



## Evaluation of self-healing ability in protective coatings modified with combinations of layered double hydroxides and cerium molybdate nanocontainers filled with corrosion inhibitors

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### ARTICLE INFO

#### Article history:

Received 2 September 2011

Received in revised form 26 October 2011

Accepted 26 October 2011

Available online 23 November 2011

#### Keywords:

Self healing  
Coatings  
Nanocontainers  
Corrosion

### ABSTRACT

Nowadays, there is a strong demand on the search of thinner, but more effective organic coatings for corrosion protection of metallic substrates, like galvanised steel, used in the automotive industry. In order to guarantee effective corrosion protection of these coatings, and because chromate-based pigments cannot be used, one of the most attractive strategies consists on the modification of the organic matrix with nano-additives filled with corrosion inhibitors, which can be released to the active sites. In this work, two different nano-additives are explored as potential self-healing materials for the development of active protective coatings. These additives are layered double hydroxides and cerium molybdate hollow nanospheres loaded with mercaptobenzothiazole, as a corrosion inhibitor. These additives were added to epoxy primers, individually, or combining the two nanoadditives in the same layer.

The electrochemical behaviour and the potential of self-healing ability were studied by electrochemical impedance spectroscopy, scanning vibrating electrode technique and scanning ion-selective electrode technique. The results reveal that both types of nanocontainers can provide effective corrosion inhibition on artificial induced defects, at different stages of the degradation process. Moreover, the results also show that there is a synergistic effect concerning corrosion inhibition and self-healing potential when a mixture of the two nanocontainers is used. The mechanism of self healing is presented and discussed in terms of effect of organic inhibitor and role of the nanocontainers, including effect of cerium ions released from cerium molybdate nanoparticles.

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## 1. Introduction

Organic coatings are the most common and cost effective method for corrosion protection of metallic parts in a wide range of technical applications. One of the main roles of the coating is to provide corrosion protection by creating a barrier that delays the corrosion attack of aggressive species. Throughout the last decades organic coatings have been widely applied for the protection of several metals with significant progress in the recent years. However, despite significant improvements in anti-corrosion coatings technologies, problems continue in the long-term protection of metals in aggressive environments, with very high costs. Moreover, the decrease of the weight of components in the transportation industry, to reduce fuel consumption and CO<sub>2</sub> emission, are also

imposing urgent challenges like the use of lightweight alloys and thinner coating layers produced by eco-friendly routes. The application of thinner coatings demands new strategies to extend their lifetime and to improve their effectiveness, as for example the development of "smart" coatings. Nowadays coatings showing self-healing ability are emerging as promising technical solutions for improved durability of painted materials. According to the literature, [1] in a smart healable material a key property is altered, in a controlled fashion, in response to the introduction of a pre-determined external stimulus. This definition can also be applied to many materials and several properties, including coatings used for corrosion protection of metallic parts. Some examples of successful smart functionalities in organic coatings have been proposed in the works by White et al. [2–4] that aim at developing self-healing ability based on encapsulated polymerising agents, for the self repair of damaged coating matrix. New synthesis routes and strategies have been reported, highlighting the potential of smart coatings for corrosion protection. Strengths and weaknesses of these

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systems have been discussed as well as scale up and related costs. A detailed review of this topic and related strategies can be found elsewhere [4,5].

The development of smart coatings, modified with nanoadditives, specially designed for the mitigation of the corrosion activity started in the early 2000's with the addition of inhibitors or sub micron particles to the coatings [6–9]. Generally, these works report an improvement of the corrosion resistance and interesting self-healing effects. The self healing ability was much improved with the use of pH sensitive reservoirs, acting as containers for corrosion inhibitors, as for example inhibitor filled particles or halloysites [10,11], polyelectrolyte layers [12,13] or pH sensitive hydroxyapatite particles [14]. The use of inhibitors encapsulated in nanocontainers is still in its infancy but it is certainly a promising approach. Another aspect of this technology, not explored so far and requiring deeper studies, is the use of mixtures of corrosion inhibitor containers, sensitive to different stimulus and able to provide corrosion protection at different stages of the coating life. This aspect is explored in this work, in which thin epoxy primer coatings modified with different inhibitor loaded nanocontainers, including their mixtures were studied. The nanocontainers used in this work are layered double hydroxides (LDH) [15] and cerium molybdate (CeMo) hollow nanospheres [16], both loaded with mercaptobenzothiazole (MBT) as a corrosion inhibitor. The modified coatings were applied on galvanised steel. The assessment of prospective self-healing ability demands for the combined use of various electrochemical techniques. In this paper we also intend to highlight the potential of three methods that are essential for effective assessment of the self-healing ability: electrochemical impedance spectroscopy (EIS) and the scanning vibrating electrode technique (SVET) combined with the scanning ion-selective electrode technique (SIET).

The results show how EIS can be powerful as a tool for the screening of promising smart protective systems and highlight the relevance of the parameters extracted from the EIS analysis to the understanding of the corrosion behaviour of the smart coatings. From the impedance results it was possible to assess the impact of the different additives (including mixtures) in the barrier properties of the coating. On the other hand, localised electrochemical techniques give detailed knowledge on the corrosion activity and self-healing extent in the presence of defects exposing the metal. The results highlight the different kinetics of inhibition of each type of additives and the synergistic effect observed when both additives are combined within the same coating.

## 2. Experimental

### 2.1. Preparation of the coated materials

Galvanised steel samples were coated with a model epoxy based coating (without anti-corrosive pigments or any other functional additives). The films were applied with a roll-coater and the dry film thickness is approximately 2  $\mu\text{m}$  in order to simulate the organic polymer matrix of anti-corrosion systems used in the automotive industry.

The coatings were modified with nanocontainers filled with corrosion inhibitor. The following additives were used: layered double hydroxides and cerium molybdate hollow nanospheres filled with 2-mercaptobenzothiazole (MBT). The preparation of LDH nanocontainers and their physical–chemical properties, including anticorrosion performance, are described in detail elsewhere [15]. First, commercial synthetic hydrotalcite ( $\text{Mg}_2\text{Al}_6(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ ) was calcined at 650 °C (2 h), to remove carbonate anions from the structure. The incorporation of MBT was achieved in a subsequent step consisting of hydration of the calcined sample, using an aqueous solution containing 0.1 M MBT in anionic form (pH 10).

XRD diffractograms acquired after the calcination–rehydration treatment showed peaks ascribed to the crystalline structure of LDHs. The loading content of MBT in the LDH (determined by HPLC) was found to be 10–13 wt.%.

The preparation and characterisation of the CeMo nanoadditives and the strategies used to encapsulate the inhibitor in these particles are reported in literature [16]. Summarily, the synthetic route consists of a two-step process. First of all, templates of anionic charged polystyrene (PS) spheres were prepared using emulsion polymerisation. Second, the PS containers were coated via the sol–gel method to form a cerium molybdate layer. Cerium molybdate hollow spheres were obtained after the burn off of the PS templates in air at 550 °C. Furthermore, the obtained cerium molybdate containers were loaded with the corrosion inhibitor MBT, using saturated solution of MBT in acetone into a sealed container under vacuum conditions. The containers are hollow with a size of  $230 \pm 20$  nm. The CeMo containers were loaded with MBT [16,17].

Two sets of modified coatings were prepared: in one set, the primer coating was loaded with LDH filled with MBT (LDH/MBT) or with CeMo filled with the same inhibitor (CeMo/MBT) in 4 wt.%. For the second set of samples, both type of containers were mixed, in equal weight amounts, to modify the primer layer, i.e. the coating was modified with a mixture of LDH and CeMo containers (same amount in total) loaded with the same inhibitor, MBT. The amount of stored inhibitor is not the same for the modified coatings because the loading capacity of each NC is different. For comparative purposes, reference coatings, i.e. coatings without additives were also prepared.

The thickness and the morphology of the coatings were determined using SEM. A JEOL – JSM7001F scanning electron microscope equipped with Oxford light elements EDS detector was used in these complementary experiments. An electron beam energy of 15 keV was applied for SEM analysis.

### 2.2. Electrochemical studies

All the coated specimens were studied by electrochemical impedance spectroscopy (EIS) in order to evaluate the effect of the containers on the barrier properties of the coating. For this purpose, coated samples were immersed in 0.5 M NaCl aqueous solution. The EIS measurements were performed using a Gamry FAS2 Femtostat with a PCI4 Controller in a frequency range from 100 kHz down to 10 mHz. All the spectra were recorded at open circuit potential, applying 10 mV sinusoidal perturbations (rms signal). A conventional three-electrode cell was used, consisting of a saturated calomel reference electrode, a coiled platinum wire as counter electrode and the coated metallic coupon as working electrode. The area of the working electrode was approximately 3.4  $\text{cm}^2$ . The electrochemical cell was placed in a Faraday cage.

The evolution of the corrosion activity and the self-healing processes were studied by the SVET and SIET techniques. To guarantee that the corrosion onset starts exactly at the same time for all the coatings, a defect was created on the coating prior immersion in 0.05 M NaCl (pH 6.5). A more diluted solution was used in this case, compared to the EIS measurements, in order to delay corrosion activity of the blank samples. With this concentration it is possible to follow the non-inhibited system for a period of time sufficient to allow effective comparisons with the inhibited samples. The defect was created by using a punch machine, which is able to create a lozenge like defect of approximately 0.2 mm side. In this controlled conditions the defect reaches the Zn layer, but not the iron substrate.

A commercial system from Applicable Electronics, controlled by the ASET program (Sciencewares), was used to perform the SVET and SIET quasi simultaneous measurements as previously reported [18].

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