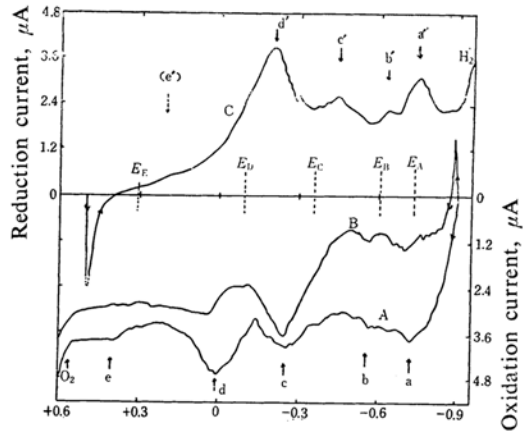

Fig. 1. Current-potential curves for a platinum electrode in 5 M KOH. A and B: oxidation curves of an electrochemically pre-reduced Pt electrode at the 1st and 3rd trials respectively from −0.9 to +0.6 V. C: reduction curve of a Pt electrode with some platinum oxides and/or hydroxides on it from +0.5 to −0.9 V.

Evidence for a Series of Redox Couples on the Surface of a Platinum Electrode and their Significance

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A series of redox couples on a platinum electrode was found by a voltammetric method as follows. A platinum electrode (approximately 0.6 cm^2 surface area) was placed in one arm of an H-cell containing 5 M potassium hydroxide solution from which air had been expelled by an inert gas. The counter electrode was Hg/HgO. The potential applied to the platinum electrode against the Hg/HgO electrode was scanned at a rate of 0.3 V. per 100 sec. from −0.9 to +0.6 V. or +0.5 to −0.9 V. and the current flow through the platinum electrode was recorded automatically. In Fig. 1 there are shown two oxidation curves for a pre-reduced platinum electrode and a reduction curve for the platinum electrode at which the oxidation curves had been taken. The presence of many peaks on these curves is evident. These peaks may not be attributed to adsorbed oxygen nor hydrogen as repeated experiments with the same electrode produced identical peaks. Peaks a, b, c, d and e on the oxidation curve may indicate the formation of five kinds of platinum oxides and/or hydroxides. The corresponding reduction peaks a′, b′, c′ and d′ can be seen on the reduction curve. The potentials (E_A, E_B, etc. in Fig. 1) between a pair of oxidation and reduction peaks can give approximate redox potentials for the redox couples. This has been verified of known redox couples such as $Ni \rightleftharpoons Ni(OH)_2$ and $Ni(OH)_2 \rightleftharpoons NiO_2$. The same experiments at a platinum electrode in 0.05 M potassium hydroxide showed also four to five peaks. The standard redox potentials in alkaline solution for the redox couples on the platinum surface were obtained from the values E_A, E_B, E_C, E_D and E_E in 5 M and 0.05 M potassium hydroxide by making correction for OH^- activity and were −0.67, −0.54, −0.25, +0.05 and (+0.3$_9$) V. vs. N. H. E. respectively.

A platinum electrode has been used to measure redox potential in solution. It is well known that the potential of a platinum electrode placed in a solution containing a redox system follows the Nernst equation. It was assumed that the platinum electrode was inert and served only as a means of transferring electrons. The present finding of a series of oxidation-reduction couples on the surface of a platinum electrode suggests a new interpretation for the behavior of a platinum electrode. When a platinum electrode is placed into a solution containing a redox system, the surface redox couples, which are probably composed of platinum oxides and/or hydroxides, are reduced or oxidized to the redox potential of the system, and the platinum electrode exhibits exactly the redox potential of the system in the solution. As the standard potentials of

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the five redox couples on the platinum surface are well distributed between the potentials of hydrogen and oxygen evolution, the potential of the platinum electrode can be kept stable at any potential depending on the redox system involved. Platinum thus can not be considered as an inert electrode as has been traditionally assumed, but rather as an active metal. Recently, existence of oxide film[1] on platinum electrodes and their important role in various electrode reactions at platinum electrode have been reported[2-5] but the redox character of these oxide films was not made clear. In addition to the new interpretation which these redox couples on platinum can give to the behavior of so-called "inert platinum electrodes", these redox couples may play an important role in the explanation of the catalytic activity of platinum in various chemical reactions.

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