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Photocathodic protection of iron oxide nanotube arrays fabricated on carbon steel

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ABSTRACT

The carbon steel (CS) was anodized to coat with vertical arrays of nanotubes in a mixture of aqueous ammonium fluoride solution and ethylene glycol. As-anodized specimens were annealed at 450 °C for 4 h in Ar ambient. The fabricated iron oxide nanotube arrays (NTA) depicted a layer of nanotubes over 500 nm in length, about 80 nm in diameter and about 30 nm in wall thickness shown from scanning electron microscope images. X-ray diffraction pattern indicated that iron oxide NTA contained α-Fe_2O_3 as the main phase and Fe_3O_4 as the secondary phase. UV–visible absorption spectra revealed iron oxide NTA significantly absorbed light up to 700 nm. Potentiodynamic polarization curves of iron oxide NTA and CS were investigated in 0.5 wt.% NaCl solutions in the dark and under illumination supplied by solar simulator. We found that iron oxide NTA shows tremendous photoeffect under alternative illumination and dark. It was seen that potential of iron oxide NTA was more negative under illumination than in the dark and the corrosion rate of CS covered with NTA was obviously less than undecorated CS. In addition, the model of photoelectrochemical anticorrosion of iron oxide NTA was explored.

1. Introduction

Photocathodic protection technique has received more and more attraction because of its unique properties of non-sacrificial photoanode that can keep metal from corrosion without using electric power and/or the other more active metal. So far, it has reported in the literature that different oxides with wide band gap (E_g) could be used as non-sacrificial photoanodes, such as TiO_2 [1–3], SnO_2 [4], ZnO [5], WO_3 [6] and $SrTiO_3$ [7] to coat and supply cathodic protection on the metals, for example, stainless steel [8], Cu [9], Ni [10] and carbon steel (CS) [11]. Many efforts have been devoted to enhance the photocathodic protection of wide band gap oxides with the techniques of particle size reduction to nanoscale [2], fabricating nanostructures (such as nanoporous [12,13], net-like structure [14], nanotube arrays [15]), doping with inorganic atom [15] and preparing composite coating (WO_3-TiO_2 [16], SnO_2-TiO_2 [17], Sb_2O_5-TiO_2 [18], MoO_3-TiO_2 [19], V_2O_5-TiO_2 [20], CdS-TiO_2 [21] and ZnS-CdS-TiO_2 [22]). It is a pity that these oxides exhibited inferior performance of photocathodic protection due to very low absorbance of the light and high contact resistance between the oxide film and metal substrate. Accordingly, these oxides can only protect the metal with more positive corrosion potential and less corrosion rates, such as stainless steel [8], Cu [9], Ni [10]. Therefore, it needs a further effort to develop new oxide film supplying photocathodic protection for carbon steel (CS) that has a comparatively more negative corrosion potential.

Among n-type semiconductors, α-Fe_2O_3 is viewed as a promising material having the advantages of sufficient visible light absorption (almost 40% of solar spectrum), stability, ample availability and low cost [23]. However, α-Fe_2O_3 had a shorter minority carrier diffusion length, higher combination rates of electrons and holes, and poor electron mobility [24]. Currently, the array of iron oxide nanotubes has become very attractive for its unique characterizations [25–28] of high photoconversion efficiency compared to porous film and nanoparticles. Mohapatra [25] reported that the photocurrent density and charge carrier density produced were more 10 times and higher than 2 orders of magnitude level by the array of nanotubes than the film of nanoparticles. Owing to excellent photoelectrochemical and electrochemical performance, nanotubes of α-Fe_2O_3 have been applied in photocatalystes [29], water splitting [25,30,31] and gas sensor [32]. However, photocathodic protection of CS by means of nanotubes of α-Fe_2O_3 was seldom reported.

In present work, we attempted to fabricate vertical arrays of nanotube directly on the surface of CS by means of anodization in a solution of fluorinated ethylene glycol in order to eliminate the contact resistance between the oxide film and metal substrate. After annealing

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at 450 °C for 4 h under Ar-atmosphere, the morphology, microstructure and absorbance with UV–visible of iron oxide nanotube arrays (NTA) were investigated. The electrochemical behaviors of iron oxide NTA in 0.5% NaCl solution including potential, potentiodynamic polarization were also of interest.

2. Experimental

2.1. Materials and methods

All chemicals and solvents used in this work were of analytical grade. Ultrapure water with electrical resistivity at 18.0 MΩ · cm was used to prepare solution. CS was supplied from China Steel Corporation Taiwan with the composition (wt.%) C 0.05%, Si 0.01%, Mn 0.25%, P 0.015%, Al 0.054%, N 0.0049% and balance Fe, and it was cut into specimens of 15 mm × 15 mm × 0.4 mm. Only one surface of a specimen was exposed to the electrolyte by masking the other surface with a thermosetting resin. The exposed surface was ground with a series of silicon carbide (SiC) papers down to 2000 grit, polished with 1 μm alumina powder, and rinsed with DI water then with alcohol. The specimen was ultrasonically treated in DI water and alcohol successively for 10 min and eventually blew with nitrogen gas for dryness.

A side of specimen coated with the film of nanotube arrays was prepared by electrochemical anodization of CS in 150 mL solution, which contains ethylene glycol (EG), 0.3 wt.% ammonium fluoride (NH_4F, Showa, 99.0%) and 3.0 vol.% ultrapure water. A piece of platinized Ti mesh was used as the counter electrode and CS as the working electrode to keep a separation of 40 mm between them in all experimental runs. The anodization was carried out at 60 °C with 50 V for 5 min.

After anodization, the specimen was washed in DI water, in ethanol for 5 s and dried in an oven at 80 °C for 4 h before further processing. After removing the thermosetting resins, the as-anodized film was annealed in argon atmosphere at 450 °C for 4 h with the heating and cooling rate at 2 °C/min.

2.2. Characterization of the specimens

The morphology of specimens covered with the film of nanotube arrays was examined by using field emission scanning electron microscopy (FE-SEM, Nano SEM 230, Nova) operated at an accelerating voltage of 10 kV. Crystalline phases of iron oxide NTA and as-anodized film were examined by using X-ray diffraction (PW3040, Philips) with Cu target ($\lambda = 0.154$ nm). The optical absorbance of iron oxide NTA and as-anodized film was examined by ultra violet-visible diffuse reflectance photospectroscopy (Cary 100 Scan, Varian) equipped with a diffuse reflectance accessory (Labsphere, DRA-CA-3300) over a range of 200–800 nm.

2.3. Photoelectrochemical tests

All electrochemical measurements were carried out in a conventional three-electrode cell where Ag/AgCl electrode used as reference electrode, a platinum wire as counter electrode and specimen (i.e., such as CS, NTA) as working electrode. Electrochemical tests were conducted by a computer-controlled potentiostat (PGSTAT 302, Autolab) in 0.5% NaCl solution. The potential reported is versus with Ag/AgCl reference electrode.

Iron oxide NTA was made to expose an area of 1 cm^2 to the testing solution with a depth of 5 mm beneath the solution surface. Iron oxide NTA of specimen faced light source. A solar simulator (69911, Newport Oriel Instrument) with a power level at 300 W was used as a light source. The intensity of the light was measured by a thermopile sensor (PCE-SPM1, Solar Irradiance Meter) to control the illumination intensity at 140 mW cm^{-2} in the illumination period of all experimental runs.

The potential of iron oxide NTA immersed in 0.5% NaCl solution was recorded under continuous illumination or dark and under alternate illumination and dark. The potentiodynamic polarization of CS and iron oxide NTA in the same solution was performed at a scan rate of 25 mV s^{-1} under illumination and in the dark. All experiments were repeated by using different specimens to confirm the reproducibility of the results.

3. Results and discussion

3.1. Characteristics of iron oxide NTA

Fig. 1 shows the FE-SEM images of film formed on carbon steel prepared in an ethylene glycol solution consisting of 3 vol.% water and 0.1 M NH_4F before and after annealing in argon atmosphere at 450 °C for 4 h. For as-anodized film, the ordered nanotube arrays with length of over 500 nm, an average pore diameter of about 80 nm and wall thickness of about 30 nm can be clearly seen in Fig. 1(a). After annealing, the pore diameter and wall thickness of iron oxide NTA decreased (Fig. 1(b)). The annealed nanotube arrays showed an inside diameter of about 60 nm and a wall thickness of about 20 nm.

The crystalline structures of annealed iron oxide NTA and as-anodized film were characterized by X-ray diffraction (XRD), as shown in Fig. 2. Only one peak of α-Fe appeared on the XRD pattern of as-anodized film. However, α-Fe_2O_3 (JCPDS Card: 33–0664) and magnetite with the chemical compound of Fe_3O_4 (JCPDS Card: 19–0629) as the secondary phase comes out in XRD pattern of iron oxide NTA. In XRD pattern, the Miller indices belong to hematite and M is state for magnetite. In Fig. 2, the main (110) peak at 35.631° indicates that a strong preferential orientation of the [110] axis vertical to the substrate, and the preferred orientation of the (001) basal plane perpendicular to the substrate. A similar prevalence of the (110) reflection is also reported by S. K. Mohapatra et al. [25]. Such preferential orientation does good to improve the conductivity of α-Fe_2O_3 that electrons can transfer within the iron bilayers paralleled with the (001) basal planes to substrate and holes hop laterally between iron double layers to reach the electrolyte interface [33]. Fig. 3 shows the UV–vis diffuse reflectance photospectrometry results of iron oxide NTA and as-anodized film. As-anodized film does not absorb in the visible wavelength range. However, iron oxide NTA can absorb both UV light and visible light due to the direct charge transfer transition from O^{2-} 2p to Fe^{3+} 3d charge and indirect transition between the Fe^{3+} 3d → 3d spin forbidden transition excitation [25]. Two absorbance plateaus come out in visible absorbance region of iron oxide. The onsets of absorbance appeared at 756 nm (band gap = 1.65 eV), which correspond to nanocrystalline consisted of mixed phases of α-Fe_2O_3 and Fe_3O_4 [34]. However, slight lower absorbance intensity of NTA is shown in the UV–vis spectrum when compared with that observed by Mohapatra et al. [25], as may relate to higher the band gap [30] caused by complex chemical structures and larger crystalline size [34] in this investigation.

3.2. Photoelectrochemical characterization

Fig. 4 depicts the potentials of NTA changed with time, which were measured in 0.5% NaCl under illumination and in the dark. When iron oxide NTA electrodes immersed into solution and exposed under illumination, the potential of the illuminated electrode sharply declines, result from the sudden electron pairs generating in the films [35]. After about 15 min, the potential decreased slowly due to accumulation of photogenerated electrons [36] and finally tended to a stable photopotential of -0.58 $mV_{Ag/AgCl}$ because the rate balance appeared between photoelectrons generated and photoelectrons scavenged [11].The response of the potential of the iron oxide NTA electrode without illumination have the similar change with that in the light, except the longer time needed for potential to reach a stable