

# Promoted Dissociative Adsorption of Hydrogen Peroxide and Persulfate Ions and Electrochemical Oscillations

## Caused by a Catalytic Effect of Adsorbed Bromine

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Adsorbed bromine on Pt and Au electrodes acts as a catalyst for dissociative adsorption of  $H_2O_2$  and  $S_2O_8^{2^-}$ , similar to adsorbed OH (and adsorbed iodine). This fact is revealed by analyses of newly found negative differential resistances and electrochemical oscillations, appearing in a potential region where the surface coverage of adsorbed bromine ( $\theta_{Br}$ ) decreases steeply. The present result further supports the generality of a catalytic effect of adsorbed electronegative species such as OH, Br, and I on the dissociative adsorption of peroxides such as  $H_2O_2$  and  $S_2O_8^{2^-}$ .

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Electrochemical oscillations in general appear in potential regions of negative differential resistances (NDRs) of current density (*j*) vs. potential (*U*) curves,<sup>1,2</sup> though the NDRs are sometimes hidden in the *j*-*U* curves by other electrochemical processes.<sup>2,3</sup> The oscillations that appear in the regions of nonhidden NDRs are called NDR oscillators, whereas those appearing in the regions of hidden NDRs (*i.e.*, in the regions of apparently positive differential resistances) are called HNDR oscillators.<sup>2,3</sup> The important difference is that the NDR oscillator appears only as a current oscillation, whereas the HNDR oscillator appears as both current and potential oscillations. There is another type of oscillation that appears in the regions of normal positive differential resistances, called CNDR oscillators, which appears by coupling with NDRs in other potential regions.<sup>4</sup>

The NDRs thus play a key role in the appearance of electrochemical oscillations. They arise from various factors<sup>2</sup> such as the formation of inactive layers at the electrode surface, the disappearance of surface catalysts, and the electrostatic repulsion between ionic electroactive species and polarized electrodes. Of these, the NDRs arising from surface catalysts are especially interesting because their study can serve for exploration of new electrocatalytic processes.

We reported previously<sup>5</sup> that adsorbed OH on Pt electrodes promoted the dissociative adsorption of  $H_2O_2$ , causing the appearance of an NDR and a current oscillation in the  $H_2O_2$ -reduction system. The catalytic effect of adsorbed OH was explained<sup>5</sup> in terms of electrical positive polarization of surface Pt atoms lying near the adsorbed OH, caused by a difference in the electronegativity between metal atoms and OH, the polarization accelerating the adsorption of negatively polarized O atoms of  $H_2O_2$ . It was also shown<sup>5</sup> that the extent of the catalytic effect strongly depended on the difference in the crystal-face (or the atomic-level) structure of the Pt surface.

This mechanism for the catalytic effect of adsorbed OH is of much interest, indicating a new type of surface process. It is also interesting in that it leads to a unique feature of the appearance of two stationary states (*i.e.*, a high-current state with  $\theta_{OH} \cong 1$  and a low-current state with small  $\theta_{OH}$ ) at the same potential.<sup>6</sup> These points imply that the mechanism deserves further confirmation. If the mechanism is true, a similar effect to adsorbed OH should be observed for other adsorbed electronegative species such as adsorbed I, Br, and Cl. Actually, we observed<sup>7</sup> that adsorbed iodine showed a similar effect. Moreover, it was shown<sup>8</sup> that the mechanism

nism could be extended to the dissociative adsorption of  $S_2 O_8^{2^-}$ . In the present work, we have studied the effect of adsorbed bromine to obtain further confirmation and generalization of this mechanism.

#### Experimental

Single-crystal Pt(111), (100), and (110) electrodes with atomically flat surfaces were prepared by the method of Clavilier *et al.*<sup>9</sup> The details of the preparation method were described elsewhere.<sup>5</sup> Polycrystalline Au (99.99% in purity) disks of about 6.0 mm diam were also used as the working electrode. The poly-Au disks were polished with 0.06  $\mu$ m alumina slurry and immersed in hot HNO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> for 10 min to remove surface contamination.

Current density (*j*) vs. potential (*U*) curves were measured with a potentiogalvanostat (Nikko-Keisoku NPGS-301) and a potential programmer (Nikko-Keisoku NPS-2), using a Pt plate ( $10 \times 10$  mm) as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The data were recorded with a data-storing system (instruNET, GW Instruments) with a sampling frequency of 1 kHz. Electrolyte solutions 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. The electrolyte solutions were kept stagnant during measurements. The ohmic drops in the solution between the working and the reference electrodes were not corrected in the present work.

#### Results

Figures 1a and b show, for reference, reported *j* vs. *U* curves for the  $H_2O_2$  reduction on an atomically flat single-crystal Pt(111) electrode in relatively low and high  $H_2O_2$  concentrations (0.2 M  $H_2O_2$ + 0.3 M  $H_2SO_4$  and 1.0 M  $H_2O_2$  + 0.3 M  $H_2SO_4$ ), respectively, under controlled-potential conditions. The cathodic current in the potential region from about +0.55 to -0.08 V is due to the  $H_2O_2$ reduction, which starts at about +0.80 V. Hydrogen evolution starts at about -0.1 V. The  $H_2O_2$  reduction current in 0.2 M  $H_2O_2$ + 0.3 M  $H_2SO_4$  shows two NDRs in regions from +0.02 to -0.08 V and from +0.25 to +0.15 V, designated as NDR-H and NDR-OH in Fig. 1a. The origins of the NDRs can be explained as follows. The  $H_2O_2$  reduction is initiated by dissociative adsorption of  $H_2O_2$ 

$$2Pt + H_2O_2 \rightarrow 2Pt-OH$$
[1]

followed by electrochemical reduction of the resultant Pt-OH

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**Figure 1.** Effect of Br<sup>-</sup> addition on *j*-*U* curves for  $H_2O_2$  reduction on Pt(111) under controlled-potential conditions. Electrolyte: (a) 0.2 M  $H_2O_2$  + 0.3 M  $H_2SO_4$ ; (b) 1.0 M  $H_2O_2$  + 0.3 M  $H_2SO_4$ ; (c) 0.2 M  $H_2O_2$  + 0.3 M  $H_2SO_4$  + 2  $\mu$ M KBr; and (d) 0.7 M  $H_2O_2$  + 0.3 M  $H_2SO_4$  + 2  $\mu$ M KBr. Scan rate: (a, c) 100 and (b, d) 10 mV/s.

The potential-independent H<sub>2</sub>O<sub>2</sub>-reduction current in the +0.55 to -0.08 V region indicates that Reaction 1 is the rate-determining step (rds).<sup>5,6,10</sup> The NDR-H arises from the suppression of Reaction 1 by the formation of underpotential-deposited hydrogen (upd-H).<sup>10,11</sup> The NDR-OH arises from a decrease in the coverage ( $\theta_{OH}$ ) of adsorbed OH (Pt-OH), which acts as an autocatalyst for Reaction 1, with a negative potential shift.<sup>5-7</sup> Namely, the rate constant,  $k_1$ , for Reaction 1 is expressed as follows

$$k_1 = k_{10} + \kappa \theta_{\rm OH}$$
 [3]

where  $k_{10}$  is a normal rate constant, and  $\kappa$  is a proportional constant. A negative shift in *U* leads to a decrease in  $\theta_{OH}$ , which in turn leads to a decrease in  $k_1$  (Eq. 3) and hence a decrease in *j*. Thus, an NDR (NDR-OH) appears. In a high H<sub>2</sub>O<sub>2</sub> concentration (1.0 M H<sub>2</sub>O<sub>2</sub> + 0.3 M H<sub>2</sub>SO<sub>4</sub>), two oscillations, called oscillation A and E, appear in the regions of NDR-H and NDR-OH (Fig. 1b). Slight shifts in potential between the NDRs and oscillations in Fig. 1a and b can be attributed to ohmic drops in the solution.

Figure 1c and d shows *j*-*U* curves when 2  $\mu$ M KBr was added to 0.2 M H<sub>2</sub>O<sub>2</sub> + 0.3 M H<sub>2</sub>SO<sub>4</sub> and 0.7 M H<sub>2</sub>O<sub>2</sub> + 0.3 M H<sub>2</sub>SO<sub>4</sub>, respectively. A new NDR, named NDR-Br in Fig. 1c, appears. In



Figure 2. The same as Fig. 1, except that Pt(100) is used and the  $H_2O_2$  concentration in (b) is 0.7 M.

accordance with the appearance of the NDR, a new oscillation, named oscillation F, appears in a solution of high  $H_2O_2$  concentration (Fig. 1d).

A similar result was obtained for Pt(100) electrodes, as shown in Fig. 2. The NDR-OH is not so prominent for Pt(100) (Fig. 2a),<sup>5</sup> and oscillation E appears only in some experiments (Fig. 2b). When Br<sup>-</sup> was added to the solutions, the NDR-Br and oscillation F appear (Fig. 2c and d), similar to the case of Pt(111). It may be noted that another oscillation, named oscillation G in Fig. 2d, is observed for Pt(100) in a region of +0.52 to +0.46 V, though the origin is unknown at present.

Figure 3 shows results of similar experiments for Pt(110) electrodes. Neither NDR-OH nor oscillation E appears for Pt(110), contrary to the cases of Pt(111) and Pt(100). Furthermore, neither NDR-Br nor oscillation F appears when  $Br^-$  was added.

Figure 4a shows a j-U curve for  $S_2O_8^{2^-}$  reduction on a polycrystalline Au-disk electrode under a controlled-potential condition. Two NDRs, NDR-OH and NDR-X (the origin of NDR-X is unknown), are observed in 0.5 M Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> + 0.5 M HClO<sub>4</sub>. The reduction of  $S_2O_8^{2^-}$  is reported<sup>12,13</sup> to proceed via the following mechanism in the potential region of NDR-OH

$$S_2 O_8^{2-} \rightarrow 2 S O_4^{-}_{ad}$$
<sup>[4]</sup>

$$2\mathrm{SO}_{4\ \mathrm{ad}}^{-} + 2\mathrm{e}^{-} \to 2\mathrm{SO}_{4\ \mathrm{ad}}^{2-}$$
[5]



Figure 3. The same as Fig. 2, except that Pt(110) is used.

Thus, the NDR-OH arises<sup>8</sup> from a catalytic effect of adsorbed OH on the dissociative adsorption of  $S_2O_8^2$  (Reaction 4), similar to the case of the  $H_2O_2$ -reduction system. Under controlled-current conditions, a potential oscillation (named oscillation  $\gamma$ ) appears in the potential region of NDR-OH<sup>8</sup> (Fig. 4c).

When  $Br^-$  ions were added to the solution, a new NDR, named NDR-Br, appears between NDR-OH and NDR-X (Fig. 4b), with the NDR-X shifted to more negative potential. In accordance with the appearance of the NDR-Br, a new oscillation, named oscillation  $\zeta$ , is observed under controlled-current conditions (Fig. 4d and e). Note that the appearances of NDR-Br and oscillation  $\zeta$  were well reproduced, but the shape of NDR-Br (or the shape of the *j*-*U* curve in a region below -0.1 V) changed from experiment to experiment, suggesting that the surface processes in this region are complicated. The wave shape of oscillation  $\zeta$  was also very complex, strongly depending on the regulated current density. More experiments are necessary to obtain a definite conclusion. In the present paper, we focus on the fact that NDR-Br and oscillation  $\zeta$  appear upon addition of Br<sup>-</sup>. Their detailed behavior and the relation to NDR-X will be discussed elsewhere.

### Discussion

The experimental results show that the addition of Br<sup>-</sup> ions to the solution causes the appearances of NDR-Br (Fig. 1c, 2c, and 4b) and the corresponding oscillations (oscillations F and  $\zeta$ , Fig. 1d, 2d, 4d, and 4e). The potential regions of NDR-Br for Pt and Au electrodes (Fig. 1c, 2c, and 4b) are in good agreement with the reported potential regions in which the surface coverage ( $\theta_{Br}$ ) of adsorbed Br



**Figure 4.** Effect of Br<sup>-</sup> addition on *j*-*U* curves for  $S_2O_8^{2-}$  reduction on poly-Au under (a, b) controlled-potential, and (c-e) controlled-current conditions. Electrolyte: (a, c) 0.5 M Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> + 0.5 M HClO<sub>4</sub>; (b, e) 0.5 M Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> + 0.5 M HClO<sub>4</sub> + 15  $\mu$ M KBr; and (d) 0.5 M Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> + 0.5 M HClO<sub>4</sub> + 12.5  $\mu$ M KBr. Scan rate: (a, b) 100 mV/s and (c, d, e) 1 mA/s.

changes largely. For example, Gasteiger *et al.* reported<sup>14</sup> that adsorbed Br on Pt(111) in 0.1 M HClO<sub>4</sub> was desorbed in a potential region from +0.10 to -0.12 V. Mrozek and Weaver reported,<sup>15</sup> by surface-enhanced Raman spectroscopy (SERS), that adsorbed Br on Pt was desorbed in a region more negative than -0.17 V. They also reported<sup>16</sup> that adsorbed Br on Au was desorbed in a region of -0.17 to -0.57 V. We can thus conclude that NDR-Br and oscillations F and  $\zeta$  arise from adsorbed Br.

The appearance of NDR-Br can be explained quite in the same way as that of NDR-OH.<sup>5,7,8</sup> If adsorbed Br acts as a catalyst for the dissociative adsorption of  $H_2O_2$  (Reaction 1) and  $S_2O_8^{2-}$  (Reaction 4), the rate constants for these reactions can be expressed as



**Figure 5.** (A) Schematic illustration of a catalytic effect of adsorbed Br on the dissociative adsorption of  $H_2O_2$  on Pt. (B) The difference in the number of Pt pairs on which accelerated adsorption of  $H_2O_2$  can occur among Pt(111), (100), and (110).

$$k_1 = k_{10} + \kappa' \theta_{\rm Br} \tag{6}$$

$$k_4 = k_{40} + \kappa'' \theta_{\rm Br}$$
[7]

where  $k_{10}$  and  $k_{40}$  are normal rate constants for Reactions 1 and 4, and  $\kappa'$  and  $\kappa''$  are proportional constants. Thus, a decrease in  $\theta_{\rm Br}$  by a negative shift in U leads to a decrease in  $k_1$  or  $k_4$  and hence a decrease in j, resulting in an NDR (NDR-Br). The Br<sup>-</sup> concentration is very low (2 or 15  $\mu$ M) in the present work and thus  $\theta_{\rm Br}$  is considerably smaller than unity, even for the saturated  $\theta_{\rm Br}$  at positive potentials. This means that a lot of empty sites  $(1 - \theta_{Br})$  are left, which allows the appearance of NDR-OH and oscillations E or  $\gamma$ , even in the presence of Br<sup>-</sup> (Fig. 1, 2, and 4).

The catalytic effect of adsorbed Br (non-zero  $\kappa'$  and  $\kappa''$  in Eq. 6 and 7) can also be explained in the same way as that of NDR-OH,<sup>5</sup> because Br is an electronegative element and adsorbed Br can induce positive polarization of surface Pt or Au atoms in the neighborhood, similar to adsorbed OH, as schematically shown in Fig. 5A. The NDR-Br and oscillation F appear most prominently for Pt(111) (Fig. 1-3), also similarly to NDR-OH and oscillation E.<sup>5</sup> This crystal-face dependence can be attributed<sup>5</sup> to the difference in the number of positively polarized Pt (or Au) atoms near the adsorbed Br among the (111), (100), and (110) faces (Fig. 5B).

Both oscillation F in the  $H_2O_2$  system and oscillation  $\zeta$  in the  $S_2O_8^{2^-}$  system appear from a common NDR (NDR-Br), as mentioned earlier, but their appearance mechanisms are quite different. The appearance mechanism for oscillation F can be estimated to be the same as that for oscillation  $E,^5$  because both oscillations E and F appear in the region of the *j*-*U* curve of the same characteristics (Fig. 1). The only difference is that adsorbed OH in oscillation  $E^5$  is replaced by adsorbed Br in oscillator F. Thus, oscillation F can be regarded as an NDR oscillator with adsorbed Br as the NDR-inducing species and the  $H_2O_2$  diffusion as a slow process.

Similarly, the appearance mechanism for oscillation  $\zeta$  can be estimated to be the same as that for oscillation  $\gamma^8$  because these oscillations are located in the region of the *j*-*U* curve of the same characteristics (Fig. 4). Previous work revealed<sup>8</sup> that oscillation  $\gamma$  was classified as an HNDR oscillator, for which the NDR-OH is hidden by an increase in *j* (or empty surface sites) by desorption of adsorbed SO<sub>4</sub><sup>2-</sup> (as a product of the S<sub>2</sub>O<sub>8</sub><sup>2-</sup> reduction) with a negative shift in *U*. The appearance mechanism for oscillation  $\zeta$  can thus be explained in the same way, by replacing adsorbed OH in oscillation  $\gamma$ .

Finally, we summarize a variety of electrochemical oscillations observed for the  $H_2O_2$  and  $S_2O_8^{2-}$  reduction systems in Table I. For oscillations whose mechanisms have not yet been fully clarified, the characteristics such as the NDR-inducing species, the slow processes, and the mechanical classification are indicated in parenthe-

Table I. A variety of oscillations appearing in the  $H_2O_2$  reduction on Pt and the  $S_2O_8^{2-}$  reduction on Pt or Au, together with their characteristics and classification.

NDD inducing		Name of oscillation <sup>a</sup>		
species	Slow process	H <sub>2</sub> O <sub>2</sub> system	$S_2O_8^{2-}$ system	Classification
Adsorbed-OH	H <sub>2</sub> O <sub>2</sub> diffusion	Oscillation E <sup>5</sup>		NDR (class III)
	$H_2O_2$ diffusion	Enhanced oscillation E <sup>7</sup> , <sup>b</sup>		NDR (class III)
	Desorption of adsorbed $Cl^{-}$ $D = Cl^{-}$	Oscillation C <sup>10,17</sup>	Oscillation $\gamma^8$	HNDR (class IV.2)
	$CI$ , Br, or $SO_4$			
Adsorbed-Br	$(H_2O_2 \text{ diffusion})$	Oscillation F <sup>c</sup>		NDR (class III)
	(Desorption of adsorbed $SO_4^{2-}$ )		Oscillation $\zeta^c$	HNDR (class IV.2)
upd-H	$H_2O_2$ diffusion	Oscillation A <sup>18-20</sup>	Oscillation $\alpha^8$	NDR (class III)
	$H_2O_2$ diffusion	Oscillation B <sup>4</sup>		CNDR (class V)
Adsorbed OH	Desorption of	Oscillation D <sup>10,17</sup>		HNDR (class IV.4)
and upd-H	adsorbed Br-			
(Unknown)	$(S_2O_8^2 \text{ diffusion})$		Oscillation $\beta^8$	HNDR <sup>d</sup> (class IV.3)
	(Desorption of adsorbed $SO_4^{2-}$ )		Oscillation $\delta^8$	HNDR <sup>d</sup> (class IV.2)

<sup>a</sup> Numerals attached on the names of oscillations refer to the reference numbers.

<sup>b</sup> Enhanced by a catalytic effect of adsorbed iodine.

c The present work.

<sup>d</sup> Determined by impedance spectroscopy (an unpublished result).

ses. We can see that the catalytic effect of adsorbed electronegative species (OH, Br, and I) is observed in a wide range of these systems, giving strong support to its generality.

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