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The Independent Electrochemical Detection of H_2O_2 and O_2 in Aqueous Alkaline Solutions on an Alkylsilanized Gold Electrode

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The cyclic voltammetric studies of H_2O_2 and O_2 in aqueous alkaline solutions were carried out on stationary gold electrodes unmodified and modified chemically with dodecyltriethoxysilane. Although two cathodic waves were observed for both H_2O_2 and O_2 on the unmodified electrode, only the second wave was observed for H_2O_2 on the modified electrode. Since the first cathodic wave of H_2O_2 overlaps that of O_2 on the unmodified electrode, the disappearance of the first wave of H_2O_2 makes it possible to distinguish O_2 from H_2O_2 on the modified electrode. The effect of alkylsilanization on the diminution and evolution of H_2O_2 or O_2 on gold electrodes was also confirmed by employing rotating ring-disk gold electrodes unmodified and modified similarly with dodecyltriethoxysilane. Furthermore, the reduction mechanism of H_2O_2 and the application of the independent electrochemical detection of H_2O_2 and O_2 are discussed.

In the last decade, the chemical modification of electrode surfaces has been intensively investigated as a means of making various functional electrodes.[1] In relation to the electrocatalysis of the modified electrodes for fuel cells, most researchers have been involved in the pursuit of a novel molecular design to accelerate electrochemical reactions.[2-4] However, for analytical purposes or mechanistic studies, we very often require the suppression of some undesirable electrode reactions to avoid the overlapping of a wave of interest with these unwanted ones. In the present paper, we demonstrate a novel electrode with a chemically modified surface for the independent detection of H_2O_2 and O_2 in aqueous alkaline solutions.

The analysis of H_2O_2 and O_2 in solutions is of great importance in the studies of fuel cells,[5-13] photocatalytic water splitting,[14-18] bioelectrochemistry,[19,20] etc. It has been difficult so far, however, to detect H_2O_2 and O_2 independently in their mixed system by electrochemical methods or by the conventional methods employed in the fields mentioned above, such as mass spectrometry and gas chromatography, since the waves of H_2O_2 and O_2 overlap each other on the electrodes and H_2O_2 is easily decomposed into O_2 and H_2O in the mass spectrometric and chromatographic apparatuses. The experimental findings described in the present paper show that the surface catalytic reduction of H_2O_2 on a polycrystalline gold electrode in aqueous alkaline solutions can be greatly suppressed by the chemical modification of the electrode surface with dodecyltriethoxysilane, while neither the reduction of O_2 nor the oxidation of H_2O_2 is affected appreciably. Namely, it is possible to detect H_2O_2 and O_2 on the electrode at different potentials without the overlapping of their waves. Recently we succeeded in finding evidence for the photolytic formation of H_2O_2 in TiO_2[21] and in $[Ru(bpy)_3]^{2+}$-modified TiO_2 aqueous suspensions by applying the present method. The present paper will describe the basis of the method in detail. The reduction mechanism of H_2O_2 will also be discussed on the basis of the new insight given by such a chemical modification.

Experimental

A gold plate and a gold ring-disk electrode were chemically modified with dodecyltriethoxysilane.[22] The chemical modification was carried out as follows. An unmodified gold plate, which had been thoroughly washed as has been described previously,[23] was immersed in a 10% silane coupling reagent solution, after which the solution was refluxed for 24 h. The reagent solution was prepared by the addition of dodecyltriethoxysilane to dry toluene. After silanization, the electrode was washed thoroughly with dry toluene. A gold ring-disk electrode was also chemically modified by the same procedure except that the ring-disk electrode was dipped in the coupling reagent solution in a desiccator at room temperature without reflux for 3 d. A gold plate or a chemically modified gold plate was used as a stationary working electrode. Electrochemical measurements with a homemade potentiostat were performed in a glass cell using, in addition, a gold plate and a saturated calomel electrode as a counter electrode and a reference electrode, respectively. Voltammetry with a gold ring-disk electrode or a chemically modified one was carried out with a Nikko Keisoku rotating ring-disk electrode system consisting of an RRDE-1 rotating ring-disk electrode drive with an SC-5 speed controller and a DPGS-1 dual potentiogalvanostat. A deaerated 0.3 mM H_2O_2 or an air-saturated aqueous solution, both containing 10 mM NaOH and 0.1 M KCl, was employed as the sample solution (1 M=1 mol dm^{-3}). All the solutions were prepared with doubly distilled water and G. R. -grade reagents. All the electrochemical measurements were performed at 25 °C.

Results and Discussion

Reduction and Oxidation of H_2O_2 on Unmodified and Chemically Modified Gold Electrodes. Figure 1A shows the cyclic voltammogram of the deaerated H_2O_2 solution on the unmodified gold electrode. On the negative sweep, starting at the rest potential of −0.13 V, two cathodic waves were observed with peak potentials of −0.2 and −0.8 V, respectively. Three mechanistic

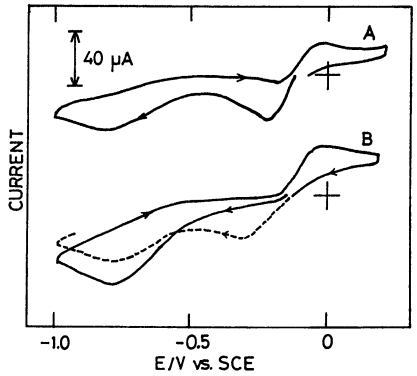

Fig. 1. Cyclic voltammograms of deaerated H_2O_2 aqueous solution on (A) an unmodified Au electrode and (B) a chemically modified Au electrode. NaOH (10 mM); KCl (0.1 M); H_2O_2 (ca. 0.3 mM); N_2 purged; sweep rate (40 mV s^{-1}); electrode area (0.79 cm^2).

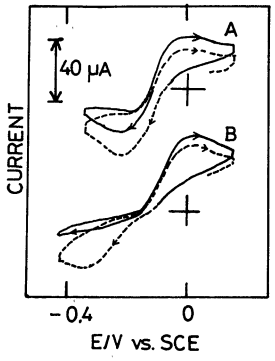

Fig. 2. Cyclic voltammograms of deaerated H_2O_2 aqueous solution on (A) an unmodified Au electrode and (B) a chemically modified Au electrode in the narrower potential range. Experimental conditions are the same as in Fig. 1.

interpretations of the first cathodic wave, with the peak potential of −0.2 V, have been presented. The first one is the surface catalytic reduction of H_2O_2, which proceeds via the adsorption of H_2O_2 on the surface of gold in the form of OH:[6,8]

$$HO_2^- + H_2O \longrightarrow 2OH(ads) + OH^- \quad (1)$$

$$2OH(ads) + 2e^- \longrightarrow 2OH^- \quad (2)$$

The second one is the surface catalytic reduction of H_2O_2, which proceeds via the adsorption of H_2O_2 on the surface in the form of O:[9]

$$HO_2^- \longrightarrow O(ads) + OH^- \quad (3)$$

$$O(ads) + e^- + H_2O \longrightarrow OH(ads) + OH^- \quad (4)$$

$$OH(ads) + e^- \longrightarrow OH^- \quad (5)$$

The third one is the reduction of O_2 generated by the chemical decomposition of H_2O_2 on the surface:[6,10]

$$2HO_2^- \longrightarrow O_2 + 2OH^- \quad (6)$$

$$O_2 + 2e^- + H_2O \longrightarrow HO_2^- + OH^- \quad (7)$$

However, the third mechanism can be ruled out because the peak potential of the first cathodic wave of H_2O_2 reduction is ca. 100 mV more positive than that of the O_2 reduction, as will be shown below. The second wave, with a peak potential of −0.8 V, may be due to the direct reduction of H_2O_2 on the gold surface:

$$HO_2^- + 2e^- + H_2O \longrightarrow 3OH^- \quad (8)$$

On the reverse scan, the cathodic current increased again in the potential region between −0.4 and −0.2 V. This indicates that the reduction shown by the first cathodic wave is limited within the narrow potential region.[6] Following the increase in the cathodic current, an anodic wave started at −0.15 V. This wave can be assigned to the oxidation of H_2O_2:[6,8]

$$HO_2^- + OH^- \longrightarrow O_2 + H_2O + 2e^- \quad (9)$$

Figure 1B shows the cyclic voltammogram of the deaerated H_2O_2 solution on the chemically modified gold electrode. In contrast with the current observed on the unmodified electrode, only one cathodic wave, with a peak potential of ca. −0.8 V, was observed. This wave can be ascribed to the direct reduction of H_2O_2 described above. The pronounced suppression of the first wave on the modified surface may result from the blocking of the catalytic sites which bind H_2O_2 in the form of OH or O. On the reverse scan, an anodic wave with an onset potential of −0.15 V was observed. This indicates that neither the oxidation of H_2O_2 to O_2 nor the direct reduction of H_2O_2 to H_2O is appreciably affected by alkylsilanization. On the second negative scan, a new wave starting at −0.1 V appeared. The peak potential of this new wave was −0.3 V which coincided with the peak potential of the first wave of the O_2 reduction, as will be shown below. This wave, therefore, can reasonably be assigned to the reduction of the O_2 which was generated on the preceding positive sweep.

Figure 2A shows the cyclic voltammogram of the deaerated H_2O_2 solution on the unmodified gold electrode recorded in a narrower potential region than that shown in Fig. 1A. All the waves can be assigned in the same way as those in Fig. 1A.

Figure 2B shows the cyclic voltammogram of the deaerated H_2O_2 solution on the chemically modified gold electrode, also recorded in a narrower potential region than that shown in Fig. 1B. On the first negative sweep, very little current flowed. On the reverse scan, consequently, a higher anodic current for the oxidation of H_2O_2 (Eq. 9) than that in Fig. 2A appeared because the irreversible transformation of H_2O_2 to H_2O was suppressed. On the second negative scan, a cathodic wave with a peak potential of −0.3 V was observed. This peak potential coincided with that of the first wave of O_2 reduction, as will be shown below. On the second

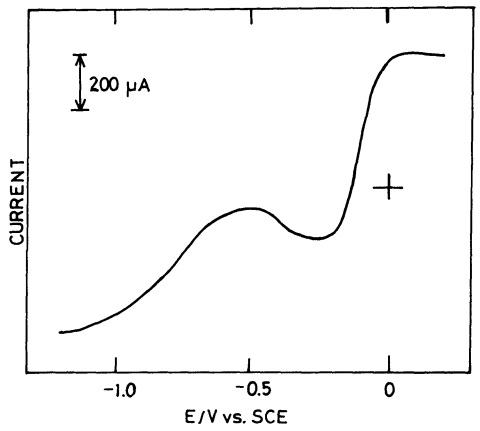

Fig. 3. Voltammetric curve of deaerated H_2O_2 aqueous solution on a rotating unmodified Au disk electrode. Sweep rate (20 mV s^{-1}); rotation speed (3600 rpm). Solution conditions are the same as in Fig. 1.

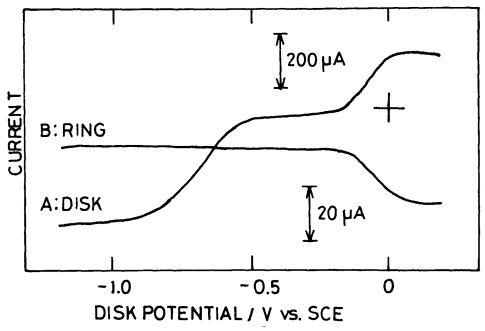

Fig. 4. (A) Current on a rotating chemically modified Au disk electrode and (B) current on a rotating chemically modified Au ring electrode for deaerated H_2O_2 aqueous solution as a function of the disk potential. Sweep rate (20 mV s^{-1}); rotation speed (3600 rpm); ring potential (−0.45 V vs. SCE). Solution conditions are the same as in Fig. 1.

positive sweep, the anodic wave height decreased a little, but the height was still much higher than that in Fig. 2A.

Figure 3 shows the current-potential curve for the deaerated H_2O_2 solution on an unmodified rotating disk electrode. This curve indicates that the oxidation wave height at anodic potentials is equal to the cathodic one at the potentials more negative than −1.0 V. This result is reasonable because both reactions, i.e., oxidation to O_2 and reduction to H_2O, are two-electron processes from H_2O_2. The dependence of these currents on the rotational speed confirmed that both currents are mass-transfer-limited. A maximal value of catalytic current was observed around −0.25 V. This also indicates that the surface catalytic reduction of H_2O_2 is limited within this potential region.

Figure 4A shows the current-potential curve for the deaerated H_2O_2 solution on a chemically modified rotating disk electrode. It is remarkable that the increase in the cathodic current between −0.15 and

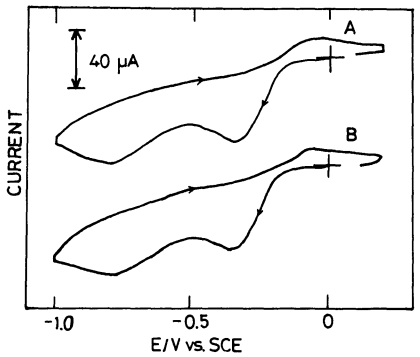

Fig. 5. Cyclic voltammograms of air-saturated aqueous solution on (A) an unmodified Au electrode and (B) a chemically modified Au electrode. Air-saturated. Other experimental conditions are the same as in Fig. 1.

−0.4 V shown in Fig. 3 was completely suppressed and that very little current flowed in the potential region. This suppression of the cathodic current corresponds to that observed on the stationary chemically modified gold electrode shown in Figs. 1B and 2B. The suppresion of the wave indicates that the chemical modification of the surface may block the catalytic sites of the gold surface. It is also seen in Fig. 4A that the magnitude of the H_2O_2 oxidation current at the potentials more positive than 0 V was smaller than that of H_2O_2 reduction current at the potentials more negative than −1.0 V. This may come from the contamination of the gold surface with impurities in the solution, which inhibits the oxidation of H_2O_2 more than the reduction of H_2O_2, since the cleaning of the gold surface by applying a more positive potential than +0.5 V, that was used for the unmodified electrode, had to be avoided for the maintenance of the modified surface.

Reduction of O_2 on Unmodified and Chemically Modified Gold Electrodes. Figure 5A shows the cyclic voltammogram of the air-saturated solution on the unmodified gold electrode. Two cathodic waves, with peak potentials of −0.3 and −0.8 V, respectively, were observed. The first wave corresponds to the reduction of O_2:[6,8-11]

$$O_2 + 2e^- + H_2O \longrightarrow HO_2^- + OH^- \qquad (10)$$

By comparing the results shown in Figs. 1—4 and 5A, we assigned the second wave to the direct reduction of H_2O_2 (Eq. 8) which had been generated by the O_2 reduction at the first cathodic wave (Eq. 10). On the reverse scan, an anodic wave starting at −0.15 V was observed. This was not observed when the sweep started first in the positive direction. The comparison of Figs. 1—4 and 5A also reveals that this anodic wave corresponds to the oxidation of H_2O_2.

Figure 5B shows the cyclic voltammogram of the air-saturated solution on the chemically modified gold electrode. The voltammogram is similar to that

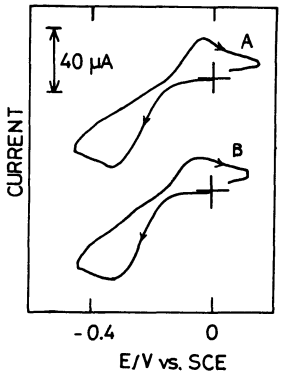

Fig. 6. Cyclic voltammograms of air-saturated aqueous solution on (A) an unmodified Au electrode and (B) a chemically modified Au electrode in the narrower potential range. Experimental conditions are the same as in Fig. 1.

recorded on the unmodified gold electrode shown in Fig. 5A. However, the ratio of the peak current of the first cathodic wave to that of the second cathodic wave, i_{p1}/i_{p2}, was slightly smaller on the chemically modified electrode shown in Fig. 5B than the ratio obtained on the unmodified one shown in Fig. 5A. On the unmodified gold electrode, the H_2O_2 generated by the O_2 reduction in the first cathodic wave (Eq. 10) was partially reduced further to H_2O by the succeeding reactions shown by the first cathodic wave in Fig. 1A (Eqs. 1, 2 or 3—5). On the other hand, since the further reactions were suppressed on the chemically modified electrode, the value of i_{p1}/i_{p2} became smaller than that on the unmodified one.

Figures 6A and 6B show the cyclic voltammograms of the air-saturated solution on the unmodified and chemically modified gold electrodes, respectively, recorded in a narrower potential region than those in Figs. 5A and 5B. The cathodic waves with a peak potential of −0.3 V indicate the reduction of O_2 to H_2O_2. On the reverse scan, the anodic waves with larger peak current than those shown in Figs. 5A and 5B were observed, since the H_2O_2 generated by the O_2 reduction at the cathodic waves (Eq. 10) was not consumed in the succeeding irreversible cathodic reaction, as is shown in Figs. 5A and 5B (Eq. 8). When the sweep started first in the positive direction, though not shown in the figures, these anodic waves were not observed on either electrode.

Figure 7 shows the disk and ring currents as a function of the disk potential for the air-saturated solution on an unmodified rotating gold ring-disk electrode. The ring potential was set at +0.16 V, where the H_2O_2 oxidation had been shown to be diffusion controlled by prior CV measurements. The current-potential curves clearly indicate that O_2 is reduced to H_2O_2 between −0.4 and −0.7 V and that O_2 is further reduced to H_2O under totally mass-transfer-limited conditions at potentials more negative than −1.0 V. A comparison of Figs. 3 and 7

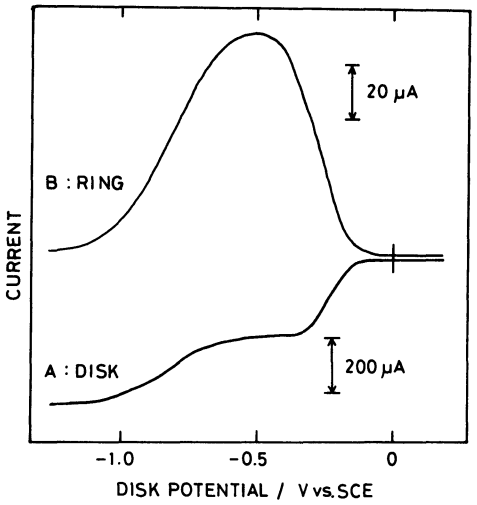

Fig. 7. (A) Current on a rotating unmodified Au disk electrode and (B) current on a rotating unmodified Au ring electrode for air-saturated aqueous solution as a function of the disk potential. Sweep rate (20 mV s^{-1}); rotation speed (3600 rpm); ring potential (0.16 V vs. SCE). Solution conditions are the same as in Fig. 1.

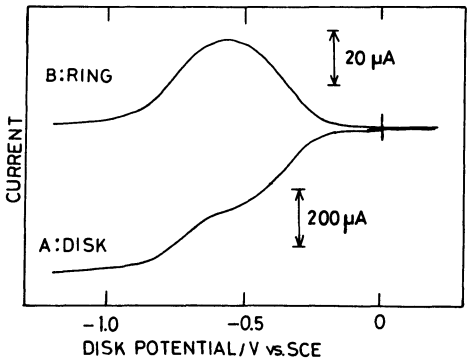

Fig. 8. (A) Current on a rotating chemically modified Au disk electrode and (B) current on a rotating chemically modified Au ring electrode for air-saturated aqueous solution as a function of the disk potential. Sweep rate (20 mV s^{-1}); rotation speed (3600 rpm); ring potential (0.10 V vs. SCE). Solution conditions are the same as in Fig. 1.

clearly shows that the potential where the H_2O_2 reduction starts is more positive than the potential where the O_2 reduction starts. This also supports the above interpretation that the intermediate of the H_2O_2 reduction between −0.2 and −0.4 V is not O_2, but adsorbed OH or O.

Figure 8 shows the disk and ring currents as a function of the disk potential for the air-saturated solution on a rotating electrode whose disk and ring electrodes had both been chemically modified. The ring potential was set at +0.1 V where the ring current reaches a plateau. In a qualitative sense, however, there was no significant difference from the result obtained on an unmodified rotating ring-disk electrode (shown in Fig. 7).

Independent Detection of H_2O_2 and O_2 on the Chemically Modified Gold Electrode. The experimental findings presented above lead to the conclusion that, on an alkylsilanized gold electrode, only oxygen can be reduced at around −0.3 V; therefore, the independent electrochemical detection of H_2O_2 and O_2 in their mixture is possible. More specifically, the concentration of H_2O_2 can be determined by its anodic or cathodic currents, and that of O_2 by its cathodic currents. Frumkin and his co-workers obtained two separate two-electron reduction waves for O_2 and H_2O_2 on an amalgamated gold electrode,[24] just as on mercury.[25] However, the use of amalgamated and other foreign-metal-adatom-modified electrodes[26] in positive potentials is limited by the dissolution of the foreign metals. In addition, the amalgamation is not suitable for modifying an optically transparent gold electrode for photoelectrochemical studies, for the stability of gold films decreases upon the amalgamation.

Figure 4B shows the ring current as a function of the disk potential for the deaerated H_2O_2 solution on a chemically modified rotating ring-disk electrode. The ring potential is set at −0.45 V, where O_2 can, but H_2O_2 cannot be reduced on the chemically modified gold electrode, as has been described above. The abrupt increase in the ring current from the residual current indicates that H_2O_2 is oxidized to O_2 at potentials more positive than −0.15 V. It should be noted that this observation is possible only on the chemically modified electrode, since, on the unmodified one, O_2 and also H_2O_2 are reduced at the potential of −0.45 V. This independent detection of O_2 is one of the most effective applications of the chemically modified electrode. In the experimental procedure of the chemical modification of the ring-disk electrode, however, the coupling solution could not be refluxed to avoid the contamination of the gold surface. The lack of refluxing sometimes causes an incomplete coverage of the electrode surface with the modifying molecules. The residual current observed at the potentials more negative than −0.15 V in Fig. 4B results from such an incompleteness, which permits the partial reduction of H_2O_2.

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