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<td>Ye, Fuxing; Ohmori, Akira</td>
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Microstructure and Photoelectrochemical Characteristics of TiO₂-ZnO Electrodes Prepared by Plasma Spraying Technique†

YE Fuxing*, OHMORI Akira**

Abstract

The photoelectrochemical characteristics of plasma sprayed porous TiO₂, TiO₂-5%ZnO and TiO₂-10%ZnO electrodes in 0.1N NaOH solution were studied through a three-electrode cell system. The microstructure, morphology and composition of the electrodes were analyzed using electron probe surface roughness analyzer (ERA-8800FE), scanning electron microscope (SEM) and X-ray diffraction. The results show that the sprayed electrodes have a porous microstructure, which is affected by the plasma spraying parameters and composition of the powders. The photo-response characteristics of the plasma sprayed electrodes are comparable to that of single crystal TiO₂, but the breakdown voltage is about 0.5V (vs. SCE). The photocurrent density increases with a decrease of donor concentration, which is calculated according to Garner-Butler model. For the lowest donor concentration of a TiO₂-5%ZnO electrode prepared under an arc current of 600A, the photocurrent density is approximately 0.4mA/cm² higher than that of the TiO₂ electrodes under 30mW/cm² xenon light irradiation. The photocurrent density increases linearly with light intensity.

KEY WORDS: (Photoelectrochemical characteristic) (Plasma spraying) (TiO₂) (ZnO) (Electrode)

1. Introduction

Since Prof. Fujishima and Honda discovered the photoelectrolysis of water on TiO₂ electrodes in 1972, extensive research has been performed to understand the fundamental principles and improve the electrode (cell) properties of TiO₂, such as light harvesting, light converting components, photocurrent density (Jsc), open circuit voltage (Voc), fill factor (FF), stability and so on. For the lower cost of polycrystalline TiO₂, compared with single crystalline TiO₂, polycrystalline n-TiO₂ has been mainly studied as a semiconductor electrode in photoelectrochemical cells. There have many techniques for the preparation of the photoelectrode, including wet chemical processing (e.g.: sol-gel, screen printing), vapor processing techniques (e.g.: CVD, PVD) and thermal oxidation of Ti. However, the electrodes prepared by the above methods have many defects, for example, the electrode adhesion strength with the substrate is generally very low, result in an increase in the ohmic resistance and then lower cell power. To improve the photocurrent density of TiO₂ electrode, one method is to obtain optimal electrical resistivity of the electrode. It is reported that ZnO additive can change the electrical resistivity of TiO₂ for the formation of defects and zinc titanates.

Thermal spraying is an economical and versatile fabrication process to produce large surface coatings with unlimited types of materials. The coatings thickness, texture and bonding strength can be controlled easily through spraying parameters, powders and spraying method etc. Moreover, plasma spray atmospheres are reductive, and it is easy to produce oxygen deficiency in plasma atmosphere. Therefore, in the present study, the TiO₂ and TiO₂-ZnO electrodes were prepared on stainless steel by plasma spraying technique. The microstructure and photoelectrochemical characteristics of the electrodes were analyzed by ERA-8800FE, SEM, X-ray diffraction and a three-electrode cell system equipped with a quartz window.

2. Materials and experimental procedures

2.1. Materials

The variation of photoelectrochemical property with particle size is associated with an increase in the specific area and a corresponding increase of light harvesting. If the size of the feedstock powder is smaller than 10μm, it is difficult to deposit coatings by thermal spraying because of the low speed of the particles. So to satisfy the two demands, the original diameter of the TiO₂ particle is held at 0.2μm, and polyvinyl alcohol is used as a binder for the thermal spraying TiO₂ powder (diameter approximately 30μm). Because the photoelec-

† Received on November 14, 2002
* Graduate Student, Osaka University
** Professor

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Microstructure and Photoelectrochemical Characteristics of TiO₂-ZnO Electrodes Prepared by Plasma Spraying Technique

trochemical property of anatase titanium dioxide is better than that of rutile, anatase TiO₂ was used as feedstock powder. The average size of the TiO₂ powder is 33.7μm. It is reported that ZnO can improve the photoelectrochemical property of the TiO₂ electrode ⁵. Therefore, to investigate the influence of ZnO additive, TiO₂-5%ZnO and TiO₂-10%ZnO powders were designed in this study. The average size of TiO₂-ZnO powder is approximately 30μm. The x-ray diffraction patterns of the feedstock powders are illustrated in Fig.1. The substrate is stainless steel (JIS SUS316).

2.2 Plasma spraying equipment

A plasma spraying system, whose commercial gun name is Plasma DYNE Gun, has been used to prepare TiO₂, TiO₂-5%ZnO and TiO₂-10%ZnO electrodes. Argon was used as a primary plasma gas and helium was used as the secondary gas. The thermal spraying parameters are illustrated in Table 1.

<table>
<thead>
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<td>Ar gas pressure (MPa) /flow (slpm)</td>
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<tr>
<td>He gas pressure (MPa) /flow (slpm)</td>
</tr>
<tr>
<td>Arc current (A)</td>
</tr>
<tr>
<td>Arc voltage (V)</td>
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<tr>
<td>Spraying distance (mm)</td>
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2.3 Analysis of the feedstock powders and sprayed electrodes

Electron probe surface roughness analyzer (ERA-8800FE) and scanning electron microscope (SEM) were used to examine the structure characteristics of the feedstock powders and the sprayed electrodes. The phase composition of the feedstock powders and the sprayed electrodes were investigated by X-ray diffraction using Cu-Kα radiation (λ=1.5405 Å) with a graphite crystal monochromator (JDX3530, JEOL, Japan).

2.4 Photoelectrochemical characteristics evaluation apparatus and process

The voltammetry was performed in a three-electrode glass cell at room temperature, in which a commercial saturated calomel electrode (SCE) was used as the reference electrode and a platinum plate (30*30mm) as the counter electrode. The electrolyte was 0.1N NaOH solution and deaerated by purging with Ar gas for 30 minutes before the experiments. The photocurrent against potential at each sprayed electrode (working electrode) was measured using a scanning potentiostat and recorded by a personal computer through an AD converter (NR-110, KEYENCE company). The sweep speed of the potential was 2mV/s

Fig.1. The X-ray diffraction patterns of feedstock powders (a:TiO₂, b:TiO₂-5%ZnO and c:TiO₂-10%ZnO powder).

in every experiment. A 500W xenon lamp was used as light source and the light intensity was measured by a UV radiometer (UVR-2, TOPCON, Tokyo, Japan) with UD-40 or UD-35 detector.

3. Results and Discussion

3.1 The microstructures of the sprayed TiO₂ and TiO₂-ZnO electrodes

Fig.2 shows the typical microstructures of TiO₂, TiO₂-5%ZnO and TiO₂-10%ZnO electrodes prepared by plasma spraying technique under the arc current of 600A. The sprayed electrodes are not very dense, containing many holes. The porosity of the specimens increases with the increasing of ZnO amount. It may result from the volatilization of Zn during the deposition process as clearly shown in Fig.3, where the hollow voids remain after the Zn gas is given off.

The density of the TiO₂-5%ZnO electrodes becomes denser with an increase of arc current as shown in Fig.4 for the much more melted feedstock powder.

The typical X-ray diffraction pattern of plasma sprayed TiO₂-5%ZnO electrodes is illustrated in Fig.5. The electrode consists of anatase TiO₂, rutile TiO₂ and Zn₂Ti₃O₈ phase. Despite the relative instability of Zn₂Ti₃O₈, the formation of Zn₂Ti₃O₈ phase rather than Zn₂TiO₄ is rational for the similarity in structure between anatase and Zn₂Ti₃O₈ when the anatase phase of TiO₂ was used in the starting mixture especially in plasma spraying process ⁶⁻⁸.

3.2 Transient photocurrent-time profile of TiO₂ electrode

Fig.6 shows a typical photocurrent-time profile of TiO₂ electrode with hand-chopped light. An anodic photocurrent spike appears immediately after the light is turned on, and then decreases continuously with time until a steady state photocurrent is reach. When the light is turned off, the photocurrent decreases quickly down to
Fig. 2. The typical microstructures of plasma sprayed TiO$_2$ (a), TiO$_2$-5%ZnO (b) and TiO$_2$-10%ZnO (c) electrode.

Fig. 3. The typical hollow voids of plasma sprayed TiO$_2$-ZnO electrode.

Fig. 4. The typical microstructures of the plasma sprayed TiO$_2$-5%ZnO electrodes under the arc current of 400A (a), 600A(b) and 800A (c).

Fig. 5. The typical X-ray diffraction pattern of a plasma sprayed TiO$_2$-5%ZnO electrode.
Microstructure and Photoelectrochemical Characteristics of TiO$_2$-ZnO Electrodes Prepared by Plasma Spraying Technique

![Figure 6](image1)  
**Fig.6.** The transient photocurrent-time profile of TiO$_2$ electrode.

![Figure 7](image2)  
**Fig.7.** The photocurrent–potential curves of the TiO$_2$, TiO$_2$-5%ZnO and TiO$_2$-10%ZnO electrode prepared under the arc current of 600A.

![Figure 8](image3)  
**Fig.8.** The relationship between photocurrent density and the arc current of TiO$_2$ (a), TiO$_2$-5%ZnO (b) and TiO$_2$-10%ZnO (c) electrode.

![Figure 9](image4)  
**Fig.9.** The relation between photocurrent density and light intensity.

Zero. The initial anodic photocurrent spike is due to instantaneous photo-induced electron transitions to the conduction band as discussed by Liu $^9$ and Salvador $^{10}$.

### 3.3 The photoelectrochemical characteristics of the sprayed TiO$_2$ and TiO$_2$-ZnO electrodes

Fig.7 illustrates the photocurrent–potential curves of the TiO$_2$, TiO$_2$-5%ZnO and TiO$_2$-10%ZnO electrode prepared under an arc current of 600A. The photo-response characteristics of the sprayed electrodes are comparable to that of single crystal TiO$_2$, but the breakdown voltage is about 0.5V (vs. SCE), which is similar to the plasma sprayed electrodes prepared by Wang $^9$. The photocurrent density of the TiO$_2$-5%ZnO electrode is higher than that of the TiO$_2$ and TiO$_2$-10%ZnO electrodes prepared under the same spraying parameters.

The conductivity of the TiO$_2$ electrode decreases with the addition of ZnO (unpublished data). It has been reported that the electrode materials for PEC conversion must have optimal conductivity for the efficient movement and lowest recombination of excited hole-electron pairs. The variation of electrode resistivity can be understood in terms of the change in electron concentration induced by the possible defect reactions and the microstructure. Furthermore, certain transition metals diffuse through these channels into lattices because TiO$_2$ contains interstitial channels in the c direction. The diffusing ions have been found to locate preferentially on either the substitutional or interstitial sites $^9$. Thus, on the one hand, the increase of resistivity for the TiO$_2$-5%ZnO electrode can be explained by substitution of Ti (0.68 Å) site with Zn (0.74 Å). As a result, the electron concentration may be reduced as expressed by the following defect equation:

$$\text{ZnO} + 2e^+ + \frac{1}{2}O_2 \rightarrow \text{Zn}^{\text{\ddagger}} + 2O^\text{*}$$

On the other hand, the increase of resistivity for the TiO$_2$-5%ZnO electrode results from the porous microstructure as shown in Fig.2 compared with the TiO$_2$ electrode. For the relative high resistivity, the

204
recombination speed of hole and electron pairs of TiO$_2$-5%ZnO electrode may decrease and then increase the photocurrent density. However, the much lower conductivity for the TiO$_2$-10%ZnO electrode may well increase ohmic loss and then lower the photocurrent density.

The photocurrent density of the electrodes prepared under an arc current of 600A is higher than that under 400A or 800A for the same powder as shown in Fig.8, and it increases linearly with the light intensity as shown in Fig.9.

3.4 The donor concentration of sprayed electrodes

The semiconductor surface properties are of paramount importance and their determination has received considerable effort. Because the donor concentration is one of the key parameters, it is obtained from the quantum efficiency measurement according to the well-known Gartner-Butler model in this study. Generally, the low donor concentration will benefit to increase the photocurrent density.

According to the Gartner-Butler model, the quantum efficiency is expressed by the following equation

$$J_{SC}^2 = \frac{2e \varepsilon_0 e \alpha^2 I_0^2}{N_d} (V - V_{FB})$$

where $J_{SC}$ is the photocurrent density, $I_0$ is the photo intensity, $\alpha$ is the optical absorption coefficient, $\varepsilon_0$ is the permittivity of free space, $\varepsilon_R$ is the relative dielectric constant, $e$ is the elementary charge, $V$ is the electrode potential, $V_{FB}$ is the flatband potential and $N_d$ is the donor concentration.

The donor concentration of the sprayed electrodes is calculated according to equation (1), and the results are illustrated in Fig.10. The donor density of the electrode under the arc current of 600A is lower than that under the arc current of 400A or 800A for the same feedstock powder, and the donor density of TiO$_2$-5%ZnO electrode prepared under the arc current of 600A is lowest comparing with the other electrodes. These are in good relation with photocurrent density shown in Fig.8. It has been previously mentioned that the photocurrent density increases linearly with the light intensity, which implies the equation (1) is fulfilled, as also reported by P. Salvador.

4. Conclusions

In this study, the photoelectrochemical performance of plasma sprayed TiO$_2$, TiO$_2$-5%ZnO and TiO$_2$-10%ZnO electrodes was systematically investigated. The plasma sprayed electrodes have photo-response characteristics and the break down voltage was about 0.5V (vs. SCE). The maximum photocurrent density of the TiO$_2$-5%ZnO electrode is about 1.45mA/cm$^2$, which is 0.4mA/cm$^2$ higher than that of the TiO$_2$ electrodes under 30mW/cm$^2$ xenon light irradiation. Furthermore, linear dependence of the photocurrent density with light intensity is obtained under a constant potential. Moreover, the donor concentration ($N_d$) is in good relation with photocurrent density in this experiment.

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