Studies on Consumption of Pt Anode in Perchloric Acid Solution

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Platinum is one of the most widely used electro-catalysts not only for water electrolysis for hydrogen production but for aqueous electrochemical industry.

In general, platinum is stable but when it is used for oxygen evolution, it happens to dissolve into the electrolyte. The rate of consumption of platinum is so small, however, the amount of consumption is not disregarded for long time electrolysis. In utilizing Pt for an industrial anode material, e.g., Pt/Ti, much attention should be paid to observe the consumption rate.

In 1M sulfuric acid at 40°C, the rate of consumption of platinum anode is proportional to the first order of the current density, and the unit consumption of 5 μg A^{-1} h^{-1} was observed [1]. In this case, formation of the Pt oxide inhibits consumption of platinum anode.

On the other hand, extraordinary consumption of Pt was observed in phosphoric acid solution [2]. In 30-70wt% phosphoric acid, platinum dissolved at the consumption rate of 19 μgcm^{-2}h^{-1} at 1 Acm^{-2}, 40°C, while, in 85wt% phosphoric acid, the rate increased to 0.91 mgcm^{-2}h^{-1} at the same current density and temperature. It is 180 times larger than in 1M sulfuric acid under the condition. In diluted phosphoric acid, the platinum surface was covered with the oxide layer and it was suggested that the corrosion was protected by the oxide layer.

In perchloric acid solutions, the same situation was indicated. Figure 1 shows the relationship between the consumption rate and temperature in perchloric acid of various concentrations. In the case of concentrated solutions, such as 4M and 8M, the rate of consumption increased with increase of the temperature. This tendency is often observed in general chemical reaction. While, in the lower concentrated solutions, like 1M and 2M, the rate of consumption decreased with increase of temperature.

Figure 2 shows the linear sweep voltammogram to negative potential after holding Pt electrode at each potential for 30 min. This figure indicates that there are two types of Pt oxide on the surface of Pt electrode. These oxides are called α and β oxide. The α oxide is formed under mild anodic conditions and reduced under wide potential range of 0.3~0.8V vs. RHE. The coverage of α oxide is limited to 2-2.2. On the other hand, the oxide reduced in the more negative narrow potential range is called β oxide. The β oxide grows very slowly under vigorous oxygen evolution conditions and would protect Pt from corrosion. The magnitude and the reduction potential of the β oxide depends on the time and the potential where the electrode is held.

Figure 3 shows the relation between the operated electrode potential and the region of corrosion and passivation of Pt and pH. Closed points show that the Pt surface is covered with Pt oxide, and Pt is protected from corrosion. On the other hand, open points indicate that there is no oxide layer on Pt, leading to easy corrosion.

In the diluted perchloric acid solutions, platinum surface is bare at low temperature, i.e., 30°C and 40°C, and the rate of consumption is rather large. However at the elevated temperature, the surface is covered with multilayered β oxide and the corrosion is protected. However in the concentrated perchloric acid, such oxide layer may be removed by the acid before accumulation and the corrosion would take place.
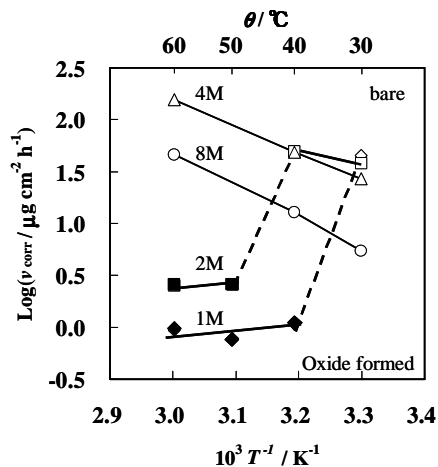

Fig.1. Dependence of consumption rate of Pt anode on temperature under electrolysis at 1Acm^{-2} in perchloric acid.
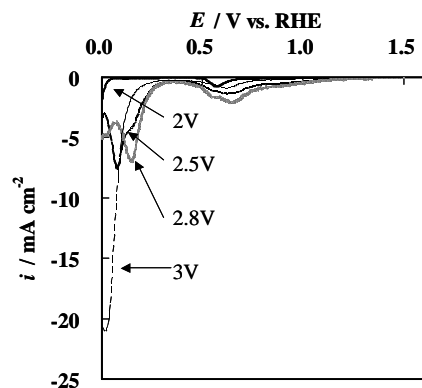

Fig.2. Linear sweep voltammograms on Pt after holding at 2-3V for 30min. in perchloric acid.

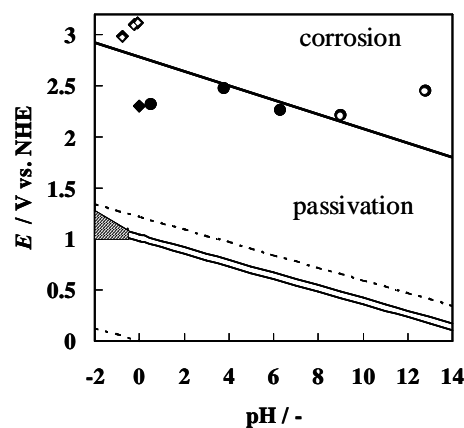Fig. 3. Potential-pH equilibrium diagram for the system platinum- water at 40°C and the region of corrosion and passivation.

[1] K. Ota et al, *J Electroanal. Chem.*, **257**, 205 (1988).
[2] N. Kamiya et al, *DENKI KAGAKU*, **65**, 1074 (1997).