Article

A Synergistic Effect between Stearic Acid and (+)- α -Tocopherol as a Green Inhibitor on Ferritic Stainless Steel Corrosion Inhibition in 3.0% NaCl Solution

Regina Fuchs-Godec

Faculty of Chemistry and Chemical Engineering, University of Maribor, 2000 Maribor, Slovenia;
regina.fuchs@um.si; Fax: +386-2-2527-774

Abstract: The synergistic inhibitory effect of stearic acid and (+)- α -tocopherol (E307) as a green inhibitor within a highly hydrophobic layer on the corrosion of low-carbon ferritic stainless steels was investigated in 3.0 wt% NaCl solution at 25 °C, focusing on long-term immersion tests. For a broader characterisation of the surface properties, especially the modified surfaces, of the samples used, the following methods were chosen: SEM was used to investigate the surface morphologies, the water contact angle to examine the wettability, while the corrosion resistance was investigated by potentiodynamic measurements and electrochemical impedance spectroscopy. The inhibition efficiency for modified ferritic stainless steel surfaces reached more than 99% after 1 h of immersion and remained the same after 5 days immersion testing when the surfaces were modified with (SA + 2.0 wt% E307) and more than 97% with (SA + 0.5 wt% E307) under the same test conditions.

Keywords: ferritic stainless steel; corrosion inhibition; E307 (vitamin E); hydrophobic layer; synergistic effect

Citation: Fuchs-Godec, R. A. Synergistic Effect between Stearic Acid and (+)- α -Tocopherol as a Green Inhibitor on Ferritic Stainless Steel Corrosion Inhibition in 3.0% NaCl Solution. *Coatings* **2021**, *11*, 971. <https://doi.org/10.3390/coatings11080971>

Academic Editors: Heping Li, Jose M. Bastidas and Daniel John Blackwood

Received: 21 June 2021
Accepted: 6 August 2021
Published: 15 August 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Despite a variety of new materials, different surface treatments such as plasma or laser surface treatment, and the development of different types of protective coating, corrosion remains a widespread problem at the top of the damage scale. Any kind of material degradation, whether fast or slow, is associated with enormous costs [1–3]. Corrosion also has economic effects that are more than just “metal loss” and is often the main cause of accidents and disasters that harm people, property and the environment. Corrosion is a material disease, and metals corrode more or less under all atmospheric conditions and especially in aggressive liquid environments. Research in this area is, therefore, crucial, because any improvement or innovation in this field contributes a significant part of the unfinished mosaic known as corrosion protection. Moreover, the toxic material released from corrosion-damaged equipment may start by polluting the environment within one country, but then spread far beyond its borders. There is thus a need to develop new, environmentally friendly corrosion inhibitors. In this context it is also important to consider the concept of a circular economy for the rational use of natural resources and different types of material, such as food additives whose expiry date has already passed (food supplements, vitamins) and which have the appropriate chemical structure for use as corrosion inhibitors.

Various types of vitamin, such as B1, B6, C and E, have already been mentioned in research as successful inhibitors of corrosion processes in aggressive environments [4–14]. Water-soluble vitamins were added directly to the corrosion medium, while fat-soluble ones (one of them was also used in this work) were used in a procedure preparing superhydrophobic self-assembled protective layers [10,11].

Superhydrophobic surfaces are generally defined as surfaces that have a water contact angle (WCA) above the value of 150°, which is now readily recognised as the “threshold

value". These surfaces have received continued attention because of their broad applications, such as self-cleaning [15], antifrosting [16] and antifogging [17], oil and water separation [18], drag reduction and surfaces with enhanced corrosion resistance in industry, oil pipelines, close cooling water circuit [19], as well as in daily life. Given the unique water-repellent properties of these surfaces, they are also capable of reducing the deterioration of metal surfaces caused by corrosion in aqueous media, and our focus is on the last of these properties. From this point of view superhydrophobic surfaces are of central interest in corrosion and surface science. It will not be superfluous to repeat that superhydrophobicity is an effect where surface roughness and chemical composition combine to generate an unusually water repellent surface, causing water to bounce and roll off.

There exists a 'wide palette' of approaches on how to achieve a superhydrophobic surface [20], such as the sol-gel method, electrospinning, electrochemical methods, and layer-by-layer method, which can be found in various review articles, like Darband et al. [21] and Guo et al. [22]. It has been confirmed that surfaces with hydrophobic properties can be an effective corrosion protection for numerous types of metal, such as steel [11,19,23–31], copper [10,32–37], nickel [38], zinc [39,40] Al-alloys [41–46] and Mg-alloys [47–51]. Carboxylic acids have been used to create hydrophobic surfaces on many different metal substrates [52–55]. Carboxylic acids adsorb to a positively charged metal surface through their carboxyl group and form a hydrophobic layer. Studies have shown that the properties of the self-assembled as-prepared hydrophobic layer are influenced by the length of the carbon chain of the carboxylic acid [52,56].

One of the most important goals of applied superhydrophobic surfaces, besides increasing the corrosion resistance of surfaces exposed to corrosive environments, is their long-term chemical stability and preservation of superhydrophobic properties. The stability of the corrosion resistance of these coatings over a long period of exposure to the aggressive conditions also remains a challenge.

Some authors have shown different approaches to the preparation of anticorrosion coatings with superhydrophobic properties, whose stability can be maintained for a longer time even in highly aggressive environments. Cao et al. reported [57] the preparation of the superhydrophobic ZnAl double hydroxide (LDH)-La film by a hydrothermal method and further modification by laurate anions. The result showed that the stable superhydrophobic ZnAl-LDH-La film was able to efficiently protect the underlying Al substrate for a long time, up to one month in 3.5 wt% NaCl solution.

Ke and his group [58] investigated a surface functionalisation approach that utilises the chemical adsorption and autopolymerisation effects of 1H, 1H, 2H, 2H perfluorodecyltriethoxysilane (FAS-17) to build a highly stable barrier coating against water and further equip it with highly reactive aluminium nanoparticles with long-term storage stability and self-activation reactivity.

Ejenstam et al. [59] presented the excellent corrosion protection properties of superhydrophobic coatings achieved with a thin composite PEA-TiO₂-HMDSO (hexamethyldisiloxane) coating system on the carbon steel. It is worth mentioning that the obtained coating maintained its protective properties almost unchanged for a period of more than 100 days in a 3 wt% NaCl solution.

Among the various engineering materials, stainless steels (SS) and other similar alloys are the most important and widely used. However, in addition to their unique properties, these metals have some limitations, with corrosion being one of them, although the use of different types of coating is one of the effective strategies for protecting them. So far, different types of barrier coatings have been developed and researched for this purpose, with both non-wetting (hydrophobic) surfaces and super-hydrophobic surfaces having attracted a lot of attention among researchers.

Several studies suggest an improvement in inhibitory efficiency when mixtures of inhibitors are used compared to a single inhibitor [60–63]. They often show synergistic effects, suggesting non-ideal behaviour, which is the reason for their extensive use in industry.

This study is actually an extension of our previous work in which we investigated the inhibition abilities of the self-assembled as-prepared hydrophobic layer formed on SS with 3.0 wt% NaCl [11] and on pure copper and copper alloy with a simulated urban rain with the pH value of 5 [10]. We have demonstrated the effectiveness of the as-prepared hydrophobic layer on the two selected systems after one hour of immersion. For this purpose, a fat-soluble vitamin E of the (+)- α -tocopherol (E307) type was used as a type of green inhibitor. After chemical etching in 10% HNO_3 , the samples were immediately immersed in the unstirred, aerated ethanol solution of stearic acid (SA) ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$) at room temperature with and without the addition of the E307. The concentrations of E307 chosen were 0.5%, 1.0% and 2.0%. We also showed that E307 as a single inhibitor had a slight effect on increasing the inhibition efficiency on copper and its alloy (Cu40Zn). The reduction in corrosion current was much lower in the case where E307 was used as a single inhibitor than in the case of SA [10]. Therefore, the focus was on the effects of the mixtures used.

The inhibition efficiency for AISI 410S reached $\approx 59\%$ when the surfaces were modified with SA only, while the values increased to over 99.0% with addition of E307.

The addition of E307 to SA (in the process of forming a hydrophobic layer) increases the inhibitory effect, probably due to a synergistic effect between the two, and this phenomenon could also be related to the esterification of SA and E307. Therefore, it was natural to extend these investigations. The main objective of the presented investigations is to demonstrate the long-term stability and effectiveness of the as-prepared hydrophobic layer on the SS AISI 410S in 3.0 wt% NaCl at 25 °C. Classical potentiodynamic measurement and electrochemical impedance spectroscopy (EIS) were used to investigate the protective effect of the self-assembled hydrophobic layer of SA, modified with E307 in the selected corrosion media. SEM was used to study the morphology while a goniometer was used to demonstrate the superhydrophobicity of these coatings. Infrared spectroscopy (ATR-FTIR) was used to characterise and identify the organic molecules in the layer.

2. Experimental

2.1. Materials and Chemicals

The low carbon ferritic stainless steel (AISI 410S) used in the experiments contained 0.04% C, 0.471% Si, 0.02% S, 13.2% Cr, 0.307% Ni, 0.213% Cu, 0.416% Mn, 0.007% Al, 0.141 Mo, and 0.024% P, the remainder being Fe. The stearic acid (Sigma-Aldrich, CAS number 57-11-4, St. Louis, MO, USA) used was pure grade (95%), while the (+)- α -tocopherol (vitamin E, E307) was also a of pure grade (97%) Sigma-Aldrich product (CAS number 59-02-9). Sodium chloride (NaCl) was obtained from KEFO. All chemicals were used as received and without further purification. The substances used had the following structures (Scheme 1):

Scheme 1. Chemical structure of Stearic acid and (+)- α -tocopherol.

2.2. Apparatus

The present investigation includes measurements on the following apparatus:

- Electrochemical measurements: Solartron 1287 Electrochemical Interface and Gamry 600™ potentiostat/galvanostat, Warminster, PA, USA controlled by an electrochemical program.

- Processing and analysis of experimental data using the following software programs: CorrView, CorrWare, Zplot and ZView programs from Scribner Associates, Southern Pines, North Carolina, USA (all version 2.80).
- ATR-FTIR: SHIMADZU-IRAffinity-1, Shimadzu Europa GmbH, Duisburg, F.R. Germany.
- Scanning electron microscope (SEM): FEI Sirion 400 NC, Eindhoven, Netherlands.
- Goniometer: Data Physics OCA 35, Filderstadt, Germany.

2.3. Pretreatment for Electrode

The specimens used in this study were cylindrical discs made of an AISI 410S type stainless steel bar with the cross-sectional area of 1.14 cm^2 . The test specimens were placed in a PTFE holder so that the surface area of 0.875 cm^2 was exposed to the solution. The specimens were mechanically abraded with a series of emery papers up to 1200 grit, rinsed in acetone and double distilled water and ultrasonically cleaned in a bath of Milli-Q water. Stronger layer adhesion can be achieved by pre-etching the metal surface (10 wt% HNO_3 for 3 min).

After etching, the samples were again ultrasonically cleaned, washed with ethanol, rinsed several times with distilled water and finally dried with compressed air.

To modify the metal surface from hydrophilic to superhydrophobic, the etched samples were immersed in a 0.05 mol L^{-1} ($\text{mol L}^{-1} = \text{M}$) ethanolic solution of SA with and without the addition of 0.5 wt% and 2.0 wt% E307, respectively, at room temperature for about 1 h to form the self-assembling layer.

2.4. Electrochemical Measurement

Electrochemical tests, including open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarisation measurements, were performed in an aqueous solution of 3.0 wt% NaCl. A conventional three-electrode configuration was used for this purpose. All potentials were measured against a saturated calomel electrode (SCE), and the counter electrode consisted of Pt.

The potentiodynamic current-potential curves were recorded by automatically changing the electrode potential from -0.7 to 0.4 V (V/SCE) at a scanning rate of 1 mVs^{-1} . The SCE was immersed in a Luggin capillary and placed in close proximity to the exposed surface of the test specimen, which was with or without a preformed self-assembled hydrophobic layer. EIS measurements were carried out within the frequency range of $100 \text{ kHz}^{-1} \text{ mHz}$ at a steady open circuit potential (OCP) disturbed by an amplitude of 10 mV (peak to peak). All experiments were performed at 25°C .

Electrochemical potentiodynamic measurements were performed after one hour of immersion and five days in a 3.0 wt% NaCl solution, and in the case of EIS measurements after one hour, 10 h, 25 h and after five days of immersion. Before each simple measurement (EIS or potentiodynamic measurements), the OCP of the working electrode was measured for 1 h to allow stabilisation of the steady-state potential.

The long-term stability of these coatings on the SS AISI 410S is, therefore, the focus of the present study.

2.5. Surface Characterisation

2.5.1. Contact Angle

The most rapid test of surface modification was performed by measuring the contact angle (CA) of a drop of water by the resting drop method. We used a commercial goniometer with the volumes of the droplets fixed at $3 \mu\text{L}$. The measurements were performed at room temperature with five replicates for each sample.

2.5.2. ATR-FTIR Analysis

The characteristics of the original solution (ethanolic solution of SA with the addition of 2.0 wt% of E307), the hydrophobic film modified on the SS electrode after immersion in the above solution at room temperature for 1 h, and the hydrophobic film modified on

the SS electrode after 5 days of immersion in the corrosion medium of 3.0 wt% NaCl were analysed by ATR-FTIR spectra. With a spectral resolution of 4 cm^{-1} and a wavenumber range of $400\text{--}4000\text{ cm}^{-1}$, the IR spectra were recorded and identified by comparison with the standard peak positions of the groups.

3. Results and Discussion

3.1. Wettability of a High-Level Hydrophobic Surface

Contact Angle Measurements

The surface wettability of the coatings was investigated by water contact angle measurements (CA). The same coating with different regions was dispensed, with at least five drops, to obtain reliable CAs. The insets in Figure 1 show the images of water droplets on the as-prepared hydrophobic coating with and without the addition of E307 in the ethanolic SA solution during coating formation and after 5 days of exposure of the treated samples to the corrosion medium.

Figure 1. SEM of the untreated and modified surface of SS type AISI 410S (a) untreated and etched surface (CA = $71.5^\circ \pm 3$) [11], (b) modified surface in SA solution for 1 h (CA = $122.8^\circ \pm 2$), (c) modified surface in SA solution with the addition of 2.0 wt% of E307 for 1 h (CA = $138.7^\circ \pm 3$) [11] and (d) modified surface in SA solution with the addition of 2.0 wt% of E307 after 5 days testing (CA = $135.1^\circ \pm 2$).

Figure 1 shows SEM images of (a) the untreated SS substrate, while images (b) and (c) show the modified surfaces of SS used in the SA solution for 1 h and in SA solution with the addition of 2.0 wt% E307 for 1 h, respectively. Moreover, the SEM image (Figure 1d) shows the surface morphology of the as-prepared hydrophobic layer (SA + 2.0 wt% E307) after 5 days of exposure to the selected corrosive medium (3.0 wt% NaCl). It has been reported that hierarchical surface structuring is usually a prerequisite for the phenomenon known as super-hydrophobicity [64].

It can be seen that the surfaces shown in Figure 1b–d are rather rough and hierarchically structured. Moreover, flowers can be seen within these structures and thus this is classified as a flower-like structured as-prepared self-assembling hydrophobic layer.

It is known that self-assembling hierarchical flower-like structures have a lot of grooves and gaps that can trap a large amount of ambient air, and in this way produce the superhydrophobic effect at room temperature. The presence of air pockets makes the contact of a water solution (corrosion medium) largely obstructed or completely inaccessible, depending on the degree of hydrophobicity (shown as CA) [65,66].

The images of water droplets on the modified surfaces, shown within the rectangles, show the hydrophobicities of the modified surfaces, with the values of CA being very close to those of superhydrophobic surfaces ($CA = 150^\circ$). As can be seen from the figure, the CA of the coating did not change significantly with time after 5 days of immersion in the corrosion solution containing 3.0 wt% NaCl.

It could be speculated that the self-assembled hydrophobic layer prepared in this way generated the superhydrophobic effect at room temperature. This is shown by the prevention of liquid penetration into the base matrix metal surface. In other words, the as-prepared self-assembled hydrophobic layers show good durability over time.

3.2. Corrosion Resistance of the As-Prepared Hydrophobic Layers—Electrochemical Results

The anti-corrosion performance of the as-prepared superhydrophobic surfaces on the stainless steel AISI 410S in the highly corrosive environment is one of the important properties to be explained and evaluated. As mentioned above, the OCP test, the potentiodynamic polarisation method and electrochemical impedance spectroscopy were chosen to investigate the corrosion behaviour of the SS AISI 410S electrode in the untreated state and treated with superhydrophobic layers in 3.0 wt% NaCl solution.

3.2.1. Open Circuit Potential

In the present study, the time dependence of the OCP of treated and untreated steel samples immersed in 3.0 wt% NaCl was monitored over a period of 5 days to estimate the corrosion behaviour of the studied samples (Figure 2).

In the case of the bare surface of SS, the OCP first decreased (i.e., became more negative) and then changed its direction to less negative values, and after about 30 h the OCP started to decrease significantly. After 5 days it dropped from -0.2 V to -0.62 V (vs. SCE). This behaviour can be interpreted as a breakdown of the oxide film formed before immersion in air or the passive film present on the surface. With respect to the chloride medium used, the onset of pitting corrosion can be predicted.

When the hydrophobic film was prepared based on the immersion of the samples in the ethanolic solution of SA without the addition of E307, the OCP decreased at the beginning and was relatively stable after 10 h. This likely indicates the more porous self-assembled hydrophobic layer.

The OCP decreased again at the beginning when 0.5 wt% E307 was added to the ethanolic solution of SA in the procedure to prepare the hydrophobic layer, but only for a relatively short time, and then it was stable with a slightly increasing mode. When the concentration of E307 added was 2.0 wt%, the OCP stabilised very quickly and its value at steady state shifted to be more positive.

All this suggests that the hydrophobic layers thus prepared containing E307 are much stabler and have better inhibitory properties, which may be related to the esterification of SA and E307 and the consequent perhaps denser structure of the self-assembled hydrophobic layer compared to the layer formed in SA without the addition of E307.

Figure 2. OCP vs. time curves ($t^{1/2}/h^{1/2}$) for SS type AISI 410S for bare and modified surfaces in 3.0 wt% NaCl at 25 °C after 5 days testing.

3.2.2. Potentiodynamic Polarisation Test

Potentiodynamic curves in a 3.0 wt% NaCl solution after 1 h of immersion and 5 days of testing for a bare SS and a surface modified by immersion in SA with and without the addition of E307 are shown in Figure 3. Compared to the bare SS, the modified surface SS showed a decrease in current density in the cathodic and anodic directions. With the presence of E307 in the hydrophobic layer, the cathodic and anodic current densities decreased by up to three decades and the corrosion current density also fell. This behaviour shows that E307 in combination with SA acts as a very effective mixed-type inhibitor. The voltammogram obtained after the 5-day immersion test shows a shift in E_{corr} compared to the immediate immersion test (after one hour of stabilisation at the OCP), where the values of E_{corr} remain practically constant around (-0.25 ± 0.01) V vs. SCE (Figure 3a). In contrast, after the 5-day immersion test the E_{corr} shifts by about 200 mV in the anodic direction (towards the nobler value) with respect to the corrosion potential obtained after 1 h of immersion at the same experimental conditions in the case with the addition of 2.0 wt% E307 to the 0.05 M ethanolic solution during the preparation of the hydrophobic layer, and for about +50 mV upon the addition of 0.5 wt% E307. The bare surface of the SS and the surface modified with SA only show a shift in E_{corr} to more negative values than originally measured. A significant reduction in the anodic current density after the 5-day immersion test (Figure 3b) is also observed, especially in the presence of 0.5 and 2.0 wt% E307 in the as-prepared hydrophobic layer, which indicates the high stability of this layer. The decrease in cathodic current density after long-term exposure is also noteworthy, although this decrease is less obvious.

Figure 3. Potentiodynamic polarisation curves (1 mVs^{-1}) for SS type AISI 410S for bare and modified surfaces in 3.0 wt% NaCl at 25°C (a) after 1 h of immersion [11] (b) after 5 days testing. (The modified surfaces were prepared by immersion of SS type AISI 410S in 0.05 M stearic acid in ethanol with and without addition of E307).

The electrochemical parameters obtained from the polarisation curves, i.e., corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic Tafel slopes (b_a), cathodic Tafel slopes (b_c), polarisation resistance (R_p) and inhibition efficiency (η), are shown in Table 1. The polarisation resistance was obtained from the linear polarisation within the potential range of $\pm 20 \text{ mV}$ with respect to E_{corr} . Extrapolation of the Tafel line allowed the calculation of the corrosion current density i_{corr} . All parameters were determined simultaneously using CorrView software, USA (version 2.80).

Table 1. Kinetic parameters for corrosion of SS type AISI 410S obtained from potentiodynamic polarisation curves for the bare and modified surfaces in 3.0 wt% NaCl at 25°C (after 1 h of immersion [11] and after 5 days testing). The modified surfaces were prepared by the immersion of SS type AISI 410S in 0.05 M SA in ethanol with and without the addition of E307.

Corrosive Media 3.0 wt% NaCl	i_{corr} (nA cm^{-2})	E_{corr} (V/SCE)	R_p ($\text{M}\Omega \text{ cm}^2$)	b_c (mV/dec)	b_a (mV/dec)	% $\eta_{i_{\text{corr}}}$	% η_{R_p}
after 1 h							
bare surface	593.50	−0.270	0.021	−109.1	104.4		
AISI 410S							
modified surface							
wt% E307							
0*	244.40	−0.233	0.065	−156.6	137.8	58.82	66.36
0.5	7.321	−0.238	1.136	−158.8	262.5	98.77	98.07
2.0	2.214	−0.272	6.573	−167.3	428.8	99.63	99.67
after 5 days							
bare surface	476.00	−0.403	0.0538	−153.9	213.3		
AISI 410S							
modified surface *							
wt% E307							
0*	155.20	−0.350	0.170	−185.1	232.7	67.39	68.44
0.5	12.270	−0.213	1.394	−141.2	246.8	97.42	96.14
2.0	0.121	−0.085	22.205	−117.9	251.3	99.97	99.75

* modified surface X4Cr13 within 0.05 M stearic acid + x wt% E307. 0* −0.05 M SA.

The surface coverage θ was calculated using the kinetic parameters measured during the corrosion processes (Equations (1) and (3)) together with the polarisation resistance R_p , the corrosion current density i_{corr} and the polarisation resistance $R_{p\text{-EIS}} = R_1 + R_2 + R_3$ (from the EIS measurements). The inhibition efficiency $\eta\%$, was calculated from the measured values of R_p , i_{corr} and $R_{p\text{-EIS}}$, in accordance with Equations (2) and (4):

$$\theta = \left[1 - \frac{i'_{\text{corr}}}{i_{\text{corr}}} \right] \quad (1)$$

$$\eta\% = \left[1 - \frac{i'_{\text{corr}}}{i_{\text{corr}}} \right] 100 \quad (2)$$

$$\theta = \left[1 - \frac{X}{X'} \right] \quad (3)$$

$$\eta\% = \left[1 - \frac{X}{X'} \right] 100 \quad (4)$$

where $X = R_p$, $R_{p\text{-EIS}}$ and $X' = R_p'$, $R_{p\text{-EIS}'}$. The notations i_{corr} , R_p and $R_{p\text{-EIS}}$ were used for the measurements without inhibitory effect, while the primed quantities i'_{corr} , R_p' and $R_{p\text{-EIS}'}$ were used when measurements were performed on the modified surfaces of SS AISI 410S in 3.0 wt% solution of NaCl (Table 1).

These results clearly show the high inhibition ability of the as-prepared hydrophobic layer in a solution of 3.0 wt% NaCl. They also indicate that the resulting layer completely stops or greatly slows down corrosion even after five days of exposure to 3.0 wt% NaCl.

3.2.3. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) methods have been recognised for years as suitable for the study and characterisation of electrode processes at various types of interface from simple to complex. The main reason is that EIS is known as a non-destructive technique and this property is very important in the field of organic coatings/films, which are of interest as anti-corrosion coatings in aqueous aggressive media [67–71]. Impedance spectroscopy analysis was thus performed to obtain more information about the structure and properties of the as-prepared superhydrophobic surfaces on the SS AISI 410S. It is known that the electrochemical behaviour of the surface of a metal sample with or without a protective layer, film or coating (hydrophobic layer or other organic coating, passive layer, etc.) exposed to an electrolyte solution can be compared with an equivalent circuit [72–76]. A suitable equivalent circuit can be used for the purpose of fitting the EIS measurements and allows the interpretation and explanation of the obtained EIS measurements, and the electrochemical behaviour of the used system (in our case, modified and unmodified surfaces of SS AISI 410S). We applied the fitting of the experimental impedance spectra using the appropriate electrical equivalent circuit (EEC) to better understand the mechanisms of the corrosive processes taking place on the surface of the studied samples. The impedance spectra in Figures 4–6 were fitted with the EEC models using a combination of resistance (R) and the constant-phase element (CPE) in series with R_s , as shown in Figure 7a,b. The data extracted from the EIS are listed in Table 2.

Figures 4–6 represent Nyquist and Bode diagrams, respectively, of the response of the bare and as-prepared superhydrophobic surfaces of the SS AISI 410S (which differed in terms of the content of added E307 within the hydrophobic layer) and their changes as a function of immersion time (1 h, 10 h, 25 h and after 5 days) in 3.0 wt% NaCl electrolyte. These plots were made sequentially for the same sample and thus show the evolution of the electrode response as a function of the immersion time in the test solution, reflecting the changes occurring either in the layer or at the interface.

The EIS obtained for different immersion times at open circuit potential shows that the composite coatings are characterised by two or three time constants. By modifying the surface of the SS AISI 410S with the as-prepared superhydrophobic layer during immersion

in the ethanol solutions of SA with and without the addition of E307, the third time constant becomes more evident. Therefore these impedance spectra were fitted with an EEC with three time constants (three R –CPE circuit elements, Figure 7b), while the bare surface of SS was fitted with the EEC model with two time constants (two R –CPE circuit elements, Figure 7a).

The Nyquist diagrams for all four selected systems show depressed semicircles. The shape of the semicircles is associated with or attributed to charge-driven responses, while the shape of the depressed semicircles indicates non-ideal capacitive behaviour. For this reason, a constant phase element (CPE) has to be used in the modelling to obtain a best fit. It should be noted that the surface heterogeneity originating from the surface roughness, porosity or inhomogeneous distribution of the electrode surface properties is the main reason for the frequency depression phenomenon, which is then considered in the CPE.

Figure 4. EIS Nyquist plots of SS AISI 410S samples for bare and modified surfaces measured after 1, 10, 25 h, and after 5 days of immersion at its open-circuit potential in 3.0 wt% NaCl at 25 °C: (a) blank, (b) SA, (c) SA + 0.5 wt%, (d) SA + 2.0 wt% E307 (measured data—dotted symbols and fitted data—solid lines).

Figure 5. Bode-phase angle plots of SS AISI 410S samples for bare and modified surfaces measured after 1, 10, 25 h, and after 5 days of immersion at its open-circuit potential in 3.0 wt% NaCl at 25 °C: (a) blank, (b) SA, (c) SA + 0.5 wt%, (d) SA + 2.0 wt% E307 (measured data—dotted symbols and fitted data—solid lines).

The impedance of CPE is described in accordance with Equation (5) [23,45,46,74,77–79]:

$$Z_{CPE} = \frac{1}{Q(i\omega)^n} \quad (5)$$

where ‘ Q ’ is denoted as the prefactor of a CPE, ‘ n ’ is the CPE index with values $0 < n < 1$, and ω is the angular frequency ($\omega = 2\pi f$). When $n = 1$, it can be considered as a true capacitor C , when $n = 0.5$, CPE represents a diffusion process, and finally, when $n = -1$, pure inductance is considered [23,80–82]. As the value of the parameter n increases, the inhomogeneity of the coating (the as-prepared hydrophobic layer) decreases.

In the EEC used to fit the experimental data (Figure 7a,b), R_s represents the resistance of the solution (or ‘IR-drop’ between the working and reference electrodes), R_1 is the resistance of the as-prepared hydrophobic layer (superhydrophobic layer), and R_2 is the pore resistance due to the penetration of the electrolyte. The porosity of the self-assembled

protective layer, and also the other minor or major defects of the layer, could represent areas where solution uptake occurs to a greater extent and the R_3 represents the charge transfer resistance. In a coating or a self-assembling hydrophobic layer, or any other type of protective layer, there are in practice always imperfections (especially pores) in its structure. Therefore, a CPE element is present in all RC-elements in the two EECs chosen. Consequently the parameter ' n ', which quantifies various physical phenomena of the surface such as roughness, adsorption of inhibitor molecules, formation of the porous layer, etc. and is an integral part of the parameter CPE, which must be taken into account when calculating the capacity of pores, surface layers or the double layer. according to Equation (6) [83–85].

$$c_x = \frac{(R_y CPE_y)^{\frac{1}{n}}}{R_y} \quad (6)$$

where ' y ' represents the number of the RC-circuits in the EEC ($y = 1, 2$ or 3).

Figure 6. Bode- $|Z|$ -module plots of SS AISI 410S samples for bare and modified surfaces measured after 1, 10, 25 h, and after 5 days of immersion at its open-circuit potential in 3.0 wt% NaCl at 25 °C: (a) blank, (b) SA, (c) SA + 0.5 wt%, (d) SA + 2.0 wt% E307(measured data—dotted symbols and fitted data—solid lines).

Figure 7. Equivalent circuits for EIS results for the: (a) bare surface of AISI 410S samples and (b) as-prepared hydrophobic surface of SS AISI 410S samples.

Some comments on the characteristic impedance values obtained by the fitting process in accordance with the selected EECs for all four types of prepared SS surfaces (bare and three different types of highly hydrophobic layers) are collected in Table 2.

It is noteworthy that the largest decrease in diameter in the case of the unmodified SS surface occurred after 5 days of immersion in a 3.0 wt% solution of NaCl. It decreased from $500 \text{ k}\Omega \text{ cm}^2$ to less than $100 \text{ k}\Omega \text{ cm}^2$, and the C_{dl} value increased from $1.105 \mu\text{F}/\text{cm}^2$ to $17.98 \mu\text{F}/\text{cm}^2$ after 10 h of exposure and to $18.902 \mu\text{F}/\text{cm}^2$ after 5 days. From the obtained values it can be concluded that the layer formed on the surface of the SS is mostly like a passive layer associated with corrosion products, where penetration of the electrolyte to the interface of the formed layer/metal surface is expected.

The C_{dl} values in the case of the modified surfaces with SA alone or in the combination of (SA + 0.5 wt% E307) and (SA + 2.0 wt% E307) are much lower and remain relatively constant (perhaps with a slight increase, but not as fast as in the case of the unmodified surface). The as-prepared hydrophobic layer (SA + 0.5 wt% E307) on the surface of the sample SS shows about three to four times higher values of C_{dl} compared to the surfaces modified with SA alone or in combination with (SA + 2.0 wt% E307), which could be attributed to higher porosity and thus higher water-uptake.

The parameter n_2 , ranging from 0.58 to 0.6 in terms of immersion time within 25 h, also indicates the presence of greater inhomogeneity on the surface. After 5 days of immersion it decreases to 0.54, indicating diffusion processes, which in turn means that both water molecules and aggressive chloride ions can penetrate more easily through the pores or defects in the self-assembling hydrophobic protective layer. On the other hand, it is worth mentioning that the resistance of this layer described by the values of R_1 is higher by an order of magnitude than in the case when the layer consisted of only SA, indicating the higher quality of the as-prepared hydrophobic layer with the addition of E307. The value of R_1 slowly decreases during the long-term test, but the resistance of the pore R_2 remains relatively constant, which can be attributed to the phenomenon that the pore is probably filled with electrolyte and does not allow access to the base metal matrix, or that the diffusion processes are very slow. It could be speculated that the pore is funnel-shaped and thus the layer/metal contact is severely constricted or even closed. Furthermore, the above statements could also be supported by the R_3 values, which are an order of magnitude higher in the cases where the surfaces were modified with (SA + 0.5 wt% E307) than in those modified with SA alone.

If the hydrophobic protective layer was made of the combination (SA + 2.0 wt% E307), all characteristic resistance parameters R_1 , R_2 and R_3 and thus the values of the polarisation resistances R_p (R_p represents the sum of all resistances contained in the EEC) additionally increased. The parameters for the inhomogeneity of the surfaces n_1 and n_2 are also increased, indicating the increase in the homogeneity of the as-prepared hydrophobic surface of the SS and consequently the highest level of protection, 99.6% in the 3.0 wt% NaCl during the long-term immersion test (5 days).

Table 2. Electrochemical impedance parameters (EIS fitting results) for SS AISI 410S (for the bare and modified surfaces) after immersion in the 3.0 wt% NaCl solution for different time at 25 °C.

Corrosive Media 3.0 wt% NaCl	R_s ($\Omega \text{ cm}^2$)	R_1 ($\text{k}\Omega \text{ cm}^2$)	n_1	C_1 ($\mu\text{F cm}^{-2}$)	R_2 ($\text{M}\Omega \text{ cm}^2$)	n_2	C_2 ($\mu\text{F cm}^{-2}$)	R_3 ($\text{M}\Omega \text{ cm}^2$)	n_3	C_3 ($\mu\text{F cm}^{-2}$)	$R_{p\text{-EIS}}$ ($\text{M}\Omega \text{ cm}^2$)	$\eta_{R_{p\text{-EIS}}}$ (%)
Bare surface AISI 410S												
1 h	6.53	0.441	0.738	1.105	/	/	/	0.501	0.766	1.105	0.501	
10 h	6.55	0.263	0.776	1.122	/	/	/	0.514	0.79	17.981	0.514	
25 h	6.42	0.629	0.728	1.169	/	/	/	0.555	0.771	12.536	0.555	
5 days	5.13	0.196	0.746	4.73	/	/	/	0.092	0.827	18.902	0.093	
modified surface AISI 410S												
							SA					
1 h	13.72	1.724	0.865	0.07	0.644	0.517	0.55	1.736	0.615	1.689	2.381	78.94
10 h	13.73	2.271	0.881	0.218	0.579	0.575	0.716	1.947	0.81	1.026	2.528	79.66
25 h	14.21	6.195	0.87	0.453	1.28	0.89	0.868	1.488	0.636	2.749	2.774	79.99
5 days	13.84	16.683	0.854	1.017	0.959	0.893	1.378	1.787	0.675	3.308	2.762	96.65
modified surface AISI 410S												
							SA + 0.5%E307					
1 h	15.13	69.991	0.918	0.04	0.11	0.588	0.119	13.998	0.627	9.215	14.178	96.46
10 h	15.82	36.001	0.9	0.033	0.268	0.604	0.368	18.072	0.667	9.152	18.376	97.2
25 h	16.29	20.499	0.829	0.025	0.803	0.583	1.078	21.576	0.754	9.306	22.399	97.52
5 days	15.81	15.47	0.88	0.043	0.242	0.542	1.246	24.079	0.669	10.111	24.337	99.62
modified surface AISI 410S												
							SA + 2.0%E307					
1 h	17.96	76.339	0.916	0.045	0.565	0.809	0.103	13.255	0.656	2.017	13.896	96.39
10 h	17.37	91.5	0.923	0.045	8.02	0.897	0.49	14.19	0.745	3.74	22.302	97.69
25 h	17.87	85.81	0.937	0.042	13.636	0.781	0.637	14.929	0.786	4.224	28.651	98.06
5 days	17.37	128.06	0.939	0.036	/	/	/	28.16	0.773	4.187	28.288	99.67

This is also confirmed by the half of the lower value of C_{dl} compared to the C_{dl} of the (SA + 0.5% E307) layer, indicating a lower possibility of penetration of the electrolyte into the as-prepared hydrophobic layer.

Figure 5a–d show the Bode impedance spectra after the immersion times of 1 h, 10 h, 25 h and after 5 days for modified and unmodified SS samples. The impedance modulus $|Z|$ (Figure 5a) at low frequency for the bare sample of SS AISI 410S decreased significantly after 5 days of immersion compared to the values after 1 h, 10 and 25 h, indicating the breakdown of the passive layer and the possible onset of a localised form of corrosion. Moreover, in the low-frequency region it can be seen that the impedance value for the hydrophobic layers prepared in this way (Figure 5b–d) is almost two orders of magnitude higher than the impedance value of the bare sample of SS AISI 410S.

Furthermore, in the long-term test for all modified samples of SS (hydrophobic layer, i.e., SA with and without addition of E307), the impedance modulus $|Z|$ does not change significantly at low frequencies. In most cases, it even increases with time. It should be noted that with the increasing concentration of E307 added in the hydrophobic layer the impedance values at low frequencies show an increasing trend. This behaviour indicates that the as-prepared superhydrophobic surface with or without the addition of E307 still exhibits protective properties during the long-term test 5 days after immersion in 3.0 wt% NaCl.

The increased amount of E307 apparently contributes to a stronger bond between the metal and superhydrophobic layer due to the formation of ester (esterification between SA and α -tocopherol). Furthermore, the as-prepared hydrophobic layer may be more densely packed for the above reason, which hinders the uptake and attack of corrosive species such as chloride ions, oxygen, water and also electrons. A higher concentration of the added E307 improves the protective property of the as-prepared hydrophobic layer compared to the layers where a lower concentration of E307 was added, or in the case where only a SA hydrophobic layer was present [10,11].

The second type of Bode diagram show the change of phase angle as a function of logarithmic frequency (Figure 6a–d). They clearly show the existence of two time constants in the case of an unmodified surface and three in the case of all types of modified SS surface. This means that the EEC consists of two or three RC-elements (Figure 7a,b).

The time constant for SA in the high-frequency range from 10^6 to 10^3 represents the properties of the hydrophobic protective layer. As the immersion time increases, this frequency window narrows, which could be a sign that the electrolyte has penetrated into the layer itself, which could greatly impair the protective properties of the layer. The phase angles of the time constant in the high-frequency region begin to decrease and have decreased by about 10° after 5 days of immersion, indicating that electrolyte and water have likely penetrated through the hydrophobic layer of SA. Considering that the R_3 values increased with time it could be suspected, as mentioned earlier, that the penetrated electrolyte has not yet reached the metal surface after 5 days of immersion.

The phase angle of the time constant in the low- and high-frequency ranges slightly increases with time in the case of the modified surface (SA + 0.5 wt% E307), while in the mid-frequency range a valley appears, indicating the penetration of the electrolyte through the pores in the layer and apparently not up to the metal surface, since R_3 is higher than in the case of the modified layer with SA alone.

In Figures 5d and 6d (SA + 2.0 wt% E307), the middle frequency region of the Bode plot shows a linear relationship between $\log |Z|$ vs. $\log f$ with a slope close to -1 , where the phase angle ranges from 0° to -80° . This shows a typical capacitive behaviour of the protected surface of SS. Moreover, the broad phase angle is attributed to the presence of three overlapped time constants (the as-prepared hydrophobic layer in the high-frequency region, the penetration of the electrolyte—the majority of which is hindered by the high-quality, low-porosity hydrophobic layer in the middle-frequency region—and the third, the charge transfer resistance in the low-frequency region). In this case, the highest value of R_3 is obtained, which confirms the maximum stability and best inhibition properties of the as-prepared hydrophobic layer of (SA + 2.0 wt% E307) on the SS AISI 410S surface.

The values of total polarisation resistance obtained from the Nyquist plots/Bode plots are in good agreement with the values obtained from potentiodynamic methods, i.e., the films deposited from ethanolic solutions of 0.05 M SA containing E307 showed significantly better protective properties even after 5 days of exposure to the aggressive 3.0 wt% NaCl solution.

3.3. Surface Characterisation

3.3.1. ATR-FTIR Analysis

The chemical composition and bonding states of the as-prepared hydrophobic layers were investigated by FTIR-ATR analysis. The focus of the ATR-FTIR analysis was to detect the presence of α -tocopherol (E307) in the modified surfaces of SS X4Cr14. There was a noticeable increase in inhibition efficiency with the addition of E307 to the ethanolic solution of SA, and thus the possible chemical changes in the composition or structure of the as-prepared hydrophobic self-assembled layer after 5 days of immersion in corrosion medium were also the subject of our interest.

Figure 8b,c show the FTIR spectrum obtained for the as-prepared hydrophobic layers on the surface of SS AISI 410S after 1 h of immersion in an ethanolic solution of SA with addition of 2.0 wt% E307 and after 5 days of immersion in a solution of 3.0 wt% NaCl, while Figure 8a shows the FTIR spectrum for the used mixture alone.

Man et al. [86], Silva et al. [87], Krilov et al. [88] and Valderrama [89] showed the characteristic absorption band of pure α -tocopherol at the wavelengths of 3473 cm^{-1} for the $-\text{OH}$ stretching band, while 2927 and 2868 cm^{-1} belong to the symmetric and asymmetric stretching vibrations of CH_2 and CH_3 , respectively. Furthermore, 1461 cm^{-1} indicates the asymmetric bending of the phenyl skeleton and methyl group (1460 cm^{-1}), 1378 cm^{-1} the symmetric bending of the methyl group, 1262 cm^{-1} , $-\text{CH}_2$, 1086 cm^{-1} for plane bending of phenyl group and 919 cm^{-1} for $\text{trans} = \text{CH}_2$ stretching. The bands at 1207 , 1110 – 1107 , and 1068 – 1062 cm^{-1} correspond to the stretching vibration of $\text{C}-\text{O}$.

In Figure 8b,c, all the above wavelengths are in agreement, except the broad peak at about 3400 cm^{-1} , which belongs to $-\text{OH}$ stretching, disappeared. Its presence is observed in Figure 8a, which shows the reaction of the ethanolic solution (SA + 2.0 wt% E307).

As mentioned in our previous works [10,11] the disappearance of the $-\text{OH}$ stretching vibrations (3300 – 3100 cm^{-1}) and the appearance of the absorption band at 1710 cm^{-1} could be related to the esterification of stearic acid and α -tocopherol E307 (carboxylic acid with an alcohol). In agreement with the above, we can undoubtedly confirm the presence of E307 in the as-prepared hydrophobic self-assembled layer. After 5 days of immersion in a corrosive medium, no significant differences in the absorption bands were observed, indicating the unchanged composition of the hydrophobic layers while confirming their high resistance and durability.

3.3.2. SEM EDAX

EDAX analysis confirmed a huge increase in carbon content on the surface of SS AISI 410S after the formation of the as-prepared hydrophobic layer. This increase is more pronounced with the addition of E307 in the 0.05 M ethanolic solution of SA during the preparation of the hydrophobic layer, which could confirm the presence of E307 in the resulting hydrophobic layer. In terms of numbers, the increase in carbon content ranged from about 0.5 wt% (bare surface) to 43.04 wt% when the surfaces were modified with SA only, and to 51.0 wt% in the case of (SA + 2.0 wt% E307) (Table 3).

Figure 8. ATR-FTIR spectra (a) for ethanolic solution of SA + 2.0 wt% of E307, (b) modified surface of SS type AISI 410S in ethanolic solution of SA with the addition of 2.0 wt% of E307 for one hour [11], (c) modified surface of SS type AISI 410S in ethanolic solution of SA with the addition of 2.0 wt% of E307 after 5 days of immersion in 3.0 wt% NaCl.

Table 3. EDAX analysis of the bare and modified surfaces of SS AISI 410S samples which were prepared by the immersion within 0.05 M SA alone and with the addition of 2.0 wt% of E307.

Bare surface		(SA)		(SA + 2.0 wt% E307)	
X4Cr13		X4Cr13		X4Cr13	
Element	wt%	Element	wt%	Element	wt%
C K	0.52	C K	43.04	C K	51.02
Si K	0.48	Si K	0.37	Si K	0.17
Cr K	16.31	Cr K	7.52	Cr K	6.71
Fe K	80.50	Fe K	49.08	Fe K	42.11
O K	1.64				
S	0.55				
Totals	100.00	Totals	100.00	Totals	100.00

4. Conclusions

Modified surfaces of SS AISI 410S in an ethanolic solution of SA with and without the addition of E307 exhibited a hydrophobic protective layer structured as a hierarchical flower-like cluster.

Of all the techniques used in this work, the presence of (+)- α -tocopherol (E307) in the as-prepared hydrophobic flower structured protective layer caused a notable increase in the corrosion inhibition properties of the modified surface of SS AISI 410S in a solution of 3.0 wt% NaCl. Furthermore, electrochemical measurements indicated that the films deposited from ethanolic solutions of 0.05M SA containing E307 have excellent protective properties, even after 5 days of exposure to a solution of 3.0 wt% NaCl.

The water contact angle (CA) for the modified layer formed on the SS type AISI 410S in the presence of SA with or without the addition of E307 was significantly larger than for the bare metal surface. It increased from 71° to almost 140°, which is very close to that seen for those surfaces with superhydrophobic properties (150°).

The significant increase in the contact angle indicates that the morphology effectively repels water, which was confirmed with the results of potentiodynamic and EIS measurements, indicating the excellent protective effect of these self-assembled layers.

In the case of SA + 2.0% E307, this structure was maintained even after 5 days of exposure to corrosive media, which was also the reason for the high value of inhibitory efficiency, which was greater than 99%.

Funding: This work was financially supported by Slovenian Research Agency-ARRS, Ljubljana (www.rrs.gov.si, accessed on 13 August 2021) under research project “Physico-Chemical Processes on the Surface Layers and Application of Nanoparticles” (P2-0006).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The author declare no conflict of interest.

References

1. Kreysa, G.; Schütze, M.; Fürbeth, W. Corrosion News. *Mater. Corros.* **2018**, *69*, 140–146. [[CrossRef](#)]
2. Hou, B.; Li, X.; Ma, X.; Du, C.; Zhang, D.; Zheng, M.; Xu, W.; Lu, D.; Ma, F. The cost of corrosion in China. *Npj Mater. Degrad.* **2017**, *1*, 1–10. [[CrossRef](#)]
3. Mazumder, M.A.J. Global Impact of Corrosion: Occurrence, Cost and Mitigation. *Glob. J. Eng. Sci.* **2020**, *5*, 4. [[CrossRef](#)]
4. Abiola, O.K.; John, M.O.; Asekunowo, P.O.; Okafor, P.C.; James, O. 3-[(4-amino-2-methyl-5-pyrimidinyl) methyl]-5-(2-hydroxyethyl)-4-methyl thiazolium chloride hydrochloride as green corrosion inhibitor of copper in HNO₃ solution and its adsorption characteristics. *Green Chem. Lett. Rev.* **2011**, *4*, 273–279. [[CrossRef](#)]

5. Hoseizadeh, A.R.; Danaee, I.; Maddahy, M.H. Thermodynamic and Adsorption Behaviour of Vitamin B1 as a Corrosion Inhibitor for AISI 4130 Steel Alloy in HCl Solution. *Zeitschrift für Physikalische Chemie* **2013**, *227*, 403–418. [\[CrossRef\]](#)
6. Solmaz, R. Investigation of corrosion inhibition mechanism and stability of Vitamin B1 on mild steel in 0.5M HCl solution. *Corros. Sci.* **2014**, *81*, 75–84. [\[CrossRef\]](#)
7. Malhotra, S.; Singh, G. Vitamins: Potential inhibitors for nickel in acidic media. *Surf. Eng.* **2005**, *21*, 187–192. [\[CrossRef\]](#)
8. Fuchs-Godec, R.; Pavlovic, M.G.; Tomic, M.V. The inhibitive effect of vitamin-C on the corrosive performance of steel in HCl solutions—Part II. *Int. J. Electrochem. Sci.* **2015**, *10*, 10502–10512.
9. Sekine, I.; Nakahata, Y.; Tanabe, H. The corrosion inhibition of mild steel by ascorbic and folic acids. *Corros. Sci.* **1988**, *28*, 987–1001. [\[CrossRef\]](#)
10. Fuchs-Godec, R.; Zerjav, G. Corrosion resistance of high-level-hydrophobic layers in combination with Vitamin E—(α -tocopherol) as green inhibitor. *Corros. Sci.* **2015**, *97*, 7–16. [\[CrossRef\]](#)
11. Fuchs-Godec, R. Effect of α -tocopherol as a green inhibitor on chloride-induced corrosion of steel. *Int. J. Electrochem. Sci.* **2019**, *14*, 10396–10409. [\[CrossRef\]](#)
12. Fuchs-Godec, R.; Pavlović, M.G.; Tomić, M.V. The inhibitive effect of vitamin-C on the corrosive performance of steel in HCL solutions. *Int. J. Electrochem. Sci.* **2013**, *8*, 1511–1519.
13. Valek, L.; Martinez, S.; Serdar, M.; Stipanovic, I. Ascorbic Acid as Corrosion Inhibitor for Steel in Alkaline Media Containing Chloride Ions. *Chem. Biochem. Eng. Q.* **2007**, *21*, 65–70.
14. Fuadi, A. Suhendrayatna Investigation of Ascorbic Acid as Environment-Friendly Corrosion Inhibitor of Low Carbon Steel in Marine Environment. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *536*, 012108. [\[CrossRef\]](#)
15. Liu, K.; Jiang, L. Multifunctional Integration: From Biological to Bio-Inspired Materials. *ACS Nano* **2011**, *5*, 6786–6790. [\[CrossRef\]](#)
16. Meuler, A.J.; Smith, J.D.; Varanasi, K.K.; Mabry, J.; McKinley, G.; Cohen, R.E. Relationships between Water Wettability and Ice Adhesion. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3100–3110. [\[CrossRef\]](#)
17. Lu, X.; Wang, Z.; Yang, X.; Xu, X.; Zhang, L.; Zhao, N.; Xu, J. Antifogging and antireflective silica film and its application on solar modules. *Surf. Coat. Technol.* **2011**, *206*, 1490–1494. [\[CrossRef\]](#)
18. Darmanin, T.; Tarrade, J.; Celia, E.; Bellanger, H.; Guittard, F. Superoleophobic Meshes with Relatively Low Hysteresis and Sliding Angles by Electropolymerization: Importance of Polymer-Growth Control. *Chem. Plus. Chem.* **2013**, *79*, 382–386. [\[CrossRef\]](#)
19. Bäßler, R.; Uhlemann, M.; Mummert, K. Inhibiting effect of octadecylamine on pitting corrosion behaviour of stainless steel type 1.4541 up to 250 °C. *Mater. Corros.* **1999**, *50*, 146–153. [\[CrossRef\]](#)
20. Xue, C.-H.; Jia, S.-T.; Zhang, J.; Ma, J.-Z. Large-area fabrication of superhydrophobic surfaces for practical applications: An overview. *Sci. Technol. Adv. Mater.* **2010**, *11*, 033002. [\[CrossRef\]](#)
21. Darband, G.B.; Aliofkhaezai, M.; Khorsand, S.; Sokhanvar, S.; Kaboli, A. Science and Engineering of Superhydrophobic Surfaces: Review of Corrosion Resistance, Chemical and Mechanical Stability. *Arab. J. Chem.* **2020**, *13*, 1763–1802. [\[CrossRef\]](#)
22. Wen, Q.; Guo, Z. Recent Advances in the Fabrication of Superhydrophobic Surfaces. *Chem. Lett.* **2016**, *45*, 1134–1149. [\[CrossRef\]](#)
23. Wang, C.-X.; Zhang, X.-F. A non-particle and fluorine-free superhydrophobic surface based on one-step electrodeposition of dodecyltrimethoxysilane on mild steel for corrosion protection. *Corros. Sci.* **2019**, *163*, 108284. [\[CrossRef\]](#)
24. Ma, Q.; Tong, Z.; Wang, W.; Dong, G. Fabricating robust and repairable superhydrophobic surface on carbon steel by nanosecond laser texturing for corrosion protection. *Appl. Surf. Sci.* **2018**, *455*, 748–757. [\[CrossRef\]](#)
25. Qian, H.; Li, M.; Li, Z.; Lou, Y.; Huang, L.; Zhang, D.; Xu, D.; Du, C.; Lu, L.; Gao, J. Mussel-inspired superhydrophobic surfaces with enhanced corrosion resistance and dual-action antibacterial properties. *Mater. Sci. Eng. C* **2017**, *80*, 566–577. [\[CrossRef\]](#)
26. Xiang, T.; Chen, D.; Lv, Z.; Yang, Z.; Yang, L.; Li, C. Robust superhydrophobic coating with superior corrosion resistance. *J. Alloys Compd.* **2019**, *798*, 320–325. [\[CrossRef\]](#)
27. Zhang, X.-F.; Chen, R.-J.; Hu, J.-M. Superhydrophobic surface constructed on electrodeposited silica films by two-step method for corrosion protection of mild steel. *Corros. Sci.* **2016**, *104*, 336–343. [\[CrossRef\]](#)
28. Sebastian, D.; Yao, C.W.; Lian, I. Mechanical durability of engineered superhydrophobic surfaces for anti-corrosion. *Coatings* **2018**, *8*, 162. [\[CrossRef\]](#)
29. Sun, W.; Wang, L.; Yang, Z.; Li, S.; Wu, T.; Liu, G. Fabrication of polydimethylsiloxane-derived superhydrophobic surface on aluminium via chemical vapour deposition technique for corrosion protection. *Corros. Sci.* **2017**, *128*, 176–185. [\[CrossRef\]](#)
30. Zhang, D.; Qian, H.; Wang, L.; Li, X. Comparison of barrier properties for a superhydrophobic epoxy coating under different simulated corrosion environments. *Corros. Sci.* **2016**, *103*, 230–241. [\[CrossRef\]](#)
31. Ejenstam, L.; Swerin, A.; Pan, J.; Claesson, P.M. Corrosion protection by hydrophobic silica particle-polydimethylsiloxane composite coatings. *Corros. Sci.* **2015**, *99*, 89–97. [\[CrossRef\]](#)
32. Liu, W.; Xu, Q.; Han, J.; Chen, X.; Min, Y. A novel combination approach for the preparation of superhydrophobic surface on copper and the consequent corrosion resistance. *Corros. Sci.* **2016**, *110*, 105–113. [\[CrossRef\]](#)
33. Xu, W.; Hu, Y.; Bao, W.; Xie, X.; Liu, Y.; Song, A.; Hao, J. Superhydrophobic copper surfaces fabricated by fatty acid soaps in aqueous solution for excellent corrosion resistance. *Appl. Surf. Sci.* **2017**, *399*, 491–498. [\[CrossRef\]](#)
34. Emelyanenko, A.M.; Pytskii, I.S.; Kaminsky, V.V.; Chulkova, E.V.; Domantovsky, A.G.; Emelyanenko, K.A.; Sobolev, V.D.; Aleshkin, A.V.; Boinovich, L.B. Superhydrophobic copper in biological liquids: Antibacterial activity and microbiologically induced or inhibited corrosion. *Colloids Surf. B Biointerfaces* **2019**, *185*, 110622. [\[CrossRef\]](#)

35. Yuan, S.; Pehkonen, S.; Liang, B.; Ting, Y.; Neoh, K.G.; Kang, E.-T. Superhydrophobic fluoropolymer-modified copper surface via surface graft polymerisation for corrosion protection. *Corros. Sci.* **2011**, *53*, 2738–2747. [\[CrossRef\]](#)
36. Cheng, Y.; Lu, S.; Xu, W.; Cao, K.; Li, J.; Zheng, Y. Controllable fabrication of superhydrophobic alloys surface on copper substrate for self-cleaning, anti-icing, anti-corrosion and anti-wear performance. *Surf. Coat. Technol.* **2018**, *333*, 61–70. [\[CrossRef\]](#)
37. Huang, Y.; Sarkar, D.; Gallant, D.; Chen, X.-G. Corrosion resistance properties of superhydrophobic copper surfaces fabricated by one-step electrochemical modification process. *Appl. Surf. Sci.* **2013**, *282*, 689–694. [\[CrossRef\]](#)
38. Khorsand, S.; Raeissi, K.; Ashrafizadeh, F. Corrosion resistance and long-term durability of super-hydrophobic nickel film prepared by electrodeposition process. *Appl. Surf. Sci.* **2014**, *305*, 498–505. [\[CrossRef\]](#)
39. Qiu, R.; Zhang, D.; Wang, P. Superhydrophobic-carbon fibre growth on a zinc surface for corrosion inhibition. *Corros. Sci.* **2013**, *66*, 350–359. [\[CrossRef\]](#)
40. Li, L.; Zhang, Y.; Lei, J.; He, J.; Lv, R.; Li, N.; Pan, F. A facile approach to fabricate superhydrophobic Zn surface and its effect on corrosion resistance. *Corros. Sci.* **2014**, *85*, 174–182. [\[CrossRef\]](#)
41. Zang, D.; Zhu, R.; Zhang, W.; Wu, J.; Yu, X.; Zhang, Y. Stearic acid modified aluminum surfaces with controlled wetting properties and corrosion resistance. *Corros. Sci.* **2014**, *83*, 86–93. [\[CrossRef\]](#)
42. Malta, M.I.C.; Vieira, M.R.S.; Da Silva, R.G.C.; Da Silva, L.M.C.; De Araújo, E.G.; Maciel, S.H.D.O.; Filho, S.L.U. Superhydrophobic Surfaces on 5052 Aluminum Alloy Obtained from LDH Film Modified with Stearic Acid for Enhanced Corrosion Protection. *Mater. Res.* **2019**, *22*. [\[CrossRef\]](#)
43. Feng, L.; Zhang, H.; Wang, Z.; Liu, Y. Superhydrophobic aluminum alloy surface: Fabrication, structure, and corrosion resistance. *Colloids Surf. A Physicochem. Eng. Asp.* **2014**, *441*, 319–325. [\[CrossRef\]](#)
44. Zhang, B.; Xu, W.; Zhu, Q.; Sun, Y.; Li, Y. Mechanically robust superhydrophobic porous anodized AA5083 for marine corrosion protection. *Corros. Sci.* **2019**, *158*, 108083. [\[CrossRef\]](#)
45. Tang, H.; Sun, J.; Yan, X.; Wu, P. Electrochemical and adsorption behaviors of thiadiazole derivatives on the aluminum surface. *RSC Adv.* **2019**, *9*, 34617–34626. [\[CrossRef\]](#)
46. Abbasi, S.; Nouri, M.; Aghdam, A.S.R. A novel combined method for fabrication of stable corrosion resistance superhydrophobic surface on Al alloy. *Corros. Sci.* **2019**, *159*, 108144. [\[CrossRef\]](#)
47. Zhao, L.; Liu, Q.; Gao, R.; Wang, J.; Yang, W.; Liu, L. One-step method for the fabrication of superhydrophobic surface on magnesium alloy and its corrosion protection, antifouling performance. *Corros. Sci.* **2014**, *80*, 177–183. [\[CrossRef\]](#)
48. Ding, C.; Liu, Y.; Wang, M.; Wang, T.; Fu, J. Self-healing, superhydrophobic coating based on mechanized silica nanoparticles for reliable protection of magnesium alloys. *J. Mater. Chem. A* **2016**, *4*, 8041–8052. [\[CrossRef\]](#)
49. Yeganeh, M.; Mohammadi, N. Superhydrophobic surface of Mg alloys: A review. *J. Magnes. Alloys* **2018**, *6*, 59–70. [\[CrossRef\]](#)
50. Zhu, J.; Jia, H. A Facile Method to Prepare a Superhydrophobic Magnesium Alloy Surface. *Materials* **2020**, *13*, 4007. [\[CrossRef\]](#)
51. Boinovich, L.B.; Emelyanenko, A.M.; Pashinin, A.S.; Gnednikov, S.V.; Egorkin, V.S.; Sinebryukhov, S.L. Mg alloy treatment for superhydrophobic anticorrosion coating formation. *Surf. Innov.* **2013**, *1*, 162–172. [\[CrossRef\]](#)
52. Boiesier, G.; Lamure, A.; Pébère, N.; Portail, N.; Villatte, M. Corrosion protection of AA2024 sealed anodic layers using the hydrophobic properties of carboxylic acids. *Surf. Coat. Technol.* **2009**, *203*, 3420–3426. [\[CrossRef\]](#)
53. Ramesh, S.P.M. Synergistic effect of Thiomalic acid and Zinc ions in Corrosion control of Carbon Steel in Aqueous Solution. *Res. J. Chem. Sci.* **2014**, *4*, 41.
54. Wysocka, J.; Cieřlik, M.; Krakowiak, S.; Ryl, J. Carboxylic acids as efficient corrosion inhibitors of aluminium alloys in alkaline media. *Electrochim. Acta* **2018**, *289*, 175–192. [\[CrossRef\]](#)
55. Yoo, S.-H.; Kim, Y.-W.; Chung, K.; Kim, N.-K.; Kim, J.-S. Corrosion Inhibition Properties of Triazine Derivatives Containing Carboxylic Acid and Amine Groups in 1.0 M HCl Solution. *Ind. Eng. Chem. Res.* **2013**, *52*, 10880–10889. [\[CrossRef\]](#)
56. Wang, S.; Feng, L.; Jiang, L. One-Step Solution-Immersion Process for the Fabrication of Stable Bionic Superhydrophobic Surfaces. *Adv. Mater.* **2006**, *18*, 767–770. [\[CrossRef\]](#)
57. Cao, Y.; Jin, S.; Zheng, D.; Lin, C. Facile fabrication of ZnAl layered double hydroxide film co-intercalated with vanadates and laurates by one-step post modification. *Colloid Interface Sci. Commun.* **2020**, *40*, 100351. [\[CrossRef\]](#)
58. Ke, X.; Guo, S.; Gou, B.; Wang, N.; Zhou, X.; Xiao, L.; Hao, G.; Jiang, W. Superhydrophobic Fluorine-Containing Protective Coating to Endow Al Nanoparticles with Long-Term Storage Stability and Self-Activation Reaction Capability. *Adv. Mater. Interfaces* **2019**, *6*, 1901025. [\[CrossRef\]](#)
59. Ejenstam, L.; Tuominen, M.; Haapanen, J.; Mäkelä, J.M.; Pan, J.; Swerin, A.; Claesson, P.M. Long-term corrosion protection by a thin nano-composite coating. *Appl. Surf. Sci.* **2015**, *357*, 2333–2342. [\[CrossRef\]](#)
60. Geuli, O.; Mandler, D. The synergistic effect of benzotriazole and trimethylsiloxysilicate towards corrosion protection of printed Cu-based electronics. *Corros. Sci.* **2018**, *143*, 329–336. [\[CrossRef\]](#)
61. Ou, H.-H.; Tran, Q.T.P.; Lin, P.-H. A synergistic effect between gluconate and molybdate on corrosion inhibition of recirculating cooling water systems. *Corros. Sci.* **2018**, *133*, 231–239. [\[CrossRef\]](#)
62. Zhang, C.; Duan, H.; Zhao, J. Synergistic inhibition effect of imidazoline derivative and L-cysteine on carbon steel corrosion in a CO₂-saturated brine solution. *Corros. Sci.* **2016**, *112*, 160–169. [\[CrossRef\]](#)
63. Fuchs-Godec, R.; Pavlović, M.G. Synergistic effect between non-ionic surfactant and halide ions in the forms of inorganic or organic salts for the corrosion inhibition of stainless-steel X4Cr13 in sulphuric acid. *Corros. Sci.* **2012**, *58*, 192–201. [\[CrossRef\]](#)

64. Barthlott, W.; Mail, M.; Neinhuis, C. Superhydrophobic hierarchically structured surfaces in biology: Evolution, structural principles and biomimetic applications. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **2016**, *374*, 20160191. [CrossRef]
65. Latthe, S.S.; Terashima, C.; Nakata, K.; Fujishima, A. Superhydrophobic Surfaces Developed by Mimicking Hierarchical Surface Morphology of Lotus Leaf. *Molecules* **2014**, *19*, 4256–4283. [CrossRef] [PubMed]
66. Jeevahan, J.; Chandrasekaran, M.; Joseph, G.B.; Raj, R.B.D.; Mageshwaran, G. Superhydrophobic surfaces: A review on fundamentals, applications, and challenges. *J. Coat. Technol. Res.* **2018**, *15*, 231–250. [CrossRef]
67. Ellingson, L.; Shedlosky, T.; Bierwagen, G.; de la Rie, E.; Brostoff, L. The Use of Electrochemical Impedance Spectroscopy in the Evaluation of Coatings for Outdoor Bronze. *Stud. Conserv.* **2004**, *49*, 53–62. [CrossRef]
68. Ates, M. Review study of electrochemical impedance spectroscopy and equivalent electrical circuits of conducting polymers on carbon surfaces. *Prog. Org. Coat.* **2011**, *71*, 1–10. [CrossRef]
69. Cesiulis, H.; Tsyntsa, N.; Ramanavicius, A.; Ragoisha, G. *Nanostructures and Thin Films for Multifunctional Applications*; Springer: Berlin/Heidelberg, Germany, 2016; ISBN 978-3-319-30197-6.
70. Bonastre, J.; Garces, P.; Galvan, J.C.; Cases, F. Characterisation and corrosion studies of steel electrodes covered by polypyrrole/phosphotungstate using Electrochemical Impedance Spectroscopy. *Prog. Org. Coat.* **2009**, *66*, 235–241. [CrossRef]
71. Amin, M.A.; Ibrahim, M.M. Corrosion and corrosion control of mild steel in concentrated H₂SO₄ solutions by a newly synthesized glycine derivative. *Corros. Sci.* **2011**, *53*, 873–885. [CrossRef]
72. Sacco, A. Electrochemical impedance spectroscopy: Fundamentals and application in dye-sensitized solar cells. *Renew. Sustain. Energy Rev.* **2017**, *79*, 814–829. [CrossRef]
73. Nady, H.; El-Rabiei, M.; Samy, M. Corrosion behavior and electrochemical properties of carbon steel, commercial pure titanium, copper and copper–aluminum–nickel alloy in 3.5% sodium chloride containing sulfide ions. *Egypt. J. Pet.* **2017**, *26*, 79–94. [CrossRef]
74. Zheludkevich, M.; Serra, R.; Montemor, F.; Yasakau, K.; Salvado, I.; Ferreira, M. Nanostructured sol–gel coatings doped with cerium nitrate as pre-treatments for AA2024-T3: Corrosion protection performance. *Electrochim. Acta* **2005**, *51*, 208–217. [CrossRef]
75. Mahato, N.; Singh, M.M. Investigation of Passive Film Properties and Pitting Resistance of AISI 316 in Aqueous Ethanoic Acid Containing Chloride Ions using Electrochemical Impedance Spectroscopy(EIS). *Port. Electrochim. Acta* **2011**, *29*, 233–251. [CrossRef]
76. Jo, B.E. Electrochemical Impedance Methods to Assess Coatings for Corrosion Protection. Technical Service Center, Materials and Corrosion Laboratory, U.S., PO Box 25007, Denver CO 80225-0007, 2019. Available online: https://www.usbr.gov/tsc/techreferences/mands/mands-pdfs/ElectrochemicalImpedanceMethods_8540-2019-03_508.pdf (accessed on 13 August 2021).
77. Nezhad, A.N.; Davoodi, A.; Zahrani, E.M.; Arefinia, R. The effects of an inorganic corrosion inhibitor on the electrochemical behavior of superhydrophobic micro-nano structured Ni films in 3.5% NaCl solution. *Surf. Coat. Technol.* **2020**, *395*, 125946. [CrossRef]
78. Liu, X.; Zhang, T.C.; He, H.; Ouyang, L.; Yuan, S. A stearic Acid/CeO₂ bilayer coating on AZ31B magnesium alloy with superhydrophobic and self-cleaning properties for corrosion inhibition. *J. Alloys Compd.* **2020**, *834*, 155210. [CrossRef]
79. Porcayo-Calderon, J.; Rivera-Muñoz, E.; Peza-Ledesma, C.; Díaz, M.C.; de la Escalera, L.M.; Canto, J.; Martinez-Gomez, L. Sustainable Development of Palm Oil: Synthesis and Electrochemical Performance of Corrosion Inhibitors. *J. Electrochem. Sci. Technol.* **2017**, *8*, 133–145. [CrossRef]
80. Abouzari, M.R.S.; Berkemeier, F.; Schmitz, G.; Wilmer, D. On the physical interpretation of constant phase elements. *Solid State Ionics* **2009**, *180*, 922–927. [CrossRef]
81. Sowa, M.; Simka, W. Electrochemical Impedance and Polarization Corrosion Studies of Tantalum Surface Modified by DC Plasma Electrolytic Oxidation. *Materials* **2018**, *11*, 545. [CrossRef] [PubMed]
82. Ni, C.S.; Lu, L.Y. Electrochemical Impedance and Modelling Studies of the Corrosion of Three Commercial Stainless Steels in Molten Carbonate. *Int. J. Corros.* **2014**, *2014*, 1–13. [CrossRef]
83. Ma, H.; Cheng, X.; Li, G.; Chen, S.; Quan, Z.; Zhao, S.; Niu, L. The influence of hydrogen sulfide on corrosion of iron under different conditions. *Corros. Sci.* **2000**, *42*, 1669–1683. [CrossRef]
84. Popova, A.; Vasilev, A.; Deligeorgiev, T. Evaluation of the Electrochemical Impedance Measurement of Mild Steel Corrosion in an Acidic Medium, in the Presence of Quaternary Ammonium Bromides. *Port. Electrochim. Acta* **2018**, *36*, 423–435. [CrossRef]
85. Martinez, S.; Metikoš-Huković, M. A nonlinear kinetic model introduced for the corrosion inhibitive properties of some organic inhibitors. *J. Appl. Electrochem.* **2003**, *33*, 1137–1142. [CrossRef]
86. Man, Y.C.; Ammawath, W.; Mirghani, M.E.S. Determining α -tocopherol in refined bleached and deodorized palm olein by Fourier transform infrared spectroscopy. *Food Chem.* **2005**, *90*, 323–327. [CrossRef]
87. Silva, S.D.; Feliciano, R.; Boas, L.V.; Bronze, M. Application of FTIR-ATR to Moscatel dessert wines for prediction of total phenolic and flavonoid contents and antioxidant capacity. *Food Chem.* **2014**, *150*, 489–493. [CrossRef]
88. Krilov, D.; Kosovic, M.; Serec, K. Spectroscopic studies of alpha tocopherol interaction with a model liposome and its influence on oxidation dynamics. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2014**, *129*, 588–593. [CrossRef] [PubMed]
89. Valderrama, A.C.S.; De, G.C.R. Traceability of Active Compounds of Essential Oils in Antimicrobial Food Packaging Using a Chemometric Method by ATR-FTIR. *Am. J. Anal. Chem.* **2017**, *8*, 726–741. [CrossRef]