details of their preparation will be described later. Polycrystalline Pt electrodes, having nearly the same shape as the single-crystal Pt electrodes, were also used. They were prepared by cutting and polishing of polycrystalline spheres, which were obtained by heating Pt wires in a hydrogen flame.

Aqueous electrolytes were prepared using special grade chemicals and pure water, the latter of which was obtained by purification of deionized water with a Milli-Q water purification system. Current density (j) vs potential (U) and j vs time (t)were measured with a potentiogalvanostat (Nikko-Keisoku NPGS-301) and a potential programmer (Nikko-Keisoku NPS-2). They were either recorded with an X-Y recorder (Riken-Denshi F-35C) or stored digitally at 1 kHz with a Mac ADIOS II/16 (GW Instruments). Ohmic drops in the solution are not corrected in the present work. Argon gas was bubbled through the electrolyte in the working-electrode compartment for 30 min to remove dissolved oxygen when j-U curves for adsorption and desorption of hydrogen atoms (upd-H) were measured in 0.3 M H₂SO₄ or HClO₄. No bubbling of argon gas was carried out in solutions containing H₂O₂, because oxygen is more or less evolved by decomposition of H₂O₂ on Pt. The structure of electrode surfaces was inspected with a scanning tunneling microscope (Nanoscope IIIa, Digital Instruments), using a Pt-Ir wire as a tip. The tunnel current was held at 1 nA, and the scan rate was 5.086 Hz.

Results

Figure 2 shows current density (*j*) vs potential (*U*) curves for a polycrystalline Pt electrode (hereafter abbreviated as a poly-Pt electrode), observed under potential-controlled conditions. Figure 2a is a curve in 0.3 M H₂SO₄ not containing H₂O₂ (pH 0.55). Two current peaks on both cathodic and anodic sides are attributed to formation and disappearance of electrochemically adsorbed hydrogen atoms, called upd-H (under-potential deposited hydrogen).^{11,18,19} The appearance of such two peaks on both sides are characteristic of poly-Pt electrodes. Figure 2b is a curve in 0.3 M H₂SO₄ containing low-concentration (0.2 M) H₂O₂. A current in a potential region from about 0.65 to 0.00 V vs NHE is attributed to H₂O₂ reduction, which starts at about 0.80 V. A hydrogen evolution current appears in potentials



Figure 2. Current density (*j*) vs potential (*U*) curves for a polycrystalline Pt (poly-Pt) electrode, obtained under potential-controlled conditions. Electrolyte: (a) 0.3 M H₂SO₄ (pH 0.55), (b) 0.2 M H₂O₂ + 0.3 M H₂SO₄, (c) 0.7 M H₂O₂ + 0.3 M H₂SO₄. Scan rate: (a) 100 mV/s, (b, c) 10 mV/s.

more negative than ca. -0.02 V. The current peaks for upd-H are missing in Figure 2b because the *j*-scale in Figure 2b is much larger than that in Figure 2a. It is to be noted that the H₂O₂-reduction current is independent of the electrode potential in a region above 0.07 V, whereas it shows the "negative slope" in a region from +0.07 to -0.02 V. The potential-independent H₂O₂-reduction current is explained by assuming that the H₂O₂ reduction is initiated by dissociative adsorption of H₂O₂

$$2Pt + H_2O_2 \xrightarrow{\kappa_1} 2Pt - OH$$
 (1)

followed by electrochemical reduction of the resultant Pt-OH

$$Pt-OH + H^{+} + e^{-\frac{k_{2}}{2}}Pt + H_{2}O$$
 (2)

and that the former (reaction 1) is a rate-determining step.¹⁵

The "negative" slope (or "negative" resistance) is caused by the suppression of the dissociative adsorption of H_2O_2 on Pt by formation of upd-H of a nearly full coverage.^{11–13} This explanation is in harmony with the fact that the negative slope starts at a potential of the most negative end of the current peaks for upd-H. Figure 2c shows a *j*-*U* curve in 0.3 M H₂SO₄ containing high-concentration (0.7 M) H₂O₂. Current oscillations, called oscillations A and B,¹¹ are both observed. Oscillation B is less pronounced in Figure 2c than in our previous work¹¹ probably because a *meniscus* electrode (see Figure 1) is used in the present work instead of a wholly immersed electrode in the previous work.

Figure 3 shows j-U curves for an atomically flat Pt(111) electrode, drawn in the same way as Figure 2. It is well-known¹⁷ that the Pt(111) electrode shows broad current peaks in a potential region from ca. 0.35 to 0.05 V vs NHE due to the formation and disappearance of upd-H, as shown in Figure 3a.



Figure 3. j-U curves for an atomically flat Pt(111) electrode, drawn in the same way as Figure 2. Electrolyte: (a) 0.3 M H₂SO₄, (b) 0.2 M H₂O₂ + 0.3 M H₂SO₄, (c) 0.7 M H₂O₂ + 0.3 M H₂SO₄, (d) 1.0 M H₂O₂ + 0.3 M H₂SO₄. Scan rate: (a) 100 mV/s, (b, c) 10 mV/s, (d) 5 mV/s.



Figure 4. An STM image of the surface of an atomically flat Pt(111) electrode used in the present work.

Anodic and cathodic current peaks in a potential region from ca. 0.55 to 0.35 V with sharp spikes at about 0.47 V in Figure 3a are attributed to adsorption and desorption of HSO_4^{-} .^{20,21} The observation of the upd-H and adsorbed- HSO_4^{-} peaks characteristic of the Pt(111) electrode, in agreement with the



Figure 5. (a-c) j-U curves for an atomically nonflat Pt(111) electrode prepared by a procedure of repeated electrochemical oxidation and rereduction, drawn in the same way as Figures 2 and 3. Electrolyte: (a) 0.3 M H₂SO₄, (b) 0.2 M H₂O₂ + 0.3 M H₂SO₄, (c) 0.7 M H₂O₂ + 0.3 M H₂SO₄. Scan rate: (a) 100 mV/s, (b, c) 10 mV/s. (d) Schematic illustration of the surface structure of atomically flat and nonflat Pt-(111) electrodes.

literature,¹⁷ clearly shows that a well-defined atomically flat Pt-(111) surface is obtained in the present work. This conclusion was also confirmed by scanning tunneling microscopy (STM) inspection, which gave an image with a clear "step and terrace" structure, as displayed in Figure 4, similar STM images are reported in the literature.²²

Figure 3b shows that a negative resistance is observed for the atomically flat Pt(111) electrode in 0.3 M H₂SO₄ containing low-concentration (0.2 M) H₂O₂, similarly to the case of Figure 2b. However, the negative resistance in Figure 3b shows a twostep structure, and its potential range extends to a more positive potential of around 0.35 V. As explained later, the negative resistance in a region from 0.10 to 0 V is attributed to the formation of upd-H, similarly to the case of Figure 2b, whereas that in a region from 0.35 to 0.10 V is attributed to another reason. In harmony with the appearance of the new negative resistance in 0.35-0.10 V, a new current oscillation, named oscillation E, appears in potentials of about 0.22-0.13 V in cases where the H₂O₂ concentration is made high, 0.7 M (Figure 3c). The conclusion that oscillation E is distinguished from oscillation A and truly a new oscillation is clearly shown by the fact that oscillation A itself appears in a region of reasonable



Figure 6. j-U curves for an atomically flat Pt(100) electrode, drawn in the same way as Figure 2. Electrolyte: (a) 0.3 M H₂SO₄, (b) 0.2 M H₂O₂ + 0.3 M H₂SO₄, (c) 0.7 M H₂O₂ + 0.3 M H₂SO₄, (d) 1.0 M H₂O₂ + 0.3 M H₂SO₄. Scan rate: (a) 100 mV/s, (b, c) 10 mV/s, (d) 5 mV/s.

potentials (-0.05 to -0.07 V) in addition to oscillation E when the H₂O₂ concentration is made much higher (Figure 3d).

To investigate whether the appearance of oscillation E is due to an effect of the atomic-level flatness of the electrode surface. atomically nonflat Pt(111) electrodes were prepared and examined. Itaya et al.²² reported, by in situ STM experiments, that surface roughening, such as schematically shown in Figure 5d, is caused by a procedure of oxidation and rereduction of an atomically flat Pt(111) surface. In the present work, the surface roughening was carried out by shifting the electrode potential stepwise to 1.75 V, where platinum oxide was formed and oxygen evolution occurred. The electrode potential was kept at 1.75 V for 3 min, and then shifted back to 0.65 V, where the surface platinum oxide was reduced and removed. This procedure was repeated three times. Parts a-c of Figure 5 show j-Ucurves for an atomically nonflat Pt(111) electrode thus prepared, drawn in the same way as Figures 2 and 3. It is seen that the curves in Figure 5 are more similar to those for poly-Pt (Figure 2) than those for atomically flat Pt(111) (Figure 3). The negative resistance in Figure 5b appears only in a narrow potential region (0.10-0.00 V), and no oscillation E appears as seen in Figure 5c, similar to the cases of parts b and c of Figure 2. The j-Ucurves for the atomically flat Pt(111) such as shown in Figure 3 were restored when the atomically nonflat Pt(111) electrodes giving the curves of Figure 5 were annealed in a hydrogen flame,



Figure 7. j-U curves for an atomically flat Pt(110) electrode, drawn in the same way as Figure 2. Electrolyte: (a) 0.3 M H₂SO₄, (b) 0.2 M H₂O₂ + 0.3 M H₂SO₄, (c) 0.7 M H₂O₂ + 0.3 M H₂SO₄, (d) 1.0 M H₂O₂ + 0.3 M H₂SO₄. Scan rate: (a) 100 mV/s, (b, c) 10 mV/s, (d) 5 mV/s.

suggesting that the atomic nonflatness of the atomically nonflat Pt(111) was restricted only to a narrow surface region (see Figure 5d).

Figures 6 and 7 show j-U curves for atomically flat Pt(100) and Pt(110) electrodes, respectively, drawn in the same way as Figures 2 and 3. The observed cathodic and anodic current peaks attributed to upd-H (Figures 6a and 7a) agreed with those reported for well-defined atomically flat Pt(100) and Pt(110),²³ indicating that the electrodes in the present work had well-defined atomic structures. The j-U curves for both the Pt(100) and Pt(110) are rather similar to those for poly-Pt (Figure 2) than those for atomically flat Pt(111) (Figure 3). However, Pt-(100) electrodes showed the negative resistance of a two-step structure (Figure 6b) though much less prominent than for Pt-(111) (Figure 3b). In harmony with this result, some of the Pt-(100) electrodes showed oscillation E in addition to oscillation A when the potential sweep was in the *positive* direction.

Figure 8 shows current (*j*) vs time (*t*) curves for atomically flat Pt(111) and poly-Pt electrodes. Figure 8a shows the wave shape of oscillation E at 0.13 V vs NHE. Parts b and c of Figure 8 are the wave shapes of oscillation A for atomically flat Pt-(111) and poly-Pt, respectively. It is clear that the wave shapes for oscillations E and A are quite different from each other. In addition, the oscillation period for oscillation E (2–10 ms) is much shorter than that for oscillation A (0.2–1 s).



Figure 8. Current density (*j*) vs time (*t*) curves, (a) and (b) for atomically flat Pt(111) and (c) for poly-Pt. Electrolyte: (a, b) 1.0 M $H_2O_2 + 0.3$ M H_2SO_4 , (c) 0.7 M $H_2O_2 + 0.3$ M H_2SO_4 . Electrode potential: (a) 130 mV (oscillation E), (b) -30 mV (oscillation A), (c) -20 mV (oscillation A).



Figure 9. j-U curves for an atomically flat Pt(111) electrode, drawn in the same way as Figure 2. Electrolyte: (a) 0.3 M HClO₄, (b) 0.2 M H₂O₂ + 0.3 M HClO₄, (c) 0.7 M H₂O₂ + 0.3 M HClO₄. Scan rate: (a) 100 mV/s, (b, c) 10 mV/s.

Figure 9 shows j-U curves in 0.3 M HClO₄-based solutions (instead of the 0.3 M H₂SO₄-based ones thus far described) for atomically flat Pt(111) to see an effect of the kind of anions in the electrolyte. The cathodic and anodic current peaks for upd-H



Figure 10. (a) j-U curves for atomically flat and nonflat Pt(111) electrodes, (b) those for atomically flat Pt(111), and Pt(100), Pt(110), and nonflat poly-Pt electrodes. Electrolyte: 0.2 M H₂O₂ + 0.3 M H₂-SO₄. Scan rate: 10 mV/s.

in 0.3 M HClO₄ (Figure 9a) are located in nearly the same potentials as in 0.3 M H₂SO₄ (Figure 3a), in agreement with the literature.^{20,21} A current peak attributed to the adsorption of ClO₄⁻ is not observed,^{20,21} contrary to the case of HSO₄-. Cathodic and anodic current peaks in 0.60–0.85 V (Figure 9a) are attributed to the adsorption and desorption of OH⁻.²¹ Though the adsorption and desorption behaviors of HSO₄⁻ and ClO₄⁻ are quite different from each other, as mentioned above, the observed negative slope and oscillation E are nearly the same between the HSO₄⁻ - and ClO₄⁻ -based solutions (Figures 3 and 9). This indicates that the appearance of oscillation E is not due to the effect of anion adsorption.

Figure 10 shows, comparatively, the H₂O₂-reduction currents and the negative resistances for various Pt electrodes in 0.3 M H₂SO₄ containing low-concentration (0.2 M) H₂O₂. The H₂O₂reduction current in 0.65-0.35 V for atomically flat Pt(111) is higher in absolute value than that for atomically nonflat Pt-(111) even in the same H₂O₂ concentration (Figure 10a). Also, the H₂O₂-reduction current in this potential region decreases in the order of atomically flat Pt(111), Pt(110), and Pt(100) and nonflat poly-Pt (Figure 10b). The differences in the H₂O₂reduction current become more prominent with the increasing scanning rate. It is also to be noted that the aforementioned "new" negative resistance in 0.35-0.10 V is observed prominently only for atomically flat Pt(111), which shows the highest H₂O₂-reduction current in 0.65–0.35 V. This result indicates that the increase in the H_2O_2 -reduction current in 0.65-0.35 V for atomically flat Pt(111) has a close relation with the appearances of the new negative resistance and oscillation E.

Figure 11 shows a phase diagram for the appearance of oscillations A and E in the case of atomically flat Pt(111) with respect to the H_2O_2 and H_2SO_4 concentrations. It seems that not only the H_2O_2 and H_2SO_4 concentrations but also their ratio are important for the appearance of these oscillations.

Mathematical Simulation

We reported in previous papers^{12,14,15} that oscillations C and D appearing in 0.40–0.00 V in the presence of a small amount of halide ions, such as Cl⁻, Br⁻, and I⁻, could be explained by taking into account a catalytic effect of adsorbed halogen (Pt–X) and an autocatalytic effect of adsorbed OH (Pt–OH) for



Figure 11. A phase diagram with respect to the H_2O_2 and H_2SO_4 concentrations: \Box , only oscillation E appears; \bigcirc , both oscillations A and E appear; \times , no oscillation appears. Electrode: atomically flat Pt-(111).

the dissociative adsorption of H_2O_2 . Namely, the appearance of oscillations C and D could be explained by expressing the rate constant (k_1) for reaction 1 in the preceding section as follows:

$$k_1 = k_{10} + \gamma' \theta_X \theta_{\text{OH}} \tag{3}$$

where k_{10} is a normal rate constant for reaction 1, γ' is a proportional constant, and θ_X and θ_{OH} are the surface coverages of Pt-X and Pt-OH, respectively. The appearance of oscillation E in 0.2–0.1 V for atomically flat Pt(111) in the present work may be explained by taking into account a similar autocatalytic effect of Pt-OH on the Pt(111) surface, i.e., by expressing k_1 as follows:

$$k_1 = k_{10} + \gamma \theta_{\rm OH} \tag{4}$$

Thus, we have made mathematical simulation on the basis of this idea.

The following reactions were considered in addition to reactions 1 and 2, in the same way as in our previous paper:¹⁵

$$Pt + H^{+} + e^{-\frac{k_{5}}{\underset{k_{-5}}{\leftarrow}}}Pt - H (upd-H)$$
(5)

$$2Pt-OH \xrightarrow{k_6} 2Pt + O_2 + 2H^+ + 2e^-$$
(6)

$$Pt + H^{+} + e^{-\frac{k_{7}}{\epsilon_{-7}}}Pt - H \text{ (on-top-H)}$$
(7)

$$Pt-H (on-top-H) + Pt-H (on-top-H) \xrightarrow{\kappa_8} H_2$$
(8)

where Pt represents schematically surface site(s) at the Pt electrode.

The differential equations were also expressed in the same way as in our previous work.¹³ From the conservation of the current, we obtain^{24,25}

$$I = jA = (U - E)/R_{\Omega} = I_{\rm C} + I_{\rm F} = AC_{\rm DL}({\rm d}E/{\rm d}t) + I_{\rm F} \quad (9)$$

where I is the total current, A the electrode area, j the current density, U the (external or applied) electrode potential, E the true electrode potential, U-E the ohmic drop between the electrode surface and the position of the reference electrode

(RE), R_{Ω} the solution resistance in the same place as above, $I_{\rm C} = AC_{\rm DL}(dE/dt)$ the charging current, $C_{\rm DL}$ the double-layer capacitance, and $I_{\rm F}$ the faradic current. Equation 9 can be rewritten as

$$dE/dt = (U - E)/AC_{\rm DL}R_{\Omega} - I_{\rm F}/AC_{\rm DL}$$
(10)

 $I_{\rm F}$ is expressed, from reactions 2 and 5–7, as follows:

$$I_{\rm F} = AF\{-k_5 C_{\rm H^+}{}^{\rm s}(1-\theta_{\rm H}-\theta_{\rm OH}) + k_{-5} \theta_{\rm H} - k_2 C_{\rm H^+}{}^{\rm s}\theta_{\rm OH} + k_6 \theta_{\rm OH}{}^2 - k_7 C_{\rm H^+}{}^{\rm s}(1-\Theta_{\rm H}) + k_{-7} \Theta_{\rm H}\} (11)$$

where $C_{\rm H^{+8}}$ is the concentration of H⁺ ions at the electrode surface and $\theta_{\rm OH}$, $\theta_{\rm H}$, and $\Theta_{\rm H}$ are the surface coverages of Pt– OH, upd-H, and on-top-H, respectively. The quantities, k_2 , k_5 , k_{-5} , k_6 , k_7 , and k_{-7} are the rate constants for the *i*th reactions (*i* = 2, 5, -5, 6, 7, and -7), which can be expressed by the Butler–Volmer equations

$$k_i = k_{i0} \exp[-\alpha_i n_i F(E - E_{i0})/RT]$$
 $i = 2, 5, \text{ and } 7$ (12)

$$k_i = k_{i0} \exp[(1 - \alpha_i)n_i F(E - E_{i0})/RT]$$

 $i = -5, 6, \text{ and } -7 (13)$

where k_{i0} is the rate constant at $E = E_{i0}$, E_{i0} the equilibrium redox potential for the *i*th reaction, α_i the transfer coefficient, n_i the number of transferred electrons, F the Faraday constant, R the gas constant, and T the temperature. Because reactions 5 and -5 (and 7 and -7) are reverse reactions to each other, we obtain $E_{50} = E_{-50}$ and $E_{70} = E_{-70}$.

The time dependences of $C_{\text{H}^{+8}}$, $C_{\text{HO}^{8}}$ (the surface concentration of H₂O₂), θ_{OH} , θ_{H} , and Θ_{H} are expressed as follows:

$$(\delta_{\rm HO}/2) \, \mathrm{d}C_{\rm HO}^{\rm s}/\mathrm{d}t = (D_{\rm HO}/\delta_{\rm HO})(C_{\rm HO}^{\rm b} - C_{\rm HO}^{\rm s}) - k_1 C_{\rm HO}^{\rm s}(1 - \theta_{\rm H} - \theta_{\rm OH})^2$$
(14)

$$(\delta_{\rm H^{+}}/2) \, dC_{\rm H^{+}}/dt = (D_{\rm H^{+}}/\delta_{\rm H^{+}})(C_{\rm H^{+}}^{\rm o} - C_{\rm H^{+}}^{\rm s}) + \{-k_{2}C_{\rm H^{+}}^{\rm s}\theta_{\rm OH} - k_{5}C_{\rm H^{+}}^{\rm s}(1 - \theta_{\rm H} - \theta_{\rm OH}) + k_{-5}\theta_{\rm H} + k_{6}\theta_{\rm OH}^{2} - k_{7}C_{\rm H^{+}}^{\rm s}(1 - \Theta_{\rm H}) + k_{-7}\Theta_{\rm H}\}$$
(15)

$$N_{0} d\theta_{\rm OH}/dt = k_{1} C_{\rm HO}^{\ \rm s} (1 - \theta_{\rm H} - \theta_{\rm OH})^{2} - k_{5} C_{\rm H^{+}}^{\ \rm s} \theta_{\rm OH} - k_{6} \theta_{\rm OH}^{\ \rm 2}$$
(16)

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$$N_0 \,\mathrm{d}\theta_{\mathrm{H}}/\mathrm{d}t = k_5 C_{\mathrm{H}^+}{}^{\mathrm{s}} (1 - \theta_{\mathrm{H}} - \theta_{\mathrm{OH}}) - k_{-5} \theta_{\mathrm{H}} \qquad (17)$$

$$N_0 \, \mathrm{d}\Theta_{\mathrm{H}}/\mathrm{d}t = k_7 C_{\mathrm{H}^+}^{\ \mathrm{s}} (1 - \Theta_{\mathrm{H}}) - k_{-7} \Theta_{\mathrm{H}} - 2k_8 \Theta_{\mathrm{H}}^{\ 2} \quad (18)$$

where $D_{\rm HO}$ and $D_{\rm H^+}$ are the diffusion coefficients for H₂O₂ and H⁺, respectively, $\delta_{\rm HO}$ and $\delta_{\rm H^+}$ the thicknesses of the diffusion layers for H₂O₂ and H⁺, respectively, and $C_{\rm HO}^{\rm b}$ and $C_{\rm H^{+b}}$ the concentrations of H₂O₂ and H⁺ in the solution bulk, respectively. A small contribution of the drift motion of H⁺ was neglected. N_0 schematically represents the total amount of surface Pt sites per unit area.

Figure 12 shows j-U curves obtained by mathematical calculations. With no or a small autocatalytic effect ($\gamma \leq 7$), only a one-step negative resistance was reproduced for low-concentration (0.2 M) H₂O₂ (Figure 12a) and only oscillation A was reproduced for high-concentration (0.7 M) H₂O₂ (Figure 12b). On the other hand, with a large autocatalytic effect ($\gamma \geq 8$), the appearance of oscillation E was reproduced together with the increase in the H₂O₂-reduction current in 0.60–0.40 V and



Figure 12. Calculated j-U curves with U scanned at a rate of 0.01 V/s. Parameter values used are as follows: $C_{\rm HO}^{\rm b} = 0.2 \times 10^{-3}$ mol cm⁻³ for (a) and (c) and 0.7×10^{-3} mol cm⁻³ for (b) and (d), $\delta_{\rm HO} = 0.01$ cm, $D_{\rm HO} = 1.7 \times 10^{-5}$ cm² s⁻¹, $C_{\rm H^{+}b} = 0.3 \times 10^{-3}$ mol cm⁻³, $\delta_{\rm H^{+}} = 0.004$ cm, $D_{\rm H} = 9.3 \times 10^{-5}$ cm² s⁻¹, A = 0.01 cm², $C_{\rm DL} = 2.0 \times 10^{-5}$ F cm⁻², $N_0 = 2.2 \times 10^{-9}$ mol cm⁻², $R_{\Omega} = 60 \ \Omega$, T = 300 K, $\alpha_i = 0.25$ (i = 2) and 0.50 ($i \neq 2$), n = 1, $k_{10} = 4 \times 10^{-2}$ cm s⁻¹, $k_{50} = 1 \times 10^{-5}$ mol cm⁻² s⁻¹, $k_{60} = 1 \times 10^{-8}$ mol cm⁻² s⁻¹, $k_{70} = 5 \times 10^{-5}$ mol cm⁻² s⁻¹, $k_8 = 5 \times 10^{-6}$ mol cm⁻² s⁻¹, $k_{20} = 1.37$ V vs NHE, $E_{50} = E_{-50} = 0.08$ V, $E_{60} = 0.67$ V, $E_{70} = E_{-70} = -0.03$ V, $\gamma = 4$ for (a) and (b) and 8 for (c) and (d).



Figure 13. Time course of oscillation E, calculated with $\gamma = 8$ and U = 0.24 V. The other parameters are the same as those for Figure 12.

the appearance of the new negative resistance in 0.35-0.10 V (Figure 12c,d). Figure 13 shows a time course of oscillation E, calculated with $\gamma = 8$. Compared with the observed oscillation (Figure 8a), the oscillation period is well reproduced, but there is a difference in wave shape, which may be due to the adoption of Nernst's diffusion-layer model with a constant thickness in eqs 14 and 15.



Figure 14. Schematic illustration of an autocatalytic mechanism in which the dissociative adsorption of H_2O_2 is accelerated on surface Pt atoms in the neighborhood of adsorbed OH.

Discussion

The experimental results have shown that the atomically flat Pt(111) electrodes show the electrochemical behavior for the H_2O_2 reduction, quite different from that of other Pt electrodes, such as atomically flat Pt(100) and Pt(110), atomically nonflat Pt(111), and poly-Pt. The behavior of the latter electrodes, i.e., the appearance of the one-step negative resistance in a narrow potential region from +0.10 to -0.02 V and the appearance of only oscillation A in this potential region, can be explained by taking into account the suppression of the H₂O₂ reduction by the formation of upd-H as reported previously.^{11–13} On the other hand, the behavior of the atomically flat Pt(111) electrode cannot be explained by this model, and a new model has to be taken into account.

As already mentioned in the preceding section, the appearance of oscillation E, together with the appearance of the new negative resistance in a potential region from 0.35 to 0.10 V and the increase in the H_2O_2 -reduction current in 0.65-0.35 V, can be explained by taking into account the autocatalytic effect of adsorbed OH (Pt-OH) for the dissociative adsorption of H₂O₂. This effect is not considered for our previous model for polycrystalline Pt.¹³ Mathematical simulation based on this model has reproduced well the essential behavior of the atomically flat Pt(111). According to this model, the increase in the H_2O_2 -reduction current in 0.65–0.35 V for Pt(111) is attributed to the autocatalytic effect of surface Pt-OH for the dissociative adsorption of H₂O₂ and the appearance of the new negative resistance in 0.35-0.20 V is attributed to a decrease of the Pt-OH concentration with a negative shift of the electrode potential. Oscillation E appears on the basis of this new negative resistance.

The difference in the electrochemical behavior between the atomically flat Pt(111) and other Pt electrodes can thus be attributed to be a difference in the efficiency of the autocatalytic mechanism (i.e., the γ value in eq 4) between these electrodes. In other words, the γ value is expected to decrease in the order Pt(111) > (100) \approx (110) \geq poly-Pt, as estimated from the magnitude of the H₂O₂-reduction current in 0.65–0.35 V (Figure 10). How can this order be explained? We tentatively assume that, as shown in Figure 14A, adsorbed OH (Pt–OH) is present at hollow sites of surface Pt atoms and that H₂O₂ is adsorbed

with negatively polarized oxygen atoms of H₂O₂ directed to surface Pt atoms. Under this assumption, it is expected that the adsorption of H₂O₂ is accelerated on surface Pt atoms in the neighborhood of adsorbed OH (Pt-OH) because they are more or less positively polarized by an electronegativity difference between the Pt atom and OH group (Figure 14A). This can be responsible for the autocatalytic effect. The differences in the γ value among various Pt electrodes can be attributed, in the first approximation, to the differences in the number of "pairs of Pt atoms" for the accelerated adsorption of H₂O₂. Figure 14B illustrates possible examples of such pairs of Pt atoms by arrows with two heads. The number of pairs of Pt atoms is 15, 12, and 6 for atomically flat Pt(111), Pt(100), and Pt(110) surfaces, respectively. Accordingly, we can expect that the autocatalytic effect of Pt-OH is the most efficient for Pt(111) and decreases in the order Pt(111), Pt(100), and Pt(110), in agreement with the experiment. The corresponding number for atomically nonflat Pt surfaces is estimated to be in the range of 6-12, because the current peaks for upd-H for atomically nonflat Pt are given by a simple sum of those for Pt(100) and Pt(110).

Finally it should be mentioned that Ross et al.²⁶ reported that the H₂O₂-reduction currents on low-index single-crystal Pt electrodes showed the negative resistance in a potential region from +0.1 to -0.3 V vs SCE, which was more prominent in the order of Pt(110), Pt(100), and Pt(111), in agreement with the new negative resistance in the present work. Ross et al. explained their negative resistance to be due to the suppression of the H₂O₂ reduction by the formation of upd-H, contrary to an explanation in the present work. However, the atomically flat Pt(111) electrodes show the negative resistance of a twostep structure (Figure 3b), and in harmony with this result, the Pt(111) (and sometimes Pt(100)) electrodes show two types of oscillations (i.e., oscillations A and E). This strongly suggests that the negative resistance for Pt(111) is composed of two components.

In conclusion, the present work has revealed that the current oscillations in the H_2O_2 -acid-Pt electrode system strongly depend on the atomic-level structure of the Pt electrode surface. The detailed analyses of the behavior, combined with mathematical simulation, have suggested the presence of an autocatalytic mechanism of adsorbed OH (Pt-OH) for the dissociative adsorption of H_2O_2 , which depends in efficiency on the atomic-level structure of the Pt surface. Further studies will serve for deeper understanding of oscillation mechanisms and mechanisms of electrochemical reactions themselves.

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References and Notes

(1) Hudson, J. L.; Tsotsis, T. T. Chem. Eng. Sci. 1994, 49, 1493.

(2) Fahiday, T. Z.; Gu, Z. H. In *Modern Aspects of Electrochemistry*; White, R. E., Bockris, J. O., Conway, R. E., Eds.; Plenum: New York, 1995; Vol. 27, p 383.

(3) Koper, M. T. M. In *Advances in Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; John Wiley & Sons: New York, 1996; Vol. 92, p 161.
(4) Krischer, K.; Luebke, M.; Wolf, W.; Eiswirth, M.; Ertl, G.

Electrochim. Acta 1995, 40, 69.

(5) Raspel, F.; Eiswirth, M. J. Phys. Chem. **1994**, 98, 7613.

(6) Eiswirth, M.; Luebke, M.; Krischer, K.; Wolf, W.; Hudson, J. L.; Ertl, G. Chem. Phys. Lett. **1992**, 192, 254.

(7) Raspel, F.; Nichols, R. J.; Kolb, D. M. J. Electroanal. Chem. 1990, 286, 279.

(8) Strasser, P.; Luebke, M.; Raspel, F.; Eiswirth, M.; Ertl, G. J. Chem. Phys. 1997, 107, 979.

(9) Markovic, N.; Ross, P. N. J. Phys. Chem. 1993, 97, 9771.

(10) Tripkovic, A.; Popvic, K.; Adzic, R. R. J. Chim. Phys. Phys.-Chim. Biol. 1991, 88, 1635.

(11) Hommura, H.; Mukouyama, Y.; Matsuda, T.; Yae, S.; Nakato, Y. Chem. Lett. **1996**, 391. Matsuda, T. Hommura, H.; Mukouyama, Y.; Yae,

S.; Nakato, Y. J. Electrochem. Soc. 1997, 144, 1988.

(12) Mukouyama, Y.; Nakanishi, S.; Nakato Y. Bull. Chem. Soc. Jpn. 1999, 72, 2573.

(13) Mukouyama, Y.; Hommura, H.; Nakanishi, S.; Nishimura, T.; Konishi, H.; Nakato, Y. Bull. Chem. Soc. Jpn. **1999**, 72, 1247.

(14) Mukouyama, Y.; Konishi, H.; Nakanishi, S.; Nakato, Y. Chem. Lett. **1998**, 1009.

(15) Mukouyama, Y.; Nakanishi, S.; Konishi, H.; Nakato, Y. J. Electroanal. Chem. 1999, 473, 156.

(16) Nakanishi, S.; Hommura, H.; Mukouyama, Y.; Matsuda, T.; Nakato, Y. Chem. Lett. **1998**, 977.

(17) Clavilier, J.; Faure, R.; Guinet, G.; Durand, D. J. Electroanal. Chem. 1980, 107, 205.

(18) Bard, A. J.; Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications, John-Wiley & Sons: New York, 1980; p 540.

(19) Nichols, R. J.; Bewick, A. J. Electroanal. Chem. 1988, 243, 445.
(20) Wieckowski, A.; Zelenav, P.; Varga, K. J. Chim. Phys. Phys.-Chim. Biol. 1991, 88, 1247.

(21) Wagner, T.; Ross, P. N. J. Electroanal. Chem. 1988, 250, 301.

(22) Itaya, K.; Sugawara, S.; Sashikata, K.; Furuya, N. J. Vac. Sci. Technol. 1990, A8 (1), 515.

(23) Furuya, N.; Koide, S. Surf. Sci. 1989, 220, 18.

(24) Koper, M. T. M.; Sluyters, J. H. J. Electroanal. Chem. 1991, 303, 73.

(25) Koper, M. T. M.; Sluyters, J. H. J. Electroanal. Chem. 1993, 347, 31.

(26) Markovic, N. M.; Gasteiger, H. A.; Ross, Jr. P. N. J. Phys. Chem. 1995, 99, 3411.