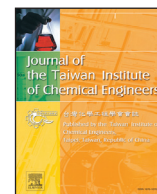




Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Investigation on corrosion protection mechanism of polyaniline nanoparticles doped with phosphoric acid by scanning Kelvin probe and other electrochemical methods

Ghasem Ebrahimi^a, Fereshteh Rezaei^{b,*}, Jaber Neshati^a

^a Corrosion Department, Research Institute of Petroleum Industry (RIPI), P.O. Box 18745-4163, Tehran, Iran

^b Coating Research Center, Research Institute of Petroleum Industry (RIPI), P.O. Box 18745-4163, Tehran, Iran

ARTICLE INFO

Article history:

Received 20 April 2016

Revised 23 September 2016

Accepted 8 November 2016

Available online xxx

Keywords:

Polyaniline nanoparticles

Phosphoric acid dopant

Scanning Kelvin probe

Surface Volta potential

Epoxy Novolac

ABSTRACT

In this research corrosion protection mechanism of Polyaniline nanoparticles (PANs) doped with phosphoric acid dispersed in the Epoxy–Novolac polymer was investigated. Scanning and transmission electron microscopy proved PANs nanometer size and uniform dispersion in Epoxy. Conductivity, EIS, Potentiodynamic, OCP measurements and Scanning Kelvin Probe technique were used to study the protection mechanism of PANs. It was proved that PANs in the coating stabilize the potential of metal in passive state via formation of protective oxide layer and passivation of pinholes on the carbon steel. Coefficient of variation of surface Volta potentials was suggested as an index for investigation on corrosion uniformity under the coatings in presence of PANs.

© 2016 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

1.1. Effect of PANs in corrosion inhibition

Polyaniline has been one of the most important topics of investigations in recent years because of its unique properties such as electrical conductivity, corrosion protection and simple synthesis methods [1–4]. Although it is well recognized that polyaniline can effect on metals corrosion protection, the mechanisms are not completely understood. It has been confirmed that the dopant used with the Polyaniline will affect the corrosion protection, since the dopant affects the PANs conductivity [5–7].

Different mechanisms have been reported for the corrosion protection ability of Polyaniline, such as barrier protection, corrosion inhibition [3,5,8], anodic protection [3,5] and metal surface passivation [2,6]. Polyaniline particles can be barriers against the aggressive anions penetration. The capability of Polyaniline in oxidizing steel substrate, shift the potential of steels to passive state, in which the steel is protected by the passive layer formed beneath the conducting polymer. It was shown that corrosion potential shifted towards more positive potentials in presence of Polyaniline and the corrosion current density was significantly reduced at the corrosion potential [2,3,6–8,8]. It has been shown that Polyaniline

stabilizes metal potential and maintaining a protective oxide layer on the metal. Oxygen reduction on the polymer film also compensate the polymer charge consumed by metal oxidation, so that stabilizes the potential of the metal in the passive state and reduces the rate of metal corrosion [6,8–10]. Polyaniline dispersed in organic coating is able to passivate the pinholes and defects by rapid oxidation of iron [3,11].

Significant properties of Polyaniline are related to Nitrogen hetero atom between Phenyl rings of Polyaniline. dopant anions can also participate into the polymeric structure [12]. The anions are essential to compensate the Polyaniline charges. Structure, properties and the concentration of these anions affect the conductivity of the PANs [11,13–15].

Polyaniline is usually in three forms, reduced leucoemeraldine base (LEB), half reduced emeraldine base (EB), and oxidized pernigraniline base (PNB). The doped or protonated EB form which is called emeraldine salt (ES) has the highest conductivity, while base forms are approximately insulators. During the Polyaniline synthesis Acidic dopant reacts with the imine nitrogens in emeraldine base and Polyaniline salt is produced as a result. As a consequence of imine nitrogens protonation, two electrons of imine nitrogens move to closest quinonoid ring and convert it to the benzenoid form. The remaining unpaired electrons on imine nitrogens, act as charge carriers in the electric conduction chain. It means that conductivity of Polyaniline would increase since the protonation of imine nitrogens produce new charge carriers [15–17]. Corrosion protection would happen because of reversible reduction-oxidation

* Corresponding author. Fax: +982144739592, +982148255139.

E-mail address: rezaeif@ripi.ir (F. Rezaei).

properties of Polyaniline. In the other words the formation and stabilization of a protective oxide layer at the metal/coating interface is accelerated by PAN's high oxidizing power due to their good conductivity. The reduced PANs can be oxidized again by the oxygen available in the system, and these frequent redox-oxidize reactions passivate the surface [8,9]. Using an acidic dopant during the Polyaniline synthesis would affect the polymer conductivity because of dopant protonation ability [5,15]. The higher corrosion protection ability of phosphate doped PANs is also due to Iron-phosphate complex formation on steel [6].

1.2. Scanning Kelvin probe (SKP)

Kelvin probe is a non-contact vibrating capacitor device that measures the potential difference between a vibrating tip and a conductive sample through measuring the AC current induced by the probe vibration [18]. Contact potential difference (CPD) between the conducting tip and sample, is also called Volta potential and defined as:

$$\text{Volta potential} = \frac{\varphi_{\text{tip}} - \varphi_{\text{sample}}}{-e} \quad (1)$$

where φ_{sample} and φ_{tip} are the work functions of the sample and tip, and e is the electronic charge. The work function is the minimum required work to extract an electron from the sample to a position outside the sample so that atomic forces effects eliminate [19–23].

Potential decrease is a phenomenon caused by Fermi level misalignment at the interface between the tip and the Iron substrate as a result of corrosion [24,25].

It was shown that the potential drop across the electrical double layer at the metal polymer interface is an important part of the measured Volta potential. Kelvin probe and the electrode potential at the buried interface is straightforward, although it includes other terms such as dipole or membrane potentials. Local corrosion beneath insulating films can be also studied using SKP [20,25,26]. In the other words giving electron by the steel substrate and progressing corrosion in presence of diffused electrolyte leads to metal surface potential drop and it can be measured by the means of Kelvin prob.

In the present paper, the effect of Polyaniline nanoparticles doped with Phosphoric acid and dispersed in Epoxy Novolac polymer matrix, on the corrosion protection of carbon steel was investigated according to electrochemical measurements and SKP results. We wanted to investigate the effect of the Polyaniline and its amount and also the effect of dopant type on the corrosion phenomena under the coating. SKP measurements were used for the determination of corrosion mechanism under the coatings and the effect of Polyaniline and its amount on the corrosion uniformity under the coating. Kelvin probe measurements are nondestructive and take place in humid air without any need to electrolyte in comparison to other electrochemical methods. One of significant improvement of this work is investigation on potential shift of steel surface to more positive values in presence of Polyaniline by the means of Kelvin prob. In the other words corrosion protection mechanism of PANs was proved by SKP technique. Another point is introducing CV as an index for discussing the corrosion uniformity under the coatings.

2. Experimental

2.1. Materials

Epoxy Novolac resin D.E.N 431 of Dow Chemical Company with Epoxy Equivalent Weight (EEW): 175 and polyamine hardener D.E.H with hardener Equivalent Weight (HW): 24 were used. The

weight mixing ratio of resin to hardener was 13:1. Aniline (analytical grade, Merck) was distilled twice under vacuum and stored in a dark place in refrigerator. Ammonium peroxydisulfate (APS) (analytical grade, Merck), H_3PO_4 acid (99 wt%, Merck) were also used.

2.2. Synthesis of PANs

Chemical oxidative polymerization of aniline was done in aqueous solution at 0–5 °C by dissolving Aniline (4.5 mmol) in 4.6 mmol of H_3PO_4 dissolved in 800 ml distilled water, and then prepared solution was ultrasonicated for 15 min in water and ice bath with a UIP 1000 HD ultrasonic instrument from Hielscher Ultrasound Technology Co. Then an aqueous solution containing 4.5 mmol of APS in 30 ml of distilled water was quickly added and the resulting solution was ultrasonicated again for 5 min in ice and water bath in order to avoid temperature increase. The polymerization was carried out at 0–5 °C for 6 h under static conditions. Afterward the deep green mixture is filtered and washed with distilled water and Acetone. Finally the Polyaniline nanoparticles sintered in an oven at 50 °C for 5 h to get PANs powder. The particle size and morphology of PANs were studied by Vega Tescan Scanning Electron Microscope (SEM).

2.3. Preparation of Epoxy nanocomposite

PANs were added to the Epoxy Novolac resin in 0.5 wt% and 1 wt%. Then the mixing was done by pearl milling for 2 h in 2000 rpm. The mild steel sheets of size 10 cm × 7.5 cm were sand blasted and washed with acetone. The hardener added to the Epoxy Novolac containing PANs before application. The mixture was then applied on the sheets by air spraying and curing of coated steel samples was carried out at room temperature in 15 days. The thickness of cured coating films were about 30 μm. The sample without Polyaniline was defined as **EP** and the samples containing 0.5 wt% and 1 wt% Polyaniline were identified as **PAN5** and **PAN10** respectively.

The transmission electron micrographs of Polyaniline-Epoxy nanocomposite films were obtained using a CM 30, Philips Co. Transmission Electron Microscope (TEM) instrument.

2.4. Conductivity measurements

Conductivity of Polyaniline doped with Phosphoric acid was measured by a four-point method using, using a Siemens B102 Voltmeter and Keithly 6221 current source [27]. In order to sample preparation, PANs were compressed with a hydraulic press at into pellets, 40 mm in diameter and 2 mm thick. Then current imposed to pellet and potential were recorded.

2.5. EIS measurements

Glass tubes were attached to the nanocomposite-coated sheets to form the electrochemical cells, in order to limit the measurable areas to 7.065 cm². The cells were then filled up with a 3.5% NaCl solution. The test cells were maintained at room temperature (20–30 °C) and the solution was refreshed frequently during the test period. EIS data were collected using a Potentiostat/Galvanostat Autolab 84,165 with Nova 1.6 software, after immersion time in the solution. The EIS measurements were performed in 3-electrode mode, using a graphite counter electrode and a saturated calomel reference electrode (SCE). All measurements were carried out on open-circuit potential (OCP), using 10 mV rms amplitude sinusoidal voltage, over a frequency range of 10⁵–10^{–2} Hz. Before each experiment, the open circuit potential was monitored for 1 min. The times required to perform this test varied between 0 and 2500 h for different samples. Three samples investigated were neat epoxy

Download English Version:

<https://daneshyari.com/en/article/4998925>

Download Persian Version:

<https://daneshyari.com/article/4998925>

[Daneshyari.com](https://daneshyari.com)