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Effects of Adsorbed Bisulfate Ion, Adsorbed Hydrogen and Surface Structure on the Oxygen Reduction at Platinum Single Crystal Electrodes

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Oxygen reduction was studied on Pt(111), Pt(100) and Pt(110) electrodes in 0.5 M H_2SO_4 and 0.1M $HClO_4$ solutions. The specific adsorption of the bisulfate ion retarded the O_2 reduction on Pt(111) and slightly on Pt(100). The adsorbed hydrogen atom did not take part in the O_2 reduction. The O_2 reduction was slow on Pt(110). Innertness of the respective electrodes in a potential range of 1.0-1.23 V was discussed in term of the specific adsorption of water molecule.

The electroreduction of oxygen is one of the most fundamental electrode reactions and receives a great interest from the point of view of water electrolysis and fuell cell. Platinum is well known as a good catalyst for the oxygen electrode reaction and a large number of works have been reported.[1)]

The present work treats with the O_2 reduction on the Pt single crystal electrodes to examine the effects of bisulfate ion, adsorbed hydrogen atom, and the surface structure. To our knowledge, the effect of the surface structure has not been studied in detail because of the surface reconstruction of the electrode at a high polarization. As will be described later, we confirmed that the low-index planes are stable under a potential sweep up to 1.2 V.

The single crystal electrodes were prepared by Clavilier's method.[2,3)] Before each measurement, the crystal was annealed in a gas + oxygen flame at ca. 600 °C for a few seconds and then quenched with Milli-Q water. The electrolytes were 0.5 M H_2SO_4 and 0.1 M $HClO_4$ solutions prepared from suprapure reagents and Mill-Q water. The electrochemical measurements were carried out by a usual potential sweep method (50 and 1 mVs^{-1}) at room temperature. All potentials in the text were referred to the reversible hydrogen electrode in the same solutions.

Figures 1-3 show the cyclic voltammograms (denoted CVs) at Pt(110), Pt(100), and Pt(111) in 0.5 M H_2SO_4 and 0.1 M $HClO_4$ saturated with Ar or O_2, respectively. These results are discussed below in terms of the surface reconstruction, effects of the adsorbed species such as bisulfate ion, hydrogen atom and water molecule, and the structure sensitiveness for the O_2 reduction reaction.

When Pt electrode is polarized in the positive direction deeply, oxygen-species are formed on the surface. Removal of the oxygen-species by negative polarization causes the surface reconstruction. Thus, the anodic polarization has been usually limited up to 1.0 V. The blank CVs up to 1.2 V in the Ar saturated 0.5 M H_2SO_4 and 0.1 M $HClO_4$ (a and b in Figs. 1-3) revealed the typical features characteristic of the respective planes and demonstrate the absence of the surface reconstruction. The low-index planes remained stable under the potential excursion up to 1.2 V. The hydrogen wave on Pt(110) (Figs. 1a and 1b) gave a sharp peak at 0.14 V in 0.5 M H_2SO_4 which has been explained due to the hydrogen atom adsorbed at the site provided from a few neighbouring Pt atoms, denoted short-range order site (S).[4] The anodic scan in 0.5 M H_2SO_4 displayed a clear peak at 1.07 V (denoted P_b) with a prepeak at 0.95 V. P_b appeared at 1.05 V in 0.1 M $HClO_4$. Figures 2a and 2b show the blank CVs on Pt(100) in 0.5 M H_2SO_4 and 0.1 M $HClO_4$. The hydrogen wave in 0.5 M H_2SO_4 revealed two clear peaks at 0.27 and 0.37 V. The latter peak has been explained due to the hydrogen atom adsorbed at the site provided on the wide terrace, denoted long-range order site (L).[4] The high anodic polarization up to 1.2 V did not reconstruct the surface in both solutions. P_b mentioned above was again noticed (Fig 2b) but to a much lesser extent. Figures 3a and 3b show the blank CVs on Pt(111) in 0.5 M H_2SO_4 and 0.1 M $HClO_4$. The hydrogen wave consisted of two parts for the weakly and strongly adsorbed hydrogens, H(w) and H(s), both being L.[4] The high anodic polarization up to 1.2 V again did not cause the surface. reconstruction. P_b was developed most clearly in 0.1 M $HClO_4$ (Fig.3b) at 1.07 V in the anodic scan but entirely absent in 0.5 M H_2SO_4 (Fig.3a). Nature of P_b is under investigation.

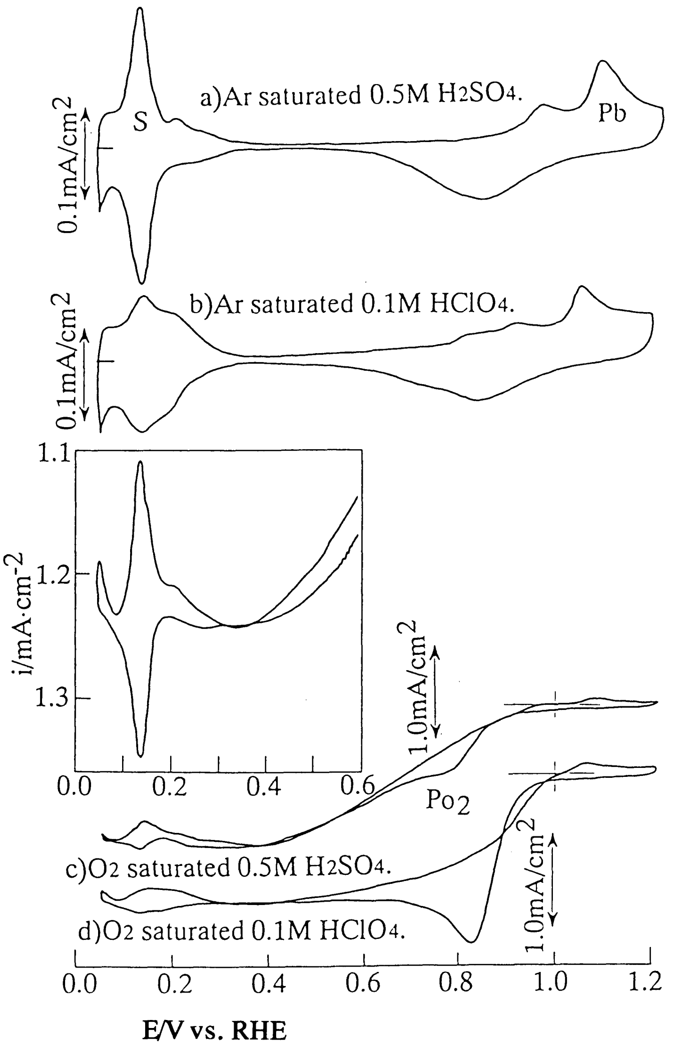

Fig.1. CVs on Pt(110). Sweep rate: 50 mVs^{-1}

This section discusses only the anodic polarization curves up to 1.2 V observed in the O_2 saturated 0.5 M H_2SO_4 and 0.1 M $HClO_4$. Results are shown in c and d of Figs.1-3. The O_2 reduction current on the respective planes reached a diffusion limiting value in the hydrogen region and decreased monotonously with a positive polarization. Above ca. 1.0 V, the O_2 reduction current became zero. The potentials at the current of a half of the limiting value(half-height potential, $E_{1/2}$) on the respective planes are summarized in Table 1.

Table 1. Half-height Potential, $E_{1/2}$ and Potential at 0.1 mA cm^{-2}, $E_{0.1}$

	$E_{1/2}$/V			$E_{0.1}$/V		
	Pt(110)	Pt(100)	Pt(111)	Pt(110)	Pt(100)	Pt(111)
0.5 M H_2SO_4	0.67	0.73	0.67	0.89	0.91	0.79
0.1 M $HClO_4$	0.87	0.83	0.86	0.89	0.93	0.92

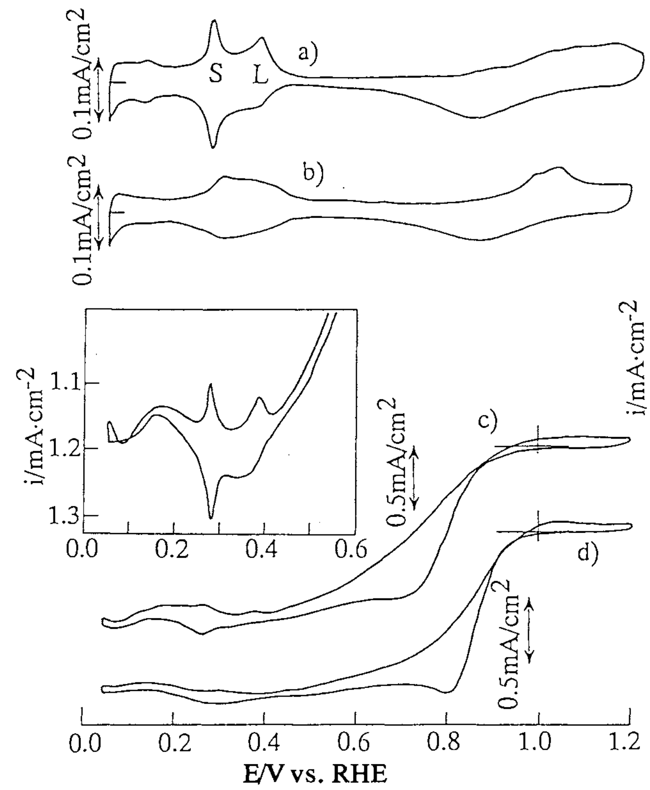

Fig.2. CVs on Pt(100). Conditions are in Fig.1.

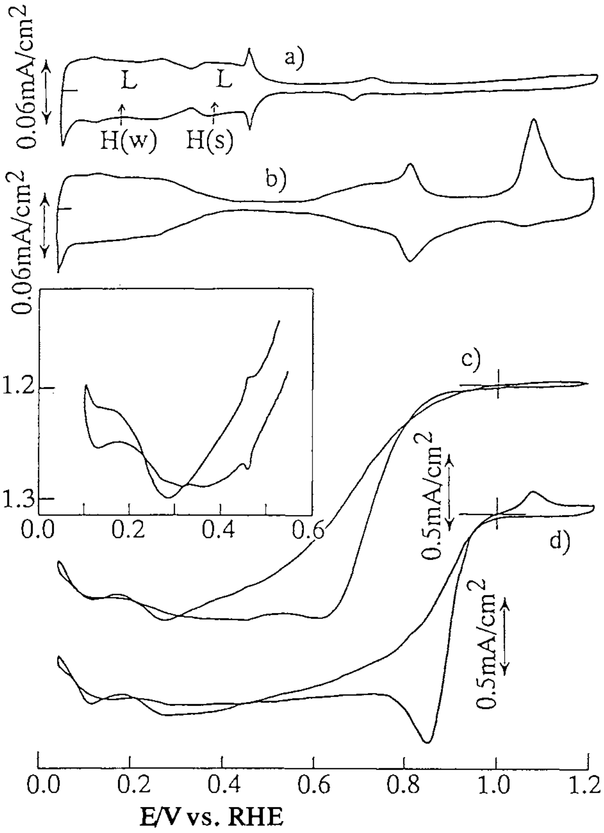

Fig.3. CVs on Pt(111). Conditions are in Fig.1.

$E_{1/2}$ in 0.1 M $HClO_4$ ranges in 0.83-0.87 V, being almost structure-independent. However, E1/2 in 0.5 M H_2SO_4 is smaller than that in 0.1 M $HClO_4$ and appears structure-dependent. The smaller value, i.e.,the slower O_2 reduction is taken due to the specific adsorption of the bisulfate ion. Recently we reported that the bisulfate ion specifically adsorbs on Pt(111) and does not on Pt(110) from the CVs for the H_2 ionization and methanol oxidation reactions.[5] The specific adsorption of the bisulfate ion on Pt(111) and to a much lesser extent on Pt(100) has been reported by Gamloa-Aldeco et al. by using a radioactive tracer method.[6] Thus, the extremely smaller value of 0.67 V on Pt(110) in 0.5 M H_2SO_4 will be attributed to another factor as will be discussed later.

Now we examine the cathodic polarization curves from 1.2 V observed in the O_2 saturated 0.5 M H_2SO_4 and 0.1 M $HClO_4$(c and d of Figs.1-3). It is interesting to note that each cathodic scan gives the O_2 reduction peak (denoted P_{O2}) before the current reaches to the limiting value. Genenally, P_{O2} is more pronounced in 0.1 M $HClO_4$ as in the case of P_b. It is, however, hard to correlate P_{O2} and P_b since P_{O2} appears even under the absence of P_b on Pt(111) in 0.5 M H_2SO_4 (Fig. 3c). The polarization above 1.0 V is the necessary condition to cause P_{O2}, since P_{O2} becomes very small or indistinguishable when the potential sweep is reversed at 1.0 V. Details will require further examination.

When the sweep rate is decreased to 1 mVs^{-1}, P_{O2} disappears and the anodic and cathodic polarization curves coinsided each other. Thus, these curves are taken as the steady polarization curves. The potentials at 0.1 mA cm^{-2} on the respective planes $E_{0.1}$ are summarized in Table 1. On Pt(110) , no difference is observed in 0.5 M H_2SO_4

and 0.1 M $HClO_4$ whereas on Pt(111) the difference is largest, 0.13 V smaller in 0.5 M H_2SO_4, in accordance with the behavior of the bisulfate specific adsorption.[5,6] The exceptionally small $E_{1/2}$ on Pt(110) in 0.5 M H_2SO_4 must be attributed to a transitional factor.

Comparison of $E_{0.1}$ in 0.1 M $HClO_4$ shows that Pt(110) is less active than Pt(100) and Pt(111) with respect to the O_2 reduction. Other structural dependences were not observed between Pt(100) and Pt(111).

The hydrogen regions of the polarization curves observed in the O_2 saturated 0.5 M H_2SO_4 (50 mVs^{-1}) are enlarged and shown just above c of Figs.1-3.

The hydrogen wave observed in the blank solution, superimposed on the O_2 reduction current in each plane except H(w) on Pt(111). This fact clearly demonstrates that the adsorbed hydrogen atom does not take part in the O_2 reduction. This conclusion contradicts the often assumed idea that the O_2 reduction proceeds via an elementary step of the adsorbed O-species + adsorbed H. It will be worthwhile to mention that the H_2 evolution reaction proceeds via the on-top hydrogen atom which is different from the adsorbed hydrogen atom giving the hydrogen wave.[7] The role of H(w) is now under investigation.

Recently we reported that the H_2 ionization and methanol oxidation reactions are greatly suppressed in a potential region above 0.9 V.[5] The same situation holds in the present O_2 reduction reaction. We conclude that these common phenomena are due to a common factor, i.e., a rigid reorientation of the water molecule at the electrode surface, so that the resulting water molecule can be precursor of the oxygen-species formed in a further high polarization.

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