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Effectiveness of lanthanum triflate activated silica nanoparticles as fillers in silane films for corrosion protection of low carbon steel

Poovarasi Balan[a,*], R.K. Singh Raman[b,c], Eng-Seng Chan[a], M.K. Harun[d], Varghese Swamy[e]

[a] Chemical Engineering Discipline, School of Engineering, Monash University Malaysia, 46150 Bandar Sunway, Selangor, Malaysia
[b] Department of Chemical Engineering, Monash University, Clayton, VIC 3800, Australia
[c] Department of Mechanical and Aerospace Engineering, Monash University, Clayton, VIC 3800, Australia
[d] Global Entrepreneur Research and Innovation Centre, University Malaysia Kelantan, 16100 Kelantan, Malaysia
[e] Advanced Engineering Program and School of Engineering, Monash University Malaysia, Jalan Lagoon Selatan, Bandar Sunway, 46150 Selangor Darul Ehsan, Malaysia

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ABSTRACT

The synergistic effects of lanthanum activated silica nanoparticle fillers in silane films on the corrosion behavior of low carbon steel have been investigated. The silane films were synthesized through hydrolysis and condensation reactions of 3-glycidoxy-propyl-trimethoxy-silane (3-GPTMS) and methyl-triethoxy-silane (MTES) in acid catalyzed condition. A new corrosion inhibitor, lanthanum triflate at 1000 ppm concentration, was used to activate silica nanoparticles before their impregnation into silane sol–gel mixtures. The morphological characteristics and elemental distribution of the coatings were investigated using scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometer (EDX), confirming crack-free coatings distributed with silica nanoparticles. The structural characteristics and adhesive properties of the silane coatings on steel substrates were analyzed using Fourier Transform Infrared Spectroscopy (FTIR) with the results suggesting the formation of Si—O—Si network and Si—O—Fe bonding. Furthermore, the wetting properties of the coatings were determined through contact angle measurements; the silane films doped with lanthanum and/or silica nanoparticles exhibited increased hydrophobicity of the coatings. The corrosion resistance of the coated steel was evaluated by using electrochemical impedance spectroscopy (EIS) fitted with electrical equivalent models (EEC). The EIS diagrams obtained for the coatings doped with fillers exhibited higher impedance values by at least an order of magnitude when compared with non-doped coatings, indicating improved barrier properties of the coatings. Moreover, the films doped with both lanthanum inhibitor and silica nanoparticles exhibited the most efficient corrosion resistance – by more than two orders of magnitude for more than 168 h – compared to the films doped with either La^{3+} or silica nanoparticles alone. The overall system responses from EIS at high and low frequencies confirmed the benefits derived from synergistic roles of lanthanum-silica nanoparticles in silane films for a long term corrosion resistance performance of low carbon steel.

1. Introduction

Development of new, effective and environment-friendly surface pre-treatments is one of the most considerably investigated method of corrosion protection research in recent times. Silane pre-treatments are one such option for environment-friendly replacement of the toxic chromate-based surface pretreatments. The organo-functional silanes are excellent coupling agents for facilitating adhesive bonding between inorganic substrates and the organic coatings [1,2]. Silane coatings primarily act as barrier coatings by impeding the rate of water and electrolyte intrusion into the substrate. Whilst silane pre-treatments are known to provide good barrier properties for metals, they remain '*passive*' during corrosion. The generation of hydroxyl ions is the most common cathodic process during corrosion of steels under aqueous conditions. As a result, pH may increase to the alkaline conditions causing decomposition of silane and disruption of the sol–gel film network. Thus, silane films need to be modified

* Corresponding author.
E-mail address: poovarasi.balan@monash.edu (P. Balan).

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to resist such deterioration and provide durable corrosion protection.

In the past, modifications to the silane films used different corrosion inhibitors, nanoparticles, and combinations thereof [3–7]. Nanoparticles used to improve barrier properties of silanes include silica [8–10], titania [11], zinc oxide [12], zirconia [6,13], ceria [4], and alumina [14]. Silica nanoparticles are particularly attractive as an additive in silane pre-treatments as they form a passive silicate layer on the metal and thereby suppressing cathodic reactions of corrosion processes for different metals including aluminum and galvanized steel [15]. Montemor and Ferreira [4] studied the role of ceria and silica nanoparticles activated by cerium ions impregnated into silane films on aluminum metals. Ceria nanoparticles were found to provide superior barrier properties due to their stability over a wide range of pH and ability to form complexes with other species. Ceria nanoparticles are also known to provide anodic inhibition to the metals [4].

The nanoparticles have been used together with organic and inorganic corrosion inhibitors such as benzotriazole and rare earth ions for improved barrier properties. The salts of rare earth elements were found to be effective for the aluminum alloys and steels [16]. The rare earth salts suppress the cathodic reaction by precipitating locally insoluble hydroxide or oxide films, which covers the active pitting.

The nitrates [16,17], sulphates[18] and chlorides [19,20] of some rare earths (e.g., cerium and lanthanum) have been used as corrosion inhibitors, including as additives to silane mixtures for metal protection [16]. Rare earth chlorides as inhibitors work well in the alkaline pH regime [19–21]. In studies conducted by Kozhukharov et al. [18], cerium sulphate doped silane film showed detrimental inhibitive effect for aluminum alloys. In their study, it was concluded that though cerium salts are generally reported as efficient inhibitors of corrosion for aluminum alloys, the anionic moiety of the Ce salt used is found to play an important role in its barrier performance. The present study is the first on the use of triflates of a rare earth (i.e., lanthanum triflate) as a corrosion inhibitor impregnated within the silane matrix for anti-corrosive protection. Lanthanum trifluoro-methane-sulfonate($C_3F_9LaO_9S_3$), also known as lanthanum triflate, is stable in water and hence eliminates the need to use any organic solvent, which makes this silane preparation environment-friendly. The present work investigates the effects of lanthanum triflate both with and without silica nanoparticles as fillers in hybrid silane sol–gel films applied on a low carbon steel. The corrosion barrier and adhesion properties of the modified silane films introduced in this work will then be compared with conventional silane films (i.e. those without any dopants).

2. Materials and methods

2.1. Materials

A typical cold rolled low carbon steel procured from Q-Panel, U.S.A was used as the metallic substrate. The nominal composition of the low carbon steel is given in Table 1. The steel was cut into coupons (6 cm × 2 cm × 1 mm) and polished to 1 μm finish. The polished coupons were then washed in an ultrasonicator with soap water and deionised (DI) water for 2 min, followed by acetone degreasing for 3 min. All samples were then treated with sodium hydroxide solution (pH 10.8) at 50 °C and washed with DI water until a water-break free surface was achieved. The specimens were subsequently dried using compressed air at room temperature before silanisation.

Table 1
Composition of cold rolled low carbon steel.

Element	Mn	C	P	S	Fe
Nominal composition (wt%)	0.25–0.6	0.13	0.04	0.050	Balance

Table 2
Types of silane coatings.

Sample reference	CN	GT	GTL	GTS	GTSL
Silane mixture	No	Yes	Yes	Yes	Yes
SiO_2 nanoparticles in silane matrix	No	No	No	Yes	Yes
$La(OTf)_3$ in final silane matrix	No	No	Yes	No	Yes
$La(OTf)_3$ concentration (ppm)	0	0	1000	0	1000
SiO_2 nanoparticles concentration (ppm)	0	0	0	300	300

The silica nanoparticles (>99.5% purity, average diameter of 10–20 nm, Sigma–Aldrich, U.S.A) were ultrasonically dispersed in an aqueous solution of lanthanum trifluoro-methane-sulfonate or lanthanum triflate ($C_3F_9LaO_9S_3$, 99.9%, Sigma Aldrich) to obtain a concentration of 300 ppm of nanoparticles by mass and 1000 ppm of lanthanum triflate by mass. This dispersed aqueous solution was then used for the preparation of the silane solution. A separate aqueous solution with the same lanthanum triflate concentration but without silica nanoparticles was also prepared.

The silane sol–gel sols were synthesized by using a mixture of 3-glycidoxy-propyl-trimethoxy-silane (3-GPTMS, Sigma Aldrich 98%) and methyl-triethoxy-silane (MTES, Sigma Aldrich, 99%) and catalyzed with 0.05 M nitric acid (HNO_3, Sigma–Aldrich, 99.9%) at a molar ratio of 2:1:10 [22]. The silane solution was stirred for three continuous days prior to application on the low carbon steel. 1 ml of dispersed silica (300 ppm solution) was added to the silane solution after 48 h of stirring. The modified sol was left under stirring for another 24 h before applying it to the substrates.

Different pre-treatments used in this work are shown in Table 2; presence of additives such as SiO_2 and/or $La(OTf)_3$ along with their concentrations are indicated. The sol–gel films were produced by dip-coating, i.e. immersion of the pre-cleaned substrate into the desired solution three times for 30 s. After the application of the coating, the samples were cured at 90 °C for 5 h in an oven and then wrapped with aluminum foil and stored until further analysis.

2.2. Corrosion characterization

Electrochemical impedance spectroscopy (EIS) was carried out using a Gamry FAS2 with a PCI4 Controller Board. The experiments were conducted at the open circuit potential with applied 10 mV of sinusoidal perturbation, using a Faraday cage at room temperature. A three-electrode system was used consisting of a saturated calomel reference electrode, graphite electrode (counter electrode) and low carbon steel with exposed sample area (~0.785 cm^2) as a working electrode. The measurements were carried out in the frequency range 100 kHz–10 mHz with 10 steps per decade. The EIS experiments were performed after prior immersion of the silane coated substrates in 0.05 M NaCl for different durations up to 336 h. The EIS measurements were duplicated three times to examine the reproducibility of the results, ensuring the same reported patterns in this study. All the EIS spectra obtained were treated for adequate equivalent electrical circuit fitting using Gamry Echem Analyst software.

2.3. Physical characteristics of the coatings

The average thickness of the coatings developed using different mixtures was measured using Elcometer 456 Coating Thickness Gauge (accuracy of ±1%). Thickness presented (Table 3) is an average of 10 measurements.

The wetting characteristics of the coated surfaces were determined using a contact angle goniometer, Rame-Hart Instrument. The precision of each measurement was of ±0.5°. Several