

Hexacyanoferrate-intercalated Layered Double Hydroxides as solution for Detection of Early-stage Corrosion of Steel

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ABSTRACT

The *in-situ* detection of corrosion and failures represents an important stage in the procedures of maintenance of metallic structures. The use of nanotechnology embedded in the protective coatings is a promising way to develop user-friendly and cost-effective corrosion detection systems and has to be explored by the coating industry. Several groups have already reported the use of coating systems containing pH indicators and fluorescent probes to detect the corrosion of the substrates. The interest of encapsulating these indicators to prevent undesired interactions and leaching from the coating has also been argued.

In this work, layered double hydroxides (LDHs) are intercalated with hexacyanoferrate to be used as corrosion indicator coating additives. Their structure is characterized as well as their toxicity towards marine species. The nanocontainers are then dispersed in a coating matrix to detect the corrosion of a steel substrate at early stage. Electrochemical impedance spectroscopy measurements are performed to monitor the response of this coating towards immersion in corrosive medium. The reaction of the color indicator with the Fe^{3+} ions liberated during corrosion produces a stable blue precipitate coloring the coating, which could be detected by optical instruments to highlight the zones of failure in the structure.

Key words: corrosion, detector, layered double hydroxides, coatings, controlled release

INTRODUCTION

In many applications using metallic parts, corrosion is a main drawback to the integrity of the structures, particularly offshore where humidity and salt lead to aggressive environments. Corrosion detection for maintenance of structures in specific field such as marine and offshore application is usually very complex and expensive,¹ making it a domain eager for innovative technology allowing to reduce costs. In this context, the functionalization of the protective coatings appears to bring opportunities for direct *in-situ* corrosion detection. A trend in this field of research is the development of formulations containing color indicator changing state when corrosion is occurring under the protective coating, making it detectable by a simple visual inspection.

Concepts based on pH indicators present in the coating already have been proven to detect early corrosion process thanks to the alkaline pH occurring locally under the protection film.² Furthermore, methods of encapsulation of corrosion indicator using organic or inorganic nanomaterials have been developed to limit the drawbacks of the systems such as interaction between coating formulation and color indicator, or leaching of the species out of the coating.^{3,4} However, these systems based on pH indicators present the drawback of being reversible or losing the color indication, allowing a “live” sensing but not a “detection”, with a constant signal visible overtime and brought up by a trigger. Also, pH indicators require to be in aqueous medium to be in their free anionic state and to present a change of color: the coating has to be hydrated, and when it dries, indication ability can be lost. To overcome this drawback, the idea is to use an indicator forming a colored substance chemically stable, which will not be altered by its environment. This work presents tests performed on steel substrates using an hexacyanoferrate salt as a color “detector”: this compound is composed of $[\text{Fe}(\text{CN})_6]^{3-}$ ions which react with the Fe cations present in the hydrated part of the coating as a result of corrosion processes, giving a strong and stable blue pigment. Furthermore, the corrosion indicator has been intercalated in layered double hydroxides (LDHs) nanocontainers as a means to protect it from eventual side

reactions with the coating matrix and to control its release. The loading of the nanocontainers, their characterization as well as their use in coatings formulations are reported hereafter.

EXPERIMENTAL PROCEDURE

Nanocontainers and coating preparation

LDH-NO₃ layered double hydroxide are obtained from Smallmatek⁽¹⁾ and are used in slurry form to perform the intercalation: 7.5g of LDH (dried mass) in slurry form is dispersed in 250ml of a 0.1M solution of the active compound (hexacyanoferrate III) salt: K₃[Fe(CN)₆]. The mixture is stirred for 24h and then filtered and quickly rinsed to obtain materials labelled LDH-[Fe(CN)₆]³⁻.

A first coating series is prepared using a water-based white enamel (AQ EM 80) produced by Synpo⁽²⁾. The additive to be studied is added to the coating formulation and thoroughly stirred to ensure homogeneity of the paint, which is then added to the corresponding hardener (AQ BU 16) and deposited on a steel substrate using a bar coater. After application of the coating formulation, the curing was performed for 24 hours at room temperature followed by 1 hour in an oven at 100°C. For comparison purposes, coatings are prepared with the blank formulation (*Reference*), with 5%wt LDH-[Fe(CN)₆]³⁻ in slurry form or with 0.18%wt non-encapsulated active compound (amount corresponding to the compound added within the LDHs, calculated using the loading of [Fe(CN)₆]³⁻ in the interlayer of the LDHs (referred hereafter as *free* [Fe(CN)₆]³⁻)).

A second type of coating is prepared using water-based lactamide modified Polyhedral Oligomeric Silsesquioxane (POSS[†]) as a matrix, where 5%wt LDH-[Fe(CN)₆]³⁻ are added. Coatings were prepared on steel plates by bar-coating and cured at 150°C for 2 hours.

The steel plates used are cold-rolled steel of nominal composition in percentage: C ≤ 0.12; Mn ≤ 0.6; P ≤ 0.045; S ≤ 0.045.

Characterization techniques

The morphology of the nanocontainers is observed under Scanning Electron Microscopy (SEM) using an electron beam energy of 25keV, and samples are prepared by drop-casting a suspension of the LDH powder on a Si wafer.

The powder X-Ray diffraction (pXRD) was recorded using a Cu K_α radiation (λ = 1.5418Å) and graphite monochromator.

Release studies are performed in seven different media: distilled water, NaCl solutions with different concentrations (0.005M, 0.05M and 0.5M), two commercial buffer solutions of pH 4 and pH 10 and an aqueous solution of NaOH with a pH10. In a typical test, 150mg of LDHs loaded with [Fe(CN)₆]³⁻ were dispersed in 20ml of solvent (3 replicates for each media) and kept under room temperature at stirring speed 500rpm for 7 days. At different time periods (0–168 h) aliquots (0.2ml) were taken from the LDHs suspension with an automatic pipette (solvent was replaced), diluted to 2ml with distilled water, filtered through 0.22µm polytetrafluoroethylene (PTFE) membrane filter and analyzed by UV-Vis spectrophotometer using a calibration method at wavelength of 420.936nm. The total loading of [Fe(CN)₆]³⁻ in the nanocontainers was determined

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