TiO_2−WO_3 Photoelectrochemical Anticorrosion System with an Energy Storage Ability

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TiO_2 coatings are known to protect some metals, including type 304 stainless steel, from corrosion on the basis of its reductive energy generated under UV irradiation. A TiO_2 coating is coupled with a WO_3 coating as an electron pool, in which the reductive energy can be stored. A WO_3 film on a type 304 stainless steel plate can be charged by a UV-irradiated TiO_2 coating on the same plate, in a 3 wt % NaCl aqueous solution, pH 5. The charged WO_3 coating can protect the stainless steel plate from the corrosion for a while even after the UV light is turned off. Thus, the TiO_2 coating protects the plate and charges the WO_3 coating during the day, and the charged WO_3 coating protects the plate during the night. The charge−discharge cycles are repeatable. A TiO_2−WO_3 composite coating also has the same effects.

Introduction

In general, metals are protected from corrosion by a corresponding passive metal compound layer (e.g., alumina-coated aluminum), painting, or a sacrificial metal coating (with a less positive corrosion potential) (e.g., galvanized iron). Among them, the passive layer and painting are effective only when the coating covers the meal surface perfectly. As for a sacrificial metal coating, its lifetime is limited because the metal coating dissolves gradually instead of the substrate metal. As an alternative to these methods, photoelectrochemical protection by semiconductors has been studied in recent years.

Tsujikawa et al. have coated a photoelectrochemically active TiO_2[1,2] on type 304 stainless steel[3,4] or copper[5] and reported that the substrate metals can be polarized at a more negative potential than its corrosion potential under UV irradiation. Similar effects have also been observed by Akashi et al. under not only UV irradiation[6,7] but also γ-ray irradiation.[8] Carbon steel can also be negatively polarized by a TiO_2 coating in a strongly alkaline solution (pH 11)[9−11] or in atmosphere.[12] Also, we have recently evidenced that corrosion of type 304 stainless steel coated with TiO_2 is actually suppressed under UV irradiation.[13] This photoelectrochemical anticorrosion system is not expensive because just a thin semiconductor film is coated on the metal surface. Additionally, the semiconductor coating is not sacrificial and is allowed to have defects (e.g., pinholes). However, the photoelectrochemical anticorrosion system is driven by light; hence, it does not work in the dark. Tsujikawa et al. have prepared a multilayer-coated carbon steel, amorphous TiO_2/anatase TiO_2/Ti−Fe oxide/α-Fe_2O_3/Fe, and found that the coated steel retains its anticorrosion effect for a while even in the dark after UV irradiation.[11,12] However, the preparation of the multilayer may be complicated from a practical point of view, and the effect was observed only in a strongly alkaline solution (pH 11)[11] or in the atmosphere.[12] Additionally, the mechanism of the effect is not well-known so far.

To solve these problems, we designed a new system, in which the photoelectrochemical anticorrosion system is combined with an energy storage system with a sufficient capacity. Figure 1 illustrates the concept. In the semiconductor, electrons in the valence band are excited to the conduction band under irradiation with appropriate light. The excited electrons are injected to the metal so as to keep its potential more negative than the corrosion potential. The excess electrons are accepted by the electron pool combined, so that the reductive energy generated at the irradiated semiconductor can be stored. After the UV light is turned off, electrons

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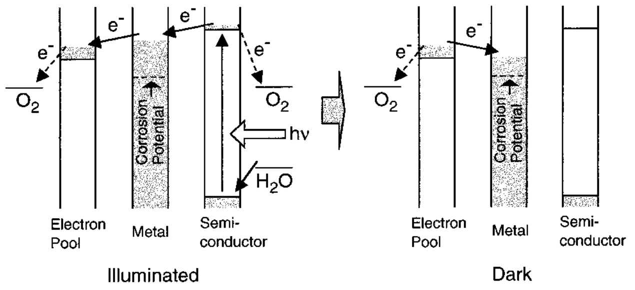

Figure 1. Mechanism of a photoelectrochemical anticorrosion system with an energy storage ability.

that have been stored in the electron pool are injected to the metal so that it is still protected from corrosion.

Characteristics required for the electron pool are as follows: (1) redox activity, (2) more positive redox potential than the conduction band potential of the semiconductor employed (the oxidized form of the electron pool should accept electrons from the irradiated semiconductor), (3) more negative redox potential than the corrosion potential of the metal (the reduced form should protect the metal from corrosion), (4) poor oxidizability of the reduced form by ambient oxygen, and (5) stability during repeated redox cycles.

In the present work, a combination of TiO_2 semiconductor with WO_3 electron pool was employed for the protection of type 304 stainless steel. It has been known that WO_3 can be reduced to tungsten bronze (M_xWO_3; M = H, Li, Na, etc.; $x \leq 1$) by photoirradiated TiO_2 in a nonaqueous electrolyte.[14] Here we characterized WO_3 as an electron pool in a slightly acidic aqueous electrolyte (pH 5). The energy storage ability and the anticorrosion effect after dark of the TiO_2-WO_3 system were demonstrated.

Experimental Section

Preparation of the Coatings. An indium tin oxide -coated (ITO-coated) glass plate or type 304 stainless steel (1 mm thick) was used as a substrate (2.5 × 4.0 cm). The stainless steel substrate was polished to a mirror finish with 0.05 mm of Al_2O_3 and rinsed with acetone.

The TiO_2 coating was prepared 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 TiO_2 coating was ca. 1.2 μm (measured by scanning electron microscopy (SEM)).

For the preparation of WO_3 coatings, crystalline WO_3 nanoparticles (Japan New Metals; diameter measured by SEM, ca. 10-500 nm) were suspended in an alkoxysilane solution (NDC-100A, Nippon Soda) (WO_3 content, 58 g L^{-1}). The suspension was coated on a substrate by spin-coating at 1500 rpm. The substrate was annealed at 200 °C for 30 min. The thus-prepared single coating (average thickness measured by SEM, ca. 0.3 μm) may be subjected to the same treatments again to obtain a double coating (average thickness, ca. 0.6 μm). In the following experiments, the single coating was used unless otherwise noted.

TiO_2-WO_3 composite coatings were prepared by a spray-pyrolysis technique at 300 °C from a 0.05 M ethanol solution of bis(2,4-pentanedionato)titanium oxide containing the WO_3 nanoparticles (2.3 g L^{-1}). The thickness of the composite coating was controlled with the amount of the suspension used (20-200 mL).

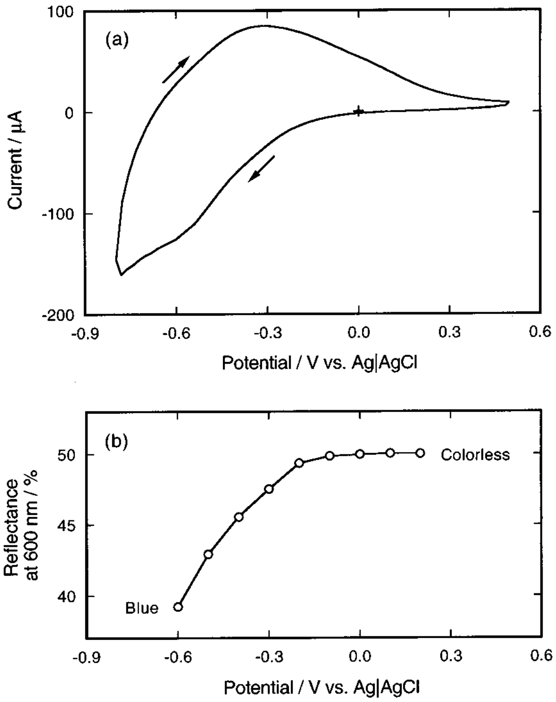

Figure 2. (a) Typical cyclic voltammogram of the WO_3 film on an ITO electrode in an air-saturated 3 wt % NaCl solution, pH 5. (b) Dependence of the steady-state reflectance (at 600 nm) of the WO_3 film on the potential.

Measurements. Electrochemical and photoelectrochemical measurements were carried out in an air-saturated 3 wt % NaCl aqueous solution, pH 5, unless otherwise noted. The area of a coated ITO electrode or stainless steel plate exposed to the solution was 1.75 cm^2. Basically, as-prepared films were used, unless otherwise noted. A digital potentiostat (HZ3000, Hokuto Denko) was used for potential measurements and cyclic voltammetry. Reflectance of WO_3 coatings were measured by using a reflectance spectrophotometer ("Handy-Spec", GY-Gardner). The light source used was a 200-W Hg-Xe lamp (Luminar Ace 210, Hayashi Tokei) together with a 365-nm band-pass filter. The light intensity was about 22 mW cm^{-2} at the sample surface.

Results and Discussion

Electrochemistry of the WO_3 Coating. First we studied electrochemical behavior of a WO_3-coated ITO electrode in a 3 wt % NaCl aqueous solution (pH 5) to examine whether the WO_3 coating can accept electrons from UV-irradiated TiO_2 under these conditions. Figure 2a shows the typical cyclic voltammogram, and Figure 2b depicts the dependence of the steady-state reflectance (at 600 nm) of the WO_3 coating on the potential. It is known that WO_3 is electrochemically reducible to a tungsten bronze, M_xWO_3 (M = H, Li, Na, etc.) as follows:

$$WO_3 + xe^- + xM^+ \rightleftarrows M_xWO_3 \qquad (1)$$

Since the color of M_xWO_3 is blue, the reduction of WO_3 (almost colorless) gave rise to a decrease in the reflectance (Figure 2b). In the solution, photopotential of a TiO_2-coated ITO electrode was −0.4 V vs Ag|AgCl, and it is obvious from Figure 2 that the WO_3 coating can be reduced partially at this potential.

Then, a WO_3-coated ITO electrode was connected to a TiO_2-coated ITO electrode that was in the same electrolytic cell, and the TiO_2 was irradiated with UV

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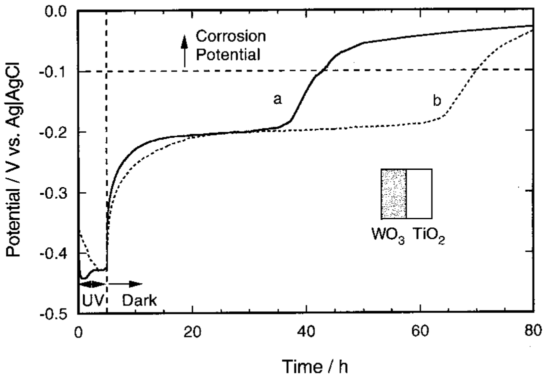

Figure 3. Changes in the potential of an ITO electrode (1.75 cm^2) coated with TiO_2 and WO_3 (area, 50% each) in an air-saturated 3 wt % NaCl solution, pH 5. The WO_3 film was a single (a) or double (b) coating. TiO_2 was irradiated with UV light for the first 5 h.

light. As a result, the reflectance of the WO_3 coating decreased, indicating that the WO_3 was reduced by the irradiated TiO_2. In other words, the WO_3 was charged with reductive energy by the TiO_2.

When WO_3 is reduced, in general, cations are intercalated into WO_3 to cancel the negative charges generated in WO_3, as eq 1 shows. In the present solution, the possible cations that can be intercalated are H^+ and Na^+ (i.e., $M^+ = H^+$ or Na^+). If the concentration of M^+ (in eq 1) decreases, an overvoltage necessary to reduce WO_3 should increase. In a 3 wt % NaCl solution, whose pH value was adjusted to 6 with NaOH, the overvoltage (measured by means of cyclic voltammetry) was almost the same as that in the pH 5 solution. In contrast, in a 0.3 wt % NaCl solution (pH 5), the overvoltage was larger (reduction and reoxidation potentials were more negative) than that in the 3 wt % solution. These results suggest that Na^+ is intercalated preferably to H^+ under the present conditions.

To reduce WO_3, TiO_2 requires an electron source. In other words, TiO_2 has to consume holes generated in its valence band. According to the band bending in the space-charge layer, holes are transported to the TiO_2 surface and react with H_2O in the present case, because the potential of TiO_2 valence band is positive enough to oxidize H_2O to O_2. On the other hand, electrons are transported to the TiO_2 bulk (TiO_2 is an n-type semiconductor) according to the band bending, then further transfer through ITO, and finally reduce WO_3. Thus, the principal reactions involved in the photoelectrochemical charging of WO_3 is described as follows:

$$TiO_2 \xrightarrow{UV} TiO_2{}^*(e^- + h^+) \tag{2}$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \tag{3}$$

$$WO_3 + xe^- + xNa^+ \rightarrow Na_xWO_3 \tag{4}$$

Incidentally, the photopotential of the WO_3 coating in the 3 wt % NaCl solution (pH 5) was about −0.07 V vs Ag|AgCl, and the coating was not charged enough by itself.

Photocharging and Self-Discharging of WO_3. Next, 50% of the surface area of an ITO electrode was coated with TiO_2, and the other 50% was coated with WO_3 (single or double coating), as the inset of Figure 3 shows. The coated electrode was soaked in the 3 wt % NaCl solution (pH 5), and then TiO_2 was irradiated with UV light. Figure 3 shows the results. During the UV irradiation, the potential of the ITO electrode was around −0.4 V vs Ag|AgCl, which is close to the photopotential of TiO_2. After the UV light was turned off, the electrode potential shifted in the positive direction to ca. −0.2 V vs Ag|AgCl, and this potential was retained for a while. This indicates that the WO_3 coating was charged by the UV-irradiated TiO_2 via the ITO electrode. At the potential of −0.2 V vs Ag|AgCl, type 304 stainless steel can be protected from corrosion at least from the thermodynamic point of view, because its corrosion potential is −0.1 to 0.0 V vs Ag|AgCl.

Finally the electrode potential in the dark shifted positively again from about −0.2 V to 0.0 V vs Ag|AgCl. This behavior should be explained in terms of discharging, which is analogous to self-discharging of a battery. That is, Na_xWO_3 is gradually reoxidized to WO_3 probably by giving electrons to dissolved oxygen (reaction 5, 6, or 7):

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{5}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{6}$$

$$O_2 + e^- \rightarrow O_2{}^{-}\cdot \tag{7}$$

Actually, the self-discharging took at least several-fold longer time in a solution deaerated with argon.

In Figure 3, the single- and double-coated WO_3 (the latter is about twice as thick as the former) that had been charged by the irradiated TiO_2 for 5 h took about 45 and 75 h, respectively, to be discharged in an air-saturated solution. This indicates that the double coating reasonably has a greater capacity than the single coating.

Capacity of a WO_3 Coating. Capacity of the WO_3 single coating was measured on the basis of the visible reflectance at 600 nm, which has positive relationship with the charge stored in WO_3. The charge stored for 1 h in the WO_3 coating (single coating, per unit area) by the UV-irradiated TiO_2 was estimated to be 1.2−1.6 C cm^{-2} based on the correlation. The discharge rate was almost constant in the dark, 0.07 μC cm^{-2} s^{-1}. Thus, the rate of oxygen reduction is about 0.7 n^{-1} pmol cm^{-2} s^{-1} if n electrons are involved in the reduction of one O_2 molecule.

Cyclability. Charge and discharge was repeated to examine the cyclability. An ITO electrode coated with TiO_2 and WO_3 (single coating) (area, 50% each) was used. WO_3 was charged in a 3 wt % NaCl solution by UV-irradiated TiO_2 for 1 h and then left until it was discharged. The time required for discharging increased initially (1−9 cycles) and then decreased gradually (Figure 4) until a constant value (~4 h) was reached.

An increase (decrease) in the discharge period should reflect an increase (decrease) in the charge−discharge capacity, an increase (decrease) in the charging rate, or a decrease (increase) in the discharging rate. The initial increase in the capacity may be explained in terms of "break-in" behavior, which is known for some electroactive films.[15] When an electrostatically neutral film is reduced (oxidized), cations (anions) are interca-

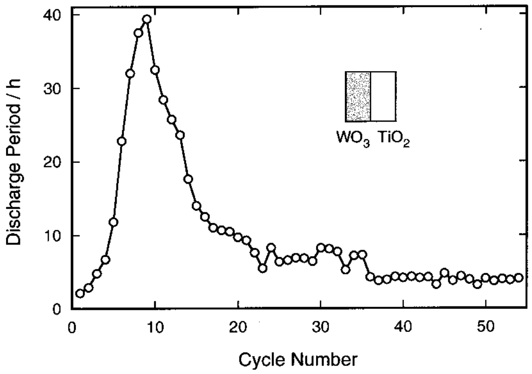

Figure 4. Change in the time required for self-discharging of the WO_3 coating in an air-saturated 3 wt % NaCl solution, pH 5. An ITO electrode (1.75 cm^2) coated with TiO_2 and WO_3 (area, 50% each) was used. The WO_3 film (single coating) was charged by the UV-irradiated TiO_2 for 1 h in each cycle.

lated into the film to cancel the negative (positive) charges generated. In the case of an as-prepared film, the initial several cycles of intercalation and deintercalation give rise to film structure changes, which sometimes increase mobility and accessible regions of the intercalated ion in the electroactive film, resulting in improvement of the redox kinetics and/or capacity. Actually, an increase in apparent redox activity has been observed for WO_3 films.[16] It is known that the water content of a WO_3 film increases during the redox cyclings,[16] indicating changes in the WO_3 film structure.

Further structure change may result in film degradation and a capacity decrease. To examine this possibility, we observed the WO_3 film surface by scanning electron microscopy before and after the repeated charge–discharge cycles (60 cycles) (Figure 5). It is apparent that the WO_3 particles observed after the cycles are smaller than those in the as-prepared film. This degradation must have given rise to the capacity decrease. However, the decrease in the capacity gradually decelerated, and the discharge period approached a constant value (~4 h). Thus, the degradation may be due to mechanical cracking caused by stress generated from Na^+ intercalation, so that the fine particles, which can relax mechanical stress more easily than the larger particles, undergo no further degradation. Actually, crystalline WO_3, which is employed here, has been reported to be stable in an acidic aqueous solution even during redox reactions, unlike amorphous WO_3.[16] On the basis of this report and our results, we anticipate that use of fine WO_3 particles will suppress the degradation, although this is beyond the scope of the present work, which is a demonstration of the potential usefulness of the present system.

Anticorrosion Effect after Dark. Next, type 304 stainless steel was used as a substrate. Two kinds of samples were prepared; one of them was coated with TiO_2 and WO_3 (single coating) (area, 50% each), and the other was fully coated with TiO_2 (see insets of Figure 6).

As Figure 6 shows, the potential of the stainless steel plate fully coated with TiO_2 (curve a) was about −0.4 V vs Ag|AgCl, where the stainless steel is not oxidized, during the UV irradiation. After the UV light was turned off, however, the potential was shifted in a few minutes to the corrosion potential of the stainless steel (−0.1 to 0.0 V vs Ag|AgCl). The potential in the dark was very unstable, indicating that the stainless steel was corroded.

In contrast, the potential of the stainless steel plate coated with TiO_2 and WO_3 (curve b) was more negative than the corrosion potential for a few hours even after the light was turned off. Actually, the unstable potential behavior reflecting corrosion of the substrate stainless steel was not observed for 4 h in the dark. These results clearly indicate that the anticorrosion effect of the TiO_2-WO_3 system is retained after dark.

Potential behavior of the ITO electrode coated with TiO_2 and WO_3 (single coating) (area, 50% each) was also examined for comparison. Even though the sample was prepared and tested in the same way as that for the coatings on the stainless steel, it took longer time to be

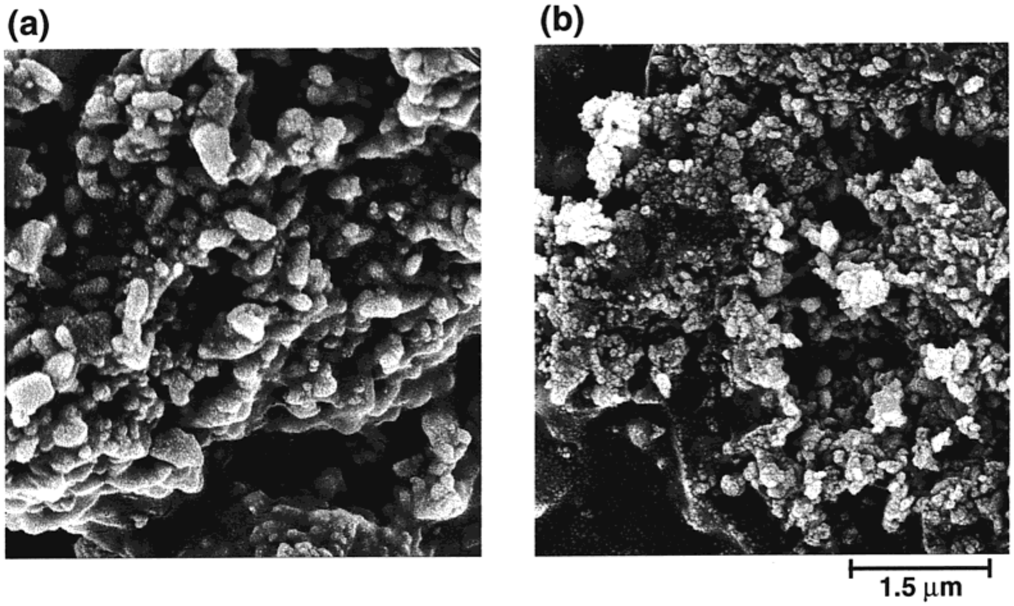

Figure 5. SEM images of the WO_3 films (single coating) before (as prepared) (a) and after (b) the charge–discharge cycles (60 cycles).

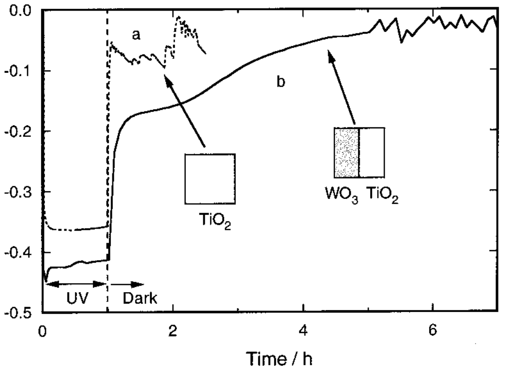

Figure 6. Changes in the potential of a type 304 stainless steel (1.75 cm^2) coated with TiO_2 (a) and that coated with TiO_2 and WO_3 (single coating) (area, 50% each) (b) in an air-saturated 3 wt % NaCl solution, pH 5. TiO_2 was irradiated with UV light for the first 1 h.

discharged (>6 h). This difference is probably due to a difference in discharging processes. That is, a reduced WO_3 coating on an ITO electrode is oxidized primarily by oxygen directly, while that on a stainless steel plate should be oxidized also by oxygen via the stainless steel. This may be reasonable because stainless steel should catalyze the oxygen reduction more efficiently than ITO does.

TiO_2−WO_3 Composite Coating. From a practical point of view, a composite coating in which TiO_2 and WO_3 are mixed is preferable to the separate coatings. As described in the Experimental Section, the composite coating used in this work consists of TiO_2 prepared by spray−pyrolysis and WO_3 particles entrapped in the TiO_2 matrix. The WO_3 content in the film was estimated by means of reflection spectroscopy. The film on an ITO electrode was reduced electrochemically at −0.8 V vs Ag|AgCl in a 3 wt % aqueous NaCl, and a decrease in the reflectance at 600 nm was measured. As a result, the decrease observed for a composite film prepared from 30 mL of the suspension (see Experimental Section) was found to be close to that for the WO_3 film (spin-coated, single coating). Thus, almost the same amount of electrochemically available WO_3 is contained in both the TiO_2−WO_3 composite film and the spin-coated WO_3 film. An ITO coated with the composite film was compared with that coated separately with TiO_2 and WO_3 (area, 50% each). The time for self-discharging after 1 h photocharging was measured for both samples. Here, note that the self-discharging time must be independent of the area of WO_3, as far as the film thickness is constant.

As a result, the composite film exhibited the discharge period of roughly 80% of that of the separately coated sample (Figure 7). As described above, photoexcited TiO_2 has not only reducing but also oxidizing ability. Since WO_3 particles are in contact with TiO_2 particles in the composite film, the oxidizing ability may interfere with the reduction of WO_3. Even so, this effect is not so severe at least in the present system, because the discharge time of the former sample was comparable to that of the latter sample. This may be because most of the TiO_2 surfaces are in contact with the solution, so that most of the photogenerated holes on the TiO_2 surfaces are consumed to oxidize H_2O, rather than the reduced WO_3. Another cause of the different discharge period might be the different surface area of TiO_2. However, it is very difficult to measure microscopic TiO_2 surface area in both of the samples. In either event, WO_3 in the composite film is also photochargeable and retains its capacity.

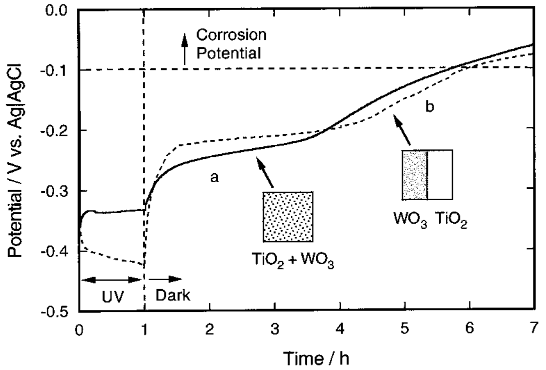

Figure 7. Changes in the potential of an ITO electrode (1.75 cm^2) coated with the TiO_2−WO_3 composite film (a) and that coated separately with TiO_2 and WO_3 (area, 50% each) (b) (see text for further detail) in an air-saturated 3 wt % NaCl solution, pH 5. The coating was irradiated with UV light for the first 1 h.

Conclusions

WO_3 coatings can be charged with a UV-irradiated TiO_2 in a 3 wt % NaCl solution, pH 5. Na^+ is preferably intercalated into WO_3 when it is charged. Type 304 stainless steel coated with TiO_2 and WO_3 (single coating) (area, 50% each) is protected from corrosion under UV illumination, and the anticorrosion effect is retained for a while even after dark, due to the stored charge. A TiO_2−WO_3 composite coating also has the same functions as does the combination of the TiO_2 coating and WO_3 coating.

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