The Activation of Platinum Electrodes by Preoxidation

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It is well-known[1-11] that the activity of a bright platinum electrode is markedly increased by anodic polarization followed by cathodic polarization. To account for the mechanism of this phenomenon, two theories, the impurity theory[4-7] and the oxidation theory[3,8-12], have been proposed. According to the former theory, the activation is due to the removal of the impurities which have been poisoning the electrode. Indeed, some kinds of impurities, even in very small amounts, poison the platinum electrode considerably[13]. On the other hand, the latter theory attributes the increase in activity to the change of nature of the surface itself caused by the successive formation and reduction of superficial oxide layers.

The present work attemps to elucidate this phenomenon by studying the effects of the conditions of the preoxidation on the decay of the activity.

Experimental

As the test electrodes, a number of square-shaped pieces having an apparent area of 1 cm² were cut out of one large plate of bright platinum. Each piece was welded to one end of a fine platinum wire, and the other end of this wire was sealed into a glass tube. The electrodes were cleaned successively with hot concentrated hydrochloric acid, hot concentrated nitric acid, and hot chromic acid and washed with distilled water. Then, after being reduced by cathodic polarization in a sulfuric acid solution, they were aged in a hydrogen atomosphere at room temperature for two weeks.

The electrolyte was 1 N hydrochloric acid for the measurement of the hydrogen overpotential and 1 N sulfuric acid for that of the anodic activation. These electrolytes were prepared from, respectively, water and hydrochloric acid, each distilled carefully several times with a quartz still, and from sulfuric acid distilled twice under reduced pressure. Hydrogen gas was prepared by the electrolysis of a sodium hydroxide solution, and it was freed from oxygen by passage through a column of palladium asbestos. The electrodes were activated by either of the two methods, i. e, the anodic polarization with a 0.1 amp./cm² current for 0.25, 1 or 28 hr. or soaking in a chromic acid solution at 80±2°C for 1, 15 or 60 min. The electrodes thus oxidized were washed repeatedly with conductivity water, reduced by cathodic polarization with a 20 mamp./cm² current for 200 sec., and then introduced into the cell containing the electrolyte saturated with the hydrogen. After the electrode had thus been let alone for a definite time at open circuit, the hydrogen overpotential was measured in the usual manner against the c. d. in order to determine the activity.

The amount of platinum oxide formed by the anodic polarization or by the soaking in the chromic acid was determined by means of chronopotentiometry with another cell with the electrolyte which was freed from oxyen by passing nitrogen gas of 99.99% purity.

The cells for the measurement of the overpotential and for the chronopotentiometry were of all-glass construction, with anode and cathode compartments separated by a fritted-glass disk, and each was equipped with a gas inlet tube. The reference electrode was a saturated calomel electrode in both cases.

All measurements were carried out in a thermostat of 15±0.1°C. All potentials quoted are on the hydrogen scale.

Results and Discussion

The relation between the c. d., i, and the hydrogen overpotential, η, may be expressed as follows[8,13]:

$$i=i_{\mathrm{k}}-i_{\mathrm{a}}=k'\mathrm{e}^{-b'\eta}-k'\mathrm{e}^{+b''\eta}$$

where i_{k} is the cathodic c. d. and i_{a}, the anodic c. d.

When the value of η is sufficiently small,

$$i=-k'(b'+b'')\eta$$

Since k', b' and b'' are constants for a given electrode, a linear relation should then hold between η and i. The slope, $\mathrm{d}i/\mathrm{d}\eta$, of this straight line is proportional to k' and may be

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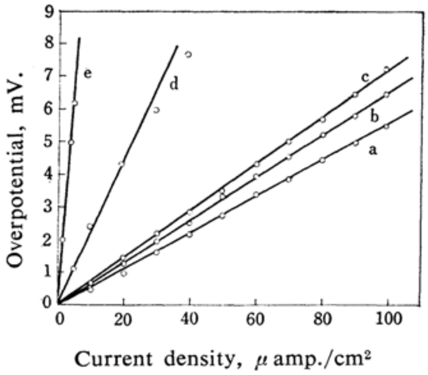

Fig. 1. Hydrogen overpotential against c. d. curves of the electrode activated by anodic prepolarization with 0.1 amp./cm² for 1 hr.

a : Immediatly after the activation
b : After standing for 3 hr.
c : 4 hr. d : 7.5 hr. e : 10 hr.

taken as a measure of the activity of the electrode[8,13]. Typical overpotential-c. d. curves for the electrode activated by means of the anodic polarization are shown in Fig. 1. It may be seen in this figure that the activity decreases with an increase in the aging time. The electrodes have almost identical activity immediately after the activation, irrespective of the pretreatment. However the rate of decay of the activity differed according to the method of pretreatment. Furthermore, in both cases the longer the pretreatment, the slower the decay, as is seen in Fig. 2. If the deactivation or the activation was caused only by either the adsorption or the desorption of the trace of impurities contained in the electrolyte, the rate of decay of the activity would be the same, irrespective of the method of activation. At any rate, it may be inferred from the above experimental facts that the surface texture, depending on the condition of preoxidation, is one of the most important factors determining the behavior of the electrode with regard to the activity. It would be reasonable to postulate that the surface texture of the electrode should be changed by the preoxidation, since the electrode surface is visibly "coarsened" when it is repeatedly oxidized and subsequently reduced, as in the case of the alternating current electrolysis[14,15].

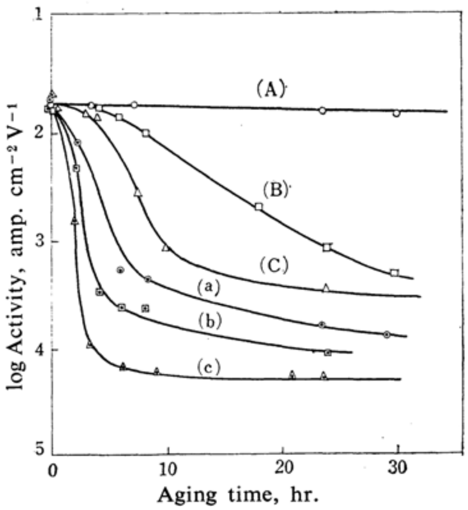

Fig. 2. Time-decay curves of activity.

(A), (B) and (C). For the electrode activated by anodic prepolarization with 0.1 amp./cm² current in 1 N H_2SO_4 for 28, 1 and 0.25 hr. respectively.

(a), (b) and (c). For the electrode activated by pretreatment of chromic acid for 60, 15 and 1 min. respectively.

When the electrodes were treated with the chromic acid solution, the amount of platinum oxide formed on the surfaces increased with an increase in the periods of soaking in the solution, as may be seen in Fig. 3. The electrode pretreated anoidically reveals, on the other hand, two rests on the chronopotentiogram (Fig. 4.). The amount of oxide reduced at the potential of the first rest is slightly more than that on the electrode pretreated with the chromic acid. The second rest did not appear until the electrode had beeen preliminarily anodically polarized for a sufficiently long time,

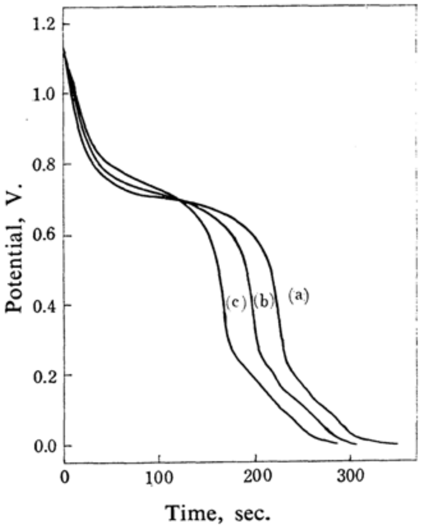

Fig. 3. Cathodic chronopotentiograms for the pretreated with chromic acid for (a) 60, (b) 15 and (c) 1 min. respectively.
$i = 10$ μamp./cm².

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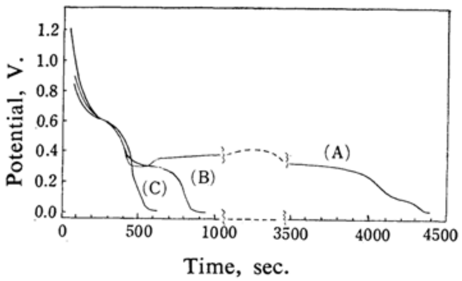

Fig. 4. Cathodic chronopotentiograms for the electrode anodically polarized with 0.1 amp./cm^2 current in 1 N H_2SO_4 for (A) 28, (B) 1 and (C) 0.25 hr. respectively, $i=10$ μamp./cm^2.

and the amount of oxide reduced at the potential increased steeply with an increase in the time of the anodic polarization.

The above experimental facts lead the present author to the following hypothesis: as the electrode is oxidized and then reduced, there is formed a very thin layer of unstable atoms, such as a freshly electrodeposited platinum, a layer which has high activity associated with a small crystallization rate[12,16]. The activity decays as the unstable active structure gradually settles down into a more stable state or as, in other words, a sort of recovery takes place in the superficial portion. It would take a long time for a thick activated layer resulting from a thick oxidized layer to recover. It is possible that the electrode is turned so as to be scarcely poisoned at all by the structure change resulting from the preoxidation. In any case, however, it is a reasonable to assume that the structural change itself plays an important part in the activation process.

Summary

The decay of the activity of bright platinum electrodes activated by means both of electrolytic and chemical preoxidations have been studied under a hydrogen atmosphere.

The life of the activity has been shown to depend upon the extent of the oxidation of the surface in the pretreatment. The structural change of surfare caused by the preoxidation appears to be responsibe for the enhanced activity.

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