Study of the Effect of Sol pH and Nanoclay Incorporation on the Corrosion Protection Performance of a Silane Sol-Gel Coating

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Abstract

This work is aimed to evaluate the role of nanoclay in the protective performance of an eco-friendly silane sol-gel layer applied on mild steel substrate in 0.1M sodium chloride solution. At the first step, the effect of pH of the silane solution, consisting of a mixture of γ-glycidoxypropiltrimethoxysilane and methyltriethoxysilane and tetraethoxysilane, on the coating performance was evaluated through electrochemical noise measurements. The values of characteristic charge as a parameter extracted from shot noise theory revealed that the sol pH determining the rate of hydrolysis can play an important role in the corrosion protection behavior of silane coatings. Then, the influence of clay nanoparticles on the corrosion protective performance of the hybrid silane film was studied through taking advantage of electrochemical techniques, including electrochemical impedance spectroscopy and polarization curves, as well as surface analysis methods. The obtained electrochemical data including the values of charge transfer resistance, coating resistance, low frequency impedance and corrosion current density showed that the silane sol gel film in the presence of clay nanoparticles can present an improved corrosion protection. The behavior was connected to an enhancement in the coating barrier properties. Moreover, FESEM and water contact angle confirmed the higher reticulation in case of the coating incorporating nanoclay.

Keywords: Silane sol-gel coating; Nanoclay; Electrochemical impedance spectroscopy; Electrochemical noise; Surface analysis

1. Introduction

Revealing excellent performance, chromate conversion coatings have attracted many attentions. However, the coatings are severely restricted due to their carcinogenic characteristic. Hence, a great deal of study has focused on finding suitable alternatives [1, 2]. As one of the most efficient approaches, hybrid silane-based coatings have been proposed resulting from the hydrolysis and condensation of silane molecules [3-5]. The major disadvantage of the coatings is to act only as a physical barrier against aggressive species towards the interface, meaning the coatings cannot provide active protection [6]. According to the literature, several factors have been studied to enhance the performance of silane sol-gel coatings. In order to improve the barrier properties, the hybrid films should be cured in the proper condition [7, 8]. The coating structure is influenced by the pH of silane solution as the parameter can determine the hydrolysis rate [5]. To top it off, the corrosion inhibitors and nanoparticles have been reported to play an important role in enhancement of the anticorrosion properties of silane layers [3, 9, 10]. Montemor et al. [11] formulated a hybrid silane layer incorporating ceria nanoparticles with enhanced protective performance. They successfully showed the inhibitive effect of the nanoparticles using scanning vibrating electrode technique (SVET). The positive effect of silica nanoparticles incorporated into the bis-sulfur silane film was reported by Van Ooij et al. [10]. The corrosion inhibitive role of SiO_2 and CeO_2 in a silane film applied on galvanized steel was compared elsewhere [12]. The experimental results in a sodium chloride electrolyte showed that the SiO_2 nanoparticles

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are not as effective as the CeO_2 particles, probably due to its lower stability and decomposition of the SiO_2 under increased alkaline conditions as those generated at the cathodic sites. When the silane network degrades, the CeO_2 nanoparticles, that are stable in alkaline conditions, might leach out and precipitate together with the zinc corrosion products, producing a more stable and protective layer. Moreover, some papers have been published reporting the impact of clay nanoparticles on the corrosion protection performance of silane film [3]. Deflorian et al. used nanoclay to improve the barrier properties of silane sol-gel layer on galvanized steel [3]. The corrosion behavior of pure aluminium coated by an eco-friendly silane sol-gel film incorporating nanoclay was also assessed by Naderi and his co-workers [13]. Although the role of clay nanoparticles in the function of silane coatings applied on Al and galvanized steel has been studied elsewhere [3, 13], no report could be found in the literature regarding the mild steel substrate.

This paper intends to investigate the effect of sol pH on the protective performance of an eco-friendly silane sol-gel film consisting a mixing of glycidyloxypropyltrimethoxysilane, tetraethoxysilane and methyltriethoxysilane applied on the mild steel substrate, employing electrochemical noise (EN) method. The silane solution used in this study is completely water based and, therefore, no organic solvent is present. Then, the corrosion protection of silane coatings without and with clay nanoparticles is compared via electrochemical impedance spectroscopy as well as potentiodynamic polarization measurements. The effect of clay nanoparticles on the film structure was also studied using FE-SEM surface analysis and water contact angle measurement.

2. Experimental

Steel panels (composition in wt. %: Fe: 97.7, C: 0.19, Si: 0.415, Mn: 1.39, P < 0.005, S < 0.005, Cr: 0.026, Mo: 0.018, Co: 0.0559, Cu: 0.0429, Nb: 0.0481) were abraded with abrasive papers starting from 100 to 1200 grit size. The samples were rinsed with distilled water and dried in air, then followed by acetone degreasing. The surface activation was performed through 7-min dipping in 25 g/l NaOH solution at 55 °C. The alkaline treatment results in the formation of a high surface density of hydroxyl groups on the substrate. The presence of Fe-OH bonds is responsible for the subsequent interaction between the substrate surface and the hydrolyzed silane molecules. The substrates were then rinsed in distilled water and blow-dried with compressed air. The silanes consisting of γ-glycidoxypropiltrimethoxysilane (γ-GPS) and methyltriethoxysilane (MTES) and tetraethoxysilane (TEOS), purchased from Aldrich, were employed in this study. In order to prepare the silane solution, 10% (w/w) of the silane mixture including an equal weight percentage of the three components was dissolved in distilled water. To investigate the effect of sol pH, the values of pH were adjusted to 2.8 and 4 using acetic acid. The mixture was then magnetically stirred at ambient temperature for 24 h at a rate of 1000 rpm, resulting in a clear and homogenous solution. The coating application process was carried out through vertical dipping of the alkaline surface pretreated samples for 120 s in the prepared silane solution. After drawing of the samples, a heat treatment in an oven was executed at 150 °C for 30 min [14].

Nanoparticles incorporation was executed using ultrasonic dispersion of 1000 ppm of nano clay (supplied by Southern Clay Products, USA), as filler into the distilled water with pH 2.8 prior to addition of the silane mixture. The suspension was then magnetically stirred at ambient temperature for 24 h at a rate of 1000 rpm. The curing process was performed in accordance with the above mentioned procedure. A summary of samples are given in Table 1.

Table 1. A brief summary of samples

sample	pH	Nano clay Concentration [ppm]
A1	2.8	0
A2	4	0
B	2.8	1000

In order to obtain impedance spectra and polarization curves, a conventional three electrode cell including the prepared sample as working electrode, a platinum counter electrode and a saturated calomel reference electrode was used. The exposure area to 0.1 M NaCl solution was 1.0 cm^2. The coating performance was monitored after 1, 4 and 8 h of immersion in the electrolyte at 25°C. EIS measurements were executed within the frequency range 100 kHz to 0.01 Hz using a sine wave of 10 mV amplitude peak to peak. A Solarton 1260 frequency response analyzer (FRA) and Potentiostat–Galvanostat EG&G Model 273A were employed for impedance measurements. Data analysis was made using Zview 3.1c software. After the samples immersed in 0.1 M NaCl solution for 4 h at 25 $^{\circ}$C, polarization curves were provided at a scan rate of 1 mV s^{-1} from -200 mV to +200 mV of OCP using a Potentiostat–Galvanostat EG&G Model 273A.

The electrochemical potential and current noise were simultaneously measured in a freely corroding system employing two nominally identical working electrodes of the same area and a saturated calomel reference electrode. The electrochemical noise measurements were performed using an Autolab instrument model PGstat 302N. The area of each electrode exposed to the solution was about 1.0 cm^2. The three electrodes were immersed in 0.1 M NaCl solution at 25 $^{\circ}$C. The noise data were recorded for 1024 s at a sampling rate of 1 s. After removing DC trend using moving average removal (MAR) method, electrochemical noise data analysis was made with NOVA 1.8 software.

In order to determine water contact angle at room temperature, the samples were horizontally placed on a sample holder. Subsequently, a drop of deionized water (about 0.18 ml) was put on the sample surface and an image was taken from the water drop. The angle between the baseline of the drop and drop boundary was measured using image analysis software. The surface analysis was carried out using a Hitachi SU8040 model field emission type scanning electron microscopy (FE-SEM).

3. Result and Discussion

At first, the effect of sol pH on the protective performance of silane coating was evaluated by electrochemical noise method. One of the approaches to obtain useful data from electrochemical noise analysis is shot noise theory which is based upon the assumption that current noise signals can be considered as packets of charge. Applying some restrictive assumptions, the charge of each electrochemical event q can be obtained from the potential and current noise signals, using the equation (1) [15]:

$$q = \frac{\sqrt{\Psi_E}\sqrt{\Psi_I}}{B} \qquad (1)$$

where Ψ_E and Ψ_I are the low frequency power spectral density (PSD) values of the potential and current noise, respectively and B represents the Stern-Geary coefficient which is dependent on the system under study [15]. To calculate q one should use Ψ_E and Ψ_I determined at low frequencies, where PSD plots take the form of a plateau. The time variations of characteristic charge for samples A1 and A2 are presented in Table 2. From the table, lower characteristic charges could be seen for the mild steel samples coated in a silane solution with pH 2.8. Further, the increase in immersion time resulted in a descending trend of q values, probably due to the coating degradation increasing water uptake. Since the magnitude of characteristic charge can be directly attributed to the anodic dissolution process as well as the mass lost during each electrochemical event at the coating/substrate interface, it could be deduced that the protective performance of silane coatings are affected by sol pH [14]. Affecting the hydrolysis reactions, the pH of silane solution can determine the rate of hydrolysis [5]. Accordingly, the hydrolysis content determining the reactivity of silane solution may affect the film homogeneity and barrier properties. In case of sample A providing more effective corrosion protection, a silane film thickness of approximately 260 nm was estimated.
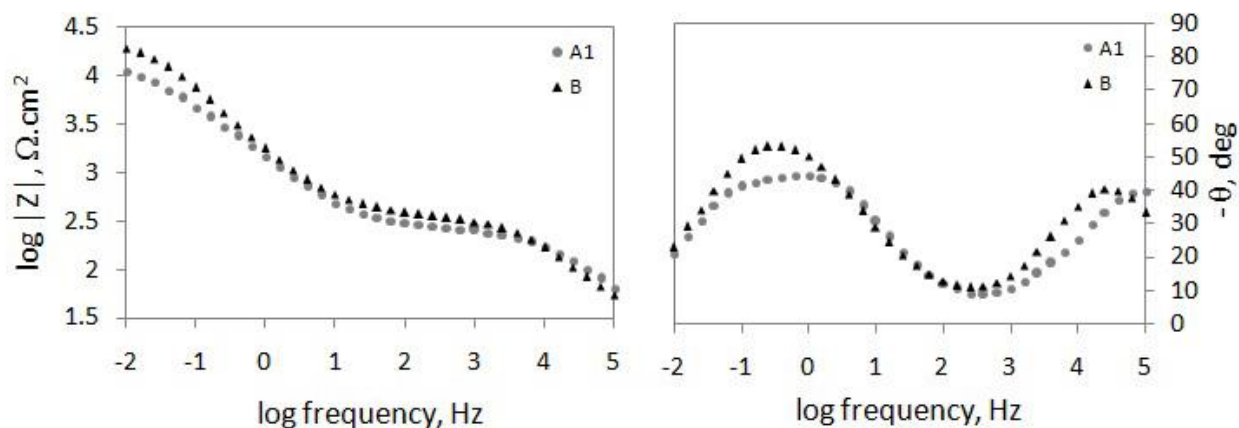
Fig. 1. Typical EIS plots of sample A1 and sample B after 8-h immersion in 0.1 M NaCl.

Table 2. Evolution of characteristic charge corresponding to samples A1 and A2

sample	immersion time in electrolyte [h]	q [C]
A1	1	2.47×10^{-9}
	4	3.55×10^{-9}
	8	4.06×10^{-9}
A2	1	3.20×10^{-9}
	4	5.06×10^{-9}
	8	5.98×10^{-9}

Fig. 2. Equivalent circuit to model the electrochemical behavior of the coated samples during 8-h exposure to the electrolyte.

Electrochemical impedance spectroscopy and polarization measurements were employed to study the role of nanoclay in the protective performance of silane coating. Typical impedance spectra of samples A1 and B after 8-h immersion in 0.1 M NaCl solution are depicted in Fig.1. From the figure, the hybrid film incorporating nanoclay could provide more effective corrosion protection as compared to the neat silane. In other words, sample B presented higher values of low frequency impedance.

As can be seen from Fig.1, two time constants appeared in the impedance spectra of both samples. First time constant in high frequency range is attributed to the silane film and the other one in low frequency domain can reflect the charge transfer process at the coating/substrate interface [3]. Fig.2, where R_s represents solution resistance, R_{ct} charge transfer resistance, CPE_{dl} double-layer constant phase element and R_f and CPE_f represent parameters connected with 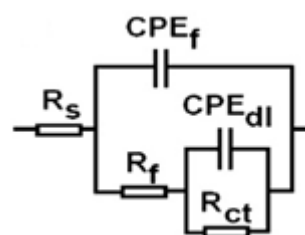the silane film, displays the equivalent circuit selected to model the behavior of samples during the whole immersion period.

Some parameters extracted from EIS spectra are given in Fig. 3. It can be seen from the bar diagrams that incorporation of nanoclay has a significant effect on the performance of silane-based coating. Within the whole immersion period, higher film resistance was obtained in the presence of nanoclay. It might be attributed to better barrier properties provided by clay incorporated film in comparison to the neat one. After 4 h of immersion in the electrolyte, the film resistance offered by sample B is approximately 8.5 times higher than that provided by sample A. The film resistance for both samples revealed a decreasing trend as time increased, probably due to the film degradation and water uptake [16]. Moreover, the superiority of the silane film with clay nanoparticles can be also observed from Fig. 3, where the R_{ct} values offered by sample B is higher than those offered by sample A1. In case of both samples, the downward trend of charge transfer resistance could suggest the
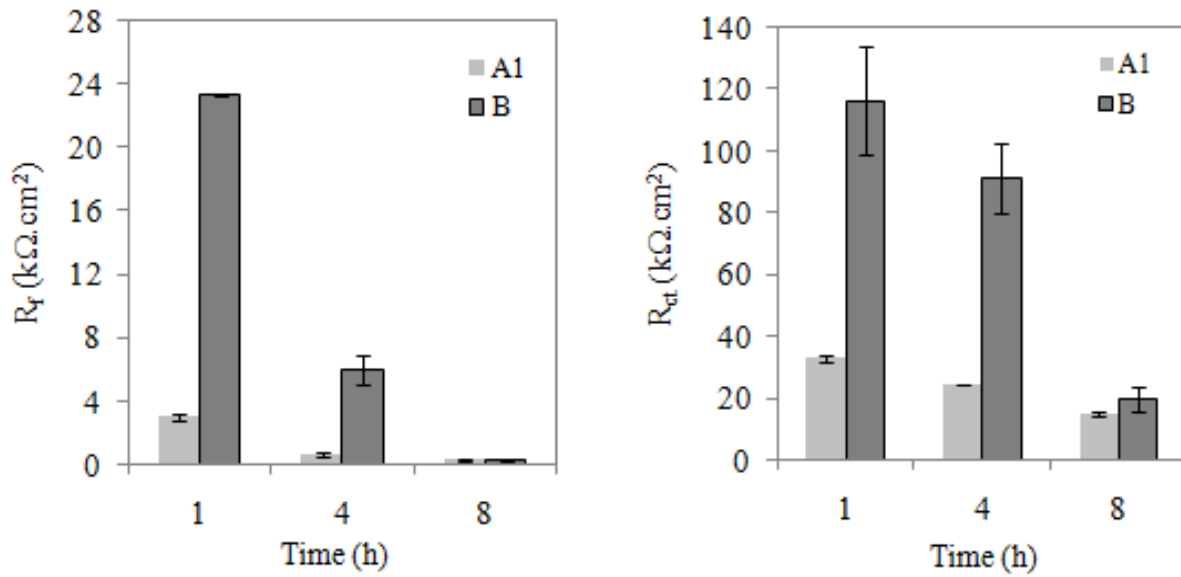
**Fig. 3.** Effect of nanoclay on the parameters coating resistance and charge transfer resistance.

progress of corrosion on the substrate surface, beneath the film [3]. In agreement with Deflorian and his co-workers [3] investigating the addition of clay nanoparticles to the formulation of the silane coating applied on galvanized steel, the nanoclay revealing barrier effect could enhance protective performance of the silane layer on mild steel substrate.

The dispersion quality of nanoclay in the silane matrix is considered as a key factor determining the protective performance. The uniform dispersion of clay nanoparticles with no agglomeration is clearly visible from Fig.4, showing the FE-SEM image of sample B. Furthermore, Fig.4 revealed effective corrosion protection of the silane layer including clay nanoparticles. In other words,

no corrosion product was detected after 4 h of immersion in 0.1 M NaCl solution.

The polarization curves of the silane coated panels in the presence and absence of nanoclay after 4 h of exposure to the electrolyte is compared in Fig. 5. Corrosion current densities extracted from the curves for samples A1 and B are 1.0×10^{-6} and 5.0×10^{-7} A.cm^{-2}, respectively. In case of sample B, the reduction of i_{corr} indicated that the corrosion of mild steel can be effectively inhibited by the silane coating with clay. The behavior may be due to the better barrier properties provided by the flake-like nanoparticles.

Water contact angle was measured to evaluate the hydrophobicity of silane layers. The Θ_{water} values obtained for samples A1 and
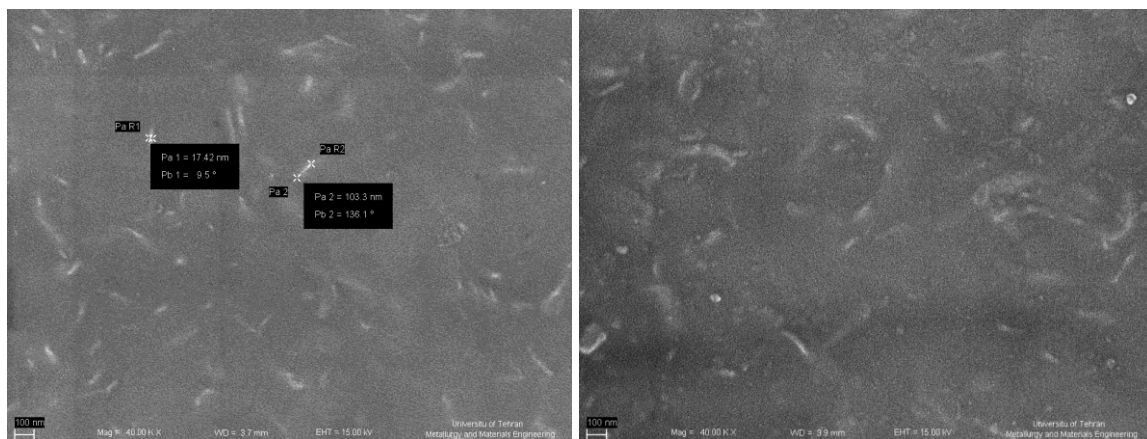
Fig. 4. FE-SEM image of sample B before immersion (left) and after 4-h immersion in the electrolyte (right).
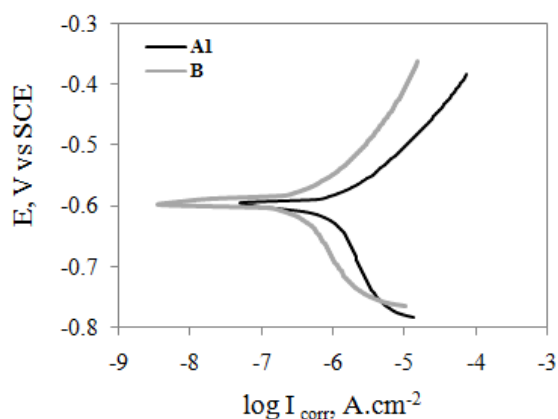
Fig. 5. Polarization curves of samples A1 and B after 4 h of immersion in NaCl solution.

B were 79.34 and 83.63, respectively. The higher water contact angle could indicate more hydrophobic nature of the nanoclay incorporated silane film, i.e. this film is less prone to water [17]. In case of sample B, higher reticulation could be responsible for higher surface hydrophilicity [18].

4. Conclusions

An eco-friendly silane layer was applied on mild steel via sol-gel method in this study. The effect of parameters sol pH and clay nanoparticles incorporation on the corrosion protection was evaluated by electrochemical techniques as well as surface analysis. The characteristic charge as a parameter extracted from electrochemical noise measurement revealed superiority of the film formed in the silane solution with pH 2.8. The significant effect of clay nanoparticles on the protective performance of silane layer was shown through electrochemical impedance spectroscopy and polarization measurements. The behavior was connected to more effective barrier properties of silane coating with nanoclay, confirmed by water contact angle and FE-SEM surface analysis.

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