Encapsulation of Dodecylamine Inhibitor on Silica Nanoparticles

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Introduction

The development of active corrosion protection systems for metallic substrates is an issue of prime importance for many industrial applications [1]. This improvement is important for substitution of protective coating systems that use chromates in their composition, which are known as the most effective inhibitors but are strongly carcinogenic [2]. Most protective coatings are applied to metallic surfaces to create a passive barrier between the metal and an aggressive environment [3]. Recent developments in surface science and technology provide new opportunities of modern engineering concepts for fabrication of active coatings, through the integration of nanoscale carriers loaded with active compounds (e.g., corrosion inhibitor, lubricant, drug, vitamin, etc.) into existing classical films. The key idea is to create nanocontainers for loading active agents with shells possessing controlled permeability specific to several triggerings (pH, ionic strength, temperature, ultrasonic treatment), and then introducing them into the coating matrix [4]. The layer-by-layer (LbL) deposition procedure is a technique extremely versatile, which involves the stepwise electrostatic assembly of oppositely charged species (e.g., polyeletrolytes and inhibitors or others: proteins, nanoparticles) on a substrate surface with nanometer-scale precision, and when added to a polymeric film allows the formation of a coating with multiple functionality [5]. Moreover, each corrosion process is accompanied by local pH changes, where the pH value can be reduced or increased depending on the metal substrate and corrosion mechanism [6]. Usually, the polyelectrolyte capsule is permeable to macromolecules and nanoparticles at low pH (<3) or high ionic strength, whereas it is in a closed state at higher pH (> 6).

Experimental

The substrates used in this study were ABNT 1020 carbon steel samples, which were previously treated with emerypapers from 120 to600 mesh grade, sequentially, and then rinsed with distilled water, alcohol and acetone. Two procedures for preparation of dodecylamine encapsulated silica particles were used. The first procedure, called protocol 1, was performed treating the silica nanoparticles with dispersion in water and without sonication between different steps (after each centrifugation step) and drying them at the final step, in an oven; the second procedure, protocol 2, was achieved by dispersing centrifuged nanocontainers (silica nanoparticles) in 1 % PVA (polyvinyl alcohol) solution and sonication by 30 min between steps and drying the final particles in air. To produce the nanocontainers 20 mL of SiO₂ (15 wt %) colloidal solution were mixed (without sonication) with 3 mL of 2 mg/mL PEI solution for 15 min. Then, the SiO₂/PEI sample was washed three times in distilled water and separated by centrifugation. The deposition of the negative PSS layer (poly-styrene sulphonate) was carried out mixing for 15 min 3 ml of 2 mg/mL PSS solution with the centrifuged SiO₂/PEI sample. Then, the SiO₂/PEI/PSS sample was washed three times in distilled water and separated by centrifugation. Deposition of the third layer (dodecylamine corrosion inhibitor) was accomplished mixing for 15 min 30 ml of an acidic solution of the inhibitor (pH 3) in a concentration of 1 mg / ml with the centrifuged SiO₂/PEI/PSS sample. Then, the SiO₂/PEI/PSS/inh sample was washed three times in distilled water and separated by centrifugation. The last two deposition steps (PSS and inhibitor) were repeated once more to ensure the highest inhibitor loading in the final LbL structure, where the resulting system has a structure of type SiO₂/PEI/PSS/inib/PSS/inib. For evaluating indirectly the amount of released inhibitor from nanocontainers prepared following protocols 1 and 2, electrochemical impedance spectroscopy (EIS) measurements in areated 0,1 mol/L NaCl solution containing 1 wt % of nanocontainers at different pH values (2.0 and 6.2) were performed. The working electrode was a carbon steel plate with exposed area of 1.0 cm², Ag/AgCl/KCl_{sat} electrode was used as reference and a platinum foil as counter electrode. The direct monitoring of dodecylmine release by direct analysis by infrared spectroscopy probe in the recipient was also accomplished.

Results and Discussion

EIS measurements using nancontainers obtained following protocol 1

Figure 1 shows the Nyquist diagrams for the carbon steel after different immersion times (60 min, 120 min, 180 min, 300 min and 1020 min) in 0.1 mol / L NaCl solution at different pH values (2 and 6.2) and containing 1% w/wt of nanocontainers treated without sonification and dried in an oven. In these diagrams it can be seen that for the condition of pH 2 there is a greater release rate in comparison to the obtained at pH 6.2, expressed by arcs of larger diameter obtained at pH 2.0 which indicates a greater permeability of the polyelectrolyte walls which are open at pH values < 3. However, at neutral pH (6.2) the polyelectrolyte walls are closed and keep the inhibitor until when local pH changes occurs due to the initiation of the corrogion process in areas of defects.



Figure 1. Nyquist diagrams for carbon steel after differentimmersion times in 0.1 mol/L NaCl at different pHs (2 and 6.2) containing 1% w/wt of nanocontainers with dodecylamine encapsulated and using the protocol 1.

EIS measurements using nancontainers obtained following protocol 2

Figure 2 shows the Nyquist diagrams for the carbon steel in different immersion times in solution of 0.1 mol / L NaCl at different pH values (2 and 6.2) and containing 1% w/wt of nanocontainers sonificated and dried in air. In this case, for the condition of pH 2 there was also a greater release rate in comparison to the obtained at pH 6.2, but the amount of inhibitor released was smaller in comparison to the obtained at pH 2 (Fig. 1) due to different final treatment given in the preparation. One possible explanation for this fact is the immersion times of the nanocontainers in 1%PVA solution. When nanocontainers were dispersed in this ,solution, a spontaneous leakage of the inhibitor was verified.(results not presented here).



Figure 2. Nyquist diagrams for carbon steel after different immersi n times in **(x1)** a carbon 2000 2500 3000 (2 and 6.2) containing 1% w/wt of nanocontainers with dodecylamine encapsulated and using the protocol 2.

Study of the release of dodecylamine inhibitor from silica nanoparticles by infrared spectroscopy

An infrared probe ReactIR from Mettler Toledo was immersed directly in aerated 0.1 mol/L NaCl solution at pH 2 containing capsules loaded with dodecylamine inhibitor, obtained by

protocol 1, during a period of 6 h and under constant stirring. Figure 3 shows the 3D graph generated by the spectra obtained during the experiment, where it can be observed the appearance of three peaks, the first located at 1100 cm^{-1} related to the poly-styrene-sulphonate, the second located at 1466 cm⁻¹ representing the amine group and the third at 1640 cm⁻¹ attributed to overlapping peaks between the poly-styrene sulphonate and poly-ethylen-imine. Therefore, one can conclude that, besides the release of the dodecylamine therewas also a release of the polyelectrolyte layers that constitute the imprisoning layers of the inhibitor. These results were corroborated by the weight loss measurements of the capsules before and after the release process (not presented here).



Figure 3. 3D graphs of spectra generated by the release of the dodecylamine with time (spectra were corrected subtracting solvent spectrum).

Conclusions

The results showed that for both procedures used in the final treatment to produce the nanocontainers there was a greater release of inhibitor at pH 2 in comparison to the obtained at pH 6.2. In addition, the use of 1%PVA solution and sonication for dispersing particles was useful for obtaining a good dispersion of the nanocontainers during the preparation and obtaining a fine powder of the final nanocontainers. On the other hand, the release rate of inhibitor was more rapid and efficient following protocol 1, which produces coarse particles of nanocontainers.

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