Consumption of Pt Anode in Phosphoric Acid

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Consumption of Pt anode was investigated in phosphoric acid of various concentration. In 30~70wt% phosphoric acid, Pt dissolved at the rate of $19 \mu\text{gcm}^{-2}\text{h}^{-1}$. On the other hand, in 85 wt% phosphoric acid, the amount increased to $0.91 \text{mgcm}^{-2}\text{h}^{-1}$ which is ca. 180 and 1800 times as much as in 1M sulfuric acid and 1M alkaline solution, respectively.

In the diluted phosphoric acid solution, the Pt surface was covered with Pt oxides during the electrolysis, which would prevent the surface from corrosion. However, in the concentrated phosphoric acid, no such oxide surface was observed. Concentrated phosphoric acid might form stable complex with Pt species, therefore the uncovered bare Pt surface is situated in the serious corrosion condition under the high overvoltage and Pt would dissolve into the solution directly instead of forming the Pt oxides.

1 INTRODUCTION

Among various kinds of fuel cells that have been studied and developed hitherto, the phosphoric acid fuel cell would be most promising and has now widely been tested for commercial use¹⁾. However, in the course of commercialization, far more longer life time and lower cost are desired. One reason that lowers the cell life time and characteristics is the reduction of the surface area of the catalyst under the corrosion of the supporting carbon materials. Under the operation of the phosphoric acid fuel cell, Pt catalyst dissolves into the electrolyte and the dissolved Pt species deposits or moves on the surface of the electrode. Therefore, the size of the Pt particles grows larger and the specific surface area decreases²⁾.

Consumption of Pt anode in sulfuric acid aqueous solution was reported³⁾ and the characteristics of the Pt species were well studied⁴⁾. On the contrary, there has been few data reported on the corrosion in the phosphoric acid aqueous solution^{2,5)}.

From this point of view, consumption of Pt anode in the phosphoric acid media has been studied and the

mechanism of dissolution was discussed. From these data, the characteristic of Pt anode in the concentrated phosphoric acid can be deduced.

2 EXPERIMENTAL

Platinum wires of which diameter and geometric surface area were 0.3mm and 1cm^2 , respectively, were wound in a coil shape and served for anodic electrolyses. The test Pt electrode was hung up on a Pt electrode holder and after the electrolyses, the electrode was detached from the holder. The used Pt wires were often used repeatedly unless their surface were seriously corroded. Although the surface of a new platinum wire is smooth, it becomes rather rough by the electrolysis. Therefore, before each electrolysis, both new and used wires were dipped in a hot aqua regia solution for 30 sec in order to keep the surface condition constant. The dipping treatment made the surface of both samples to be the same and the roughness factor was around 2.

Junsei Chemical Co.'s analytical grade 97wt% sulfuric acid and guaranteed reagent grade 85wt% phosphoric acid were dissolved in ultra pure water that passed through a Millipore filter and were served for electrolyses. The electrolyte was deaerated by passing N_2 gas through the solution and the electrolyses were performed under the agitated condition. The temperature was kept constant in a water bath to be

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40°C. The consumption of the electrodes was examined under the constant current electrolysis. The amount of the consumed Pt was determined by weighing the electrode before and after the electrolysis on a semimicrobalance. Here the consumption of Pt was considered to occur due to two ways, i.e., one is to dissolve into the electrolyte as ions or complexes and another is to degrade as the highly oxidized platinum oxide (this oxide is called the Pt oxide hereafter). This oxide is soluble in a hot hydrochloric acid. In this case, the amount of Pt in the Pt oxide was determined by a dithizone-benzene method^{6,7}.

The overvoltage of the electrodes for Tafel's plots was obtained by using a current interrupting method in order to eliminate the IR drop.

3 RESULTS AND DISCUSSION

3.1 Voltammograms of Pt in various concentration of H_3PO_4

Figure 1 shows the voltammograms of Pt in 1M H_2SO_4 (a), and 30 (b) and 85wt% (c) of phosphoric acid solution. In the diluted phosphoric acid solution, i.e., 30 wt.%, the voltammogram is almost the same as that observed in 1M sulfuric acid solution. The shape of the voltammograms taken at 50 and 70wt% is also the same as that of 30 wt%. The quantity of electricity for hydrogen adsorption and desorption in the lower potential region, is nearly the same as in other solutions at different concentration. However, the quantity of electricity for the oxygen adsorption (or formation of PtO) at 0.8-1.5 V vs. RHE and the reduction at 0.9-0.7V, decreases with the increase of the concentration as shown in Fig. 1. Figure 2 shows the dependence of the charge for formation and reduction of PtO as well as the charge for desorption of H_{ad} on the concentration of phosphoric acid. In this figure, the vertical axis indicates the ratio of the charge at each concentration to that in 30wt% solution. From the charge for hydrogen desorption from Pt surface taken at 1M H_2SO_4 solution, the roughness factor (R.F.) of the surface was determined to be 2.31. In 30wt% solution, the charge for desorption of hydrogen was nearly the same as that obtained in 1M H_2SO_4 . From Fig. 2, it is shown that the quantity of electricity for desorption of H_{ad} does not change much with increase of the concentration. Opposite to the small change for H_{ad} , the charge for formation and reduction of PtO decreases much with increase of the concentration. Hydrogen adsorption

Fig.1 Voltammograms of Pt in H_2SO_4 and H_3PO_4 solution.

(a) 1M H_2SO_4 , (b) 30wt% H_3PO_4 , (c) 85wt% H_3PO_4

Fig. 2 Relation between the ratio of the quantity of electricity for desorption of H_{ad} and formation of PtO and conc. of H_3PO_4 .

and desorption on Pt surface would take place rapidly. On the other hand, the formation and reduction of PtO would occur slowly and therefore the quantity of electricity for the reaction largely depends on the amount of water molecules. Counting the charge for formation of PtO in 1M H₂SO₄ to be 1, the value is 0.96 and 0.75 in 30 and 85 wt% H₃PO₄, respectively.

3.2 Consumption of Pt with time, V_{corr}

Figure 3 shows the amount of consumption of Pt with time in 60 and 85 wt% H₃PO₄ solutions. The amount of consumption increased with time and the relation is in the first order. From the data, the rate of consumption, V_{corr} can be obtained by deviding the amount of consumption by time.

$$V_{\text{corr}} = (\text{the amount of consumption}) / t \quad (1)$$

The rate in the 60 wt% solution is almost the same order of the one obtained in 1M H₂SO₄ solution³⁾. However, the value is extraordinary larger in the 85 wt% solution.

Fig. 3 Relation between weight loss and time at 40 °C, 1Acm².

3.3 Consumption of Pt at different concentration of H₃PO₄

Figure 4 shows the consumption in 30-85wt% phosphoric acid under the electrolysis at 1Acm⁻² for 40h. At the concentration of less than 70wt%, the amount of consumption was as small as in the sulfuric acid solution as shown above and the red brown Pt oxide was found on the surface of the electrodes. Figure 5 shows a SEM photograph of the Pt surface

Fig. 4 Relation between weight loss and concentration of phosphoric acid after electrolysis for 40h at 40 °C, 1Acm².

Fig. 5 SEM photograph of Pt surface after electrolysis for 50h in 30wt% phosphoric acid at 1Acm².

taken under electrolysis for 40h in the 30wt% H₃PO₄. It looks like the dried mud swamp and the shingle shaped pieces was partially stripped. These oxide pieces were soluble in the hot HCl solution and the amount of the Pt included in the oxide was determined by the spectroscopic method. The amount of Pt in the Pt oxide was about 60% in the total amount of consumption.

The amount of consumption increased urgently as the concentration was raised higher than 70wt%. On the contrary, the amount of Pt oxide became smaller with increase of the concentration and no Pt oxide was observed in 85wt% solution. In the lower concentration than 70wt%, the oxide layer would take

part in to protect the surface from corrosion. In the concentrated phosphoric acid solution, however, the bare Pt surface is faced to the severe corrosive condition. In this case, the amount of Pt consumption reached as much as 30mgcm^{-2} . After 40h electrolysis in 85wt% H_3PO_4 , the electrode got clearly thinner and the solution was contaminated with black particles. First stage of the corrosion would be dissolution into the solution as ions or soluble complexes. The Pt ions-phosphate complex and its solubility are at the present time unknown. Although the discussion is not beyond the speculation, the first stage of the corrosion should be caused by the high solubility of Pt ions or their complexes.

As shown in the above voltammograms, the electricity for PtO formation decreased with increase of the concentration of phosphoric acid. This decrease would be due to the decrease of the amount of free water molecules. The formation of PtO that is shown in the voltammograms in Fig.1 is just the absorption of oxygen onto the surface of Pt and this layer should be one or two layers from the calculation of electricity. In the prolonged electrolysis, the multilayer, highly oxidized Pt oxide would form if the enough water molecules are present on the Pt surface. In the concentrated H_3PO_4 , the formation of the oxide layer would be retarded by lack of water molecules.

In the diluted sulfuric acid solution, the Pt oxide layer was also found^{8,9)} under the same electrolysis as shown above. However, when the electrolysis was carried out in the sulfuric acid solution that includes a small amount of organic materials, such as acetonitrile, the oxide layer was not observed⁹⁾. And the amount of the consumption was extraordinary raised¹⁰⁾ just as in the concentrated phosphoric acid (Table 1). When the surface of Pt is not covered with protective oxide, the bare Pt surface would be faced to the severe corroding condition. Like in the case of the concentrated phosphoric acid, the first stage of the corrosion should be forming and dissolution of Pt ions or soluble Pt complex rather than forming the Pt oxide layer. In the presence of acetonitrile, cyanide ion was formed by the electrolysis⁹⁾. Cyanide ion is a good complexing ligand and would take part in the acceleration of the consumption of Pt. Table 1 shows the rate of consumption, V_{corr} of Pt anode in the various electrolytes. In 85wt% H_3PO_4 solution, no such acceleration by acetonitrile was observed. Once the Pt surface is uncovered with protective Pt oxide layer, the formation and dissolution of Pt ions would

Table 1 Rate of consumption (V_{corr}) of Pt anode in various electrolytes at 1Acm^{-2} , 40°C .

Electrolyte	$V_{\text{corr}}/\mu\text{gcm}^{-2}\text{h}^{-1}$
85Wt% H_3PO_4	910
85Wt% H_3PO_4 +0.5M CH_3CN	740
30Wt% H_3PO_4	19
1M H_2SO_4	5
1M H_2SO_4 +1M CH_3CN	750
1M NaOH	0.5
1M NaOH+1M CH_3CN	780

proceed fast. The effect of acetonitrile was also observed in alkaline solution such as NaOH solution. The discussion shall be made in another report later.

Figure 6 shows the amount of consumption of Pt in 85wt% phosphoric acid with time up to 120h. It increased with time almost linearly. The rate of consumption, i.e., the amount of consumption divided by time, V_{corr} at 20 to 50h after the start of electrolysis was $0.91\text{mgcm}^{-2}\text{h}^{-1}$. However, the precise observation showed the rate of consumption at the start of electrolysis was slightly larger than that observed at the steady state (after ca. 20h). In this initial stage, the bright surface of Pt became gradually rough. And the rate of consumption gradually

Fig.6 Relation between weight loss and time at 40°C , 1Acm^{-2} in 85wt% H_3PO_4 .

decreased with time after 60h. In this stage, the total amount of consumed Pt reached to about 1/3 of the initial Pt weight. Since the geometrical surface area is related to the square root of the weight, the change of weight at the shorter time period is small and does not give serious effect on the corrosion mechanism. However, after 60h, the weight change was huge and the geometrical surface area should have been smaller than that of the initial stage by 20% and also the solution was contaminated with dissolved Pt species. The consumption curve may not be elucidated with the simple mechanism.

3.4 Dependence of Pt consumption on the current density

The V_{corr} observed in the 30wt% phosphoric acid, 1M sulfuric acid and 1M NaOH solutions¹¹⁾ was summarized in Table 1. The value in 85wt% is about 180 times as large as the one in sulfuric acid solution, and 1800times larger than the one in NaOH solution.

Figure 7 shows the consumption in 85wt% at the current density of 0.2, 0.4, 0.6, 0.8 and 1Acm^{-2} up to 50h. The V_{corr} was obtained between 20 and 50h. The relation between V_{corr} and the current density was plotted in Fig. 8. The V_{corr} was small under the small current density but it increased gradually when the current density was raised to 0.6Acm^{-2} and V_{corr} got a linear relation to the current density. Assuming all the data fall on the linear relation except at the low current density, the unit consumption of Pt anode, i.e., U_{corr} can be obtained by dividing V_{corr} by current density. The U_{corr} of $910\mu\text{A}^{-1}\text{h}^{-1}$ was obtained. This value is

Fig. 7 Relation between weight loss and time at various current densities.

Fig. 8 Average rate of consumption of Pt anode in 85 wt% phosphoric acid between 20 and 50h.

density operated at the high current density. The mechanism of consumption at the high current density may be different from those at the low current density.

3.5 Tafel's plots

Figure 9 shows the Tafel's plots of Pt anode in 30 and 85wt% phosphoric acid solution. Under the current density of less than 0.1Acm^{-2} , the slopes for both concentration are almost the same and the Tafel's coefficient is about 120mV that is larger than that obtained in sulfuric acid solution³⁾ i.e., 90mV and the mechanism in this case may be different from that in sulfuric acid solution. The number of electrons in the

Fig. 9 Tafel plots of Pt anode in 30 and 85 wt% phosphoric acid at 40°C.

rate determining step and the transfer coefficient would be 1 and 0.5 are expected, respectively. In 85wt% phosphoric acid solution, the slope extremely increased under the current density of larger than 0.1 A cm^{-2} . The slope is too large to be elucidated by the general charge transfer mechanism. This may be due to the insufficient water transfer in the 85wt% solution under the higher current density.

As shown in Fig. 8, the linear relation between V_{corr} and i (current density) was assumed and from these data, the following equation was derived.

$$V_{\text{corr}} = k i \quad (2)$$

where k is the constant and in this case, k is nearly equally to 1. Utilizing this equation, the relation between the potential, E and the current density, i can be replaced by

$$E = 2.49 + 0.118 \log V_{\text{corr}} \quad (3)$$

for the lower current density region in 85wt% phosphoric acid solution and

$$E = 3.44 + 1.06 \log V_{\text{corr}} \quad (4)$$

for the higher current density region.

If the U_{corr} is constant, the time for consumption of 1 mg Pt should be $1/V_{\text{corr}}$. Therefore, from the equations (3) and (4), the time can be determined. These relations may not be applied directly to the actual case for the fuel cell electrodes or other corrosion mechanism. Anyhow, if the Pt is placed under a certain potential the V_{corr} would be derived by the above relationship.

4 CONCLUSION

In the phosphoric acid solution of which concentration is lower than 70wt%, the Pt anode was protected by the Pt oxide that formed on the surface under the long time electrolysis and the amount of degraded Pt was as little as in the sulfuric acid solution. However, as the concentration was raised higher than 70wt%, the oxide layer becomes thinner and the amount of dissolution of Pt increased rapidly. This enormous dissolution would be due to the large solubility product of the complex between the

dissolved Pt ion species and phosphoric acid ligand, and therefore, it would be difficult to form the protective oxide layer on the surface of the Pt anode. The rate of corrosion, V_{corr} of Pt anode in the concentrated phosphoric acid solution, was $0.91 \text{ mg cm}^{-2} \text{ h}^{-1}$ and this value was 180 and 1800 times as large as in the 1M sulfuric acid and 1M alkaline solutions.

The operating condition of the cathode in the practical phosphoric fuel cell is a little different from those in this experiment. However, the extrapolation of the data, e.g., Tafel's plots, to the practically operated condition, would be helpful to clear the mechanism of the degradation of the Pt catalyst.

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