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Double-doped zeolites for corrosion protection of aluminium alloys

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ABSTRACT

This work has introduced a new doping concept to develop self-healing anticorrosive coatings by synergistic and controlled release of corrosion inhibitors. NaY zeolites were double doped in a two-step process with cerium and diethyldithiocarbamate (DEDTC) as these are known efficient corrosion inhibitors for AA2024-T3. The corrosion efficiency and mechanisms were evaluated by a combination of optical, analytical and electrochemical techniques. It was observed that the inhibitors deposit on the metallic surface with preference for intermetallic particles. Current density measurements of the samples revealed that the double doped NaY zeolite was able to provide both immediate and sustained corrosion protection for the alloy substrate. Moreover, impedance analysis of hybrid sol–gel coatings with 10% wt. of the most relevant doped zeolites revealed distinctive release events from the coatings containing the doped zeolites. The results confirm the potential of this double doping concept which can be extrapolated to other carriers and inhibitors for an effective environmentally friendly active corrosion protection. It is believed that the double doping concept can be extrapolated to fields other than corrosion protection.

1. Introduction

The search for environmentally friendly alternatives to Cr(VI) based coatings has boosted in recent times due to the urgent need to substitute this highly effective but toxic and carcinogenic corrosion inhibitor [1]. As part of this on-going search, focus has been placed on the synergistic effects of inhibitor combinations aiming at improved corrosion protection [2]. Rare earth organophosphates (organo-REM) are one kind of new multifunctional corrosion inhibitors showing synergistic corrosion protection [3,4]. One of the most feasible mechanisms leading to synergy of these compounds is the selective deposition of Ce on cathodic intermetallics and the formation of an organic film by the organic part of the inhibitor covering the entire surface [5]. Despite the many advances in the direction of these organo-REM synergistic inhibitors in aqueous solution, the implementation of these into organic matrices has not led to many studies [6]. Nevertheless, the implementation of new corrosion inhibitors into organic coatings brings associated challenge of the potential incompatibility between inhibitor and matrix.

The use of nano and micro carriers has been proposed in order to decrease the inhibitor-matrix interactions and control the release of the inhibitors in a process described as a self-healing concept where the inhibitor is only released when required by triggers such as changes in pH or ion exchange [7]. Successful inhibitor-doped carriers described in literature include the use of phyllosilicates such as cerium doped bentonite [8] and vanadate doped hydrotalcites [9], and nanoporous materials such as benzotriazole doped silica [10] and molybdenum, zinc, alkaline earth metals and cerium doped zeolites [11,12]. What these reported systems have in common is that they have been doped with a single corrosion inhibitor not addressing thus synergy possibilities as explored in individual inhibitors such as the organo-REMs.

In the present study, we demonstrate that the concept of double inhibition process shown in corrosion inhibitors can be extrapolated to concepts of controlled release from carriers. In this manner, carriers doped with two types of inhibitors can potentially lead to synergistic effects offering a more efficient protection of the underlying metal. For this work, we employed NaY zeolite as the carrier material. Zeolites are microporous cage-structured aluminosilicate crystals used in multiple applications due to their high ion exchange and adsorption capabilities. Despite being applied primarily as catalysts in the petroleum and petrochemical industry, they are also employed in other areas such as agriculture, detergent manufacturing and wastewater treatment [13,14]. For the corrosion inhibitors, cerium(III) nitrate hexahydrate (Ce) and sodium diethyldithiocarbamate trihydrate (DEDTC) were selected

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as dopants for their known individual efficiency as corrosion inhibitors of AA2024 [15,16]. Their size was also a factor since the dopants have to be sufficiently small to enter the supercage and pores of the employed NaY zeolite carrier, namely between 0.74 and 1.3 nm as exposed in the experimental section. The morphology and composition of the inhibitor doped zeolites were also investigated. In addition, different approaches on evaluating the corrosion resistance of inhibitor doped zeolites and sol–gel coatings were performed.

2. Experimental

2.1. Materials

NaY zeolite (CBV-100) was purchased from Zeolyst International. Sodium diethyldithiocarbamate trihydrate (DEDTC), cerium(III) nitrate hexahydrate (Ce), tetraethyl orthosilicate (TEOS), 3-glycidoxypropyltrimethoxysilane (GLYMO) and concentrated HNO_3 were purchased from Sigma–Aldrich. The NaCl crystals used with at least 99% purity was purchased from Acros Organics. The AA2023-T3 sample was supplied by Akzo Nobel N.V. All solutions used in the inhibitor doping and in the corrosion experiments were prepared using Milipore® Elix 3 UV filtered water as solvent.

2.2. Preparation of inhibitor-doped zeolites

The ion-exchange process was carried out by mixing zeolite (5.0 g) in the corrosion inhibitor solution (100 mL) at a known concentration inside a 250 mL flask fitted with condenser and controlled at 60 °C in oil bath with stirring at 200 rpm for 1 h. The inhibitor concentration was calculated based on the cation exchange capacity (CEC) of NaY zeolite which is approximately 4.19 milliequivalence g^{-1} zeolite ($Na_2O \sim 13\%$ wt.). For cerium, 0.1 M cerium nitrate hexahydrate solution was used which is about 33% more available corrosion inhibitor than the CEC of NaY zeolite to ensure maximum ion exchange. To perform the second doping sequence, sample of NaY–Ce (2.0 g) prepared initially was weighed and then mixed with 0.15 M DEDTC solution (55.0 mL). The DEDTC solution was mixed with NaY–Ce at ambient temperature of 22.5 °C for 30 min with 200 rpm mixing speed using the same set-up in the ion-exchange. After each mixing, all samples were vacuum filtered using Whatman® grade 595 and the filtrates were collected for analyses on their final concentrations. All inhibitor solutions were sampled prior to mixing to determine their actual initial concentrations. The inhibitor loaded Y zeolite materials were washed with water three times using the same volume as the inhibitor solution used. All washed samples were dried in a vacuum oven at 60 °C for at least 24 h.

The inhibitor doped zeolite samples were characterized using FE SEM-EDS (Jeol JSM-7500F). ICP-OES (Spectro Arcos EOP) was used to analyze cerium concentration in the solution and the data were used to calculate the amount of cerium uptake in the zeolite. To estimate the amount of DEDTC corrosion inhibitor contained in the Y zeolite, UV–Vis (Perkin-Elmer Lambda 35) was used to determine the concentration of the sampled DEDTC solutions at 282 nm absorbance. A calibration line was first developed by preparing DEDTC solutions at known concentrations and measuring their absorbance at 282 nm. The absorbance values are then plotted against the known concentrations and the extinction coefficient or molar absorptivity constant ($\varepsilon = 13{,}322\ L\ cm^{-1}\ mol^{-1}$) was obtained from the linear calibration plot with R^2 value of 0.9997 which is in close agreement with one reported from literature [17]. The value of molar absorptivity ε was used to calculate the concentrations of the sampled DEDTC solutions using Beer–Lambert's law.

2.3. Preparation of the hybrid sol–gel coatings

Three batches of hybrid sol–gel epoxy coatings were made; one containing the undoped NaY zeolite, one with cerium doped zeolite (NaY–Ce) and one doped with both cerium and DEDTC (NaY–Ce–DEDTC). The hydrolysis of sol solution was prepared by mixing TEOS, GLYMO and 0.05 M HNO_3 (1.15:2.62:1 weight ratio) for 2 h at room temperature. The resulting solution was added with either 10% wt. of the pre-weighed undoped zeolite or doped zeolite pigments (accounting the total weight of components used in the coating) and then shear mixed at 2500 rpm for 5 min. To improve adhesion and stability of the coating, the sol solution containing the zeolite pigment was also mixed with Epikote 828 with 1:1 weight ratio (TEOS + GLYMO:Epikote 828) at 2500 rpm for 5 min. Finally, the sol mixture was added with the curing agent Ancamine 2500 with 1:1.89 weight ratio (GLYMO + Epikote 828:Ancamine 2500) and then mixed at 2500 rpm for 5 min prior to application on AA2024-T3 panel.

Prior to application of the coating, the AA2024-T3 panels were abraded with Scotch Brite 3 M "Clean N Finish grade AVFN" to remove the top native oxide layer and degreased with acetone. In order to clean the surface and improve the adhesion of the sol–gel coating to the substrate the panels were then pretreated in an alkaline aqueous solution of 2 M NaOH for 10 s followed by rinsing with water and then air dried. The sol–gel coatings were applied on the pretreated substrate by using a spiral bar coater producing a thickness of 100 μm. After coating, the samples were cured first at ambient temperature for 24 h then inside a vacuum oven at 40 °C for 2 h and then at 60 °C for another 2 h. Afterwards, the coated panels were stored inside a dessicator prior to the EIS tests.

2.4. Corrosion testing procedure and characterization

A potentiostat/galvanostat (Autolab PGSTAT 302 N) connected to a flat electrochemical cell as described and illustrated elsewhere [18] together with a Faraday cage to avoid external interferences was used for all of the potentiodynamic polarization test (PPT) experiments. In the PPT set-up, the substrate sample or working electrode (WE) was AA2024-T3 which was clamped vertically and a platinum gauze counter electrode was placed opposite to it. The reference electrode used was Ag/AgCl which was placed in between the previous two electrodes. The exposed area of the AA2024-T3 substrate was 0.65 cm^2. Before placing the AA2024-T3 sample on the electrochemical cell, each test panel was polished to remove the native oxide layer using 800, 1200 and 4000 grit SiC papers, rinsed with water followed by ethanol and then dried using compressed air. The AA2024-T3 samples were immersed in 0.05 M aqueous NaCl solution with the inhibitor-doped zeolites at different time intervals of 30 min, 3 and 24 h. A fixed amount of zeolite and doped zeolites (0.13 g) was used for each test solution (250 mL) of 0.05 M NaCl with a maximum particle diameter of 50 μm (325 mesh) while the pure inhibitors were each at 1 mm concentration in the NaCl solution. The pigments were magnetically stirred in solution at 200 rpm during the immersion tests. After each sample was exposed to the solution, OCP evolution was recorded for 5 min prior to the start of potentiodynamic scan. The scan range and scanning rate applied were −200 mV to +200 mV vs. OCP polarization at 1 mV s^{-1}, respectively. From the plot of polarization curves, the corrosion current density was obtained via Tafel extrapolation as described from literature [19,20]. The potentiodynamic tests at specified immersion time were performed at least in duplicates. To verify the trend of corrosion