Photoelectrochemical Cathodic Protection of Steel Using a TiO₂ Photoanode and Sunlight

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Metal corrosion was successfully prevented using a TiO₂-based photoelectrochemical system (1). Under UV illumination (30-W blacklight), TiO₂/ITO electrode either in hole-scavenging medium (formate solution or formate in solidified agar) or in pure water (pH 5.6 or pH 11.0) supplied photogenerated conduction band electrons to an electrically connected steel electrode with the generation of photocurrent (I_{ph}) and shifted the coupled-potential (E_{ph}). In this galvanic pair, the steel and the TiO₂ electrode acted as a cathode and a photoanode, respectively.

Using formate as hole scavenger, the photoanode supplied external current (~ 20 µA) with polarizing the steel electrode cathodically from -0.1 to about -0.8 V (vs. SCE), which is essentially a variation of the impressed current cathodic protection (2).The performance of the photo-cathodic protection little depended on the light intensity as long as there were enough photons to compensate the dark corrosion current of the steel. The corrosion prevention of the steel connected to the photoanode 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 UV-illuminated TiO₂ electrode, while it quickly corroded to be covered by red-brown rusts in the absence of light. An outdoor test under solar light also demonstrated a similar effect of corrosion prevention, which verified the possibility of using solar light for corrosion prevention. Various experimental parameters affecting the new photo-cathodic protection system were investigated and discussed in detail.

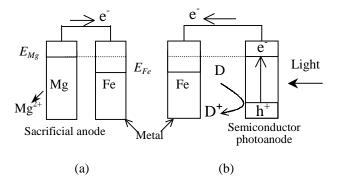
When there was water (pH 5.6, air-equilibrated) only without any added hole scavenger in the TiO₂ photoanode compartment, corrosion took place on the steel surface. However, the steel electrode did not experience any corrosion with the deaerated TiO₂ cell at both pH 5.6 and 11.0 and even with the air-equilibrated TiO₂ cell at pH 11.0. It was postulated that removing dissolved oxygen in water increased the rate of electron transfer to the steel electrode (3) and that basic pH shifted both the flat band potential of TiO₂ and the coupled photopotential of the steel electrode to the negative direction.

REFERENCES

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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 stands for hole scavengers. The dashed lines represent the electrochemical potential of the electrons generated in the anode.

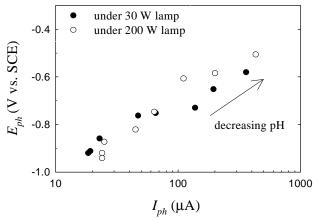


Figure 1. E_{ph} plotted as a function of I_{ph} . The experimental conditions were with the TiO₂ photoanode in formate-containing agar gel and 0.05 M K₂CO₃ in the corrosion cell.

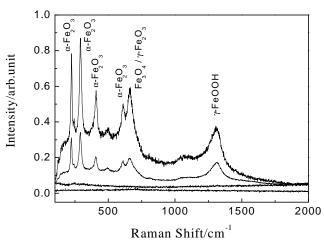


Figure 2. Raman spectra of the steel surface corroded under different illumination conditions: (in the order of bottom to up) an initial steel surface, continuously illuminated sample under 30-W lamp, sunlight illuminated (16-hr day plus 14-hr night) sample in the open air, and a control sample not connected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