# THE ENHANCEMENT OF THE CORROSION RESISTANCE OF ALUMINIUM AND VTES-COATED ALUMINIUM BY USING A GREEN INHIBITOR

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*Aluminium is widely used in various industries due to its superior properties, such as anticorrosive protection. Several methods are employed for the enhancement of these properties and consist basically in modifying the metallic substrate or the composition of the aggressive media.*

*This paper presents the effect of the addition of a green inhibitor (garlic extract) in the composition of the aggressive media on the anticorrosive properties of aluminium and vynil-trietoxysilane coated aluminium. Electrochemical impedance spectroscopy was employed for the characterisation of the corrosion protection properties of the metallic substrate exposed to 0.05 M phosphoric acid solution, at different temperatures.*

**Keywords**: anticorrosive properties; aluminium; vynil-trietoxysilane coated aluminium; electrochemical impedance spectroscopy

## 1. Introduction

Aluminium and aluminium alloys are among the most widely used metals in various industries, such as automotive, aircraft manufacturing, food packaging, and metallurgical applications [1]. Aluminium has the advantage of an increased anticorrosive protection provided by the rapid formation of a protective compact oxide layer. In order to achieve better corrosion prevention, it has been used two main approaches, namely the substrate modification with various coatings and the use of corrosion inhibitors. In the first case, various substances are used as coatings for the metallic substrates. For the specific case of aluminium, coatings based on cerium and lanthanum salts, zinc, Zr–Ti, $Cr^{3+}$ and phosphate are used for the pre-treatment of the metallic surface. In recent years, an increased interest has been granted to the use of silanes as an environmental-friendly alternative to the conventional coatings. Various papers on the use of silane-coated aluminium

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substrates are available and prove their increased barrier protection against the contact between some aggressive media and the substrate [1-7]. Moreover, the anticorrosive protection properties of the silane films may be enhanced by modifying the composition of the silane layer by adding reinforcement agents and modifying the surface of the substrate [8-12]. Basically, a uniform silane film provides higher corrosion resistance to the metallic substrate. There are two important factors that contribute to the obtaining of a uniform coating, namely the hydrolysis time of the silane solution and the thermal treatment of the films after the deposition [9, 13-15]. One of the main parameters that relate closely to the anticorrosive protection properties of a coating is the polarization resistance [13, 14, 16-18]. Electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and open circuit potential (OCP) are employed to evaluate the behaviour of the coating in aggressive media [19, 20]. The second method for corrosion control consists in modification of the aggressive media by means of corrosion inhibitors. Among these, green inhibitors have received an increased interest, as they are biodegradable and do not contain harmful compounds. Several papers have reported the use of such compounds for the inhibition of the corrosion of aluminium in acidic and alkaline media. The ones with a high inhibiting efficiency in acidic media are onion and garlic extracts [21, 22].

This paper depicts the effects of modifying the composition of the aggressive media on the anticorrosive properties of aluminium and aluminium coated with vinyl-triethoxysilane (VTES). The effect of addition of natural garlic extract in the aggressive media consisting of 0.05M phosphoric acid was characterised at different temperatures by means of electrochemical impedance spectroscopy.

## 2. Experimental part

The aluminium samples were mechanically pre-treated before the EIS tests in order to remove the aluminium oxide naturally formed on the surface of the samples. It has been employed two types of emery paper (800 and 1200) for the surface polishing; then the samples were degreased with ethanol (Merck), rinsed with distilled water and dried. For the coated samples, it has been used a deposition solution that consists of a 5% vyniltrietoxysilane (VTES) solution in ethanol (Merck). This solution was left to stand for 24h in order to ensure the hydrolysis of the silane. The coatings were obtained from the deposition solution by the sol-gel deposition method, at a deposition time of 10 minutes. In order to ensure optimum conditions for the hydrolysis process, the complete removal of organic compounds from the glassware is required, and thorough cleaning of the glass containers with ozone-enriched water was performed [23]. For the electrochemical impedance spectroscopy measurements, a 50 mL thermostatic three electrode cell that consists of a saturated Ag/AgCl reference electrode

(Radiometer Analytical), a platinum mesh counter electrode (Radiometer Analytical), an aluminium working electrode, respectively a VTES coated aluminium and a 0.05M $H_3PO_4$ electrolyte solution (Sigma Aldrich) was employed. The electrochemical cell employed consists of a 50 mL glass cell provided with a double wall cell, where water is constantly circulated in order to maintain a constant temperature inside the cell. In order to test the inhibition effect of the natural extract, it has been enriched the phosphoric acid solution with different amounts of garlic extract (10, 20, 50 and 100 µL). Moreover, the effect of the inhibitor was tested at two temperatures of the corrosive media (30°C and 40°C). The EIS measurements were conducted by applying a sinusoidal potential perturbation of 10 mV and scanning a frequency range between 100 kHz and 100 mHz, carrying out 10 measurements per decade. A computer controlled VoltaLab 40 PGZ301 potentiostat used in connection with the supplied VoltaMaster 4.0 software was used to control the potentiostat and for data processing.

## 3. Results and discussions

Electrochemical impedance spectroscopy being a non-destructive technique gives valuable information concerning the corrosion behaviour and the ability of some layers to block the ionic conduction to the metallic surfaces without interfering or destroying the samples. In this particular case, EIS was used to evaluate in influence of the garlic extract on the behaviour of some aluminium and VTES coated aluminium samples in a $H_3PO_4$ solution by means of the polarization resistance. Fig. 1 depicts the Nyquist plots of the most representative samples of aluminium and VTES-coated aluminium in the presence and absence of inhibitor.

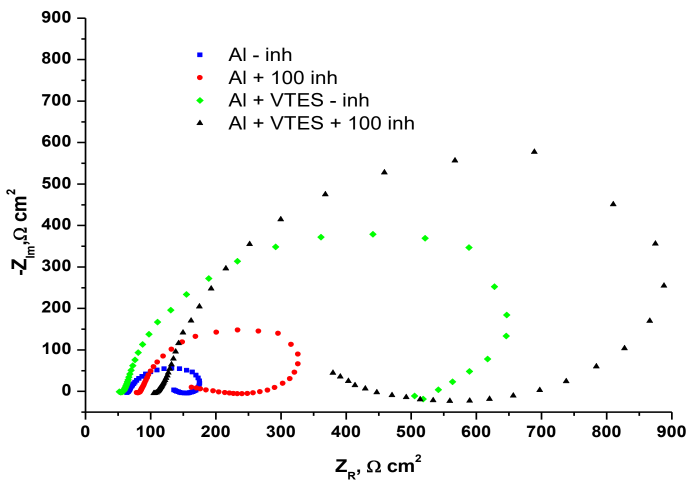


Fig. 1. Nyquist plots for the analysed aluminium samples: without inhibitor (■), with 100 µL of inhibitor (●), with VTES (♦), with VTES and inhibitor (▲) in a $H_3PO_4$ solution

The recordings of the Nyquist plots were subjected to a circular regression to the data represented in these plots and the main parameters were directly given by the VoltaMaster 4.0 software. The polarisation resistance ($R_p$) and capacitance (C) resulting from EIS for all samples are presented in tables 1 and 2.

In table 1, may be seen the influence of the garlic extract from the values of the polarization resistance, values that increase with increasing the concentration of the inhibitor, for the samples analyzed at the same temperature. Another observation would refer to the contribution of the VTES coating, coating that increases the polarization resistance up to 4 times, for the samples analyzed at 30°C, and up to 3 times for the ones analyzed at 40°C.

The values of the capacitance recorded for the VTES coated samples show that uniform and compact layers of silane were deposited on the aluminium substrate, which provide a barrier for the attack of the aggressive media, and corroborated with the effect of the garlic extract lead to improved corrosion resistance for the aluminium substrate.

*Table 1.*

**The values of the polarization resistance, capacitance and correlation coefficient extracted from the Nyquist plots for the samples analysed at 30°C.**

| | Types of samples | $R_p$, $\Omega\cdot cm^2$ | C, $\mu F\cdot cm^{-2}$ | $R^2$ |
|---|---|---|---|---|
| S1 | Al | 133.50 | 37.650 | 0.999 |
| S2 | Al + 10 µL inhibitor | 202.30 | 24.850 | 0.998 |
| S3 | Al + 20 µL inhibitor | 265.30 | 23.980 | 0.863 |
| S4 | Al + 50 µL inhibitor | 280.60 | 17.920 | 0.991 |
| S5 | Al + 100 µL inhibitor | 312.20 | 20.380 | 0.998 |
| S6 | Al + VTES | 545.60 | 9.277 | 0.974 |
| S7 | Al + VTES + 10 µL inhibitor | 548.90 | 12.440 | 0.997 |
| S8 | Al + VTES + 20 µL inhibitor | 674.20 | 9.063 | 0.997 |
| S9 | Al + VTES + 50 µL inhibitor | 339.50 | 9.375 | 0.997 |
| S10 | Al + VTES + 100 µL inhibitor | 1203.00 | 8.359 | 0.997 |

*Table 2.*

**The values of the polarization resistance, capacitance and correlation coefficient extracted from the Nyquist plots for the samples analysed at 40°C.**

| | Types of samples | $R_p$, $\Omega\cdot cm^2$ | C, $\mu F\cdot cm^{-2}$ | $R^2$ |
|---|---|---|---|---|
| S1 | Al | 59.48 | 42.270 | 0.915 |
| S2 | Al + 10 µL inhibitor | 61.12 | 26.030 | 0.992 |
| S3 | Al + 20 µL inhibitor | 64.01 | 15.710 | 0.995 |
| S4 | Al + 50 µL inhibitor | 73.26 | 13.720 | 0.944 |
| S5 | Al + 100 µL inhibitor | 75.51 | 13.320 | 0.997 |
| S6 | Al + VTES | 184.10 | 13.650 | 0.975 |
| S7 | Al + VTES + 10 µL inhibitor | 654.70 | 7.680 | 0.987 |
| S8 | Al + VTES + 20 µL inhibitor | 710.30 | 2.823 | 0.984 |
| S9 | Al + VTES + 50 µL inhibitor | 842.60 | 2.984 | 0.995 |
| S10 | Al + VTES + 100 µL inhibitor | 892.00 | 3.568 | 0.995 |

In order to obtain a better quantification of the results, it has been calculated an inhibiting effect of the natural inhibitor as follows [24, 25]:

$$\varepsilon = \left(1 - \frac{R_0}{R_i}\right) \times 100,\% \qquad (1)$$

Where: $R_0$ is the value of the polarization resistance of the aluminium sample in $H_3PO_4$ solution without any inhibitor, $R_i$ is the value of the polarization resistance of the aluminium samples in $H_3PO_4$ solution with different amounts of inhibitor, respectively of the VTES coated aluminium samples in the $H_3PO_4$ solution with and without the inhibitor.

Similar findings about the anticorrosive protection properties of the VTES-coatings have been reported in some previous works, such as [10]. The present work goes a bit further and introduces the presence of a green inhibitor in the aggressive media.

The values of the inhibiting effect of the natural inhibitor and of the VTES coating are presented in table 3 and in Fig. 2.

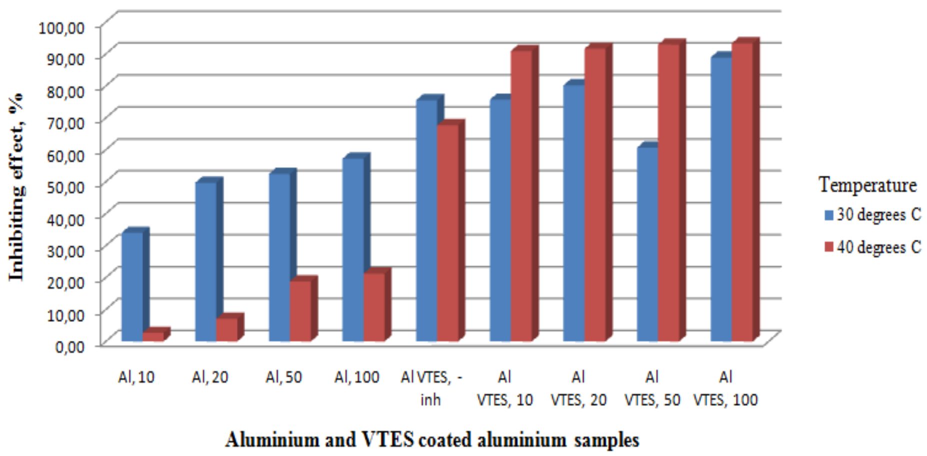


Fig. 2. The values of the inhibiting effect of the VTES coating and of the natural inhibitor at 30 and 40˚C

At a 40˚C temperature, the inhibiting effect of the natural extract increases with increasing its concentration. Also, the effect of the VTES coating deposited on the aluminium surface may be seen. At a temperature of 30°C, the trend of the inhibiting effect is also an increasing one, with one exception. For an added amount of the extract of 50 μL, the smallest effect registered for the VTES coated samples is registered, which is even smaller than the one analyzed in an inhibitor free solution. For the investigated aluminium samples, the inhibiting effect of the garlic extract has by far lower values when the temperature of the aggressive media is 40°C than the ones recorded at 30°C. Meanwhile, in the case of the

VTES coated aluminium, the inhibiting effect of the garlic extract increases with the temperature of the aggressive media, values over 90% being recorded.

## 4. Conclusions

The effect of a garlic extract on the anticorrosive protection properties of aluminium and VTES-coated aluminium was investigated using electrochemical impedance spectroscopy. The behaviour of the metallic substrate exposed to a 0.05M phosphoric acid solution was investigated at different temperatures (30°C and 40°C). The results showed that the VTES-coated aluminium has a better corrosion resistance. The values of the polarization resistance increase with increasing the concentration of the inhibitor for a given temperature. The VTES coating increases the polarization resistance by up to 4 times for the samples analyzed at 30°C, and up to 3 times for the ones analyzed at 40°C.

The inhibiting effect of the garlic extract has lower values at a temperature of the aggressive media of 40°C compared to 30°C. For the VTES-coated aluminium, the inhibiting effect of the garlic extract increases with the temperature of the aggressive media, values over 90% being recorded.

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