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Electrochemical investigation of high-performance silane sol-gel films containing clay nanoparticles

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ABSTRACT

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Keywords: Silanes Montmorillonite nanoparticles EIS TEM Galvanised steel Cerium oxides Silane sol-gel coatings are widely used as adhesion promoters between inorganic substrates, such as metals, and organic coatings. The aim of these pre-treatments is to enhance the corrosion protection performance of the organic coating improving the adhesion to the substrate and acting as a barrier against water and aggressive ions diffusion. It is a matter of fact that the silane sol-gel pre-treatments do not provide an active protection against corrosion processes except for the partial inhibition of the cathodic reaction. Inorganic pigments can improve the barrier properties of the silane sol-gel film, enhancing the resistance against corrosion. In this study, different amounts of montmorillonite nanoparticles were added to a water based silanes mixture in order to improve the barrier properties of the sol-gel coating. Hot dip galvanized steel was used as substrate. The sol-gel film consists of a combination of three different silanes, GPS, TEOS and MTES. The clay nanoparticles used in this study were mainly neat montmorillonite. The proper concentration of filler inside the sol-gel films was determined comparing the corrosion resistance of silane layers with different nanoparticles contents. Additionally, the effect of CeO₂ and Ce₂O₃ enriched montmorillonite particles. The EIS analysis and the polarization measurements demonstrated that the optimal amount of neat montmorillonite nanoparticles is about 1000 ppm. The same electrochemical techniques highlighted the limited effect of the cerium oxides grafted to the clay nanoparticles on the corrosion resistance of the silane sol-gel film. The TEM analysis proved the presence of a nanocrystalline structure inside the silane sol-gel film due to the formation of crystalline silica domains.

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1. Introduction

Organosilane molecules are widely studied as coupling agents for the development of environmentally friendly pre-treatments for many metals [1–7]. The potential of these hybrid molecules for the replacement of chromate conversion treatments as well as their corrosion protection properties have been the topic of a huge number of studies which are reported elsewhere in literature [8–14]. Despite being one of the most attractive ways to replace chromium compounds, silanes sol-gel films do not provide the metallic substrate with an active inhibition of the corrosion processes. It was demonstrated that silane sol-gel films provide a thin, but efficient barrier against oxygen diffusion to the metal interface [15], that, usually, improves the resistance against corrosion. However, when water and aggressive ions reach the metallic substrate, silane sol-gel films do not ensure any active protection of the metal. Several attempts have been made to find out a strategy to provide the silane sol-gel film with an active corrosion inhibition potential. The potential of rare earth compounds as environmentally friendly corrosion inhibitors embedded in the silane sol-gel layer has been investigated by many authors [16–18]. Among the different rare earth compounds, the effectiveness of both cerium oxides [19,20] and salts [21–23] as corrosion inhibitors has been demonstrated.

This paper aims at investigating the effect of neat sodium montmorillonite nanoparticles on the properties of silane mixture sol-gel films for the protection of galvanized steel. The idea is to embed the nanoparticles into the silane sol-gel film. After hydrolysis, silanes molecules can graft to the montmorillonite nanoparticles [24], embedding the clay into the hybrid organosilane network. In this paper, the interaction between the montmorillonite nanoparticles and the silanes molecules was investigated, as well as the electrochemical properties of the silane sol-gel film filled with the clay nanoparticles. In addition, clay nanoparticles containing a certain amount of cerium oxides (in particular, CeO_2 and Ce_2O_3) were tested to check the effect of a modified clay surface on the properties of the silane sol-gel layer. Cerium oxides have been proved to be corrosion inhibitors [19], even if the corrosion inhibiting mechanism through which they act is still not completely understood.

For this purpose, a mix of three different silanes molecules such as γ -glycidoxypropiltrimethoxysilane (γ GPS), tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) was used for sol-gel

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matrix to embed the nanoparticles. The balance between the different silanes molecules provides the sol–gel film with improved corrosion protection properties [25].

The characterization of the different silane sol-gel films containing clay nanoparticles was performed by means of electrochemical techniques such as electrochemical impedance spectroscopy and polarization measurements. In addition, exposition in the salt spray chamber and analysis with transmission and environment scanning electron microscopy (TEM and ESEM) were performed. The properties of the different silanes sol-gel systems were characterized and the corrosion protection properties of the clay nanoparticles enriched systems were analyzed and discussed.

2. Experimental

2.1. Materials

Hot dip galvanized steel sheets (zinc–aluminium alloy, 0.25 wt% Al) used as substrate for the application of the silane sol–gel films were purchased from Arcelor Mittal, Belgium. The etching solution for the activation of the surface was an alkaline degreaser, containing KOH (Gardoclean[®], supplied by Chemetall, Germany). The organosilane molecules employed were γ -glycidoxypropiltrimethoxysilane (99% pure), tetraethoxysilane (99% pure) and methyltriethoxysilane (99% pure), all purchased from Degussa and used as received without further purification. The neat clay mineral used as filler was a sodium montmorillonite (supplied by South Clay Products, USA), also called cloisite. The cerium oxides grafted to the montmorillonite nanoparticles were Ce₂O₃ and CeO₂. 5 wt% Ce₂O₃ enriched montmorillonite nanoparticles and 5 wt% CeO₂ enriched montmorillonite nanoparticles were used additionally.

2.2. Samples preparation

The clay nanoparticles were ultrasonically dispersed in water. The pH of the dispersion was modified to 3.5 adding hydrochloric acid. Concentrations of 250, 500 and 1000 ppm of neat montmorillonite particles in the solution were tested. Higher nanoparticles concentration value affects the stability of the dispersion of inorganic particles in the solution at this pH value. The dispersion of inorganic particles into water was added to a 10 wt% of silanes mix consisting of an equal weight percentage of γ -glycidoxypropiltrimethoxysilane (99% pure), tetraethoxysilane (99% pure) and methyltriethoxysilane (99% pure). Thus, the final composition in the glass flask consists of 10 wt% silane mixture and 90 wt% dispersion of montmorillonite nanoparticles in acidified water. The galvanized steel sheets were cut to a size of $100 \text{ mm} \times 60 \text{ mm}$ and then degreased with acetone and ultrasounds for 15 min. The chemical etching was performed by dipping the samples into the alkaline degreaser for 5 min at 50 °C. After rinsing in tap water and then in deionised water, the galvanized steel samples were dipped for 2 min in the different silane solutions. A heat treatment in an oven at 150 °C for 15 min followed after the drawing of the samples. Table 1 summarizes the labels of the different samples object of the study.

1000 ppm of Ce_2O_3 and CeO_2 enriched montmorillonite particles were dispersed into the silane mixture, applied to the substrate and cured following the same procedure previously described for the neat montmorillonite particles.

2.3. Experimental techniques

The electrochemical properties of the silane sol-gel films were monitored by means of electrochemical impedance spectroscopy (EIS). Electrochemical tests were performed using a Princeton

Table T			
Preparation	of the	sol-gel	films.

Name of the sample	Silane sol-gel films		
	Amount of clay nanoparticles in the silane solution used for film preparation (ppm)	Curing temperature (°C)	
250 ppm cloisite	250		
500 ppm cloisite	500	150	
1000 ppm cloisite	1000	150	
Silane sol-gel matrix	_		

Applied Research Potentiostat 273A and Schlumberger HF Frequency Response Analyser SI 1255. A classical three electrodes arrangement was used. A Ag/AgCl reference electrode (+0.207 V vs SHE) and a platinum ring counter electrode were used. Electrochemical impedance measurements were performed using signal amplitude of 10 mV respect to the open circuit potential and the freguency range from 10^5 to 10^{-2} Hz. Five points per frequency decade were collected. The immersed area was 6.15 cm^2 . The impedance measurements were collected regularly with the time of immersion in the electrolyte. To complete the electrochemical characterisation both cathodic and anodic polarization curves, were acquired. The same experimental setup as for the impedance measurements was used. The scan rate was 0.2 mV/s, the IR drop was considered negligible. The tests were performed after 1 h of immersion in the electrolyte. For both, impedance and polarization curves, the conductive solution was 0.1 M sodium chloride. The corrosion resis-



Fig. 1. Impedance modulus (a) and phase (b) of the silane sol-gel coating modified with different amount of clay nanoparticles (neat, 250, 500 and 1000 ppm) after 1 h of immersion in 0.1 M sodium chloride solution.

tance of the silane films was also investigated by exposition of the samples in the salt spray chamber in compliance with the ASTM B117 standard. Both a Philips CM12 transmission electron microscope (TEM) and a Philips XL30 environmental scanning electron microscope (ESEM) were used to collect images of the samples. The analysis and interpretation of the ring electron diffraction patterns was performed using the modelling software Process Diffraction [26–29], while for the spot patterns the modelling software CaRIne 3.1 [30] was used.

3. Results and discussion

3.1. Sol-gel films containing clay nanoparticles

First of all, the effect of different amounts of neat montmorillonite nanoparticles on the properties of the silane sol–gel films was investigated. Fig. 1 shows the impedance modulus and phase diagrams for the different silane sol–gel films containing 250, 500 and 1000 ppm of cloisite nanoparticles, respectively, after 1 h of immersion. For comparison, also the spectra of the silane sol–gel film without nanoparticles are shown. All the different amounts of montmorillonite nanoparticles improve the electrochemical properties of the sol–gel films compared to the unfilled sol–gel matrix (see Fig. 1). The corrosion protection properties of the unfilled silane sol–gel matrix were investigated in a previous study [25] and are



Fig. 2. Impedance modulus (a) and phase (b) of the silane sol-gel coating modified with different amount of clay nanoparticles (neat, 250, 500 and 1000 ppm) after 1 week of immersion in 0.1 M sodium chloride solution.



Fig. 3. Equivalent electric circuit used for the fitting of the experimental spectra: electrolyte resistance (R_{el}), sol-gel film resistance (R_{silane}), constant phase element related to the coating capacitance (Q_{silane}), charge transfer resistance (R_{ct}) and double layer capacitance (Q_{dl}).

recalled here in Figs. 1 and 2 for comparison. The Impedance Phases of the nanoparticles enriched sol gel films, shown in Fig. 1b, clearly indicate two time constants: the high frequency time constant is related to the sol–gel film [31], while the second time constant probably corresponds to the response of the substrate. The values of the low frequencies impedance at 10^{-2} Hz are between 4×10^5 and $2 \times 10^6 \Omega \text{ cm}^2$ for all the sol–gel films containing nanoparticles. During the first hour of immersion, the low frequency impedance of the silane sol–gel matrix is around $10^5 \Omega \text{ cm}^2$, significantly lower than the best value of the montmorillonite filled sol–gel film. In the first hour of immersion all the sol–gel films filled with different amounts of nanoparticles have very similar protection properties.



Fig. 4. Silane sol-gel film resistance (a) and constant phase element (b) for the silane sol-gel coating modified with different amounts of clay nanoparticles (250, 500 and 1000 ppm) with time of immersion in 0.1 M sodium chloride solution.



Fig. 5. Charge transfer resistance of the silane sol-gel coatings modified with different amounts of clay nanoparticles (250, 500 and 1000 ppm) with time of immersion in 0.1 M sodium chloride solution.

Another difference is noticeable: the silane sol-gel matrix shows three different time constants, while the silane sol-gel film filled with the nanoparticles just two. The third time constant has been investigated in several studies [32] and it is likely to be related to the properties of a silane molecules structure arranged on the metal oxide. It is likely that the presence of the nanoparticles leads to strong changes in the structure of the hybrid films.

After a few days of immersion in the aggressive solution, the differences among the sol–gel films become remarkably larger. In Fig. 2 the EIS spectra after one week of immersion in the electrolyte are shown. The film obtained from a solution containing

1000 ppm of nanoparticles maintains the value of the low frequencies impedance very close to the value measured after the first hour of immersion. The film obtained from a solution containing 500 ppm of nanoparticles shows a slight decrease of the impedance in the low frequency domain, while the sample obtained from a solution containing 250 ppm of nanoparticles shows an evident drop (two orders of magnitude) of the low frequency impedance, reaching values close to the sample without nanoparticles. Notice that for this last sample the time constant related to the presence of the sol-gel film is no more observable (see Fig. 2b). In order to better understand the electrochemical properties of the montmorillonite filled sol-gel films, the impedance spectra were fitted using a R(R(Q(RQ))) equivalent circuit (see Fig. 3) [33]. The first resistance is the electrolyte resistance, the second corresponds to the silane sol-gel film resistance (R_{silane}), the first constant phase element is related to the silane sol-gel film capacitance (Q_{silane}), while the other time constant is representative of both the Faradaic resistance of the metal interface (R_{ct}) and the double layer capacitance (Q_{dl}). The results of the fitting procedure are reported in Fig. 4, which shows the values of the silane sol-gel resistance (Fig. 4a) and the constant phase element related to the sol-gel film capacitance (Fig. 4b) estimated from the acquired impedance spectra. The values of the "n" exponent related to the CPE (Q_{silane}) associated to the silane sol-gel films is approximately 1 for all the investigated samples and, therefore, the CPE (Q_{silane}) can be considered as the capacitance of the sol-gel film. Notice that after 100 h of immersion it is no more possible to extract the value of the silane sol-gel film resistance of the 250 ppm cloisite sample, because it becomes too low and the fitting model cannot find a correct value for this parameter. It is clear that sample with 1000 ppm cloisite provides the best corrosion protection among the different samples since the resistance values of this coating are the highest compared to coatings with lower cloisite content after all immersion times in the aggressive solution. In addition, as shown in Fig. 5, the charge transfer



Fig. 6. ESEM image of the silane sol-gel coating modified with 250 ppm of clay nanoparticles (a) before the immersion in the aggressive solution and ESEM images of the silane sol-gel coatings modified with different amount of clay nanoparticles (250 ppm (b), 500 ppm (c) and 1000 ppm (d)) after 10 days of immersion in 0.1 M sodium chloride solution.

resistance on the surface of this sample is almost constant for all immersion times in the sodium chloride solution. It is commonly accepted [34] that the charge transfer resistance is inversely proportional to the corrosion rate (depending on the reactive area). Thus, as far as the performed experimental tests are concerned, the sample with 1000 ppm cloisite seems to ensure the highest degree of protection for the galvanized steel substrate among the studied sol-gel coatings. Sample 500 ppm cloisite shows values of the charge transfer resistance which, even if lower, are comparable with the values of sample 1000 ppm cloisite. On the other hand, the sample obtained from a solution containing 250 ppm of nanoparticles shows a continuous decrease of the charge transfer resistance, indicating the progression of a corrosion process. After 240 h of immersion in the aggressive solution, the area of each sample affected by the electrolyte was analyzed by means of scanning electron microscopy. Fig. 6 depicts the appearance of the area of the three different samples affected by the electrolyte. Zinc corrosion products (lighter particles in Fig. 6b) are observable on the surface of sample with 250 ppm cloisite. In accordance with the electrochemical measurements, this is an evidence of an advanced corrosion process occurring on the surface of this sample. The surface of the other two samples does not show any accumulation of zinc corrosion products and the sol-gel film surface seems to be intact. For comparison, the appearance of the surface of the 250 ppm cloisite sol gel film before immersion is shown in Fig. 6a. The appearance of the silane sol-gel films other two samples (500 and 1000 ppm) before the immersion in the aggressive solution is exactly the same of sample 250 ppm cloisite.

In order to complete the electrochemical characterization, potentiodynamic curves were also acquired. Fig. 7 shows the anodic and cathodic polarization curves for the samples object of the study. For comparison, the behaviour of the alkaline degreased bare zinc and the unfilled silane sol-gel matrix are also reported. Comparison of the anodic polarization curves shows that the main difference regards the particularly low anodic current of 1000 ppm cloisite sample. All the silane sol-gel films show a higher resistance of both the anodic and cathodic polarization curve compared to the bare galvanized steel. This difference is huge for all the samples (two or three orders of magnitude) for the cathodic polarization, while, except for the sample 1000 ppm cloisite, it is slight for the anodic polarization. Among the silane sol-gel covered samples, the 1000 ppm cloisite samples show the lowest value of the cathodic current densities, even if the values of the other samples are comparable. All the montmorillonite filled samples show lower cathodic and anodic currents than the silane sol-gel matrix. It is likely that the presence of the montmorillonite nanoparticles affects the barrier properties of the silane sol-gel film, leading to a decrease of both anodic and cathodic currents. Probably the presence of the hybrid sol-gel film reduces the active areas of the metal directly in contact with the electrolyte. All the studied sol-gel films shows a remarkable decrease of the cathodic current densities of the underling metal. On the other hand, except for the sol-gel coating produced with 1000 ppm of cloisite, the anodic current densities of the other samples are just slightly lower than the anodic current density of the bare zinc. This fact can be related to the good oxygen barrier properties of the studied sol-gel films which lead to low cathodic current densities of all the investigated samples.

The concentration of 1000 ppm of clay nanoparticles of the diluted silane solution leads to the formation of a sol-gel film with improved protection properties as proved by high impedance values. Indeed, this sol-gel film seems to maintain the better protection of the substrate against corrosion during all the testing time (about 200 h). The properties of the 1000 ppm cloisite samples were further investigated by means of TEM observation. The aim of this technique was to determine the effect of the nanoparti-



Fig. 7. Anodic (a) and cathodic (b) polarization curves for samples modified with different amounts of clay nanoparticles (250, 500 and 1000 ppm cloisite) and bare zinc.

cles on the structure of the silane sol-gel film. Fig. 8a, c and d depicts the appearance of the silane sol-gel film and reports the electron diffraction spectra (b). By collecting an electron diffraction pattern all over the portion of film depicted in Fig. 8a it is possible identify, after a proper modelling of the electron diffraction patterns, the presence of the structure of montmorillonite [26-30]. The montmorillonite nanoparticles are highlighted in Fig. 8a by dot circles. It was possible to detect and localize the montmorillonite nanoparticles selecting a convenient diffraction angle (which undergoes Bragg scattering related to the crystallographic structure of the montmorilonite particles) and observing the sample in "dark field". Fig. 8b reports the electron diffraction pattern collected over the area depicted in Fig. 8a. Notice that both a ring and a spot pattern are visible. Modelling the dot pattern of Fig. 8b with the pattern-solving software CaRIne 3.1 [30] it is possible to observe that it corresponds to the montmorillonite crystals, while the ring pattern is related to the presence of a nano-crystalline phase. The solution of the ring pattern carried out using the modelling software Process Diffraction [26-29] leads to the conclusion that the nano-crystalline phase consists of a hexagonal structure of silicon oxide. It is likely that the inorganic fraction of the hybrid molecules arranges itself in a nano-crystalline phase. In Fig. 8c and d it is possible to appreciate the presence of the nano-crystalline domains, present as dark dots dispersed in the film (highlighted by the arrows in Fig. 8d). It



Fig. 8. TEM images of the 1000 ppm cloisite silane sol-gel film (a, c and d) and electron diffraction pattern (b) of the highlighted areas in image (a).

was possible to detect the presence of the nano-crystalline domains acquiring and analysing electron diffraction patterns on over the dark areas in Fig. 8d. The presence of nano-crystalline domains was investigated more in depth. Fig. 9 reports other crystalline phases observed by means of TEM. For both the two crystalline phases depicted in Fig. 9a and c the corresponding electron diffraction pattern are reported in Fig. 9b and d, respectively. The modelling of the diffraction patterns performed using Process Diffraction [26–29] leads to the conclusion that the nano-crystalline phase is, also in this case, silica arranged in an hexagonal crystalline habit. In Fig. 9



Fig. 9. TEM image of the 1000 ppm cloisite sol-gel film, (a) and (c), and their corresponding electron diffraction pattern, (b) and (d) respectively.



Fig. 10. TEM images of two different montmorillonite nanoparticles or agglomerates of montmorillonite nanoparticles.

it is possible to appreciate nano-crystalline domains of different extent and appearance. It is likely that some of these domains are self-arranged during the curing, while other grows surrounding a montmorillonite particles. The dimension and appearance of the montmorillonite particles were also investigated in order to clarify the nature of the crystalline domains. The clay nanoparticles were ultrasonically dispersed in ethanol and than observed by TEM. Fig. 10 depicts, for example, two different particles. Despite the use of high magnification, it is not easy to differentiate between single montmorillonite particles and aggregation of a certain number of particles. However, considering Fig. 10b, it is possible to observe the presence of a small particle (or aggregates of smaller particles) that probably act as nucleant for the formation of crystalline domains in the hybrid matrix.



Fig. 11. Silane sol-gel film resistance (a) and charge transfer resistance (b) for the silane sol-gel coatings modified with different kinds of clay nanoparticles with time of immersion in 0.1 M sodium chloride solution.



Fig. 12. Anodic (a) and cathodic (b) polarization curves of silane sol–gel films modified with different kinds of clay nanoparticles.



Fig. 13. Silane sol-gel films with different kinds of nanoparticles after 1 week of exposure in the salt spray chamber.

3.2. Sol-gel films containing cerium oxides

In the previous section (see Section 3.1) it was evidenced that the concentration of 1000 ppm of nanoparticles in the starting solution enhances the corrosion protection of the sol-gel film. As previously specified, 1000 ppm of, respectively, neat montmorillonite, 5 wt% Ce₂O₃ enriched montmorillonite and 5 wt% CeO₂ enriched montmorillonite and 5 wt% CeO₂ enriched montmorillonite and 5 wt% CeO₂ enriched montmorillonite, were dispersed in the diluted silanes solution to obtain three different sol-gel films. The films were obtained following the procedure previously described in the experimental part. The corrosion protection properties of these sol-gel films were evaluated, as before, by means of electrochemical impedance spectroscopy. Fig. 11 shows the silane sol-gel resistance (a) and the charge transfer resistance (b) for the different sol-gel films with the time of immersion in the aggressive solution. The fitting of the impedance spectra was carried out using the previously discussed equivalent electric circuit.

The resistance values of the different clay nanoparticles filled sol-gel films are comparable. The decrease of the resistance follows the same trend for all samples, with little differences only during the very last days of immersion. This is an evidence that the clay nanoparticles tailored with cerium oxides improve the barrier properties of the silane sol-gel film as well as the neat montmorillonite particles. However, as shown in Fig. 11b, the film with neat montmorillonite embedded leads to a slightly better corrosion protection compared to the films with cerium oxides-modified clay nanoparticles. In Fig. 11b, no remarkable differences between the two different cerium oxides are visible. The charge transfer resistance trends over immersion time of both samples are more or less the same, showing a progressive decrease of the corrosion resistance. Instead, the sol-gel film filled with neat montmorillonite shows stable values of the charge transfer resistance up to 200 h of immersion. Only after this period of exposure time a decrease of the charge transfer resistance is appreciable. However, despite the initial differences, the final values of the resistance, after 336 h of immersion are similar.

The potential of the cerium oxides as surface modifiers was investigated by means of both anodic and cathodic polarization measurements. Fig. 12 shows the anodic (a) and cathodic (b) polarization curves for these sol-gel films and, for comparison, for the bare galvanized steel. In Fig. 12, there is no evidence of a beneficial effect on either the cathodic or anodic reaction kinetics related to the presence of the cerium oxides on the surface of the particles. The silane sol-gel matrix filled with neat montmorillonite again shows the best performance, indicated by the lowest cathodic and anodic currents.

To detect possible differences among the differently filled sol-gel films, salt spray testing was performed. Fig. 13 reports the qualitative results of the exposure, after 1 week. The bare galvanized steel samples show a huge amount of zinc corrosion products on the surface while the samples covered with the sol-gel films filled with neat montmorillonite and CeO₂ enriched montmorillonite are still protective and no zinc corrosion products are observable. Instead, the zinc corrosion products are visible on the surface of the sample covered with the silane sol-gel film filled with clay nanoparticles enriched with Ce₂O₃.

The surface modification of montmorillonite nanoparticles with cerium oxides, therefore, does not improve the protective properties of the sol–gel film. In fact, the properties of the sol–gel films obtained using montmorillonite modified with cerium oxides are the same, or even worse, than of the sol–gel layer obtained using neat montmorillonite. It is likely that the surface modification of montmorillonite nanoparticles, may affect the performances of the silane films, by influencing the silane–clay interaction due to the presence of the oxides.

4. Conclusions

Montmorillonite nanoparticles and cerium oxides enriched montmorillonite nanoparticles were tested as fillers inside silane sol-gel films. The amounts of 250, 500 and 1000 ppm of montmorillonite nanoparticles were tested as fillers inside the starting silane mixture. It was proved that the concentration of about 1000 ppm of neat montmorillonite nanoparticles in the silane solution improves the corrosion protection properties of the produced silane sol-gel film by means of electrochemical testing and exposure in the salt spray chamber. The TEM images of the silane sol-gel films containing montmorillonite nanoparticles highlighted the presence of two crystalline phases, one corresponding to the clay and the other corresponding to hexagonal silica nanostructured domains. In addition, it was demonstrated that the surface modification of the montmorillonite particles with cerium oxides do not improve the barrier properties of the silane sol-gel film, leading to the conclusion that it is likely that the interaction between the montmorillonite and the silane molecules is the critical point to obtain high performances sol-gel films. The presence of the cerium oxides does not improve the corrosion protection properties of the silane sol-gel film in which they are embedded.

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