Corrosion protection mechanisms of carbon nanotube and zinc-rich epoxy primers on carbon steel in simulated concrete pore solutions in the presence of chloride ions

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ABSTRACT

This study investigates the electrochemical characterization of carbon nanotube and zinc-rich epoxy primers (CNT-ZRPs) on carbon steel in simulated concrete pore (SCP) solutions in the presence of chloride ions. The mechanistic performance of CNT-ZRPs was characterized by adding different zinc content. The electrochemical results indicated a dominant barrier protection effect for the coating with 60 wt% Zn while there was a mixed corrosion protection mechanism for the coating with 70 wt% Zn and a dominant cathodic protection mechanism for coatings with higher zinc content (80 wt% and 90 wt% Zn). These barrier and cathodic protection control mechanisms were characterized quantitatively by electrochemical and high-resolution techniques.

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1. Introduction

Reinforced concrete structures exhibit high corrosion resistance due to their highly alkaline conditions (pH 12.5–13). Carbon steel can be used for rebar since it forms a passive oxide layer consisting of iron oxide (γ-Fe_2O_3) and magnetite (Fe_3O_4), which prevents and controls the corrosion-induced deterioration [1–5]. Economic advantages are also an important characteristic of ferrous alloys since they represent cost-effective solutions. Nevertheless, carbon steels are susceptible to halides in electrolyte solutions such as chloride ions, and these charge entities can influence the breakdown of the passive layer and the appearance of localized attack [5–8]. Following corrosion or activation processes, damage to concrete structures can be more severe when corrosion products induce high mechanical stresses that cause the formation of cracks in the concrete surface and even collapse of the structure [9,10].

Several coating systems have been studied to control or mitigate rebar deterioration due to corrosion processes, including inorganic, organic, and hybrid protective coatings [11–15]. Zinc-rich epoxy primer (ZRP) has been applied since the 1930s due to its anti-

corrosion properties [16]. These composite materials exhibit two protection mechanisms when an electrolyte penetrates into the organic binder. First, ZRPs provide cathodic protection by acting as sacrificial anodes when they are in electronic contact with the carbon steel surface [17]. Once cathodic protection is no longer active, ZRPs start to provide barrier protection due to the characteristic nature of the epoxy binder and the formation of zinc corrosion products on both the carbon steel surface and within the binder. These products fill in pores and reduce the amount of electrolyte that reaches the steel surface [18].

Nevertheless, it has been reported that high zinc content (>90 wt%) is not sufficient to ensure cathodic protection for a long time, especially for zinc particles with spherical geometry where there is only a single contact between two adjacent particles [19]. In such conditions, self-corrosion of zinc particles due to the presence of oxygen and water will lead to rapid loss of the electrical connection among themselves and with the carbon steel surface [19]. In addition, a high amount of zinc particles can reduce the adhesion to the metal substrate and create difficulties in spraying due to high viscosity and poor dispersion [20]. Therefore, studies have been performed to develop ZRPs with high electrical conductivity but with lower amounts of zinc particles [21–23].

An attractive option for improving ZRP performance is associated with the presence of carbon nanotubes (CNTs) integrated within the binder. CNTs provide excellent mechanical and electrical

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Table 1
Chemical composition of simulated concrete pore (SCP) solution in presence of chloride ions.[*]

	[KOH]	[NaOH]	[Ca(OH)$_2$]	[NaCl]
Molarity (M)	0.08	0.02	0.001	0.1

[*] The chemical composition of the simulated concrete pore solution provides a chloride to hydroxide ratio of 1.

properties, large surface area, high thermal stability, and chemical inertness [23–25]. CNTs can interconnect the zinc particles and provide higher electrical conductivity with which the percolation threshold can be reached with a lower zinc concentration compared with the traditional zinc-rich epoxy primer (90 wt% Zn content) [23]. Counter effects in the coating performance have been reported due to the formation of microgalvanic cells between CNTs and metal compounds resulting in the acceleration of the oxygen reduction reaction [26]. Different works have also shown effective improvement in the corrosion protection of composite coatings using CNTs by distributing the electrical current to prevent localized attack in the metal surface. In addition, CNTs can provide barrier protection to composite coatings as pore fillers within the epoxy coating [27–29].

In this work, the influence of CNTs on the corrosion protection mechanism of CNT-ZRPs was evaluated in simulated concrete pore solution in the presence of chloride ions by electrochemical impedance spectroscopy (EIS). Coating systems were studied with a fixed amount of less than 1 wt% CNTs and four different zinc contents (60 wt% Zn, 70 wt% Zn, 80 wt% Zn, and 90 wt% Zn). Evolution of the corrosion performance of these systems was also observed by localized electrochemical impedance spectroscopy (LEIS), scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS) to support the electrochemical mechanism findings.

2. Experimental procedure

2.1. Electrolyte solution

The electrolyte used simulates a concrete pore solution contaminated by chloride ions. Table 1 shows the chemical concentration of each of the species in this solution. Sodium chloride (NaCl) was added to investigate the influence of chloride ions on the corrosion degradation process. All used chemicals were analytical grade and water was deionized with the highest purity. The resulting electrolyte had a chloride to hydroxide ratio of 1 that corresponds to a sodium chloride concentration of 0.1 M and a pH of 12.87. This chloride to hydroxide ratio ([Cl$^-$]/[OH$^-$]) was higher than the critical chloride concentration reported for concrete structures, which has been established as around 0.6 [30–32]. All testing procedures (except for localized electrochemical impedance spectroscopy) were performed by using concrete pore solution.

The solution was selected based on previously studies [33–38]. It is important to clarify that this solution does not include all chemical species contained in real cement concrete pore solutions such as fly ash, silica fume, gypsum, etc. However, sodium hydroxide (NaOH), potassium hydroxide (KOH), and calcium hydroxide (Ca(OH)$_2$) represent the chemistry of the concrete in a controlled environment and the electronic properties of the passive film formed at the steel surface used as the reinforced material [38].

2.2. Coating samples

Carbon nanotubes and zinc-rich epoxy primers were provided by Tesla NanoCoatings company. The coating formulation corresponds to a solvent-based two component epoxy-polyamide
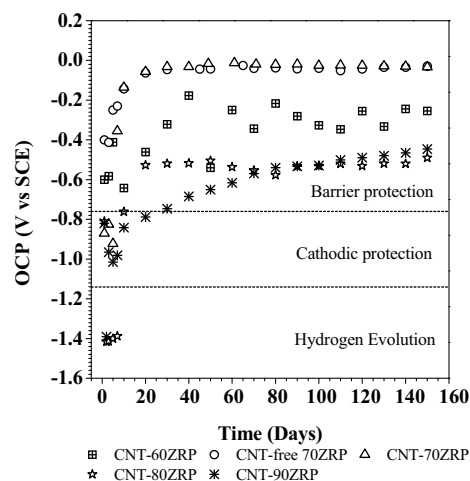

Fig. 1. OCP evolution for CNT-ZRPs with different zinc contents immersed in the SCP solution during 150 days.

primer that incorporates sacrificial zinc particles in spherical configuration together with carbon nanotubes. To prepare the zinc-rich coating formulations, epoxy resin (Tesla P1150ASAS) was mechanically mixed with a fixed composition of <1 wt% of carbon nanotubes (CNT). After CNTs were completely dissolved in the epoxy resin, different weight percentages of zinc particles were added gradually to the mixture while stirring at room temperature. Finally, a stoichiometric amount of hardener (Tesla P1150BSAS) with a weight ratio (epoxy resin: hardener) of 2:1, was added to the mixture and sonicated for 5 min. The different coating formulations are listed in Table 2. The prepared coatings were air sprayed on AISI 1008 carbon steel (UNS G10080) with a chemical composition (maximum nominal composition in wt%) of 0.60% Mn, 0.15% C, 0.030% P, 0.035% S and balance Fe. The dimensions of the substrate panels were 152 × 76 × 1 mm. Prior to the application of coatings, steel panels were sandblasted followed by degreasing with acetone and drying at room temperature. The coating systems were allowed to cure for 6 h at 60 °C and then, they were kept at room temperature for seven days before exposure to the electrolyte solution. Samples were exposed by using a glass tube fixed on the coating surface by an O-ring and a metal clamp that exposed a surface area of 4.67 cm^2. The dry film thickness was measured by an Elcometer 456 coating thickness gauge.

2.3. Electrochemical measurements

Electrochemical measurements were conducted using a Biologic SP-200 Research Grade Potentiostat/Galvanostat/FRA. A conventional three-electrode cell was used at room temperature. The coated samples served as the working electrodes, a saturated calomel electrode (SCE) was used as the reference electrode, and Pt/Nb mesh electrode of 2 cm diameter was the counter electrode. The electrochemical testing procedure included measurements of open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) during 150 days. Open circuit potential was measured for 10 min following impedance measurements in a frequency range of 100 kHz to 10 mHz at 6 points/decade with 10 mV amplitude. All electrochemical impedance spectroscopy measurements were performed at the open circuit potential. The impedance results were fitted with equivalent electrical circuits using the Z Fit tool of the EC-lab software. All electrochemical tests were performed in duplicate to guarantee reproducibility of the OCP and EIS measurements.