BILAYERED PHOTOANODES FOR CATHODIC PROTECTION OF COPPER

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1. Introduction

The ability of sol-gel derived TiO_2 coatings to protect copper from corrosion under ultraviolet (UV) illumination was reported by Yuan and Tsujikawa in 1995 [1]. The basic principle of a photocathodic protection is that a semiconductor photoanode coupled with the metal, generates conduction band (CB) electrons upon band-gap irradiation, which are transferred to the metal substrate thereby shifting its potential to more negative values. The main advantage of this method is that the photoanode does not get consumed during the process of protection unlike a sacrificial type cathodic protection. However, in the case of TiO_2 coated on copper, the photeffect was realized only for heat treatment temperatures above 600 ^{o}C. There was always an intervening Cu_2O/CuO layer formed between the Cu sample and the TiO_2 coating. So, when copper coated with TiO_2 was illuminated with UV light, there was an initial p-type effect as Cu_2O is a p-type semiconductor and after a long time shifted to an n-type photoeffect, indicating the reduction of Cu_2O and/or CuO by the photogenerated electrons from TiO_2. It was concluded that sol-gel derived TiO_2 coatings needed to be heat-treated at 600 –700 ^{o}C in an inert atmosphere for cathodic protection of copper. The well-known disadvantage of a pure TiO_2 coating is that they are functional only under illumination and once the light is cut-off, the photoeffect disappears instantaneously. Hence, the objective of this work was two-fold namely to reduce the heat-treatment temperature of the photoanodic protective coatings on copper and to find out a system that would store electrons during illumination and release them during dark so that there is a continued cathodic protection in the dark conditions.

2. Theoretical background

An easy method of efficient charge separation would be to use another semiconductor whose CB level is below that of TiO_2 so that as soon as there are photogenerated CB electrons in TiO_2, they are immediately transferred to it. Furthermore, if the coupled semiconductor is capable of charge storage, then the n-type effect could persist even after the illumination has been stopped. The important factors that one has to bear in mind are:

1. instantaneous and sufficient n-type photoeffect upon illumination
2. low cathodic current and high anodic current
3. good memory effect and
4. high electrical conductivity of the film so that a facile electron transfer to substrate occurs

SnO_2 is a potential candidate semiconductor material that can be coupled to TiO_2 because of the favourable position of its CB (-0.5 V vs NHE; TiO_2 – 0 V vs NHE at pH 7). Our previous studies showed that in case of a composite SnO_2-TiO_2 coupled photoanode, a 1:1 composition yielded the best results compared to the other compositions [2] and a bilayered composite showed better properties compared to a monolayer composite [3].

3. Experimental

TiO_2, SnO_2 and Sb_2O_3 doped SnO_2 sol solutions were used to make the bilayer electrode. Copper plates of dimensions 3 cm x 2.5 cm polished to 1 μm were used as the substrates. A 0.1-0.2 μm thick bilayer coating of Sb_2O_3 doped SnO_2 followed by a SnO_2-TiO_2 mixture was made by spin coating technique. Heat treatment at different temperatures starting from 100 ^{o}C up to 500 ^{o}C was done in a N_2 atmosphere for 20 min. Electrochemical measurements were carried out in a 0.3 % deaerated NaCl solution and open circuit potentials (OCP) were measured with reference to a saturated calomel electrode under dark and UV illumination. A platinum strip was used as the counter electrode for polarization measurements.

4. Results and Discussion

A comparison of the results for one cycle of rest potential measurements in dark and under illumination for different heat treated samples is given in Fig. 1. It can be seen that the 200 ^{o}C heat treated sample showed highly negative potentials even in the dark conditions and an instantaneous n-type photoeffect on illumination whereas the 400 and 500 ^{o}C HT samples showed an initial p-type effect followed by an n-type effect. Even the as-coated Copper samples showed a desirable photoeffect and memory effect. However, a comparison of the polarization curves for the samples showed that the 200 ^{o}C HT sample showed a higher anodic photocurrent compared to the other samples. This makes us to conclude that a 200 ^{o}C HT is sufficient to induce a efficient photoeffect, reduces the cathodic current and gives a good memory effect, thereby satisfying all criteria that one looks for in a photoanode. This temperature is not too high for an industrial processing and coating big structures. The study has proved for the first time the use of a bilayered photoanode capable of offering a continued non-sacrificial cathodic protection in dark also.

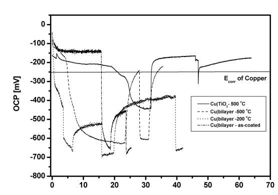

Fig. 1. OCP versus time

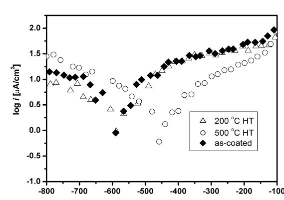

Fig. 2. Polarization curves under illumination for different HT samples

5. Conclusion

A bilayered photoanode consisting of Sb_2O_3 doped SnO_2 and SnO_2+TiO_2 was found to be promising for use in the corrosion protection of copper under UV illumination and dark.

References

1. J. Yuan and S. Tsujikawa, J. Electrochem. Soc. **142** (10) (1995) 3444.
2. R. Subasri and T. Shinohara, Electrochem. Comm., **5** 897 (2003).
3. R. Subasri, T. Shinohara and K. Mori (to be communicated)