



Contents lists available at ScienceDirect

## Journal of the Taiwan Institute of Chemical Engineers

journal homepage: [www.elsevier.com/locate/jtice](http://www.elsevier.com/locate/jtice)

# Electrochemical investigations of the corrosion resistance of a hybrid sol–gel film containing green corrosion inhibitor-encapsulated nanocontainers

Mazdak Izadi<sup>a</sup>, Taghi Shahrabi<sup>a,\*</sup>, Bahram Ramezanzadeh<sup>b,\*\*</sup><sup>a</sup> Department of Materials Engineering, Faculty of Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran<sup>b</sup> Department of Surface Coatings and Corrosion, Institute for Color Science and Technology (ICST), P.O. Box 16765-654, Tehran, Iran

## ARTICLE INFO

## Article history:

Received 18 July 2017

Revised 6 October 2017

Accepted 30 October 2017

Available online xxx

## Keywords:

Nettle nanocontainers

Corrosion inhibition

EIS

Silane bi-layer

Active protection

## ABSTRACT

In the present study, the effect of Nettle loaded nanocontainers (Nettle-NCs) on the active corrosion inhibition properties of a silane bi-layer coating was studied. In addition, the synergistic inhibition between the Nettle-NCs and zinc acetate (ZA) was studied. Results obtained from electrochemical impedance spectroscopy (EIS) test demonstrated the effective synergistic corrosion inhibition of mild steel by silane coating containing Nettle-NCs and ZA. The active performance of Nettle-NCs/Silane bi-layer coatings on the MS panels was studied by electrochemical impedance spectroscopy (EIS) and salt spray tests.

© 2017 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

## 1. Introduction

Corrosion is the main cause of metal structures destruction in various industries [1]. There are several methods to protect metallic structures from corrosion damages. Materials selection, corrosion inhibitors incorporation, cathodic and anodic protection, and application of protective coatings are the most convenient methods in industries for retarding the metals corrosion [2]. Among these methods, application of the corrosion protective coatings on metals is the most effective way to protect metals against harsh environments [3]. Corrosion protective coatings are divided into three categories: Metallic, organic, and inorganic coatings [4]. Organic coatings are commonly used as protective coatings due to several advantages such as availability, good adhesion to the substrates, low cost, and proper chemical resistance [5,6]. However, diffusion of corrosive agents into the organic coatings during maintenance is inevitable. In addition, most of the organic coatings only provide a physical barrier against electrolyte and do not show any active inhibition properties when there is a slight damage in the coating matrix. So the aggressive agents diffuse into the polymer–

metal interface and accelerate corrosion process and deteriorate the adhesion bonds between the coatings and metal substrates [7,8].

In recent years, the silane films have been used for pretreatment of metallic substrates before organic coatings application. Silanes play as an important role in adhesion improvement of the organic coatings on metallic substrates [9,10]. Also, the silane films have dense and cross-linked siloxane network and act as a good barrier against diffusion of water, oxygen, and other aggressive agents into the substrate/coating interface [11,12]. Al-saadi et al. [13] investigated the influence of Bis [triethoxysilyl] ethane silane coating on the corrosion resistance of mild steel in the chloride medium. They indicated that the silane coating significantly improved the corrosion resistance of mild steel in 0.6 M NaCl solution. Tetraethylorthosilicate (TEOS) and 3-methacryloxypropyltrimethoxysilane (MPS) were utilized by Chou et al. [14] to prepare protective coating on the stainless steel substrate. The electrochemical analysis confirmed excellent corrosion protection of sol–gel coating through forming a physical barrier which separated the anode from the cathode. Despite the mentioned advantages, like other types of coatings, the corrosion inhibition performance of a silane coating is limited to the barrier effect [3]. In addition, most of the silane coatings highly tend to deterioration in exposure with corrosive media and because of that they do not show good protection performance at long exposure times.

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [mazdak.izadi@modares.ac.ir](mailto:mazdak.izadi@modares.ac.ir) (M. Izadi), [tshahrabi34@Modares.ac.ir](mailto:tshahrabi34@Modares.ac.ir) (T. Shahrabi), [ramezanzadeh@aut.ac.ir](mailto:ramezanzadeh@aut.ac.ir), [bahram1362r@gmail.com](mailto:bahram1362r@gmail.com) (B. Ramezanzadeh).

<https://doi.org/10.1016/j.jtice.2017.10.039>

1876-1070/© 2017 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Incorporation of corrosion inhibitors and inhibitor containing nanoreservoirs into the silane coatings is an effective approach for achieving active inhibition properties. Yan et al. [15] used electrodeposited silica interlayer as the reservoir of inhibitors (polyvinylpyrrolidone and zinc gluconate) for active protection of mild steel substrate. They embedded corrosion inhibitors into the porous sol-gel silica film and applied epoxy coating on the active intermediate film. The considerable improvement in the corrosion resistance of the coated samples was proved using electrochemical tests on the intact and scratched mild steel panels. Cerium salt activated nanoparticles were utilized by Zandi et al. [16] as nanocontainers in silane hybrid coating on electro-galvanized steel samples. Results of salt spray test and electrochemical techniques indicated that the silane coatings containing  $\text{CeO}_2\text{-ZrO}_2$  nanoparticles had lower anodic and cathodic current densities and higher impedance magnitude which approved the active performance of the coatings. Alinejad et al. [17] investigated the influence of an eco-friendly silane sol-gel coating with  $\text{ZnCl}_2$  on the corrosion protection properties of mild steel substrate. They observed that incorporation of zinc cations into the silane coating decreased the corrosion damage of mild steel. Also, deposition of zinc hydroxide and oxide was mentioned as the main protection mechanism of the active system through field emission-scanning electron microscopy (FE-SEM). Wang and Akid [18] used mixture of tetraethoxysilane and cerium nitrate as active surface coating for corrosion protection of mild steel. The considerable corrosion resistance of the silane hybrid coating was due to release of the encapsulated rare earth inhibitor at the coating defects, resulting in cerium hydroxide precipitation which hinders the cathodic reactions.

Direct incorporation of inhibitors into the organic coatings causes several disadvantages such as destructive interaction between the corrosion inhibitor molecules and the coating components, disruption of coating curing process, and uncontrollable release of inhibitors into the coating structure. All of these directed the researchers' attention toward using corrosion inhibitors in the form of containers [19]. There are several methods to synthesize nanocontainers [20]. Among these techniques, layer-by-layer procedure based on oppositely charged polyelectrolytes assembly has several advantages such as facile synthesis process, long-term and smart release of inhibitors, pH-sensitivity, and solid core containers attainment (nanoparticles and pigments which act as barrier agents in the coatings after releasing inhibitors from nanocontainers) [21,22]. In this method, two polyelectrolyte layers form polymeric shell on the nanoparticles surface and corrosion inhibitors can be entrapped between these two layers. The main mechanism in assembly process is electrostatic interaction. In the first step, a polyelectrolyte layer with opposite charge related to the nanoparticles is deposited. In the second step, the inhibitor molecules can be loaded on the polyelectrolyte layer. Then, by adding the second oppositely charged polyelectrolyte (related to first layer), the inhibitor molecules can be isolated and any destructive interaction can be avoided. Also, the polycation/polyanion pair is susceptible to the pH changes and swells at specified pH ranges, leading to the corrosion inhibitors release [23,24]. According to the fact that the corrosion process is accompanied with pH changes, the layer-by-layer formed containers based on oppositely charged polyelectrolytes assembly have special ability to employ as inhibitors reservoirs in organic coatings and have been studied by a large number of researchers [25–29].

Different corrosion inhibitors are used in industries and most of these inhibitors are synthetic, expensive, and harmful to the environment [30,31]. Accordingly, usage of organic green compounds as corrosion inhibitors instead of common industrial chemicals is attractive issue and investigated through many studies [32–35]. Plant extracts, which consist of various phenolic constituents with

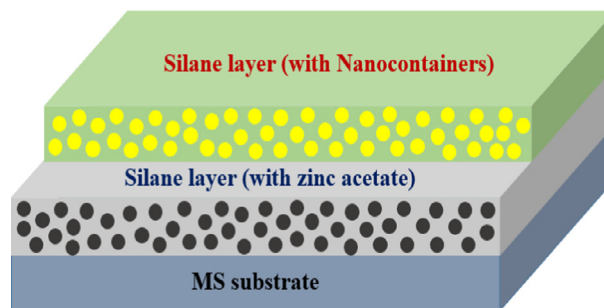


Fig. 1. Schematic illustration of active silane bi-layer coating on MS substrate.

polar functions (S, O, or N) and  $\pi$  electrons, are susceptible to interact with transition metals such as Fe and form chelates which deposit on the metal surfaces and reduce corrosion rate [36–38]. Nettle leaves extract with chemicals such as histamine, quercetin, serotonin, and caffeic acid is a good corrosion inhibitor for steel substrates [37,38].

In regard to the active silane coatings, there are no considerable reports about employment of nanocontainers based on L-b-L method loaded with green inhibitors (Nettle extract). In this study, Nettle-NCs were synthesized by L-b-L method. The polyaniline (PANI)/polyacrylic acid (PAA) pair polyelectrolytes were used to entrap Nettle molecules as corrosion inhibitors. Also, ZA was used to induce the synergistic effect with inhibitor molecules in the active silane bi-layer coatings. The final layout of active nanocomposite silane bi-layer coating is illustrated in Fig. 1.

## 2. Experimental

### 2.1. Materials

Tetraethylorthosilicate (TEOS,  $\text{C}_8\text{H}_{10}\text{O}_4\text{Si}$ ) and triethoxymethylsilane (TEMS,  $\text{C}_7\text{H}_{18}\text{O}_3\text{Si}$ ), acetic acid ( $\text{C}_2\text{H}_4\text{O}_2$ ), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), zinc acetate ( $\text{Zn}(\text{O}_2\text{CCH}_3)_2$ ), sodium hydroxide (NaOH), sodium dodecyl sulfate (SDS,  $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$ ), and ammonium persulfate (APS,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) were supplied by Merck Co. Polyacrylic acid (PAA), aniline monomer, and myristic acid (MA,  $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ ) were purchased from Sigma Aldrich Co. and were used without further purification. Mild steel (CK10) panels (wt.%, 0.1% C, 0.45% Mn, max 0.4% Si, and about 99% Fe) with  $30 \times 20 \times 1$  mm and  $100 \times 35 \times 1$  mm dimensions were used for corrosion studies. Nettle leaves were picked from Northern Foothills of Alborz Mountain, Iran, dried away from the sunlight and gathered for aqueous extraction step.

### 2.2. Synthesis of $\text{Fe}_3\text{O}_4$ nanocontainers

The  $\text{Fe}_3\text{O}_4$  nanoparticles (NPs) were synthesized by adding NaOH to the mixture solution of  $\text{FeCl}_3/\text{FeCl}_2$  [39]. The resulted solution was transferred into the autoclave and  $\text{Fe}_3\text{O}_4$  nanoparticles were collected with a magnet after washing step. The nettle extract was prepared through heating the Nettle leaves in an aqueous solution at  $70^\circ\text{C}$  for 4 h. After that, the supernatant was separated by a filter paper and the resulted solution was exposed to heating until a pasty product was obtained. The Nettle extract was dried and stored in refrigerator. The L-b-L process was done in a multistage procedure to precipitate all three layers on the surface of NPs. After 15 min homogenization of nanoparticles, the 10 g/L NPs suspension in deionized water was prepared and a 2 g/L solution of myristic acid in methanol was added to the prior suspension. The steric stabilization of NPs by MA was performed through an ultrasound assisted step ( $60^\circ\text{C}$  for 45 min) in an ultrasound bath. The functionalized NPs were separated by centrifugation (SW14R Froilabo)

Download English Version:

<https://daneshyari.com/en/article/7105114>

Download Persian Version:

<https://daneshyari.com/article/7105114>

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