SrTiO₃-WO₃ Photocatalysis Systems with an Energy Storage Ability

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SrTiO₃ photocatalyst was combined with an energy storage material, WO₃, to fabricate a new photocatalysis system, envisaging application to, *e.g.*, protection of metals from corrosion. The SrTiO₃-WO₃ composite system stores reductive energy under UV irradiation, as does the TiO₂-WO₃ system. Since SrTiO₃ exhibits more negative photopotential (*ca.* -0.5 V vs Ag | AgCl) than TiO₂ (*ca.* -0.4 V), the SrTiO₃-WO₃ system can be charged more rapidly. In addition, self-discharging of the SrTiO₃-WO₃ system on the basis of aerobic re-oxidation of the system is slower than that of the TiO₂-WO₃ system.

Key Words : SrTiO₃-WO₃ Photocatalyst, Reductive Energy Storage, Photoelectrochemical Anti-Corrosion Effect, Photoelectrochemical Oxygen Reduction

1 Introduction

Photocatalyst is one of the promising devices for the conversion of the light energy into chemical energy, or in some cases (*e.g.*, electrocatalytic anti-corrosion systems), electric energy. Redox reactions proceed on the surface of a photocatalyst under light irradiation.¹⁻³⁾ However, light is essential for the redox reactions, so that the reactions always suffer from irregularity; the reactions are not driven "after dark". To solve this conventional problem, we have developed a new photocatalysis system with an energy storage ability, by combining TiO₂ photocatalyst with WO₃.⁴⁾ The photo-excited electrons of TiO₂ are accepted by WO₃ as an electron pool; the reductive energy generated at the UV irradiated TiO₂ can be stored in the WO₃.

The reducing ability of photocatalysts has been exploited to protect metals from corrosion,⁵⁻⁸⁾ for instance, by coating the metals directly with a photocatalyst film. Furthermore, hydrogen peroxide generated by photocatalytic reduction of oxygen ($\text{O}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow \text{H}_2\text{O}_2$)⁹⁾ should contribute to an anti-bacterial effect. We have demonstrated in the previous reports that the TiO₂-WO₃ composite system can keep the anti-corrosion effect⁴⁾ for type 304 stainless steel and the bactericidal effect¹⁰⁾ even after dark. We believe that light energy can be utilized more effectively by using our system.

To make this system more practical, it is very important to improve efficiency of the energy storage; the greater amount of electrons are desired to be stored in the shorter time. However, if the TiO₂ content in the composite is increased, the relative content of WO₃ decreases instead, giving rise to a decrease of the specific capacity as well as energy density of the composite. Thus, in the present work, we selected SrTiO₃ as a photocatalyst¹¹⁾ instead of TiO₂ because its flatband potential is

more negative than that of TiO₂.^{8,12)} The larger overpotential applied to WO₃ by illuminated SrTiO₃ increased the rate of electron transport from SrTiO₃ to WO₃. Additionally, better use of the electron capacity of WO₃ was achieved.

2 Experimental

2.1 Preparation of the coatings

A TiO₂ coating was prepared on an ITO-coated glass plate by a spray-pyrolysis technique at 300°C from a 0.05 M ethanol solution of bis(2,4-pentanedionato)titanium oxide (Tokyo Kasei). The average thickness of the resulting TiO₂ coating was *ca.* 1.2 μm (measured by scanning electron microscopy, SEM). The crystalline phase of the TiO₂ coating was anatase.⁷⁾ The size of the ITO glass plate used was 2.5 × 4.0 cm, unless otherwise noted.

A SrTiO₃ coating was also prepared on an ITO glass plate by a spray-pyrolysis technique at 300°C from a 0.02 M methanol solution of bis(2,4-pentanedionato)titanium oxide (Tokyo Kasei) and strontium 2,4-pentanedionate (Alfa). The SrTiO₃ coating obtained was annealed at 500°C. As a result, peaks showing perovskite crystallization were observed by an XRD measurement, although the signals were not very strong. The average thickness of the resulting SrTiO₃ coating was *ca.* 1.5 μm (measured by SEM).

For the preparation of WO₃ coatings, crystalline WO₃ nanoparticles (Japan New Metals; diameter measured by SEM, *ca.* 10-500 nm; monoclinic phase) were suspended in an alkoxysilane solution (NDC-100 A, Nippon Soda) (WO₃ content, 58 g L⁻¹). The suspension was coated on an ITO glass plate by spin-coating at 1500 rpm. The substrate was annealed at 200°C for 30 min. The average thickness of the resulting WO₃ coating was *ca.* 0.3 μm (measured by SEM).

Fig. 1 Changes in the potential of a WO_3 -coated ITO electrode (1.75 cm^2) in an air-saturated 3 wt% NaCl solution at pH 5. The WO_3 coating was charged at (a) -0.3 , (b) -0.4 or (c) $-0.5 \text{ V vs. Ag} \mid \text{AgCl}$ for the first 1 h.

2. 2 Measurements

Electrochemical and photoelectrochemical measurements were carried out in a 3 wt% NaCl aqueous solution (pH 5) unless otherwise noted. A platinum electrode and a $\text{Ag} \mid \text{AgCl} \mid \text{KCl}(\text{sat.})$ electrode were used as counter and reference electrodes, respectively. The area of a coated ITO electrode exposed to the solution was 1.75 cm^2 . An as-prepared WO_3 -coated ITO electrode was used in each measurement. A digital potentiostat (HZ 3000, Hokuto Denko) was used for electrochemical measurements. The light source used was a 200-W Hg-Xe lamp (Luminar Ace 210, Hayashi Tokei) together with a 365-nm bandpass filter in front of a quartz window incorporated into a conventional electrolytic cell. The light intensity was 20 mW cm^{-2} at the sample surface.

3 Results and Discussion

3. 1 Electrochemical charge-discharge behavior of WO_3 coatings

First, a WO_3 -coated ITO electrode was polarized by using a potentiostat at $-0.3 \text{ V vs. Ag} \mid \text{AgCl}$ for 1 h in a 3 wt% NaCl aqueous solution at pH 5, and then the open circuit potential (OCP) was monitored in the same solution (Fig. 1). After the polarization, the OCP shifted in the positive direction to *ca.* -0.22 V , then the potential was retained at this value for about 3 h, and finally the potential shifted again positively to the initial OCP, -0.1 to 0.0 V . This behavior is explained in terms of charging of the WO_3 coating under polarization at -0.3 V and self-discharging at -0.22 V , as we have reported previously.⁴⁾ The charging corresponds to reduction of WO_3 to a tungsten bronze, M_xWO_3 ($\text{M} = \text{H}, \text{Li}, \text{Na}, \text{etc.}; x \leq 1$):

The self-discharging corresponds to reoxidation of M_xWO_3 to WO_3 by dissolved oxygen:⁴⁾

The electrons are consumed by oxygen to produce $\text{O}_2^{\cdot -}$, H_2O_2 and/or H_2O .

Behavior of a WO_3 -coated ITO electrode, to which a

Fig. 2 Changes in the potential of a WO_3 -coated ITO electrode (1.75 cm^2) in an air-saturated 3 wt% NaCl solution at pH 5. The WO_3 -coated electrode was connected with a (a) TiO_2 - or (b) SrTiO_3 -coated ITO electrode (1.75 cm^2) as illustrated in the inset, and then the TiO_2 or SrTiO_3 was irradiated with UV (20 mW cm^{-2}) for the first 1 h.

different polarization potential of -0.4 V or $-0.5 \text{ V vs. Ag} \mid \text{AgCl}$ had been applied for 1 h, was also examined for comparison. Although similar behavior was observed in each case, the discharge time strongly depended on the polarization potential. If the cut-off potential is defined to be -0.20 V , the discharge time, T_{dis} , was 3.4, 11.0 or 15.9 h when the polarization potential was -0.3 , -0.4 or -0.5 V , respectively. According to the cyclic voltammogram of the WO_3 -coated ITO electrode that we have reported in the previous paper,⁴⁾ the reduction current increased with shifting the electrode potential in the negative direction in the range of -0.3 to -0.5 V . This suggests that, at more negative potentials, the charging is faster due to a larger overpotential applied and therefore a greater amount of charges can be stored in a constant period. This kinetic effect should be chiefly responsible for the dependence of T_{dis} on the applied potential.

Moreover, if the cut-off potential was defined to be -0.23 V , the discharge time was increased from 0.7 to 2.6 h by changing the polarization potential from -0.3 to -0.5 V . This means that the maximum utilizable capacity of the WO_3 coating can be increased slightly by applying more negative potentials, as expected from our previous spectroelectrochemical data.⁴⁾ This slight increase in capacity may be explained in terms of redox-based charging (like a battery) and/or electrostatic charging (like a capacitor). As for the former, since WO_3 has redox potentials not only at -0.2 – -0.3 V but also at more negative potentials, some of the more negative redox levels might also be charged at -0.5 V .

3. 2 Photoelectrochemical charge-discharge behavior of WO_3 coatings

Next, a WO_3 -coated ITO electrode was electrically connected to a TiO_2 -coated ITO electrode. These two electrodes were soaked in 3 wt% NaCl aqueous solutions and these solutions were ionically connected with a salt bridge. The TiO_2 -coated electrode was irradiated with UV light for 1 h as the inset of Fig. 2 shows. During the UV irradiation, the potential of the WO_3 -coated electrode was around $-0.4 \text{ V vs. Ag} \mid \text{AgCl}$, which is close to the photo-potential of TiO_2 .⁴⁾ After the UV light was turned

Fig. 3 Discharge time T_{dis} (cut-off potential = -0.20 V vs. Ag | AgCl) for the WO_3 coating as a function of the average potential E_{av} of the WO_3 -coated electrode during the electrochemical (●; data from Fig. 1) or photoelectrochemical (○, TiO_2 ; ▲, $SrTiO_3$; data from Fig. 2) charging.

off, the potential showed similar behavior to that observed after the electrochemical polarization (Fig. 2). This indicates that the photo-excited electrons of TiO_2 were accepted by the WO_3 , as has been reported.⁴⁾ The discharge time T_{dis} (cut-off potential = -0.20 V) was 3.4 h.

On the other hand, when a WO_3 -coated electrode was connected to a $SrTiO_3$ -coated ITO electrode, the WO_3 -coated electrode exhibited a potential of about -0.5 V during the UV irradiation. The discharge time T_{dis} (cut-off potential = -0.20 V) was 10.9 h. This value is more than 3-fold larger than that in the case of photoelectrochemical charging by TiO_2 . This difference may also be explained chiefly in terms of the different charging rates.

3. 3 Quantitative comparison of discharge time

On the basis of the results in Fig. 1, the discharge time T_{dis} (cut-off potential = -0.20 V) was plotted as a function of the charging potential in Fig. 3. As a result, a linear relationship appeared. We also plotted in Fig. 3 the T_{dis} values for the photoelectrochemical systems against the potentials of the WO_3 -coated electrode during the UV-irradiation. However, both TiO_2 - and $SrTiO_3$ -connected systems exhibited smaller T_{dis} values than those expected from the electrochemically obtained data. This suggests that the oxygen reduction occurred not only on the WO_3 coating but also on the TiO_2 or $SrTiO_3$ coating, which was connected to the WO_3 , resulting in the faster self-discharging. In this case, the electrons from WO_3 , of which energy is lower than that of the conduction bands in TiO_2 and $SrTiO_3$, may have transferred via surface levels. Actually, Bard *et al.*¹³⁾ have reported that many redox species can be reduced at TiO_2 electrodes at less negative potentials than the flatband potential.

However, the degree of suppression of the T_{dis} value for the $SrTiO_3$ -connected system (27%) was much smaller than that for the TiO_2 -connected system (75%). This may reflect that the oxygen reduction rate at the $SrTiO_3$ surface is slower than that at TiO_2 surface, though the influence of the intrinsic surface area has not yet been considered. If so, the slow self-discharging of

the $SrTiO_3$ -connected system is favorable from a practical point of view for the application to anti-corrosion systems,⁴⁻⁸⁾ because the $SrTiO_3$ - WO_3 system would be able to retain anti-corrosion effect for longer period than the TiO_2 - WO_3 system⁸⁾ reported previously.

4 Conclusions

We demonstrated that the $SrTiO_3$ - WO_3 composite system exhibits a couple of advantageous properties in comparison with the TiO_2 - WO_3 system; quicker photoelectrochemical charging and slower self-discharging. In addition, WO_3 redox levels with more negative potentials could be reduced by using $SrTiO_3$; thermodynamically utilizable capacity of WO_3 might also be increased and discharge potential may become more negative. This will be studied in further detail. If a more negative potential can be retained during discharge period, the system will be applicable to anti-corrosion systems for metals with more negative corrosion potentials, *i.e.*, metals ready to corrode. Work is currently underway to investigate these points.

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