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Sorption and Desorption Behaviors of Hydrogen over Very Small Palladium Particles in Perchloric Acid

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The saturated amount of adsorbed hydrogen over well defined very small palladium particles has firstly been determined by a cyclic voltammetry in an aqueous solution of $HClO_4$. The amount of absorbed hydrogen into them was also measured. The sorption and desorption behaviors over them were similar to those over palladium atoms deposited on a gold plate.

Although the adsorption behavior of hydrogen on palladium electrodes in acidic solution have been examined by many investigators, clear separation of the adsorbed hydrogen from the absorbed one has not well been succeeded.[1,2] As for the adsorbed state of hydrogen over palladium particles, on the other hand, a few investigators have examined for the electrochemically deposited palladium on gold plate electrodes.[3-5] In those papers, both the anodic and cathodic peaks for the adsorbed state of hydrogen were presented as well as that for the absorbed hydrogen; however, the shape of the "palladium particles" on the gold plate could not been characterized.

In this cyclic voltammetry study, the characteristic peaks for either adsorption and desorption of hydrogen over palladium particles embedded on a non-metallic substrate; i.e. a glassy carbon (GC), have been examined, and the shape of the palladium particles has also been characterized by a transmission electron microscopy (TEM).

Palladium particles were embedded on a glassy carbon rod (Tokai Carbon, Ltd., GC-32S, 0.53 cm in diam.) by a vacuum evaporation technique. Before the evaporation of palladium, the base of the rod was polished with a cloth and alumina powder (ca. 0.3 µm in diam.), and then washed in distilled water and acetone. The amount of palladium deposited onto the base of the glassy carbon support was determined with a quartz thickness monitor, (Anelva, EVM-32B), i.e. the amount of deposited palladium was measured as

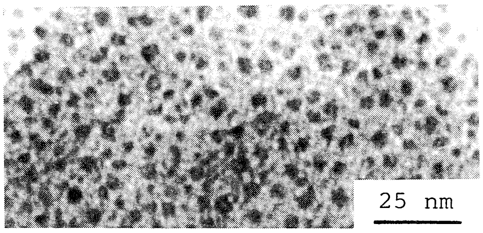

Fig.1. A transmission electron micrograph of a Pd/GC model catalyst-electrode before the electrochemical measurement. The amount of deposited palladium atoms; M = 3.5×10^{15} Pd atoms cm^{-2}. Mean diameter of the palladium particles; $\bar{d}$ = 3.2 nm. Small dark spots are the images of the palladium particles.

the mass. A typical transmission electron micrograph (TEM, JEOL, JEM-200CX, bright field) of the Pd/GC catalyst-electrode is shown in Fig.1. The main special merit of this electrode is that any effect of pore structure on the reaction process can be neglected due to the flatness of the support.6) Electrochemical measurements were carried out by using a glass beaker cell which was filled with 0.2 dm^3 of 0.1 mol dm^{-3} $HClO_4$ solution at 30 °C.

Figure 2 shows typical cyclic voltammograms for three Pd/GC and a glassy carbon electrodes under steady state. On the voltammograms, we can find four cathodic (P_{c1} — P_{c4}) and three anodic (P_{a1} — P_{a3}) peaks. P_{c1} is due to the evolution of molecular hydrogen, while P_{c4} is due to the reduction of palladium oxide formed over the top-layer of the palladium particles, probably as a form of PdO. The anodic peak P_{a1} (shoulder) seems to originate from the anodic oxidation of the

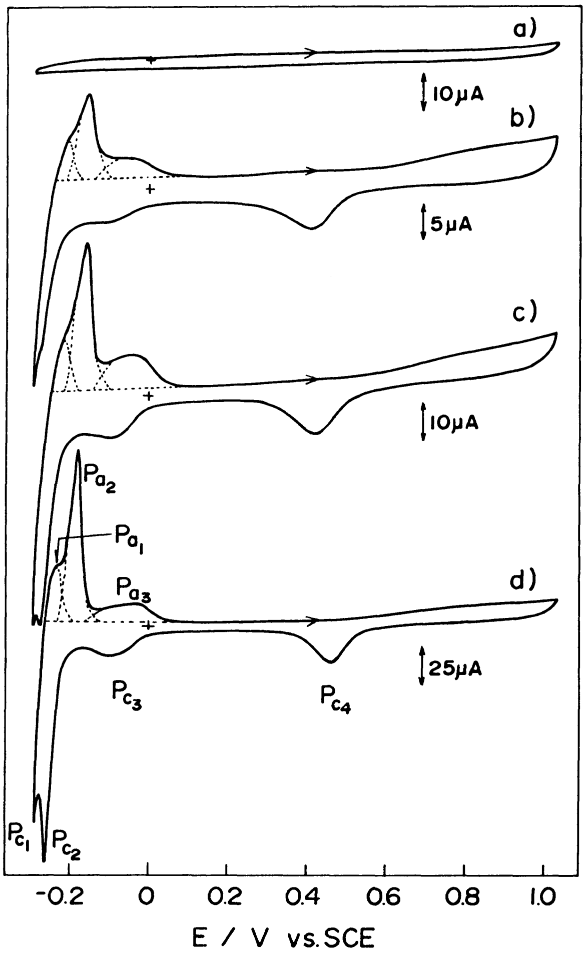

Fig.2. Steady state cyclic voltammograms for three Pd/GC and a glassy carbon electrodes.
Electrolyte : 0.1 mol dm^{-3} $HClO_4$, 30 °C. Sweep rate : 30 mV s^{-1}.
Working electrode : a) glassy carbon (geometric surface area; S_g = 0.22 cm^2), b) Pd/GC (real surface area determined by a cyclic voltammetry; S_r = 0.052 cm^2, M = 2.8 x 10^{15} Pd atoms cm^{-2}, $\bar{d}$ = 2.5 nm), c) Pd/GC (S_r = 0.15 cm^2, M = 6.9 x 10^{15} Pd atoms cm^{-2}, $\bar{d}$ = 3.8 nm), d) Pd/GC (S_r = 0.24 cm^2, M = 14 x 10^{15} Pd atoms cm^{-2}).

molecular hydrogen evolved just before the anodic sweep, while the peak might partially include the oxidation current for absorbed hydrogen. When the negative inverse potential was more negative than the potential shown in Fig.2, P_{a1} grew large and its tail extended up to the potential range of P_{a3}. In order to reveal whether the anodic peaks P_{a2} and P_{a3} are caused from adsorbed species of hydrogen or absorbed one, the amount of electricity passed for each anodic peaks are plotted in Fig.3 against the electricity used for the reduction of the adsorbed oxygen which saturated over the top-layer of the palladium particles. The determination of the latter was performed by the method reported by Wood$^{7)}$ [see in Fig.4]. It is worth noting that the amount of hydrogen atoms for P_{a3} is almost equal to that of adsorbed oxygen atoms which saturated over the palladium particles. The amount of hydrogen oxidized at P_{a2}, on the other hand, is much greater than that of oxygen saturated on the palladium particles. Thus, P_{a2} and P_{a3} can be assigned as the oxidation peaks of absorbed and adsorbed hydrogens,respectively. Our assignment for the anodic peaks essentially corresponds to those by Chevillot et al.$^{4)}$ and Shimazu and Kita,$^{5)}$ while they have used Pd/Au systems. As insisted by Shimazu and Kita, the adsorbed hydrogen can be a precursor of the absorbed hydrogen, and the absorbed hydrogen is oxidized via the adsorbed state.

Just before the anodic oxidation of absorbed hydrogen in palladium particles

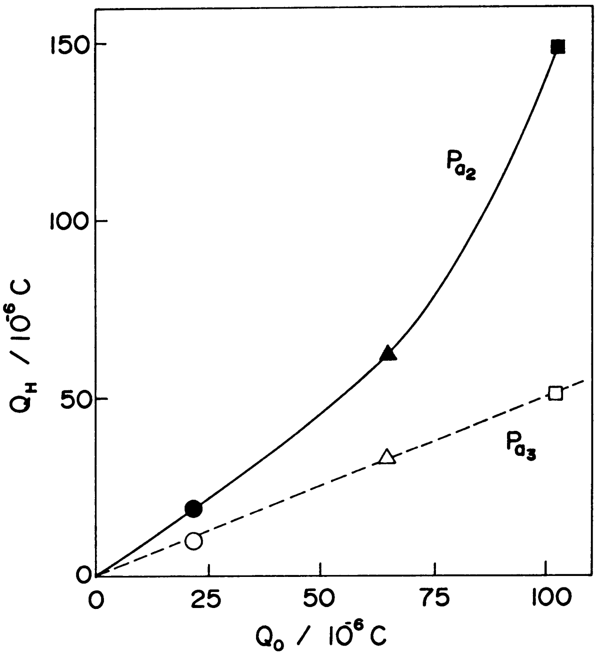

Fig.3. Relation between the amount of electricity passed for the oxidation of each peak hydrogen species, P_{a2} and P_{a3}, and that for the reduction of the adsorbed oxygen saturated on the top-layer of the palladium particles.
Experimental condition : see in the caption of Fig.2 and text.
Amount of palladium evaporated : ○, ● (M = 2.8 x 10^{15} Pd atoms cm^{-2}, $\bar{d}$ = 2.5 nm); △, ▲ (M = 6.9 x 10^{15} Pd atoms cm^{-2}, $\bar{d}$ = 3.8 nm); □, ■ (M = 14 x 10^{15} Pd atoms cm^{-2}). Q_H : amount of electricity passed for the oxidation of adsorbed hydrogen for each peaks.

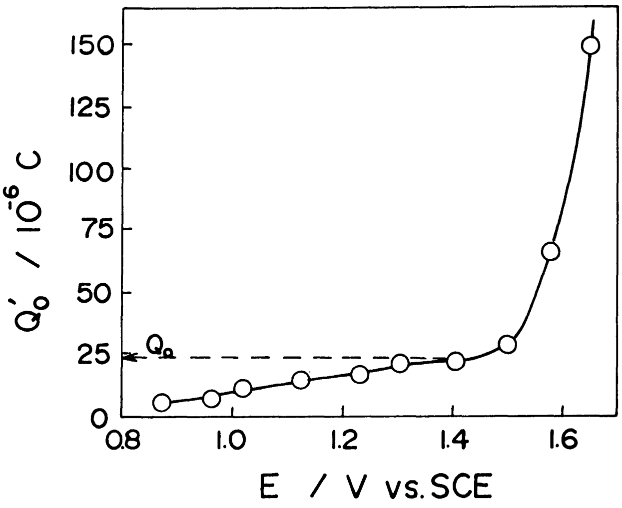

Fig.4. Determination of the amount of electricity passed for the reduction of the adsorbed oxygen saturated on the top-layer of the palladium particles.

Experimental condition : see in the caption of Fig.2. Working electrode : Pd/GC (M = 2.8 x 10^{15} Pd atoms cm^{-2}, $\bar{d}$ = 2.5 nm). Q_0' : amount of electricity passed for the reduction of the adsorbed oxygen. Q_0 : amount of electricity passed for the reduction of the adsorbed oxygen saturated on the top-layer of the palladium particles.

(P_{a2}) for each electrodes, the compositions can be presented as $PdH_{0.2}$, $PdH_{0.26}$, and $PdH_{0.3}$ for the voltammograms b), c), and d) in Fig.2, respectively. Notable effects of the size of palladium particles on the features of the voltammograms are that both the peak potentials of P_{c2} and P_{c4} shifted to the higher potential with increasing the size of palladium particles, while those of P_{a2} and P_{a3} decreased.

The observation of palladium particles after the electrochemical measurement by TEM and the effect of the electrolysis condition on the amount of absorbed hydrogen into the palladium particles are now under investigation.

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