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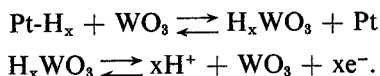
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To develop a new electrode material in the hydrogen electrode reaction, minute amounts of platinum have been doped into tungsten and tungsten (VI) oxide by platinum plating followed by a heat-treatment. In this way electrocatalytic activity similar to that of platinum electrode in the hydrogen electrode reaction was obtained with the electrode loaded with relatively thick platinum followed by heat-treatment at 500°C. For the platinum doped tungsten or tungsten oxide electrode treated at above 500°C, however, no enhancement of the electrocatalytic activity was observed.

1. Introduction

Platinum has been known as a best material for the electrocatalyst in the electrolysis of water and also in the hydrogen-oxygen fuel cell. Because of high cost of platinum, there have been many attempts to develop the new electrode materials in which the least quantities of platinum is required. In this respect, an electrode material produced by an addition of minute amounts of platinum into tungsten or tungsten (VI) oxide has been proposed as an effective electrocatalyst for the hydrogen electrode reaction¹⁾⁻⁵⁾. Hobbs and Tseung²⁾ discussed the high performance of platinum doped tungsten (VI) oxide electrode in the hydrogen electrode reactions assuming a 'bronze route' mechanism. The proposed mechanism is as follows:



Randin et al.^{3,4)} also discussed the bronze route mechanism similar to that of Hobbs and Tseung.

In this study, minute amounts of platinum have been doped into tungsten or tungsten (VI) oxide by platinum plating followed by a heat-treatment. The effects of platinum doping on the electrocatalytic activities of the electrodes were studied for the hydrogen electrode reaction by means of the potentiostatic method.

2. Experimental

2.1 Pretreatment and anodization of tungsten substrate

Tungsten rods (1.5 mm ϕ) used as a substrate were mechanically polished successively with finer grain emery papers (#0, 3, and 5), and then treated by electrolytic dissolution process in 10% NaOH solution at 0.1 Acm⁻² for 1 min. Some of tungsten rods were anodized prior to the platinum plating. Anodization was carried out in

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0.4 M KNO_3 -0.04 M HNO_3 solution at room temperature by applying a constant voltage across the tungsten rod anode and graphite cathode. When a constant voltage was supplied, anodic oxygen evolution took place at the tungsten electrode in the initial stage and it gradually decreased due to the formation of semiconducting oxide layer on the tungsten surface. The current through the circuit fell down to a constant value less than 0.1 mAcm^{-2} , indicating that the thickness of oxide layer approached a limiting value. Tungsten (VI) oxide film thus obtained gave a definite thickness, and showed a characteristic interference color depending on the applied voltage. At an applied voltage of 10, 25 or 50 V, for example, tungsten surface colored light brown, blue and pale green, respectively. The thickness (δ) of the film with the applied voltage (V) gave a linear relationship as shown below⁶⁾:

$$\delta = 1.86 V + 4.03 \quad (\text{nm}).$$

Oxide films formed in this manner are known to be non-crystalline structure.

2.2 Platinum plating

10 gdm^{-3} hexachloroplatinic (IV) acid solution at 25°C was used as a platinum plating bath. The anode was two sheets of platinum plate. Tungsten or tungsten (VI) oxide rod prepared by the procedure stated above was used as a substrate of platinum plating. Platinum plating was carried out at a current density of 0.5 mAcm^{-2} . Current efficiency of the platinum plating in this bath varied widely with the plating condition, but it may be assumed to be about 50% in the electrolysis at the low current densities. The deposit thickness was controlled by changing the plating time, and the thickness estimated for 60 s (30 mC) plating was about 3.5 nm.

In order to diffuse platinum into the substrate, platinum plated tungsten or tungsten oxide were heat-treated at the different temperatures from 400° to 800°C for 30 min in vacuo.

2.3 Electrochemical measurement

Platinum plated tungsten rod (10 mm lengths) was sealed in a polyethylene tube so as to expose 0.49 cm^2 as a working electrode. This type of electrode was placed in a conventional H-type cell. A saturated calomel electrode (SCE) was used as a reference electrode, and platinum mesh electrodes were used as an anode. Electrochemical measurement was carried out in $0.5 \text{ M H}_2\text{SO}_4$ solution at 25°C . Electrolyte was prepared from extra pure sulfuric acid and doubly distilled water. Current-potential curves were measured by the potentiodynamic method with a slow sweep rate (50 mVmin^{-1}) in the electrolyte saturated with hydrogen gas. Potentiodynamic measurement with more rapid sweep rate (250 mVmin^{-1}) in the potential range between -0.25 and $+1.5 \text{ V}$ vs. SCE was also carried out to determine the effects of heat-treatment and anodic pre-anodization of substrate.

3. Results and Discussion

3.1 Cyclic voltammetry

Figure 1 shows the voltammograms measured with platinum, tungsten and

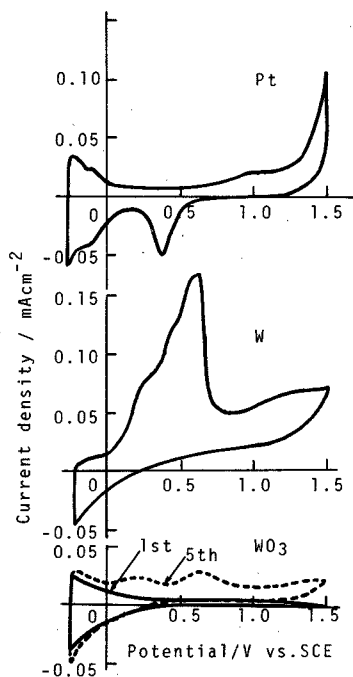


Fig. 1 Cyclic voltammograms obtained with platinum, tungsten or tungsten oxide electrodes in nitrogen saturated 0.5 M H_2SO_4 (Sweep rate: 250mVmin^{-1})

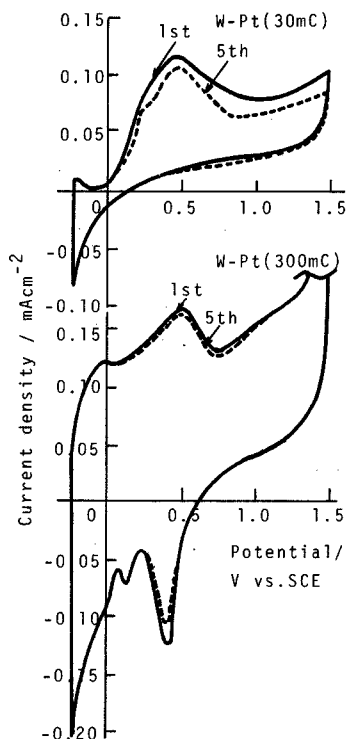


Fig. 2 Cyclic voltammograms obtained with W-Pt (30 mC or 300 mC) electrodes in nitrogen saturated 0.5 M H_2SO_4 (Sweep rate: 250mVmin^{-1})

tungsten (VI) oxide electrodes in nitrogen saturated 0.5 M H_2SO_4 solution at a sweep rate of 250mVmin^{-1} . A characteristic reduction peak of platinum oxide appeared at 0.4 V in the curve for the platinum electrode. In the case of tungsten electrode, an oxide formed at about 0.5 V was reduced just in the potential region where hydrogen adsorption occurs. The peak current corresponding to the oxidation of the electrode was not observed in the voltammogram obtained from the tungsten oxide electrode.

Cyclic voltammograms obtained on the platinum plated tungsten electrode are shown in Fig. 2. The polarization behavior observed with the platinum (30 mC) plated tungsten electrode, W-Pt (30 mC), was found to be almost the same as that obtained with tungsten electrode. There was no essential difference in the curves measured on W-Pt (30 mC), W-Pt (60 mC) or W-Pt (100 mC). The voltammogram obtained with the W-Pt (300 mC), however, shows the characteristic features of platinum and also of tungsten electrodes.

Cyclic voltammograms obtained with platinum plated tungsten (VI) oxide electrodes (WO_3 -Pt) are demonstrated in Fig. 3. The current for tungsten oxide formation at 0.5 V vs. SCE successively increased with increased cycles but the cathodic current at -0.25V was found to be almost constant during the cyclic measurements. These results indicate that the reduction current at -0.25V is due

to not only the adsorbed hydrogen on the surface but also the reduction of oxide layer on the substrate. The coexistence of tungsten oxide and platinum in the form of layer by layer seems to give no influence on the hydrogen electrode reaction.

Figure 4 shows the change in the voltammogram with the heat-treated W-Pt (300 mC) electrode as a function of heat-treatment temperature. Heat-treatment at 500°C leads to a significant decrease in the current density for the cyclic voltammogram, and results in the identical electrochemical behavior with smooth platinum electrode itself. This result may be explained by the assumption that the platinum layer recrystallizes and covers the entire electrode surface upon heat-treatment at 500°C. With increased heat-treatment temperature above 500°C, the electrochemical behavior of the W-Pt (300 mC) electrode was found to be similar to that of the tungsten electrode.

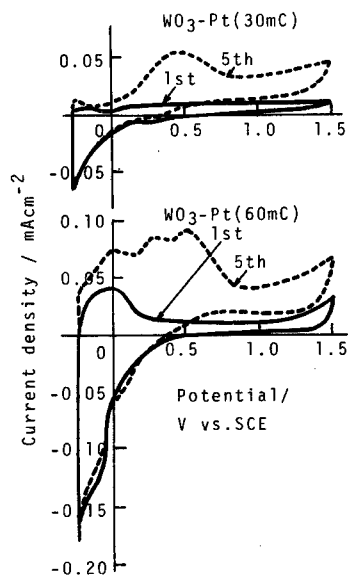


Fig. 3 Cyclic voltammogram obtained with $\text{WO}_3\text{-Pt}$ (30 mC or 60mC) electrodes in nitrogen saturated 0.5 M H_2SO_4 (Sweep rate: 250 mVmin^{-1})

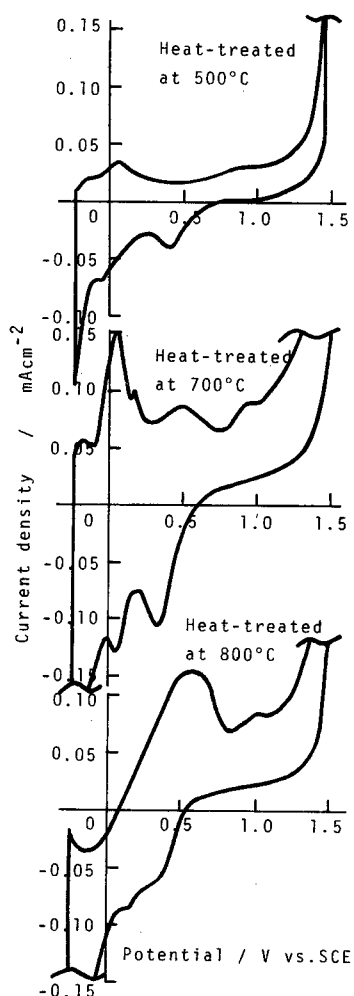


Fig. 4 Cyclic voltammograms obtained with heat-treated W-Pt (300 mC) electrodes in nitrogen saturated 0.5 M H_2SO_4 (Sweep rate: 250 mVmin^{-1})

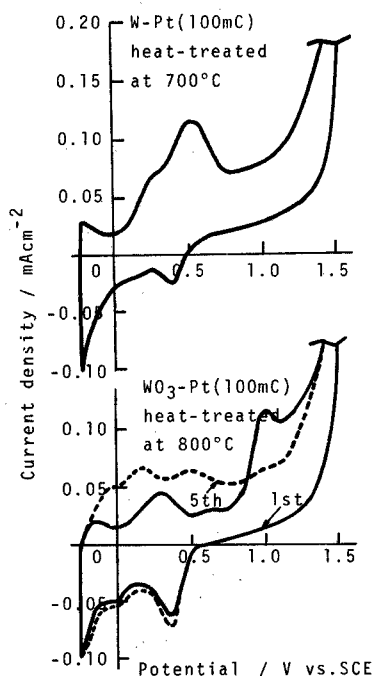


Fig. 5 Cyclic voltammograms obtained with heat-treated W-Pt and WO₃-Pt electrodes in nitrogen saturated 0.5 M H₂SO₄ (Sweep rate: 250 mVmin⁻¹)

An addition of a small amount of group VIII transition elements to tungsten powder generally accelerates mass transport along the interface of the additives with a tungsten particle.⁷⁾ The platinum layer on the W-Pt electrode might be able to diffuse into substrate by the high temperature heat-treatment. Therefore, upon heat-treatment at 800°C for 30 min, the electrochemical behavior of W-Pt (300 mC) electrode turned into that of tungsten electrode. It means that the relative diffusion up to about 35 nm takes place along the interface between platinum and tungsten by the heat-treatment at 800°C for 30 min. According to these results, platinum doping into tungsten and tungsten oxide substrate was performed in the following manner; platinum is plated with a quantity of less than 100 mC (about 12 nm), and then diffused into tungsten or tungsten oxide by a heat-treatment at a temperature below 800°C for 30 min.

Cyclic voltammograms obtained on the heat-treated W-Pt electrode at 700°C and also on the heat-treated WO₃-Pt electrode at 800°C in vacuo are shown in Fig. 5. It is expected that the platinum doped in the WO₃ layer enhances the formation of H_xWO₃ which was assumed to accelerate the hydrogen electrode reaction. The formation and oxidation of H_xWO₃ are said to occur in the potential range from -0.25 to +1.0 V vs. SCE²⁾. In this potential region, however, electroscorption and desorption of hydrogen also take place simultaneously. The current peak for the reaction step proceeding through H_xWO₃ formation, therefore, can not be distinguished in the voltammogram.

3.2 Polarization behavior of as-deposited electrodes

Figure 6 shows the cathodic and anodic polarization curves measured with the W-Pt electrodes in a 0.5 M H_2SO_4 solution saturated with hydrogen. Polarization behavior measured by a similar manner with WO_3 -Pt electrode is shown in Fig. 7. In this experiment, the tungsten (VI) oxide substrates were prepared by an anodic oxidation at an applied voltage of 50 V.

Polarization behaviors on tungsten and tungsten (VI) oxide electrodes are also given in the figures. The electrocatalytic activity of the tungsten (VI) oxide electrode without platinum loading was found to be lower than that of tungsten electrode for the cathodic reduction of hydrogen. With a small amount of platinum loading on the tungsten and tungsten (VI) oxide surface, the electrocatalytic activities of the electrode for the cathodic reduction of hydrogen increased significantly.

The WO_3 -Pt electrode, platinum plated with the electricity less than 40 mC, shows the lower activity in the hydrogen electrode reaction than the corresponding W-Pt electrode. The difference in the activity of the electrode seems to arise from the change in the surface resistance of the substrate. Thickness of the tungsten (VI) oxide layer formed on the tungsten substrate with an applied voltage of 50 V is calculated to be about 70 nm⁶⁾. Thickness of platinum layer on the WO_3 -Pt (40 mC) electrode is calculated to be about 5 nm. Thick oxide layer in comparison with a platinum layer leads to a high resistance, since the specific resistance of WO_3 is appreciably high, i.e. $2 \times 10^5 \Omega\text{cm}$.

With increased quantity of platinum deposited above 60 mC, difference between

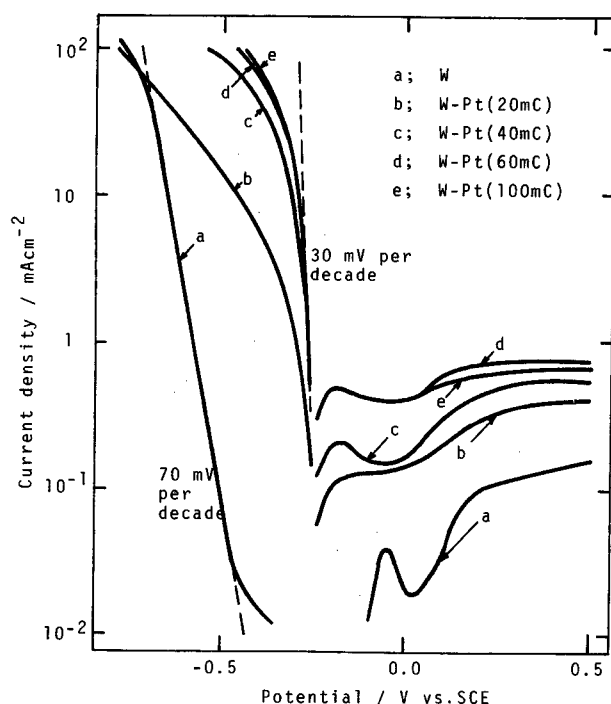


Fig. 6 Potentiodynamic current-potential curves measured on W-Pt electrodes in hydrogen saturated 0.5 M H_2SO_4 (Sweep rate: 50 mVmin^{-1})

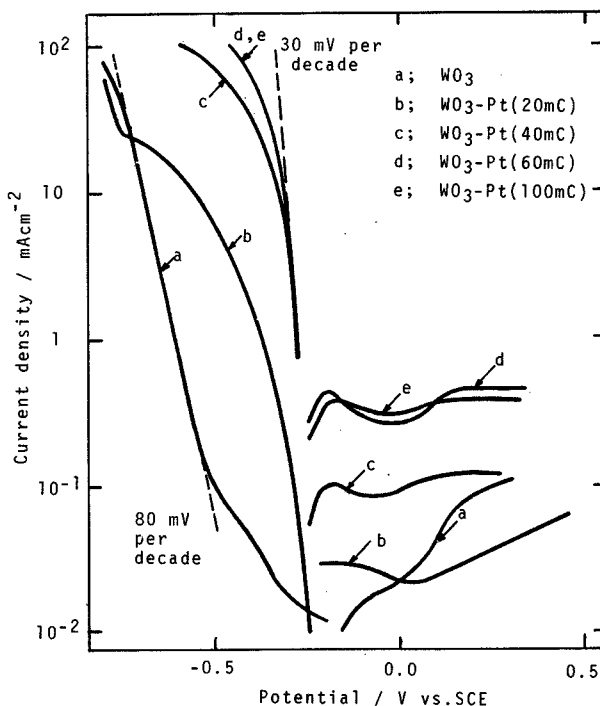


Fig. 7 Potentiodynamic current-potential curves measured on $\text{WO}_3\text{-Pt}$ electrodes in hydrogen saturated 0.5 M H_2SO_4 (Sweep rate: 50 mVmin^{-1})

the electrocatalytic activities of W-Pt and that of $\text{WO}_3\text{-Pt}$ electrodes disappeared. The polarization behavior observed on these electrodes seemed to be very similar to that obtained on bright platinum under similar conditions. These results indicate that the effect of substrates on the activity of platinum plated electrode diminished when the quantity of platinum exceeds 7 nm in thickness (about 20 monolayers). Another reason to give the similar characteristics for both W-Pt ($\geq 60 \text{ mC}$) and $\text{WO}_3\text{-Pt}$ ($\geq 60 \text{ mC}$) electrodes may also be attributed to the reduction of WO_3 during the cathodic polarization by the hydrogen which evolved more intensively on the electrode loaded with the thick platinum layer. This aspect may be supported by the fact that tungsten oxide surface changed its color from pale green to metallic appearance of tungsten itself during the polarization measurement.

3.3 Polarization behavior of heat-treated electrodes

Effects of heat-treatment have been examined on the activity of tungsten and tungsten (VI) oxide electrodes loaded with platinum. Figure 8 shows the polarization curves measured in the hydrogen saturated 0.5 M H_2SO_4 solution on the W-Pt and $\text{WO}_3\text{-Pt}$ electrodes heat-treated in vacuo. Tungsten (VI) oxide substrate was formed by an anodic oxidation of tungsten at a cell voltage of 75 V in 0.4 M $\text{KNO}_3\text{-}0.04 \text{ M HNO}_3$ solution.

Electrocatalytic activity of the W-Pt electrodes decreased with an increase in the heat-treatment temperature as shown in Fig. 8. These results may be attributed to the fact that the diffusion of platinum into the underlying tungsten layer brought

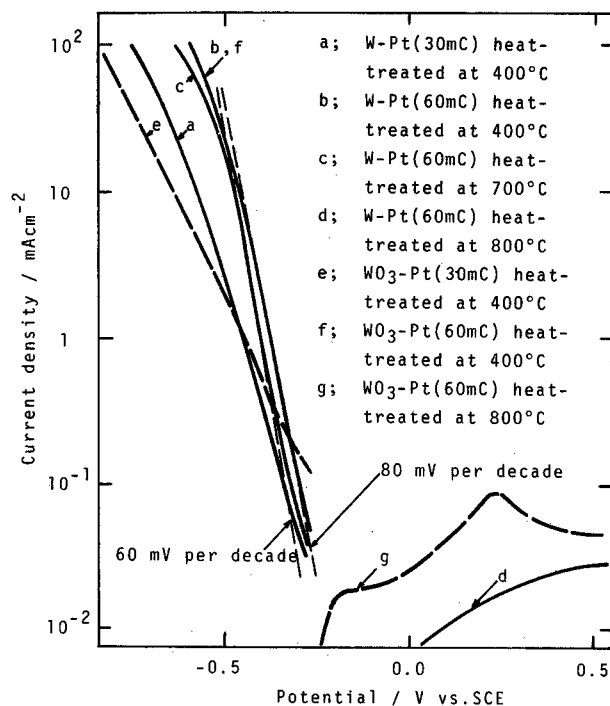


Fig. 8 Potentiodynamic current-potential curves measured on heat-treated W-Pt and WO₃-Pt electrodes in hydrogen saturated 0.5 M H₂SO₄ (Sweep rate: 50 mVmin⁻¹)

about a decrease in the surface coverage of platinum. Since the amount of diffused platinum increased with an increase in heat-treatment temperature, W-Pt electrode heat-treated at the higher temperatures above 500°C gave rise to less effective performance in the hydrogen electrode reactions.

Electrocatalytic activity of the WO₃-Pt electrodes was also reduced by the heat-treatment. If the platinum is widely dispersed in the tungsten oxide substrate by the heat-treatment, it is expected that H_xWO₃ bronze may be easily formed²⁾ not only on the electrode surface but also beneath the surface layer, and promotes the hydrogen electrode reaction. Contrary to the expectation, no improvement in the electrocatalytic activity of the heat-treated WO₃-Pt electrode was observed.

On the as-plated WO₃-Pt (≥60 mC) electrode as well as pure platinum electrode, the polarization curves obtained for hydrogen evolution reaction gave a Tafel slope of 30 mV per decade. The heat-treated W-Pt and WO₃-Pt electrodes, however, gave the Tafel line having the slope of 60–80 mV per decade. Difference in the electrocatalytic activities between the heat-treated W-Pt and WO₃-Pt electrodes was relatively small. These results imply that platinum atoms are the mutual accelerating species for the hydrogen evolution and also hydrogen oxidation reactions.

4. Conclusion

An attempt was made to develop the tungsten or tungsten oxide electrodes doped

with platinum by means of platinum plating followed by heat-treatment. The tungsten and tungsten oxide electrodes loaded with platinum more than 100 monolayers and heat-treated to recrystallize the surface platinum layer at 500°C for 30 min in vacuo gave rise to the electrocatalytic activity similar to that of platinum itself in the hydrogen electrode reaction. The heat-treated W-Pt and WO₃-Pt electrodes at above 500°C which is assumed to have the dispersed platinum particles in the tungsten or tungsten oxide substrate, however, gave less effective performance in the hydrogen evolution and also oxidation reactions.

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