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Polyaniline for corrosion prevention of mild steel coupled with copper

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Abstract

Polyaniline emeraldine base/epoxy resin (EB/ER) coating was investigated for corrosion protection of mild steel coupled with copper in 3.5% NaCl solution. EB/ER coating with 5–10 wt% EB had long-term corrosion resistance on both uncoupled steel and copper due to the passivation effect of EB on the metal surfaces. During the 150 immersion days, the impedance at 0.1 Hz for the coating increased in the first 1–40 days and subsequently remained constant above $10^9\ \Omega\,\text{cm}^2$, whereas that for pure ER coating fell below $10^6\ \Omega\,\text{cm}^2$ after only 30 or 40 days. Immersion tests on coated steel–copper galvanic couple showed that EB/ER coating offered 100 times more protection than ER coating against steel dissolution and coating delamination on copper, which was mainly attributed to the passive metal oxide films formed by EB blocking both the anodic and cathodic reactions. Salt spray tests showed that 100 μm EB/ER coating protected steel–copper couple for at least 2000 h.

Keywords: Mild steel; Copper; Galvanic corrosion; Polyaniline; Electrochemical impedance spectroscopy

1. Introduction

Conducting polymers such as polyanilines (PANIs) have been extensively investigated for corrosion control [1–3]. PANI exists in various interchangeable states as described elsewhere [4]. In addition to the conducting emeraldine salt (ES) of PANI, the non-conducting emeraldine base (EB) of PANI was also widely examined and found to offer efficient corrosion protection on iron/steel. For example, McAndrew [5] observed that EB film had a very high pore resistance ($2 \times 10^8\ \Omega\,\text{cm}^2$) on mild steel in 3.5% NaCl solution, and EB blended coatings showed improved corrosion resistances. In previous work, we reported that an EB/epoxy resin (ER) coating containing only 1% EB on mild steel passed 2000 h salt spray test, whereas pure ER coating stood only 600 h [6]. There are relatively few reports on PANIs for corrosion prevention of nonferrous metals like copper [7–10]. Brusic et al. [7] showed that spin-coated EB and its derivatives films reduced the corrosion rate of copper in water by a factor of at least 50.

Owing to the wide variations in experimental procedures used like the test methods, coating type and corrosive media, the corrosion protection mechanism of EB is still under discussion. Though McAndrew [5] and Brusic et al. [7] believed that EB acted as an efficient barrier through formation of a dense and strong adherent polymer film, Araujo et al. [11] reported that EB did not protect steel in 0.01 M Na_2SO_4 solution due to poor barrier property and adhesion. Fahlman et al. [12] demonstrated with X-ray photoelectron spectroscopy (XPS) that EB provided anodic protection to iron/steel in humidity air by inducing the formation of a passive iron oxide film, which was also confirmed by other workers [6,13,14]. However, Cook et al. [15,16] argued that EB could not passivate steel in 0.1 M HCl or NaCl solution since there was no active–passive transition upon anodic polarization of the exposed metal at pinholes in the coatings. Kinlen et al. [17] used scanning reference electrode technique to show that passivation of steel in water occurred only for ES coatings. The conducting property of PANI was also stressed by many other authors for the passivation of iron/steel [10,18,19] or copper [8,9].

Accelerated corrosion of a metal electrically connected with a more noble metal is one of the most common forms of corrosion. Though galvanic corrosion can be mitigated by using organic coatings [20,21], currently there is very little work on PANI coating for its prevention. Wessling [22] evaluated an ES coating (CORRPASSIV) for corrosion prevention of steel coupled with copper. In this report, we prepared an EB/ER coating

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and used it to protect steel–copper couple in 3.5% NaCl solution. Corrosion resistance of the coating on the coupled metals was examined through full immersion and salt spray tests; whereas that on the uncoupled metals was investigated by electrochemical impedance spectroscopy (EIS) for 150 days in order to further understand the protective action of EB through a long-term evaluation study.

2. Experimental

2.1. Sample preparation

20A mild steel and copper (99.9 wt%) plates of 5 cm × 5 cm were polished with emery paper to 600 grit and degreased in acetone ultrasonically. EB/ER blend was prepared by ball milling calculated amount of EB powder (a product of Ben'an Co. licensed under this lab, its number average molecular weight was 40,000 with polydispersity index of 3.7) with E-51 epoxy resin (a bisphenol A diglycidyl ether with epoxide number of 0.51, supplied by Jiangsu Sanmu Group, China) in xylene for 4 h. The blend was mixed with the hardener (NX2015, Cardolite) and cast onto the metal surfaces using a draw bar to form an air-dried film of about 20 μm thickness. By adjusting the amount of EB used, a series of EB/ER coatings were made with EB contents in the dried films of 1, 3, 5, 7 and 10% (w/w). Optical microscopic analysis with a LEICA optical microscope revealed that EB was well dispersed in these coatings as particles of typically 10–15 μm in diameter. As a reference, pure ER coating with the same thickness was made under similar conditions.

Samples for XPS analysis were made from copper plates of 1 cm × 1 cm, which were cut from the above pretreated copper plate and further polished with alumina paste to 1 μm and degreased in acetone ultrasonically before applying the 20 μm EB/ER coating with 10% EB.

For full immersion tests of coating on steel–copper couple, samples were prepared as follows: the steel and copper plates (5 cm × 5 cm) coated with the same coating were fixed in parallel with double-face adhesive on a glass substrate (9 cm × 15 cm), leaving the coating upward. Silver conductive adhesive was then used to fill the gap between the coated metal plates to electrically connect the metals. After the silver adhesive was hardened, the sample was sealed with paraffin/colophony mixture to create an exposed area of 3 cm × 3 cm for each coated metal surface. The distance between the exposed areas was 1 cm. Care was taken to avoid exposure of the gaps between the coated metals and the glass substrate, and also the silver adhesive since silver might become a third metal in the galvanic couple. A schematic of the coated steel–copper couple is shown in Fig. 1.

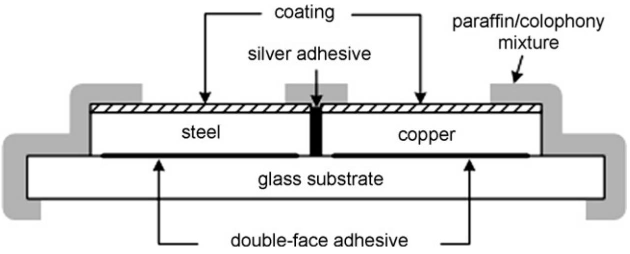

Fig. 1. Schematic of a coated steel–copper couple.

For salt spray tests, coupon assemblies simulating possible practical material combination were used. Each assembly consists of a 20A mild steel plate (0.1 cm × 6.5 cm × 11 cm) held together with a copper (99.9 wt%) plate (0.6 cm × 2.5 cm × 7 cm) by two 304 stainless steel fastener units. Each fastener unit consists of a M8 bolt, two washers and a nut. After surface pretreatment (polished by emery paper to 600 grit and degreased in acetone ultrasonically), the two metallic plates were fixed together and coated with ER or EB/ER coating before they were fastened. For the uneven assembled metallic surfaces, the coatings were applied by spray-coating with approximate 100 μm thickness. Washers and sleeves of polytetrafluoroethylene were used to insulate the bolts and nuts from the metal plates. The back and edges of the steel plate were protected with ER coating and paraffin–colophony mixture, respectively. The results in Fig. 10 show photographs of the coated metallic assemblies.

2.2. EIS measurements

EIS measurements were performed on a Solartron 1287 electrochemical interface coupled with a Solartron 1255B Frequency Response Analyzer. A three-electrode cell arrangement was used. The cell was prepared by sticking a polymethylmethacrylate pipe onto the coated metal (5 cm × 5 cm) to delimit a circular surface area of the working electrode of 7.07 cm^2. A graphite rod and a saturated Ag/AgCl electrode were used as counter and reference electrodes, respectively. The electrolyte solution was 3.5% NaCl solution. The tests were performed at room temperature (25 ± 2 °C) in a Faraday cage to minimize external interference. The data were collected at the open circuit potential (OCP) with a 20 mV sinusoidal ac perturbation over a frequency range of 100 kHz–0.1 Hz.

2.3. XPS analysis

XPS analysis was carried out on a VG Scientific ESCALAB 250 spectrometer with Al Kα X-ray source (1486.5 eV). The coated copper was wrapped with paraffin/colophony (1/1, w/w) mixture on the edges and uncoated side and then immerse in 3.5% NaCl solution for 20 days. After the immersion, the coating was removed mechanically to examine the underlying metal surface. The spectra were collected using pass energy of 20 eV at take-off angles of 90°. Sputter depth profiles were obtained with a 2 mm × 2 mm Ar^+ beam at 2 keV. Surface charge effect was compensated by referencing the adventitious C 1s peak at 284.6 eV.

2.4. Immersion tests

The coated steel–copper samples were fully immersed in 1 L 3.5% NaCl solution in polyethylene film sealed beakers. The solution temperature was controlled at 40 °C in order to shorten the test period. The solutions were periodically sampled for determining the amount of dissolved iron on a Perkin-Elmer