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An Effect of Heat-treatment on the Activity of Titanium Dioxide Film Electrodes for Photo-sensitized Oxidation of Water

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Synopsis. When an anodic oxide film of titanium and a pyrolytically prepared TiO_2 film were subjected to a heat-treatment in an argon atmosphere, their activities for photo-sensitized oxidation of water were improved.

The photo-sensitized oxidation of water on an illuminated rutile electrode[1] has been studied recently by many investigators with a special interest in photo-emf cells.[2,3] The electrochemical properties of TiO_2 film electrodes prepared by a variety of methods, such as chemical vapor deposition,[4,5] anodic oxidation,[5-7] thermal oxidation,[6,8,9] pyrolysis of titanium salts,[10] and spraying by a plasma jet,[8] as well as of single crystal rutile, have been investigated in connection with the photo-sensitized oxidation. The following points can be noticed in these investigations: (1) the anodic oxide film shows far less activity than that of single crystal rutile; (2) the films prepared by the thermal oxidation do not always have the same properties, but have some possibility of giving the same activity as that of single crystal rutile if a suitable preparation condition is chosen; and (3) the activities of the pyrolytically prepared film for oxygen adsorption and for photo-sensitized oxidation of chloride ions are influenced by the preparation temperature of the film.

It is suggested by the above information that the heat-treatment has a great influence on the activity of a TiO_2 film electrode for the photo-sensitized oxidation of water. The present study was conducted, therefore, to elucidate the effect of the heat-treatment on the activity of TiO_2 films. Anodically formed and pyrolytically prepared films were chosen for the TiO_2 films.

Experimental

A rectangular titanium sheet ($20\times10\times0.5$ mm) was anodically oxidized in ethylene glycol containing 100 g/l sodium borate.[11] Sodium borate was purified by recrystallization from distilled water twice, and ethylene glycol was distilled twice. When the titanium electrode was oxidized with a constant current of 0.5 mA/cm^2, its potenial increased with the oxidation time until it reached around 20 V *vs.* S.C.E., after which no further potential rise occurred. After the polarization under this condition for 20 min, the current density was changed to 1 mA/cm^2 and maintained at that value until the potential reached a desired value. The heat-treatment was conducted under an argon atmosphere at a desired temperature for 1 h. Pyrolytic TiO_2 films were prepared by the same procedure as that described previously,[12] except that a solution of 0.1 mol·dm^{-3} $TiCl_3$–20% HCl containing a few drops of 30% H_2O_2 was subjected to the pyrolysis. A 500 W xenon arc lamp was used as a light source and monochromatic light was obtained by using the grating of a spectrophotometer (Shimadzu, QB-50).

Results and Discussion

The activity of an anodically formed oxide film for the photo-sensitized oxidation of water was poor, as expected. When the film was heat-treated at 700 °C, however, it became almost as active as single crystal rutile. Figure 1 shows the polarization curves of an electrode formed at 50 V. In the measurement of each polarization curve, the photo-intensity was maintained at the same value. Trials of the heat-treatment at 800 °C were failures due to the fact that the film flaked off in some patches from the substrate. The polarization curves in 0.5 mol·dm^{-3} Na_2SO_4 and 1 mol·dm^{-3} NaOH were almost the same as those in Fig. 1, except that they shifted cathodically depending on the pH values of the electrolytes.

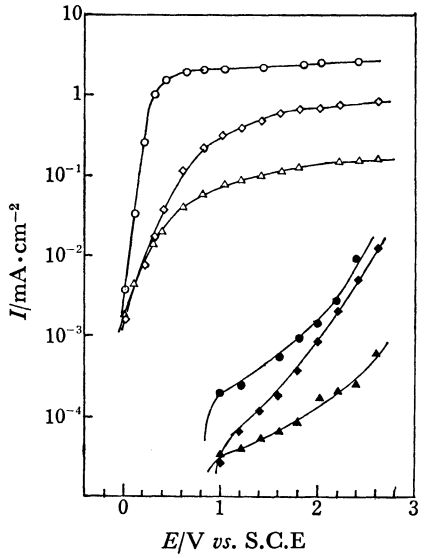

Fig. 1. Influence of heat-treatment on current-potential curves of anodic oxide films on titanium. Temperature of heat-treatment; -○-, -●-: 700°C, -◇-, -◆-: 600 °C, -△-, -▲-: non-heat-treatment, open symbol: under illumination, closed symbol: in the dark.

X-Ray diffraction patterns of the oxide film showed that the initial film formed by the anodization was amorphous and changed into rutile modification by the heat-treatment, as expected from the transformation of anatase to rutile by the heat-treatment.[13,14] It was also observed that the crystallization of the film was promoted with an increase of the temperature of the heat-treatment. Hence, one of the reasons for the increase of the activity is this crystallization. Another effect of the heat-treatment is to bring about an increase of the electrical conductivity of the film, as is usually

observed in single crystal rutile, although the determination of the carrier concentration of the film by Mott-Schottky plots before and after the heat-treatment was unsuccessuful, because the film thickness was so thin that the length of the space charge layer exceeded the film thickness by anodic polarization beyond a fairly low anodic potential.[4] As for the film thickness, it increases at a rate of 20—30 Å/V in the anodization.[11,15] Thus, the oxide film thickness formed at 50 V amounts only to 1000—1500 Å. By the heat-treatment, there is a possibility that the titanium substrate extracts oxygen from the oxide film,[16] by which a decrease in the film thickness would be expected. It was theoretically predicted that there is an optimum carrier concentration for a semiconductor electrode to attain a high quantum yield of a photo-sensitized reaction,[17] and the experimentally found optimum concentration was in the order of as high as 10^{18} carriers/cm^3.[18]

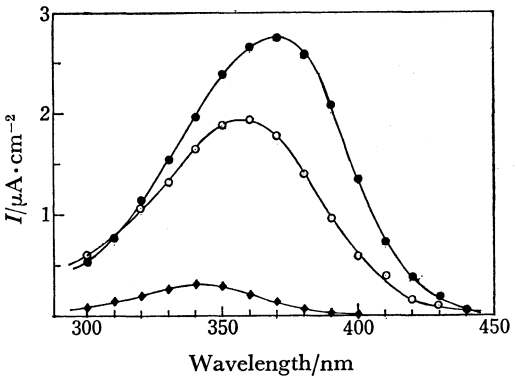

Fig. 2. Photo-current spectra of anodic oxide films on titanium.
-●- Heat-treated at 700 °C, -○- heat-treated at 600 °C, -◆- non-heat-treated.

Figure 2 gives the anodic current spectra of the film with and without the heat-treatment. By the heat-treatment, the photo-current at 2.0 V distinctly increased and its maximum occurred at a longer wavelength. Since the electrode was illuminated through the electrolyte, excitation of hole-electron pairs must be most predominant in a layer near the film/electrolyte interface. The results shown in Fig. 2, therefore, suggest that the probability of carrier recombination in the process in which electrons move from the excited sites to the substrate was decreased by the heat-treatment.

The above mentioned effects of the heat-treatment were also observed on a pyrolytic oxide film. The pyrolytic oxide film had a history of high temperature (450 °C) preparation. Nevertheless, the as-prepared film showed a poor activity.

When the activated TiO_2 film electrode was used as the electrode for the photo-sensitized oxidation of water in 0.5 mol·dm^{-3} H_2SO_4, a gradual deterioration of the activity was noticeable due to the oxidation of the electrode surface, as was already reported for a single crystal electrode.[3,19] From the above results, however, it is suggested that a TiO_2 film will be as effective as single crystal rutile as a semiconductor electrode if the film consists of highly crystalline TiO_2 with an appropriate conductivity.

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