

Using Solar Light for Metal Corrosion Prevention

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Metal corrosion was successfully prevented using a TiO₂-based photoelectrochemical system. Under illumination of 30-W UV ($\lambda_{\max} = 365$ nm; 130 W cm⁻²), TiO₂ electrode in contact with solidified hole scavenging medium, a mixture of formate with agar, supplied photogenerated conduction band electrons (I_{ph}) to an electrically connected steel electrode as its mixed-potential (E_{ph}) shifted negatively. In this galvanic pair, the steel and the TiO₂ electrode acted as a cathode and a non-sacrificial photoanode, respectively. As E_{ph} shifted to positive direction under more corrosive conditions, I_{ph} logarithmically increased under a constant light intensity (30 W or 200 W). However the effect of light intensity on I_{ph} was negligible, implying that its performance little depends on the light intensity as long as there are photons enough to compensate the dark corrosion current of the steel. The corrosion prevention of the steel connected to the system was obvious enough to be detected by the naked eyes. The shiny surface of the steel electrode remained intact in a corrosive electrolyte solution as long as it was connected to the system, while it quickly corroded to be covered by red-brown rusts in the absence of light. Iron oxides detected by Raman spectroscopy also formed much less intensively, meaning that the steel connected to the illuminated photoanode system was protected from corrosion. Through an outdoor test, a natural solar light also exerted a similar effect of prevention, promising high applicability of the system.

Keywords : cathodic protection, photoelectrochemistry, TiO₂, photoanode, solar light.

1. Introduction

In recent we reported a novel cathodic protection,¹⁾ which was carried out with a simple TiO₂-photoanode connected to carbon steel with electrical wire. The basic strategy of corrosion protection is that irradiated TiO₂ photoanode generates photoelectrons sufficient to protect steel in a corrosive environment as shown in Fig. 1 (a). As reported, a new coupled TiO₂-steel potential was placed between the photoanode photopotential (E_{ph}) and the steel corrosion potential (E_{corr}) with simultaneous cathodic photocurrent (I_{ph})²⁾ from the photoanode to the steel. Through a preliminary test, optimal coating thickness of TiO₂ for the photoanode was found to be ~ 10 nm, and the concentration effect of hole scavenging formate was saturated over 0.05 mol/L. Below pH 7, E_{ph} shifted to the negative side with increasing pH in the photoanode cell with showing a Nernstian behavior, yet after pH 7, the E_{ph} was not changed with increasing pH. In this work effects of corrosion environment on metal coupled with the photoanode were investigated under light of low intensity. The behavior of the couple was described quantitatively, and finally the system was considered in a practical view.

2. Experimental

For TiO₂ electrode, 4 ml of TiO₂-aqueous suspension (5wt%) was spread on ITO glass for coated area to be 14.8 cm². After one minute the bulk on the conductive glass was discarded. The TiO₂ electrode was dried in air for 1 hour and heated at 450 °C for 30 minutes. The procedure was repeated when higher coating thickness was needed. A carbon steel electrode employed was cut circular (area 1.66 cm²), mechanically polished with SiC emery paper down to 2000 grade, rinsed with acetone, and finally blown with air. All surfaces and edges of the steel except one circular flat surface were covered with epoxy resin. For application of the photoanode to outdoor test, the TiO₂ electrode was made like a solar panel incased in a plastic Petri dish ($\lambda_{\text{transmit}} > 300$ nm), in which a hole was drilled to connect the KCl-salt bridge as shown in Fig. 1 (b). The ohmic potential drop of the salt bridge was negligible. Solid-phase hole-scavenging medium (1g agar-added 1M formate) was sealed in the solar panel. Photopotentials and photocurrents were measured by a potentiostat (EG&G, Model 263 A), which was connected to a computer to monitor the change of potential and current. All results

Fig. 1. Schematic diagrams of corrosion prevention using semiconductor photoanode. (a) Comparison of the present photo-cathodic system with a conventional sacrificial anode method (b) experimental setup.

for electrochemical experiment were obtained with a Galvanic Corrosion mode in M 352 program supplied by EG&G. The potentiostat that runs a Galvanic corrosion experiment with 'SoftCorr III' software, in effect, functions as a zero-resistance ammeter. To analyze the corroded surface of the carbon steel immersed in various electrolytes, Raman spectroscopy (Renishaw system 3000) was employed. Excitation wavelength was the 632.8-nm line of He-Ne laser.

3. Results and discussion

3.1 Effect of light intensity

Solar panel-type electrode described in Fig. 1 (b) was employed as a photoanode for protecting a steel electrode. As compared between artificial UV light and the solar light in Fig. 2, the natural solar light produced the highest photocurrent when the solar panel was connected to the steel electrode. The increase of the photocurrent with time might be attributed to the increase of solar angle since the initial photocurrent was measured before noon. From this photocurrent comparison, one can confirm that the solar panel will successfully act as a sufficient photoanode under actual solar light if it protects the steel electrode under a less intensive artificial light than an actual solar light.

In Fig. 3, E_{ph} and I_{ph} were measured as a function of pH in the corrosion cell under a constant light intensity. The dark corrosion currents (I_{corr}) of the steel electrode increased from 0.1 to 360 ($\mu A/cm^2$) with lowering pH from 11 to 2. As E_{ph} shifted to the positive direction under more corrosive conditions (lower pH), I_{ph} logarithmically increased even under a constant light intensity. There was little dependence on light intensity (30 vs. 200 W lamp). Although the present system is essentially identical to a

Fig. 2. Effect of light intensity. Solar panel-type TiO_2 photoanode was connected to the steel electrode which was placed in water adjusted to pH 4. Light intensity was 58, 100, 130 W/cm^2 , 1.54, and 1.55 mW/cm^2 for 10, 20, 30, 200, and sunlight, respectively.

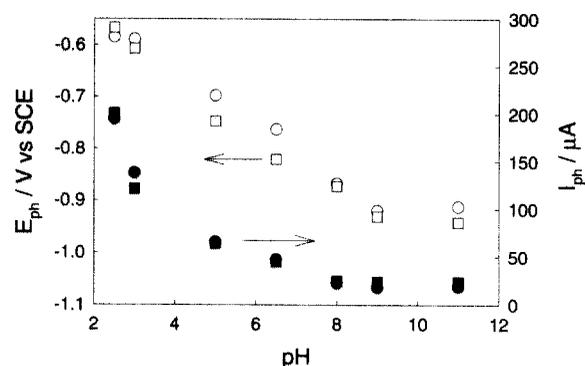


Fig. 3. E_{ph} (open symbols) and I_{ph} (filled symbols) as a function of pH under 30W (circles) or 200W (squares) illumination.

typical photoelectrochemical cell that converts light into electricity where I_{ph} is proportional to the light intensity, it is clearly distinguished from the latter by the fact that its performance little depends on the light intensity as long

Fig. 4. Potential changes with light on-off cycles. The steel electrode was immersed in 10g/L NaCl for 18 hours during the test. 18:18-hr continuous illumination; 3/3: Repeated 3-hr illumination and 3-hr darkness 9/9: 9-hr illumination and 9-hr darkness.

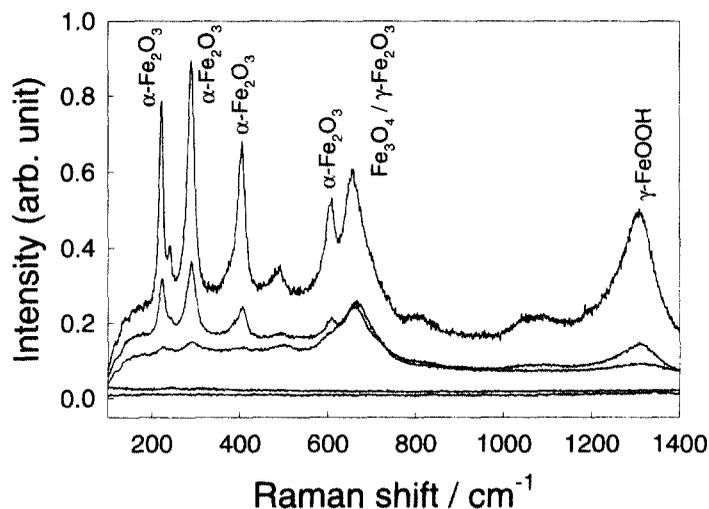


Fig. 5. Raman spectra of the steel surface corroded in Fig. 4. From bottom to up: an initial steel surface; a continuously (18) illuminated; 3/3; 9/9; and a control (dark).

as there are photons enough to compensate the dark corrosion current.

3.2 Corrosion prevention using a solar panel

To prove the performance of the photo-cathodic protection, the steel electrode was corroded by immersing itself in a corrosive solution, 10g/L NaCl for 18 hours. The 30-W lamp illuminated the photoanode continuously or intermittently in order to investigate the effect of periodicity of sunlight on the corrosion of steel. Fig. 4 shows the

potential change in the presence or absence of light. When the photopotential was maintained below $-0.77V_{SCE}$, the borderline of corrosion immunity region, the steel could be protected.

Iron oxides formed on the surface of steel electrode in Fig. 4 were compared with each other in Fig. 5. The surface of the steel electrode that was connected to the continuously illuminated photoanode hardly generated oxides. The shiny steel surface remained intact. The periodical illumination, however, did not perfectly prevent the

formation of oxides. It is interesting that the steel was less corroded in the 3-hr light on/off test than in the 9-hr one though the same amount of photons was given in both cases. This might be due to the presence of critical oxide-formation time at which steel fully reacts with interfacial solution and forms oxides on its surface.

4. Conclusions

TiO₂-based photoelectrochemical system prevented steel corrosion by supplying photogenerated electrons to the steel. When the corrosion environment became acidic, the I_{ph}

increased to compensate for the corrosion current with accompanying positive increase of the Eph. Even with much lower UV intensity (113 μW cm⁻²) than the solar light, corrosion prevention could be achieved.

References

1. H. Park, K. Y. Kim, and W. Choi, *Chem. Commun.*, 281 (2001).
2. D. A. Jones, *Principles and Prevention of Corrosion*, Prentice-Hall, p. 439, 1996.