A novel photoelectrochemical method of metal corrosion prevention using a TiO_2 solar panel

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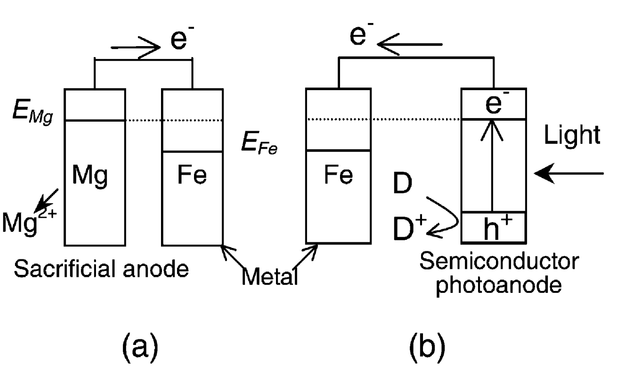
By using a simple TiO_2 solar panel connected to a steel electrode, the concept of photoelectrochemical metal corrosion prevention has been demonstrated to be feasible in utilizing solar light for corrosion inhibition.

Ever since Fujishima and Honda[1] reported the water splitting reaction on illuminated TiO_2 electrodes, semiconductor photoelectrochemistry has been applied to a wide variety of issues such as chemical or electrical conversion of solar energy,[2] pollutant degradation,[3] and superhydrophilic materials,[4] all of which are based on photo-induced charge transfer processes at the semiconductor interface. Here we report another novel application of semiconductor photoelectrochemistry: *metal corrosion prevention*.

The common strategy of corrosion prevention is to change the potential of the corroding metal by pumping electrons in, which is widely known as cathodic protection.[5] When using a sacrificial anode that is more active (negative) in corrosion potential than the metal to be protected, the electrons generated from the corroding sacrificial anode are transferred to the metal object to reduce its corrosion rate [Scheme 1(a)]. The basic idea of this investigation is to replace the sacrificial anode with a semiconductor photoanode that generates conduction band (CB) electrons upon band-gap illumination [Scheme 1(b)]. Previous work by Yuan and Tsujikawa,[6] which reported that the potential of a TiO_2-coated copper substrate drastically shifted toward the less noble (negative) direction under illumination, suggests the idea of using a semiconductor photoanode for corrosion prevention is plausible.

Corrosion prevention experiments were carried out with a photoelectrochemical set-up that consists of a flat solar panel containing a semiconductor (TiO_2) photoanode in a hole-scavenging medium and a steel electrode immersed in an aqueous solution. The semiconductor photoanode was prepared by applying a TiO_2 (Degussa P25) suspension (5 wt%) to an indium tin oxide (ITO) glass slide (Delta technology, 14.8 cm^2). The TiO_2 coated slide was dried in air for 1 h and annealed at 450 °C for 30 min. Electrical contact was made by attaching copper wire with silver paste at the uncoated edge of the ITO slide. The TiO_2/ITO electrode was placed in the solid-phase hole-scavenging medium (6.8 g sodium formate per g agar gel) and encased in a transparent Petri dish to form a flat solar cell. The carbon steel electrode was circular (surface area: 1.66 cm^2) and mechanically polished. The backside and edges of the steel electrode were covered with epoxy resin to expose the flat surface to the aqueous solution in the corrosion cell. The TiO_2/ITO electrode and the steel electrode were galvanically coupled through an external circuit and the two cells were connected by a salt bridge (saturated KCl in agar contained in a flexible Tygon tube). When necessary, 0.05 M K_2CO_3 was added as a supporting electrolyte to the cathodic compartment (corrosion cell) in order to eliminate any possible ohmic potential drop. The light source was 10 W blacklight lamps (1, 2 and 3 lamps for 10, 20 and 30 W illumination, respectively) or a 200 W mercury lamp. The intensities of UV light ($300 < \lambda < 400$ nm) (to excite the TiO_2 photoanode) were estimated to be 58, 100, 135 μW cm^{-2} for 10, 20 and 30 W illumination and 1.53 mW cm^{-2} for the 200 W lamp. Natural solar light UV intensity has been measured to be 1.55 mW cm^{-2} around noon. The TiO_2/ITO electrode was illuminated from the ITO side. Potentials (*vs.* SCE) and currents during illumination were measured using a potentiostat (EG&G, model 263A).[7] The corroded steel surface was analyzed by a Raman spectrometer (Renishaw system 3000) in backscatter geometry with an excitation wavelength of 632.8 nm (He–Ne laser).



Scheme 1 Schematic representation of metal (Fe) corrosion prevention using (a) a conventional sacrificial anode (*e.g.* Mg) and (b) a semiconductor photoanode investigated in this study; D represents hole scavengers while dashed lines represent the electrochemical potential of the electrons generated in the anode.

Fig. 1(a) shows the changes of potentials and currents in the galvanic couple of the TiO_2 photoanode (solar panel) and the steel electrode in acidic water (pH 4) when the photoanode is illuminated under different sources of light. Under illumination, the coupled photopotential, E_{ph}, immediately shifted to more negative potential with a concurrent increase of photocurrent, I_{ph}. The open circuit potential (E_{oc}) of the TiO_2 anode in the solar panel under 30 W illumination was −0.9 V (*vs.* SCE). Comparing this with E_{oc} of the steel electrode (−0.44 V *vs.* SCE), the illuminated TiO_2 anode can supply CB electrons to the metal electrode to protect the metal cathodically by setting a new mixed potential of the couple, E_{ph}. As monitored in this study the value of E_{ph} remained constant under illumination up to 35 days. Natural solar light was as effective as use of a 200 W lamp in inducing changes in E_{ph} and I_{ph}. In addition, a blank test was performed in the absence of added hole scavengers where E_{ph} and I_{ph} were measured to be *ca.* −0.45 to −0.50 V (*vs.* SCE) and 8 μA under 30 W illumination. Various alcohols and organic acids were tested as hole scavengers of which formate was found to show the best performance.

E_{ph} and I_{ph} were measured as a function of pH in the corrosion cell under constant light intensity [Fig. 1(b)]. The dark corrosion currents (I_{corr}) of the steel electrode increased from 0.1 to 360 μA cm^{-2} on lowering the pH from 11 to 2. As E_{ph} shifted in the positive direction under more corrosive

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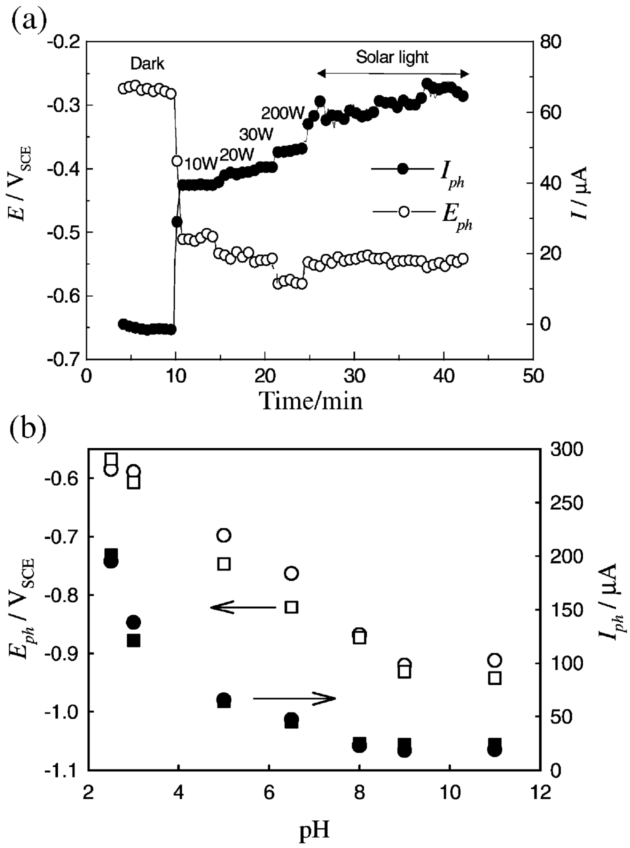

Fig. 1 (a) The change of E_{ph} and I_{ph} in the galvanic couple of a TiO_2 photoanode and the steel electrode when the photoanode was irradiated by 10, 20, 30 or 200 W lamp or solar light. (b) E_{ph} (open symbols) and I_{ph} (filled symbols) as a function of pH under 30 W (circles) or 200 W (squares) illumination.

conditions (lower pH), I_{ph} logarithmically increased even under constant light intensity. There was little dependence on light intensity (30 *vs.* 200 W lamp). Although the present system is essentially identical to a typical photoelectrochemical cell that converts light into electricity where I_{ph} is proportional to the light intensity,[2a] it is clearly distinguished from the latter by the fact that its performance depends little on the light intensity as long as there are enough photons to compensate the dark corrosion current.

Evidence of corrosion prevention of the steel connected to the solar panel was obvious enough to be detected visually. The shiny surface of the steel electrode remained intact in a corrosive electrolyte solution as long as it was connected to the solar panel, while it quickly corroded and was covered by red–brown rust in the absence of light. The progress of corrosion was quantitatively assessed by measuring the Raman spectra of steel surfaces. Fig. 2 compares the Raman spectra of the steel surface corroded in 0.05 M K_2CO_3 solution at pH 6 for 30 h under different illumination conditions. All the peaks generated as a result of corrosion are ascribed to various phases of iron oxides.[8] While the steel surface connected to a continuously illuminated photoanode showed no sign of iron oxide formation, a thick layer of iron oxides covered the steel surface under the dark condition. The steel sample tested under the natural solar light showed an intermediate level of iron oxide formation since more than half of the total corrosion time was during night time or when cloudy.

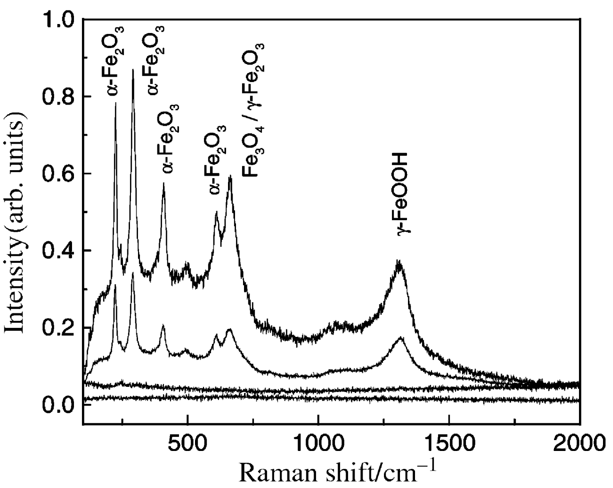

Fig. 2 Raman spectra of the steel surface corroded under different illumination conditions (from the bottom up) of an initial steel surface; a continuously illuminated sample (30 W lamp); sunlight illuminated (16 h day plus 14 h night) sample in the open air; and a control sample not connected to the photoanode.

It has been clearly demonstrated in this work that a simple TiO_2 solar panel can prevent metal corrosion. In view of the fact that the conventional sacrificial anode must be buried or immersed in the medium along with the metal object to be protected and be replaced periodically,[5] use of a photoanode installed on the ground level is easier to maintain. Although the TiO_2 photoanode itself is non-sacrificial, the TiO_2 solar panel is sacrificial since the formate added as a hole scavenger is irreversibly oxidized. However, the hole scavenging medium could be easily refilled to make it regenerative. A similar approach could be possible by using a silicon-based solar cell although it is not economically feasible. Even though the present method suffers from several limitations such as the absence of light at night[9] and the depletion of the hole-scavenging medium, it verifies the possibility of using solar light for corrosion inhibition and could be developed into an alternative or ancillary corrosion prevention method.

Notes and references

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9 This could be overcome by charging a battery connected to the solar panel by day and switching the discharging current to the metal object at night. In a preliminary experiment we confirmed that the progress of corrosion was reduced when a rechargeable battery was connected to the steel electrode at night.