

Special Issue Reprint

Advances in Corrosion and Protection of Materials (Second Edition)

Edited by
Renato Altobelli Antunes

mdpi.com/journal/metals

Advances in Corrosion and Protection of Materials (Second Edition)

Advances in Corrosion and Protection of Materials (Second Edition)

Guest Editor

Renato Altobelli Antunes



Basel • Beijing • Wuhan • Barcelona • Belgrade • Novi Sad • Cluj • Manchester

Guest Editor

Renato Altobelli Antunes
Center for Engineering,
Modelling and Applied Social
Sciences (CECS)
Federal University of the ABC
(UFABC)
Santo André
Brazil

Editorial Office

MDPI AG
Grosspeteranlage 5
4052 Basel, Switzerland

This is a reprint of the Special Issue, published open access by the journal *Metals* (ISSN 2075-4701), freely accessible at: https://www.mdpi.com/journal/metals/special_issues/1OU42OCG65.

For citation purposes, cite each article independently as indicated on the article page online and as indicated below:

Lastname, A.A.; Lastname, B.B. Article Title. <i>Journal Name</i> Year , <i>Volume Number</i> , Page Range.
--

ISBN 978-3-7258-5515-5 (Hbk)

ISBN 978-3-7258-5516-2 (PDF)

<https://doi.org/10.3390/books978-3-7258-5516-2>

Contents

About the Editor	vii
----------------------------	-----

Renato Altobelli Antunes

Advances in Corrosion and Protection of Materials (Second Edition)

Reprinted from: <i>Metals</i> 2025 , <i>15</i> , 642, https://doi.org/10.3390/met15060642	1
--	---

Faten M. Abu Orabi, Sultan T. Abu-Orabi, Oaima A. Fodeh, Faisal K. Algethami, Abdel Monem M. Rawashdeh, Tareq T. Bataineh, et al.

Ajuga orientalis L. Extract as a Green Corrosion Inhibitor of Aluminum in an Acidic Solution: An Experimental and DFT Study

Reprinted from: <i>Metals</i> 2024 , <i>14</i> , 1227, https://doi.org/10.3390/met14111227	4
---	---

HeeKwon Shin and SeKwon Oh

Effects of CTAB (Cetyltrimethylammonium Bromide) and Betaine as Corrosion Inhibitors on the Galvanic Corrosion of Cu Coupled with Au on Print Circuit Board in Etching Solution

Reprinted from: <i>Metals</i> 2024 , <i>14</i> , 1090, https://doi.org/10.3390/met14091090	24
---	----

HeeKwon Shin and SeKwon Oh

Effective Corrosion Inhibition of Galvanic Corrosion of Cu Coupled to Au by Sodium Dodecyl Sulfate (SDS) and Polyethylene Glycol (PEG) in Acid Solution

Reprinted from: <i>Metals</i> 2024 , <i>14</i> , 1080, https://doi.org/10.3390/met14091080	33
---	----

Nathalia Sartori da Silva, Aila Cossovan Alves, Jaine Aparecida da Silva Pereira, Leandro Antonio de Oliveira, Mara Cristina Lopes de Oliveira and Renato Altobelli Antunes

Corrosion Properties and Surface Chemistry of Graphene Oxide-Coated AZ91D Magnesium Alloy in Sodium Chloride Solution

Reprinted from: <i>Metals</i> 2024 , <i>14</i> , 1019, https://doi.org/10.3390/met14091019	42
---	----

Jianbo Jiang, Nannan Li, Bingqin Wang, Fangfang Liu, Chao Liu and Xuequn Cheng

A Study on the Influence of Different Defect Types on the Corrosion Behavior of Q235/TA2 Composite Plates in a Marine Environment

Reprinted from: <i>Metals</i> 2024 , <i>14</i> , 652, https://doi.org/10.3390/met14060652	64
--	----

Paula Lima Braga, Denise Criado Pereira de Souza, Mara Cristina Lopes de Oliveira and Renato Altobelli Antunes

Effect of Graphene Oxide as an Anodizing Additive for the ZK60A Magnesium Alloy: Correlating Corrosion Resistance, Surface Chemistry and Film Morphology

Reprinted from: <i>Metals</i> 2024 , <i>14</i> , 210, https://doi.org/10.3390/met14020210	85
--	----

Citlalli Gaona-Tiburcio, Jesús Manuel Jáquez-Muñoz, Demetrio Nieves-Mendoza, Erick Maldonado-Bandala, Maria Lara-Banda, Manuel Alejandro Lira-Martinez, et al.

Corrosion Behavior of Titanium Alloys (Ti CP2, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-4V and Ti Beta-C) with Anodized and Exposed in NaCl and H₂SO₄ Solutions

Reprinted from: <i>Metals</i> 2024 , <i>14</i> , 160, https://doi.org/10.3390/met14020160	105
--	-----

Peter Rodič, Barbara Kapun and Ingrid Milošev

The Effect of Pore Sealing in a Multilayer Si–O–Zr/Al₂O₃ Coating Designed to Protect Aluminium from Corrosion

Reprinted from: <i>Metals</i> 2023 , <i>13</i> , 1960, https://doi.org/10.3390/met13121960	129
---	-----

Regina Buier, Gabriella Stefania Szabó, Gabriel Katona, Norbert Muntean and Liana Maria Muresan Influence of pH on the Inhibiting Characteristics of Cresol Red Incorporated in Chitosan Coatings on Zinc Reprinted from: <i>Metals</i> 2023 , 13, 1958, https://doi.org/10.3390/met13121958	152
Vojka Gardić, Žaklina Z. Tasić, Marija B. Petrović Mihajlović, Milan B. Radovanović and Milan M. Antonijević Corrosion Behavior of the Cu ₂₄ Zn ₅ Al Alloy in Sodium Sulfate Solution in the Presence of 1-Phenyl-5-mercaptotetrazole Reprinted from: <i>Metals</i> 2023 , 13, 1863, https://doi.org/10.3390/met13111863	170
María Jesús Jiménez-Come, Francisco Javier González Gallero, Pascual Álvarez Gómez and Jesús Daniel Mena Baladés Corrosion Behaviour Modelling Using Artificial Neural Networks: A Case Study in Biogas Environment Reprinted from: <i>Metals</i> 2023 , 13, 1811, https://doi.org/10.3390/met13111811	186

About the Editor

Renato Altobelli Antunes

Renato Altobelli Antunes is a full professor at the Center for Engineering, Modeling and Applied Social Science of the Federal University of the ABC (UFABC). His research activities are currently centered on the study of the corrosion mechanisms of metallic materials, protection methods, scanning probe techniques and the correlation between surface chemistry and the corrosion behavior of light alloys and steels. Prof. Antunes is a guest editor for the journal *Metals*. He has been awarded the Research Productivity Grant from the Brazilian agency CNPq (Brazilian National Council for Scientific and Technological Development) since 2015.

Advances in Corrosion and Protection of Materials (Second Edition)

Renato Altobelli Antunes

Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas (CECS), Universidade Federal do ABC (UFABC), Santo André 09210-580, Brazil; renato.antunes@ufabc.edu.br

1. Introduction and Scope

As modern civilization, through its extensive use of metallic materials, has given rise to progressively more aggressive environmental conditions, corrosion resistance has become a prominent issue. The foundations of this challenging scenario are based on a solid understanding of corrosion mechanisms and protective methods. The current knowledge in this field is rapidly growing from intense research activity.

In its second edition, this Special Issue will provide a forum for the corrosion research community as a source for new developments and innovations in this field.

2. Contributions

This volume comprises 11 research papers that cover different topics related to corrosion mechanisms and protection methods of metallic materials. In the first paper, Jiménez-Come et al. (contribution 1) developed a model based on artificial neural networks (ANNs) to predict the corrosion susceptibility of different stainless-steel grades in simulated biogas environments. The precision and accuracy values reached 96.8% and 96.6%, depending on the input data. The breakdown potential of the stainless steel was considered a relevant parameter to attain high-precision modeling, along with its composition, indicated by the pitting resistance equivalent number (PREN).

Gardic et al. (contribution 2) studied the effect of 1-Phenyl-5-mercaptotetrazole (PMT) as a corrosion inhibitor for the Cu₂₄Zn₅Al alloy in sodium sulfate solution. Depending on the PMT concentration, the formation of a protective film on the surface of the copper alloy was attained, decreasing its corrosion rate.

Buier et al. (contribution 3) prepared cresol-red loaded chitosan coatings on zinc substrates as a protective method in sodium sulfate solutions with different concentrations. The anionic cresol-red interacted with positively charged chitosan, acting as a corrosion inhibitor for zinc. The corrosion resistance was monitored for up to 55 days by electrochemical impedance spectroscopy, increasing with respect to the initial immersion time due to the interaction between the cresol-red dye and the chitosan layer.

Rodic et al. (contribution 4) combined two protection strategies to protect commercially pure aluminum substrates from corrosion. They prepared one hybrid Si-O-Zr sol-gel coating and, thereafter, a 100 nm thick Al₂O₃ layer produced by thermal atomic layer deposition (ALD), which was used to seal the coating pores. This strategy was effective at improving the corrosion resistance of the aluminum substrate.

Gaona-Tiburcio et al. (contribution 5) tested the effectiveness of anodization treatment to protect Ti CP2, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-4V, and Ti Beta-C from corrosion in sodium chloride and sulfuric acid solutions. The corrosion protection ability of the anodized layer was dependent on its thickness and, ultimately, on the alloy's composition. The anodized films were less uniform for alloys with higher concentrations of β -stabilizing elements.

Anodizing is also an important corrosion protection method for magnesium and its alloys. Braga et al. (contribution 6) explored this strategy to improve the corrosion resistance of the ZK60A Mg alloy (Mg-Zn-Zr), using graphene oxide as an additive in an anodizing bath. The corrosion resistance was dependent on the graphene oxide concentration added to the solution, which was maximized at 1 g/L due to a better distribution within the anodized film.

Jiang et al. (contribution 7) studied the influence of different surface defects (point and line defects) on the corrosion resistance of carbon steel–titanium composite plates in a simulated marine solution. These composites are typically used for structural applications, such as bridges, pipelines, and offshore platforms. The corrosion mechanism was affected by the relative thickness between the carbon steel and titanium plates.

Graphene oxide coatings can be deposited on magnesium alloys to improve their corrosion resistance. This approach was used by Silva et al. (contribution 8), who produced graphene oxide coatings on the AZ91D Mg alloy using a simple immersion-based process and an intermediate silane layer to promote better adhesion to the substrate. Corrosion resistance was remarkably affected by the coating morphology, which, in turn, depended on the concentration of graphene oxide in the coating-forming solution.

The galvanic corrosion between Cu and Au in print circuit boards (PCBs) takes place during the etching process, which is part of PCB manufacturing. Shin and Oh (contribution 9) evaluated the corrosion inhibition efficiency of sodium dodecyl sulfate (SDS) and polyethylene glycol (PEG) in the galvanic corrosion of Cu/Au couples. PEG showed a better inhibition efficiency than SDS. In another publication (contribution 10), cetyltrimethylammonium bromide (CTAB) and betaine were evaluated as corrosion inhibitors for the same type of galvanic couples. The best inhibition efficiency was obtained for betaine (99.1%), which adsorbed copper and gold surfaces, while CTAB preferentially adsorbed on copper surfaces and exhibited an inhibition efficiency of 92.3%.

Orabi et al. (contribution 11) evaluated the *A. orientalis* L. extract (AO) as a green corrosion inhibitor for aluminum in acidic solutions. Using electrochemical tests and DFT simulation studies, the inhibition mechanism of the AO extract was identified. It exhibited a mixed-type inhibition mechanism (anodic and cathodic) and reached approximately 68% inhibition efficiency.

Acknowledgments: As Guest Editor, I am very grateful to all the reviewers and authors who contributed to this Special Issue, as well as to the Editorial staff for their dedicated support throughout the entire publication process.

Conflicts of Interest: The author declares no conflicts of interest.

List of Contributions:

1. Jiménez-Come, M.J.; Gallero, F.J.G.; Gómez, P.A.; Baladés, J.D.M. Corrosion behaviour modelling using artificial neural networks: A case study in biogas environment. *Metals* **2023**, *13*, 1811.
2. Gardic, V.; Tasic, Z.; Mihajlovic, M.B.P.; Radovanovic, M.B.; Antonijevic, M.M. Corrosion behavior of the Cu₂₄Zn₅Al alloy in sodium sulfate solution in the presence of 1-Phenyl-5-mercaptotetrazole. *Metals* **2023**, *13*, 1863.
3. Buier, R.; Szabo, G.S.; Katona, G.; Muntean, N.; Muresan, L.M. Influence of pH on the inhibiting characteristics of cresol red incorporated in chitosan coatings on zinc. *Metals* **2023**, *13*, 1958.
4. Rodic, P.; Kapun, B.; Milosev, I. The effect of pore sealing in a multilayer Si-O-Zr/Al₂O₃ coating designed to protect aluminium from corrosion. *Metals* **2023**, *13*, 1960.
5. Gaoma-Tiburcio, C.; Jáquez-Muñoz, J.M.; Nieves-Mendoza, D.; Maldonado-Bandala, E.; Lara-Banda, M.; Lira-Martínez, M.A.; Reyes-Blas, H.; Baltazar-Zamora, M.A.; Landa-Ruiz, L.; Lopez-Leon, L.D.; et al. Corrosion behavior of titanium alloys (Ti CP2, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-4V and Ti Beta-C) with anodized anod exposed in NaCl and H₂SO₄ solutions. *Metals* **2024**, *14*, 160.

6. Braga, P.L.; Souza, D.C.P.; Oliveira, M.C.L.; Antunes, R.A. Effect of graphene oxide as na anodizing additive for the ZK60A magnesium alloy: Correlating corrosion resistance, surface chemistry and film morphology. *Metals* **2024**, *14*, 210.
7. Jiang, J.; Li, N.; Wang, B.; Liu, F.; Liu, C.; Cheng, X. A study on the influence of different defect types on the corrosion behavior of Q235/TA2 composite plates in a marine environment. *Metals* **2024**, *14*, 652.
8. Silva, N.S.S.; Alves, A.C.; Pereira, J.A.S.; Oliveira, J.A.; Oliveira, M.C.L.; Antunes, R.A. Corrosion properties and surface chemistry of graphene oxide-coated AZ91D magnesium alloy in sodium chloride solution. *Metals* **2024**, *14*, 1019.
9. Shin, H.K.; Oh, S.K. Effective corrosion inhibition of galvanic corrosin of Cu coupled to Au by sodium dodecyl sulfate (SDS) and polyethylene glycol (PEG) in acid solution. *Metals* **2024**, *14*, 1080.
10. Shin, H.K.; Oh, S.K. Effects of CTAB (cetyltrimethylammonium bromide) and betaine as corrosion inhibitors on the galvanic corrosion of Cu coupled with Au on print circuit board in etching solution. *Metals* **2024**, *14*, 1090.
11. Orabi, F.M.A.; Abu-Orabi, S.T.; Fodeh, O.A.; Algethami, F.K.; Rawashdeh, A.M.; Bataineh, T.T.; Al-Mazaideh, G.M.; Al-Qudah, M.A. *Ajuda orientalis* L. extract as a green corrosion inhibitor of aluminum in an acidic solution: An experimental and DFT study. *Metals* **2024**, *14*, 1127.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Ajuga orientalis L. Extract as a Green Corrosion Inhibitor of Aluminum in an Acidic Solution: An Experimental and DFT Study

Faten M. Abu Orabi ¹, Sultan T. Abu-Orabi ², Omaima A. Fodeh ³, Faisal K. Algethami ⁴,
Abdel Monem M. Rawashdeh ³, Tareq T. Bataineh ³, Ghassab M. Al-Mazaideh ⁵ and Mahmoud A. Al-Qudah ^{3,*}

¹ Faculty of Arts and Sciences, The World Islamic Sciences and Education University, P.O. Box 1101, Amman 11947, Jordan; faten.aladwan@wise.edu.jo

² Department of Medical Analysis, Faculty of Science, Tishk International University, Erbil 44001, Iraq; sultan.abuorabi@tiu.edu.iq

³ Department of Chemistry, Faculty of Science, Yarmouk University, P.O. Box 566, Irbid 21163, Jordan; 2020104002@alumni.yu.edu.jo (O.A.F.); rawash@yu.edu.jo (A.M.M.R.); tariq.b@yu.edu.jo (T.T.B.)

⁴ Department of Chemistry, College of Science, Imam Mohammad Ibn Saud Islamic University (IMSIU), P.O. Box 90950, Riyadh 11623, Saudi Arabia; falgethami@imamu.edu.sa

⁵ Department of Pharmaceutical Chemistry, College of Pharmacy, University of Hafr Al Batin, P.O. Box 1803, Hafr Al Batin 31991, Saudi Arabia; gmazaideh@uhb.edu.sa

* Correspondence: mahmoud.qudah@yu.edu.jo; Tel.: +962-77420029; Fax: +962-27211117

Abstract: The inhibitory effect of *A. orientalis* L. extract (AO) on aluminum corrosion in a 1.0 M HCl solution was investigated utilizing weight loss, electrochemical polarization, electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM). The results show that AO is a potent inhibitor in an acidic environment, and that the inhibition potency increases with concentration. Temperature investigations showed that, in an acidic medium, the efficiency decreased, increased, and then decreased as the temperature rose. Adsorption isotherms from Freundlich, Temkin, El Awady, and Redlich–Peterson (R-P) approximated the inhibitor’s adsorption properties. For the inhibitory behavior, a physical and chemical adsorption mechanism is proposed. The adsorption process’s thermodynamic parameters (E_a , ΔH^* , and ΔS^*) were determined and explained. The inhibitor, AO, was identified as a mixed-type (anodic and cathodic) inhibitor based on polarization studies. According to the SEM findings, the inhibitor partially covers the metal surface, providing it with a respectable level of protection. The weight loss, electrochemical polarization, EIS, scanning electron microscopy (SEM), and quantum chemical calculations show a strong agreement, indicating that the AO extract is a highly effective inhibitor of aluminum in an acidic solution.

Keywords: electrochemical polarization; *A. orientalis*; physical adsorption; langmuir isotherm; aluminum

1. Introduction

The issue of corrosion is one that practically all metals and alloys face. Corrosion happens when metals and alloys are subjected to specific environmental factors. Rust is frequently produced when the metal in question reacts with its environment. A metal surface and oxygen interact physiochemically to generate oxides or salts, which is referred to as corrosion [1,2]. A lot of work has been performed in the last few years to figure out what causes rust, how it works, and what factors have a great effect on the lifetime of metallic materials [3].

Because of its low density and, thus, low weight, Al and its alloys have been widely used in a variety of sectors. Al and Al-alloys are also widely used due to their high electrical conductivity, thermal characteristics, and superior corrosion resistance. However, aluminum corrosion can occur under specific conditions, making its prevention a key

scientific challenge [1–8]. Corrosion on aluminum surfaces is usually quite visible, even in its early stages, as a general etching, pitting, or roughness of the aluminum surfaces. This reaction is accompanied by a change in the oxidation state of Al from 0 to +3. These three electrons are captured by 3H^+ . Aluminum corrosion produces aluminum hydroxide $\text{Al}(\text{OH})_3$, which is a water-insoluble, white, gelatinous precipitate [9].

There are several ways to avoid corrosion, but they all generally involve taking precautions to keep metal surfaces isolated from corrosive conditions or changing the environment in some way [10].

The three main categories of corrosion prevention are cathodic, anodic, or mixed corrosion inhibitor procedures. Anodic or cathodic corrosion reactions can be stopped by covering the metal surface or changing the activation energy of the redox process during corrosion [11].

The majority of corrosion inhibitors are poisonous, expensive, and non-biodegradable manmade compounds. As a result, finding ecologically friendly inhibitors is desirable. The importance of plant extracts has grown as a result of their status as a sustainable, eco-friendly, and readily accessible source of a diverse array of inhibitors. Natural compounds have been employed to prevent the corrosion of many metals in a variety of situations in the past. Researchers have found that green corrosion inhibitors provide places for electrons to move, and functional groups with oxygen, nitrogen, sulfur, and phosphorous atoms provide electrons to help the inhibitor stick to the metal's surface [12–20]. Complex organic species, like anthocyanins, diterpenoids, sterols, ionones, iridoids, flavonoids, glycosides, alkaloids, tannins, anolides, and triterpenes, are thought to be the reason why the extracts of the plants are so good at stopping corrosion [11–20]. Several techniques are used to track the impacts of corrosion and to monitor the corrosion process. These include weight loss, Tafel polarization, hydrogen penetration, linear polarization resistance, and other techniques [15].

In recent studies on corrosion inhibitors, researchers have increasingly turned to quantum chemistry techniques to improve the effectiveness of potential inhibitors [21,22]. The use of the density functional theory (DFT) and computer science has provided valuable tools for studying natural product molecules in this context. The DFT approach has proven particularly useful, as it offers the improved treatment of electron interactions compared to post-Hartree–Fock (HF) methods [22,23]. The DFT has been extensively applied to quantify various characteristics, such as chemical structure, kinetic properties, and thermochemistry, across different types of carbohydrates.

Investigating the viability of employing *A. orientalis* methanolic extract (AO) as a corrosion inhibitor is the goal of the current investigation. Due to their accessibility and ease of application, a lot of publications on the use of natural substances or plant extracts as corrosion inhibitors have recently been published in the literature. This study examined AO as a corrosion inhibitor of aluminum in an acidic solution. The use of this plant as a corrosion inhibitor is not mentioned in any publication. This study also examined the impact of temperature on the effectiveness of inhibition, as well as the evaluation of some thermodynamic parameters using chemical and electrochemical methods. Furthermore, for the first time, this study utilizes a combination of weight loss analysis, electrochemical polarization, scanning electron microscopy (SEM), and quantum chemical calculations to investigate the protective efficiency of the AO methanolic extract for aluminum in an HCl solution.

2. Materials and Methods

2.1. Collection and Pretreatment of Plant Samples

The ariel parts of *A. orientalis* (AO) were collected from the Ajloun region throughout the flowering season. Each sample was cleaned with running water before being dried for 30 days. Before extraction, the dried plant was powdered [18,23].

2.2. Preparation of Plant Extract

The crude was extracted from the solid matrix by using the Soxhlet extraction method. A 30 g portion of the ground plant was used, and the thimble was filled with it. The first step included extracting fatty acids using 500 mL of petroleum ether as a solvent. With 500 mL of methanol, the remaining plant matter was extracted over a period of around 24 h by reflux. The leftover crude was employed as a possible corrosion inhibitor once the solvent was dried using a rotary evaporator. A stock solution of the inhibitor was prepared by dissolving 1.0 g of the crude extract in 1000 mL of pure methanol (1000 ppm). All polarization and weight loss studies utilized diluted solutions of this stock.

2.3. LC-ESI-MS/MS

The secondary metabolized compounds of interest were screened using a Bruker Daltonik Impact II ESI-Q-TOF System (Bremen, Germany) and Bruker Daltonik Elute UHPLC system (Bremen, Germany) in negative (M-H) electrospray ionization modes similar to the procedure described in the literature [18,24].

2.4. Specimen Preparation

For the experiments using acidic media, rectangular, aluminum foil specimens with measurements of 3 cm in length, 1 cm in width, and 0.3 mm in thickness were employed. For additional experiments in an acidic medium, cylindrical, pure aluminum specimens that were 1.5 cm high and 2 cm in diameter were employed. Before performing all measurements, the specimens were polished using metallographic emery paper up to 1200 grits [16–20], rinsed with distilled water and acetone, and dried with tissue paper. To shield them from the outside environment, the samples were kept in a desiccator.

2.5. Weight Loss Measurements

Weight loss measurements were carried out for aluminum specimens in the absence and presence of the inhibitor at different concentrations (80, 120, 160, 200, 240, and 300 ppm) in a 1.0 M HCl solution. Aluminum samples were placed in test tubes with 15 mL of diluted solution, and weight loss measurements were taken for each exposure period of 2, 4, and 6 h at 30 °C. The experiment was repeated at temperatures of 35 °C, 40 °C, 45 °C, and 50 °C at a fixed time (4 h). A water thermostat that could be adjusted to 0.1 °C was used throughout this trial. The aluminum coupons were taken out of the test solution after the required time had passed, cleaned with distilled water and an acetone solution, thoroughly dried, and then reweighed. Using an electronic balance, the weight reduction was measured to the nearest 0.0001 g (Mettler HK 160, Mettler-Toledo Ltd., Leicester, UK). The mean value of the weight loss was reported after studies in triplicate were carried out.

2.6. Electrochemical Measurements

Two electrochemical techniques, namely Tafel polarization and electrochemical impedance spectroscopy (EIS), were used to study the corrosion behavior. All electrochemical measurements were carried out using a CorrTest potentiostat (CS350, Wuhan, China). The cell consisted of a platinum counter electrode, an Ag/AgCl reference electrode, and an aluminum rod (0.2 cm²) as the working electrode. Potentiodynamic polarization measurements were carried out at a scan rate of 1 mV s^{−1} at ±250 mV with respect to the open circuit potential (OCP). The linear Tafel segments were extrapolated to the corrosion potential to obtain the corrosion current density. EIS measurements were performed for the open circuit potential (OCP) at room temperature at a frequency range of 100 kHz to 0.01 Hz and with an amplitude of 10 mV. All electrochemical results were analyzed using CorrTest software (CS Studio5 version). Each electrochemical measurement was run in triplicate to verify the reproducibility of the results.

2.7. Surface Analysis (Scanning Electron Microscopy (SEM))

A scanning electron microscope (SEM FEI Quanta 200, Geology Department, Faculty of Science, Yarmouk University/Jordan) was used to analyze the morphology of the aluminum specimens. The surface of the investigated aluminum specimens was analyzed before and after immersion for 4 h at 30 °C in 1.0 M of HCl in the absence and presence of the plant extract.

2.8. DFT Computational Details

This study utilized molecular calculations based on the DFT to explore the electronic properties of the major compounds that were found in the studied plant extract. The calculations were made in both the gas phase as well as the acidic solution employing the B3LYP functional as well as a 6-31G*(d,p) basis set. The molecular structures were optimized using Gaussian 09 (G09) software along with DFT-B3LYP functions [25]. Quantum chemical parameters that included the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap (ΔE_{gap}) between E_{HOMO} as well as E_{LUMO} , and other relevant descriptors, such as the chemical potential (χ), global softness (σ), absolute hardness (η), fraction of electron transferred (ΔN), and electrophilicity index (ω), were determined [26]. These computed parameters were obtained from the calculations, offering insights into the compounds' electronic structure as well as reactivity. The computational details provided in this study assist in developing a better understanding of the chemical characteristics of the compounds being investigated, as well as their possible applications.

3. Results and Discussion

3.1. Identification and Elucidation of the Compounds Using LC-MS/MS

The methanol extract of AO was further analyzed by LC-ESI-MS/MS [18,24]. The results indicate that Succinic acid (1), Catechol (2), 8-O-acetylharpagide (3), 3,7,3',4',5'-Pentahydroxyflavone (4), and Kaempferol-7-O-glucoside (5) are the main components detected in the crude extract (Figure 1) [18,23,24].

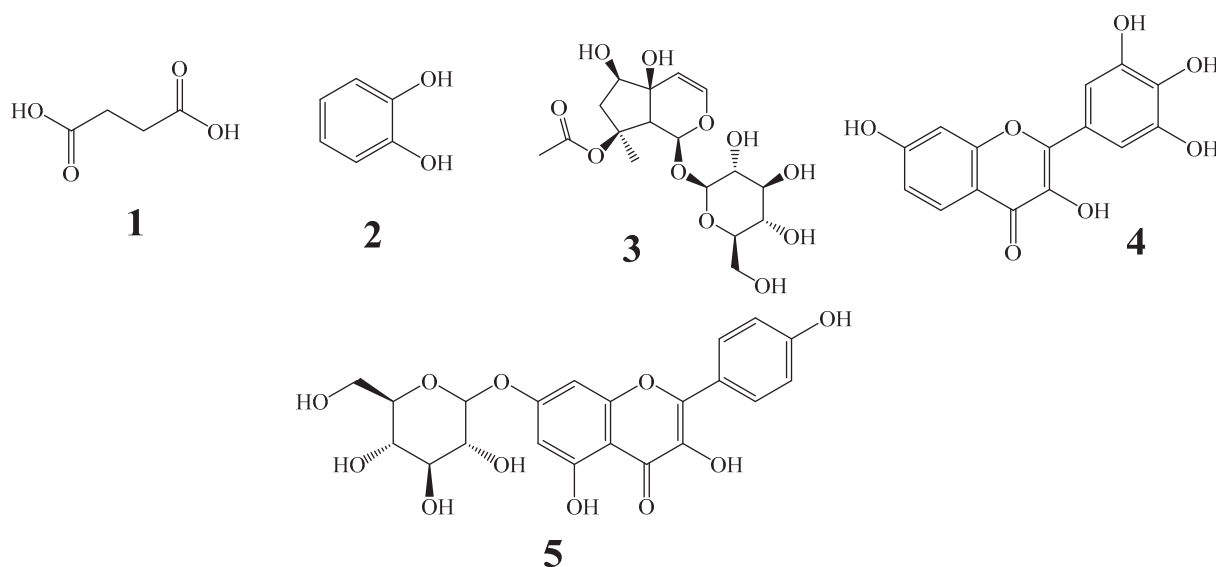


Figure 1. The main components of the methanol extract of AO.

3.2. Effect of Inhibitor Concentration

At 30 °C, for various immersion times (2 h, 4 h, and 6 h), for various concentrations of the extract (80–300 ppm), and in the presence and absence of AO, the weight loss (ΔW) of

aluminum in 1.0 M of HCl was examined. The reduction in weight was quantified to the closest 0.0001 g. Equation (1) provides the weight loss:

$$\Delta W = W - W^0 \quad (1)$$

where W and W^0 are the weigh losses of the aluminum specimens in the presence and absence of the inhibitors (AO), respectively. Figure 2 shows the weight loss (ΔW) as a function of the immersion time in the 1.0 M HCl solution. Different concentrations of AO were used at 30 °C. Aluminum weight loss was measured over a period in both the presence and absence of various concentrations of AO. Figure 2 demonstrates that the ΔW values (mg) of Al decrease as the inhibitor concentration increases. This is because the metal increases the surface coverage with an increase in AO concentration, which effectively separates the aluminum surface from the medium [13,15,27].

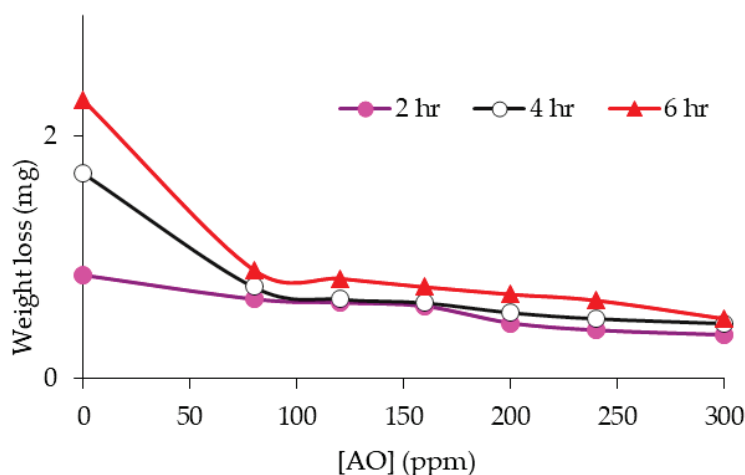


Figure 2. Variation in ΔW with time at different concentrations of AO in 1.0 M of HCl at 30 °C.

The inhibition efficiency (%IE) and the extent of metal surface coverage (θ) are calculated according to Equation (2):

$$\%IE = \theta \times 100 = \left[1 - \frac{W}{W^0}\right] \times 100 \quad (2)$$

Table 1 summarizes all the results of the calculated inhibition efficiencies at 30 °C in the presence of the inhibitor. These tests were conducted at 30 °C at different time periods using different inhibitor concentrations. The highest efficiency in an acidic medium (1.0 M HCl) was (78.3%), which was obtained after 6 h at the maximum tested concentration of the inhibitor (300 mg/L). The capacity of organic molecules to bind to metal surfaces is the major factor that determines how effective they are at preventing corrosion. This adsorption may take place when organic inhibitor molecules displace water molecules [28].

Table 1. Inhibition efficiencies of Al using different concentrations of AO at 30 °C.

Conc. (ppm)	(%IE)		
	(2 h)	(4 h)	(6 h)
80	23.3	55.3	60.9
120	26.7	61.2	63.9
160	30.2	62.9	67.0
200	46.5	67.6	69.6
240	53.5	70.6	71.7
300	58.1	72.9	78.3

3.3. Effect of Temperature

We noticed that the efficiency in an acidic medium decreases with the increasing temperature until the temperature reaches 40 °C, and then begins to increase until the temperature reaches 50 °C (Figure 3). This is the result of physical adsorption, which then turns into chemical adsorption. Similar results have been reported in the literature for other cases and are similarly explained [29,30].

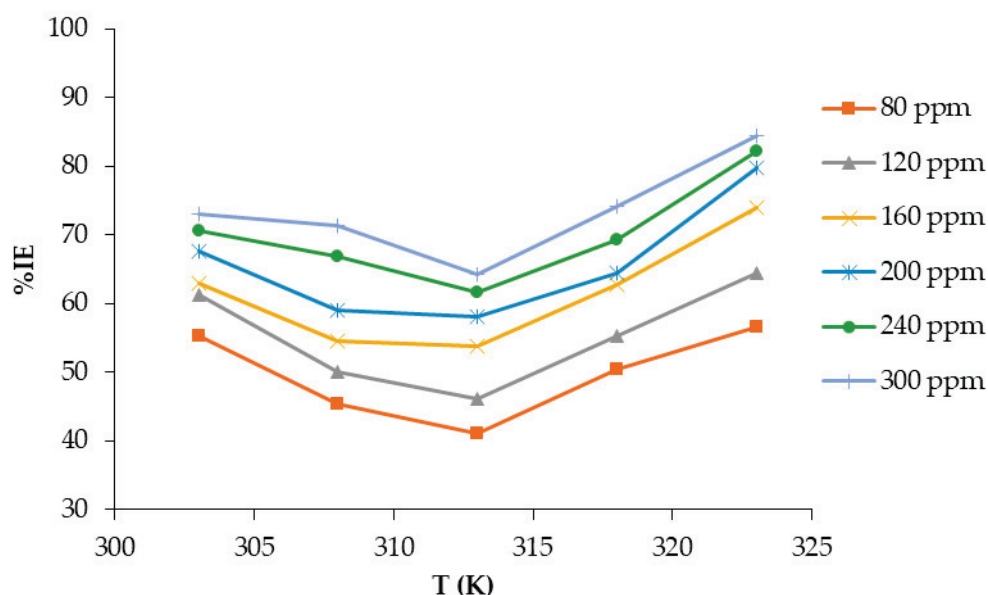


Figure 3. The change in the inhibition efficiency of Al in 1.0 M of HCl as a function of inhibitor concentration and temperatures.

In this study, the impact of changing the temperature on the corrosion rate was investigated. Five different temperatures (30, 35, 40, 45, and 50 °C) were used at different concentrations of AO as the inhibitor. The corrosion rate of Al is estimated by using Equation (3) (Table 2):

$$R_c = \frac{\Delta W}{A \times t} \quad (3)$$

where R_c is the corrosion rate, ΔW is the weight loss in mg cm, A is the area in cm^2 , and t is the time in hours.

Table 2. Corrosion rates ($\text{mg/h}\cdot\text{cm}^2$) at various temperatures in 1.0 M of HCl.

Conc. (ppm)	R_c ($\text{mg/h}\cdot\text{cm}^2$)				
	303 K	308 K	313 K	318 K	323 K
0	0.071	0.092	0.108	0.171	0.336
80	0.032	0.050	0.064	0.085	0.146
120	0.028	0.046	0.058	0.076	0.119
160	0.026	0.042	0.050	0.064	0.088
200	0.023	0.038	0.045	0.061	0.068
240	0.021	0.030	0.042	0.053	0.060
300	0.019	0.026	0.039	0.044	0.053

The Al corrosion rate (R_c) varies, as can be seen in Table 2, when different inhibitor concentrations are present during constant immersion in 1.0 M of HCl. For this experiment, a 4 h immersion period was chosen. The results demonstrate that, when the temperature

risers, corrosion rates also rise. Usually, raising the temperature speeds up corrosion, which in turn accelerates the metal's rate of dissolution [20].

3.4. Thermodynamic Considerations

The activation energy (E_a) for the corrosion of Al in 1.0 M of the HCl solution in the absence and presence of different concentrations of AO were calculated using the Arrhenius-type Equation (4):

$$\text{Log } R_c = \text{Log } A - \frac{E_a}{2.303RT} \quad (4)$$

According to the data, the corrosion rates in both inhibited and uninhibited solutions increase with the rising temperature, whereas they decrease as the inhibitor concentration rises.

The temperature dependence of the corrosion rate can be seen as an Arrhenius-type process, the rate of which is determined by Equation (4):

Figure 4 shows the plots of $\log(R_c)$ versus $1/T$ for 1.0 M HCl solutions with and without the inhibitor. Calculated activation energy (E_a) values are listed in Table 3.

$$\text{Log} \left(\frac{R_c}{T} \right) = \text{Log} \left(\frac{R}{Nh} \right) + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303RT} \quad (5)$$

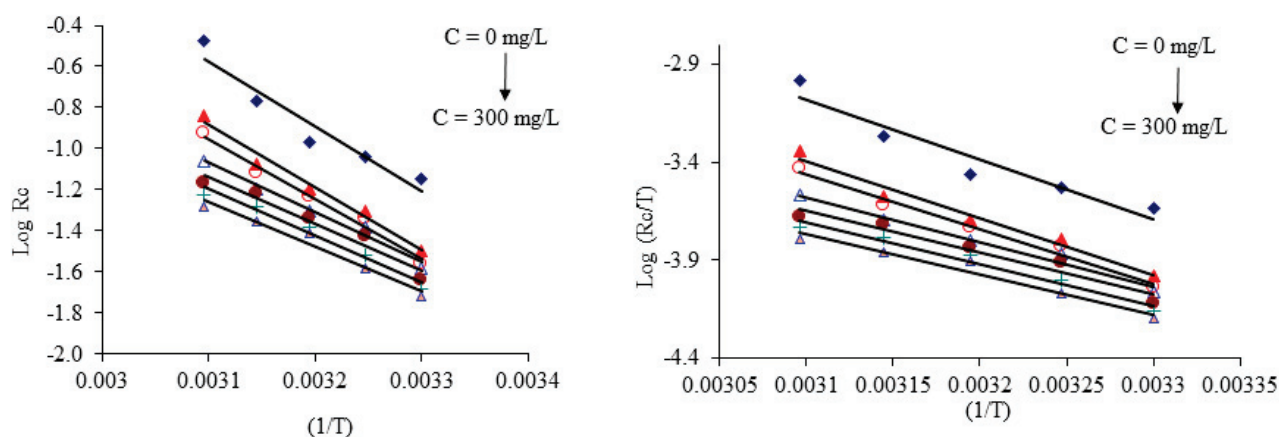


Figure 4. Arrhenius plot and plot of $\log R_c/T$ vs. $1/T$ for Al corrosion in 1.0 M of HCl at 4 h due to different concentration (from $C = 0$ mg/L to $C = 300$ mg/L).

Table 3. E_a , ΔH^* , and ΔS^* values at various concentrations of AO in 1.0 M of HCl.

Conc. (mg/L)	R^2	ΔS^* (J/mol. K)	E_a (kJ/mol)	ΔH^* (kJ/mol)
0	0.9159	−0.08	60.49	57.89
80	0.9760	−0.09	58.21	55.61
120	0.9815	−0.10	56.04	53.44
160	0.9782	−0.13	46.17	43.57
200	0.9482	−0.14	43.41	40.80
240	0.9685	−0.14	43.24	40.63
300	0.9614	−0.15	41.40	38.80

The thermodynamic characteristics of activation, such as ΔH^* and ΔS^* , were computed using the transition state Equation (5).

As a result, a straight line is obtained when $\log(R_c/T)$ is plotted versus $(1/T)$. This plot is shown in Figure 4. The slope $(-\Delta H^*/2.303R)$ and intercept $(\log(R/Nh)) + (\Delta S^*/2.303R)$

of each line are used to calculate ΔH^* and ΔS^{**} values. Table 3 shows the results. It is obvious that E_a values are lower in the presence of the varied concentrations of **AO** than in their absence. Corrosive inhibitors that rely on weak electrostatic forces are less effective at higher temperatures, while stronger chemisorptive inhibitors (which form chemical bonds with the surface) tend to perform better in such conditions. This result, related to a decrease in the activation energy with increasing the temperature and an increase in the inhibitory efficiency, points to a chemisorption process [31,32]. As we have already mentioned, **AO** shows that the limiting species chemisorb onto the aluminum surface in an acidic solution [33].

The enthalpy of activation values continuously reduced from 57.89 kJ/mol to 38.80 kJ/mol from the uninhibited solution to the greatest inhibitor concentration (300 mg/L) in the acidic solution. The positive values of ΔH^* indicate that the dissolution of aluminum in an acidic medium is endothermic, meaning the process requires the absorption of heat from surrounding environment.

Chemical adsorption is thought to be the cause of the inhibitory action in situations like these, where ΔH^* -inhibited < ΔH^* -uninhibited, and then continuously decreased with the rise in inhibitor concentration. However, the enthalpy values in this study are greater than the typical physical adsorption heat, but less than the typical chemical adsorption heat, indicating that both physical and chemical adsorption processes are likely comprehensive adsorption [34].

ΔS^* values are negative, implying that the activation complex is the rate-determining step signifying an association rather than a dissociation mechanism, resulting in reduced disordering [35–37].

3.5. Adsorption Behavior

The ability of a corrosion inhibitor to be absorbed on the metal surface determines its efficiency. Adsorption isotherms provide information on the interaction of adsorbed particles not only with one another, but also with a metal surface; therefore, it is critical to understand the adsorption mechanism, which can provide key information about the inhibitor's and the metal surface's reactance [38]. To determine which adsorption isotherm model best explains adsorption, the corrosion rate (R_c) and the size of inhibitor surface coverage (θ) were fitted into the various adsorption isotherm models. Langmuir, Temkin, Frumkin, Freundlich, El Awady, Redlich–Peterson (R-P), Dubinin–Radushkevich, and Flory Huggins adsorption isotherms are the most often used isotherm models in corrosion research.

Different types of adsorption equations were tested in an acidic medium, and the results of **AO** adsorption on an aluminum surface were applicable to R-P adsorption, Freundlich, Temkin, and El Awady isotherms.

The experimental results for the tested inhibitor were used to calculate the Freundlich adsorption isotherm:

$$\log \theta = \log K_{ads} + (1/n) \log C \quad (6)$$

where θ is the size of the surface covered, C is the concentration, K_{ads} is a constant associated with the adsorptive equilibrium constant, and n is a constant that depends on the nature of the adsorbent.

Figure 5a depicts the plot of $\log \theta$ against $\log C$ derived from the aforesaid Freundlich equation.

Table 4 summarizes the equilibrium constants, K_{ads} , for the adsorption of **AO** on aluminum in an acidic solution at various temperatures obtained using the regression equation of the linear plot in Figure 5a.

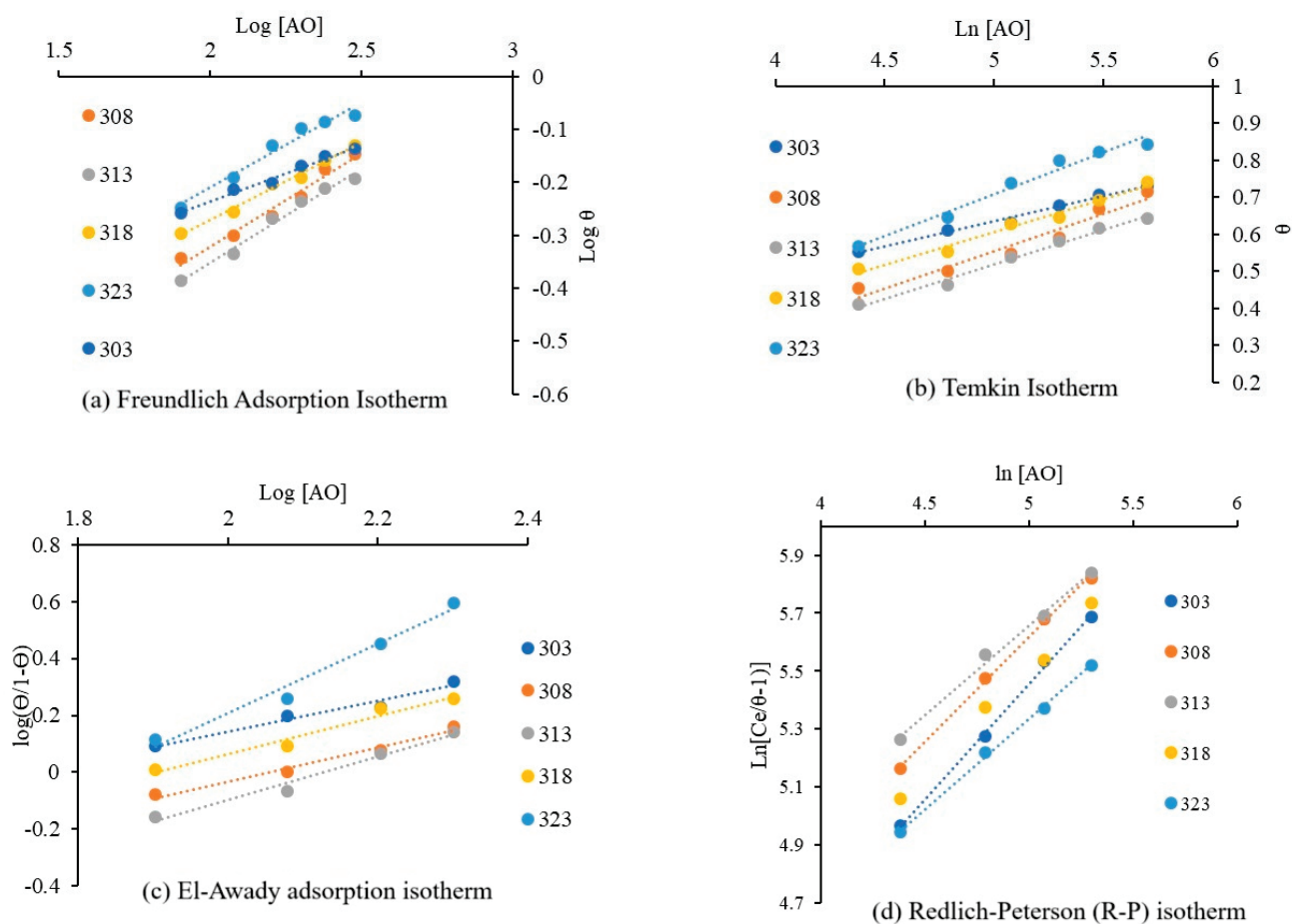


Figure 5. Adsorption model of AO on aluminum surface at different temperatures (303 K, 308 K, 313 K, 318 K and 323 K) in 1.0 M of HCl. (a) Freundlich Adsorption Isotherm, (b) Temkin Isotherm, (c) El-Awady adsorption isotherm and (d) Redlich-Peterson (R-P) isotherm.

Table 4. Adsorption parameters for the adsorption of AO on aluminum in 1.0 M of HCl for a 4 h immersion period at different temperatures.

Adsorption Isotherm	Temp. (K)	303	308	313	318	323
Freundlich Adsorption Isotherm $\log \theta = \log K_{ads} + (1/n) \log C$	R^2	0.9868	0.9717	0.9836	0.9882	0.9665
	Slope	0.2113	0.3513	0.3572	0.2930	0.3207
	Intercept	−0.6584	−1.0242	−1.0660	−0.8579	−0.8509
	K_{ads}	0.2196	0.0946	0.0859	0.1387	0.1410
	ΔG_{ads} (kJ/mol)	−30.99	−29.34	−29.57	−31.31	−31.84
	$1/n$	0.2113	0.3513	0.3572	0.2930	0.3207
Temkin Isotherm $\theta = -\frac{1}{2a} \ln C - \frac{1}{2a} \ln K_{ads}$	R^2	0.9853	0.9497	0.9863	0.9822	0.9748
	Slope	0.3107	0.4616	0.4271	0.4130	0.5177
	Intercept	−0.0400	−0.4478	−0.4082	−0.2914	−0.4158
	$\log K$	−0.1287	−0.9702	−0.9559	−0.7055	−0.8030
	K	0.7434	0.1071	0.1107	0.1970	0.1574
	a	7.41	4.99	5.39	5.58	4.45
	ΔG_{ads} (kJ/mol)	−34.06	−29.66	−30.23	−32.23	−32.14

Table 4. Cont.

Adsorption Isotherm	Temp. (K)	303	308	313	318	323
El Awady Adsorption Isotherm $\text{Log}\left(\frac{\theta}{1-\theta}\right) = \text{Log}K_{ads} + y \text{Log}C$	R ²	0.982	0.940	0.987	0.975	0.984
	slope	0.595	0.841	0.756	0.776	1.150
	Intercept	−1.047	−1.726	−1.606	−1.494	−2.086
	1/y	1.682	1.190	1.323	1.288	0.870
	K _{ads}	0.090	0.019	0.025	0.032	0.008
Redlich–Peterson (R-P) Isotherm $\text{Ln}\left(K_R \frac{C_e}{\theta} - 1\right) = \text{Ln}(a_R) + \beta \text{Ln}(C_e)$	R ²	0.9990	0.9914	0.9949	0.9979	0.9924
	slope	1.2613	1.5227	1.5424	1.4058	1.4542
	Intercept	−1.8800	−3.5225	−3.7372	−2.7402	−2.7802
	α _R	0.1526	0.0295	0.0238	0.0646	0.0620
	β	1.2613	1.5227	1.5424	1.4058	1.4542
	K _R	1				

According to each parameter calculated for each isotherm mentioned above, the best isotherm will be the Freundlich one, in an acidic medium. The R² values are excellent and the K_{ads} values correspond to the behavior of the inhibitor, which decreased when the temperature was raised from 303 K to 313 K, but the value then increased when the temperature was raised from 318 K to 323 K.

In general, values of ΔG_{ads} around −20 kJ mol^{−1} or lower are consistent with electrostatic contact, while values around −40 kJ mol^{−1} or higher are associated with chemical interactions [39]. In this study, ΔG_{ads} values are higher than for normal physical adsorption but lower than for typical chemical adsorption, indicating that both physical and chemical adsorption activities are likely to occur, and ΔG_{ads} values are negative, showing that the adsorption process is spontaneous [39]. The value of K is an approximation of the adsorption capacity, whereas 1/n is a function of adsorption strength in the adsorption process [38]. The (n^{−1}) values are less than one in the acidic medium at all temperatures. This indicates normal adsorption and a favorable sorption process [38].

The Temkin model is another well-known adsorption isotherm that has also been widely used to describe the mechanism of action of corrosion inhibitors. It offers some insights into the type of interactions occurring in the adsorbed layer, in contrast to others discussed to date. This is how the model is expressed:

$$e^{-2a\theta} = K_{ads}C \quad (7)$$

Based on the sign of the parameter, the molecular interaction parameter is utilized to identify whether attraction or repulsion occurs in the adsorbed layer. To obtain linear plots of θ against ln C (Figure 5b), the equation's linearized form can be used.

$$\theta = -\frac{1}{2a} \text{Ln}C - \frac{1}{2a} \text{Ln}K_{ads} \quad (8)$$

The K_{ads} and ΔG_{ads} values are evaluated and presented in Table 4. The value of K_{ads} describes the strength with which the inhibitor molecules bind to the metal surface.

The El Awady isotherm was used to study the strength of adsorption of AO on the surface of Al, as well as the likelihood of the creation of a multi-molecular layer of adsorption (Figure 5c):

$$\text{Log}\left(\frac{\theta}{1-\theta}\right) = \text{Log}K_{ads} + y \text{Log}C \quad (9)$$

where y is the number of inhibitor molecules that can fit in a single active site, θ is the size of the surface covered, C is the concentration, and K_{ads} is a constant associated with the adsorptive equilibrium constant.

$$K_{ads} = K^{\frac{1}{y}} \quad (10)$$

If the value of $1/y$ is less than one, the inhibitor may create many layers on the metal surface, and if it is more than one, the inhibitor molecule will occupy multiple active sites [40]. The values of $1/y$ that were obtained were greater than one, indicating that each inhibitory molecule was affixed to many active sites on the Al surface. It might be because AO contains several compounds.

The Redlich–Peterson (R-P) isotherm can be applied to both homogeneous and heterogeneous systems due to its great degree of adaptability. The R-P isotherm, in contrast to the Langmuir, Freundlich, and D-R isotherms, has three parameters in a single equation [41]. The R-P isotherm has a linear form, which is:

$$\ln\left(K_R \frac{C_e}{\theta} - 1\right) = \ln(a_R) + \beta \ln(C_e) \quad (11)$$

where β is an exponent between 0 and 1, K_R (L/g) and α_R (L/mg) $^{1/\beta}$ are the R-P isotherm constants, respectively. The R-P isotherm approximates Henry's law at low concentrations and approaches the Freundlich isotherm at high concentrations. This isotherm has three parameters; hence, the use of linear regression analysis is more difficult. To apply this isotherm, the isotherm parameter K_R ($K_R = 1$) was varied in order to produce the highest regression, R^2 , for the linear plot of $\ln[C_e/\theta - 1]$ against $\ln C_e$. The slope and intercept of this plot are displayed in Figure 5d, and the constants α_R , β , and R were calculated. Table 4 presents the obtained regression R^2 , α_R , and β values.

3.6. Potentiostatic Polarization Measurements

To examine the impact of the inhibitor (AO) on the corrosion behavior of the Al electrode, polarization measurements were performed. Tafel plots (potential-versus-log current) are shown in Figure 6. The cathodic and anodic Tafel curves were used to compute the corrosion current. Along the linear part of each curve, a straight line can be superimposed. The slope of the straight line fits of the linear regions of the anodic and cathodic Tafel yields the Tafel constants β_a and β_c , respectively, whereas the slope of the current-potential curve close to the corrosion potential determines the polarization resistance (R_p) in Ωcm^2 . Table 5 summarizes other data, including the corrosion potential (E_{corr}), corrosion current density (I_{corr}), polarization resistance (R_p), and corrosion rate (R_c).

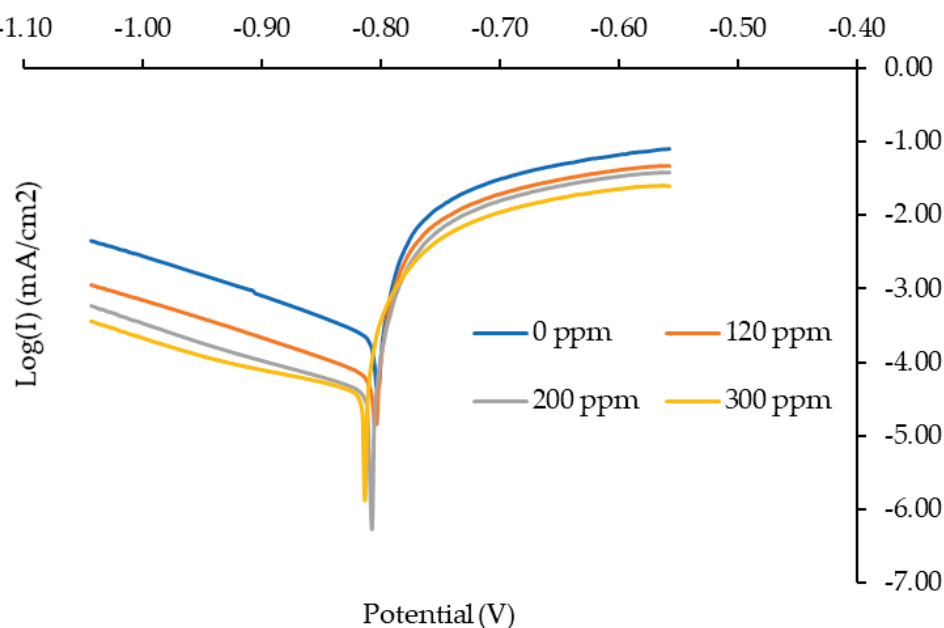


Figure 6. Potentiodynamic polarization curve for aluminum in 1.0 M of HCl at various concentrations of AO at 30 °C.

Table 5. Electrochemical corrosion parameters of aluminum in the absence and presence of various concentration of AO in 1.0 M of HCl.

[inhibitor] (mg/L)	E _{corr} (V)	I _{corr} (mA/cm ²)	β _a (mV/dec)	−β _c (mV/dec)	R _p (kΩcm ²)	I%	R _c mm/y
Blank	−0.794	18.68	413.87	199.23	3.13	-	80.32
120	−0.798	12.27	560.16	204.40	5.30	34.31	52.76
200	−0.805	8.788	578.40	183.64	6.89	52.90	37.79
300	−0.807	6.710	645.28	198.79	9.82	64.00	28.85

Table 6 shows that, as the concentration of the inhibitor increases, the corrosion current density (I_{corr}) decreases. This clearly shows that AO stops the aluminum from rusting in acidic conditions. Both anodic and cathodic processes are suppressed, as is shown by the polarization curves for the acidic medium (Figure 6). According to the results in Table 5, the corrosion potential (E_{corr}) and corrosion current density (I_{corr}) values alter as the inhibitor concentration increases. Additionally, it was noted by [42,43] that, if an inhibitor's corrosion potential displacement is greater than 85 mV relative to the blank's corrosion potential, the inhibitor can be categorized as either cathodic or anodic. Aluminum's corrosion potential (E_{corr}) is little altered by the extract when compared to a blank, shifting by around (4.2–13.6) mV cathodically in an acidic solution. According to this finding, the extract decreases the anodic dissolution and delays the cathodic hydrogen evolution reaction. It also operates as a mixed-type inhibitor. By regulating both the anodic and cathodic processes, polyphenolic substances clearly prevent corrosion [44,45]. The possibility of protonated species of the extract components in acidic solutions could explain this. The protonated species are likely to compete with the hydrogen ions at the aluminum cathodic sites, which will slow down the release of hydrogen.

Table 6. Electrochemical impedance parameters for Al corrosion in the 1.0 M HCl solution containing various concentrations of AO.

[OA] (mol/L)	R _s Ωcm ²	R _{ct} Ωcm ²	n	C _{dl} μF·cm ^{−2}	Y ₀ (Ω ^{−1} s ⁿ cm ^{−2})	I.E.
Blank	1.29	32.82	0.74	594.88	2.43 × 10 ^{−3}	
120	2.24	57.87	0.74	484.46	1.65 × 10 ^{−3}	43.29
200	1.76	87.15	0.73	360.75	1.21 × 10 ^{−3}	62.34
300	2.51	102.13	0.74	430.32	1.29 × 10 ^{−3}	67.87

The electrons of aromatic rings and the lone pair electrons of oxygen atoms participate in adsorption at the anodic sites, which reduces aluminum's anodic dissolution. The significantly reduced corrosion current (I_{corr}) and corrosion rate, along with an increase in polarization resistance (RP) values, provide additional proof that the effectiveness of the inhibition increased with the extract concentration and reached a maximum value at 300 ppm in the acidic medium. These findings are in line with the previously discussed weight loss measurements. The corrosion rate (R_c) is computed as follows:

$$R_c = \frac{0.129 \times E.Wt \times I_{corr}}{d.A} \quad (12)$$

I_{corr} = corrosion current (μA/cm²), E.Wt = equivalent weight of Al, d = density of Al, g/cm³, and A = area in cm².

The presence of AO significantly slows down the corrosion rate, which causes both the anodic and cathodic curves to move to lower current densities. In other words, the

inhibitor (AO) in the 1.0 M HCl solution slows both the cathodic and anodic processes of aluminum electrodes.

Electrochemical impedance spectroscopy (EIS).

The Nyquist plots displayed in Figure 7 reveal semicircles for all systems over the studied frequency range. The diameter of the semicircles in the presence of AO is larger than that in the blank solution, and increases with the inhibitor concentration. This indicates that the impedance of the inhibited substrate increases with the inhibitor concentration. It is clear from the figure that there is a single semicircle that shows a single charge transfer process during dissolution. The impedance spectra were analyzed by fitting information to the equivalent circuit model (Figure 8). In the equivalent circuit model, R_s represents the solution resistance between the working and reference electrodes; R_{ct} is the charge transfer resistance, and it corresponds to the resistance between the metal and outer Helmholtz plane [46,47].

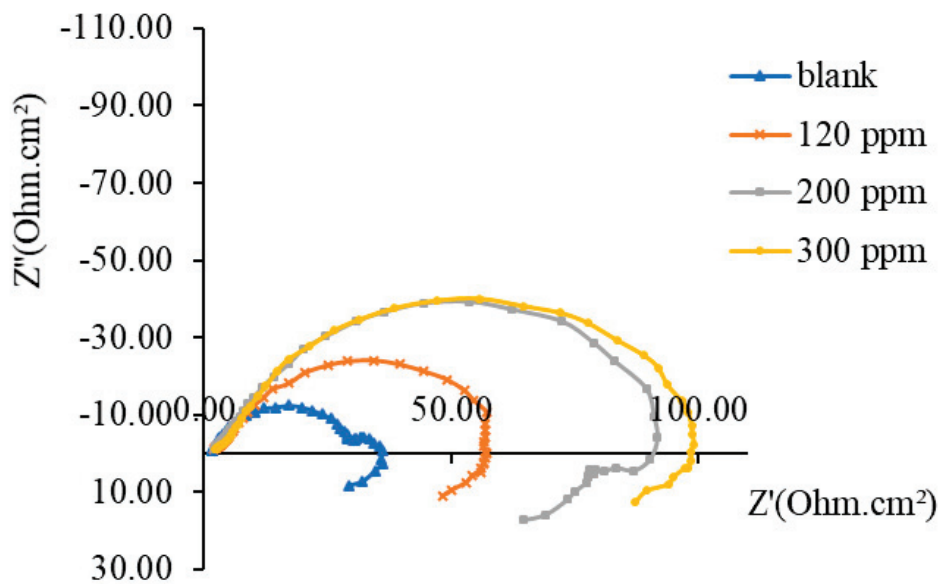


Figure 7. Nyquist plots for Al corrosion in the 1.0 M HCl solution and with the examined inhibitor (AO) at 303 K.

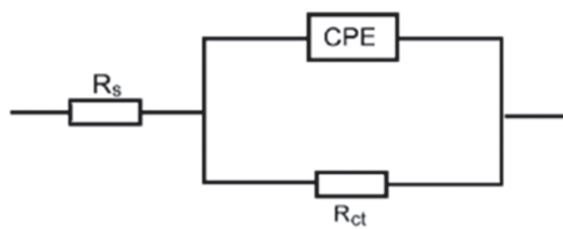


Figure 8. Electrochemical equivalent circuit utilized to fit the EIS results for Al corrosion in the 1.0 M HCl solution and with the examined inhibitor (AO).

The impedance of a CPE is presented as:

$$Z(\text{CPE}) = Y_o^{-1} (j\omega)^{-n} \quad (13)$$

where j is the imaginary root, ω is the angular frequency, Y_o is the magnitude, and n is the exponential term, whereas ω is the angular frequency ($\omega = 2\pi f$, the frequency in Hz) and n is the phase-shift, which provides details about the degree of surface inhomogeneity.

The impedance data listed in the Table 6 indicate that the addition of the extract increases the values of R_{ct} and reduces the value of the electrochemical double-layer capacitance (C_{dl}). The increase in the R_{ct} value is attributed to the formation of the protective

film on the metal/solution interface [40,46]. The decrease in C_{dl} indicates the increase in the thickness of the electric double layer [47]. The interfacial double-layer capacitance (C_{dl}) values are estimated using Formula (14):

$$C_{dl} = Y_o(2\pi f_{max})^{n-1} \quad (14)$$

where f_{max} is the frequency at which the imaginary component of the impedance attains a maximum value (Z''_{max}).

This result suggests that the extract molecules inhibit the corrosion of Al by adsorption on the Al surface, thereby causing an increase in R_{ct} values and a decrease in C_{dl} values [48].

The inhibition efficiency from the impedance data was estimated by comparing the values of the charge transfer resistance in the absence and presence of the inhibitor as follows:

$$\%IE = \left[\frac{R_{ct}^i - R_{ct}^o}{R_{ct}^i} \right] \times 100 \quad (15)$$

where the values of the charge transfer resistance with and without AO are denoted by R_{ct}^i and R_{ct}^o , respectively. The magnitude and trend of the obtained values presented in Table 6 are in close agreement with those determined from gravimetric measurements and electrochemical polarization measurements.

3.7. Scanning Electron Microscope (SEM)

The surface morphology of the tested aluminum is determined by scanning electron microscopy. The surface morphology of Al exposed to 1.0 M of HCl in the absence of plant extract is shown in Figure 9B. These data point to uniformly severe corrosion and the production of adherent amorphous corrosion products in the absence of an inhibitor. Such corroded patches may have formed as a result of aggressive H^+ assault in acidic environments, which led to the dissolution of the alumina layer.

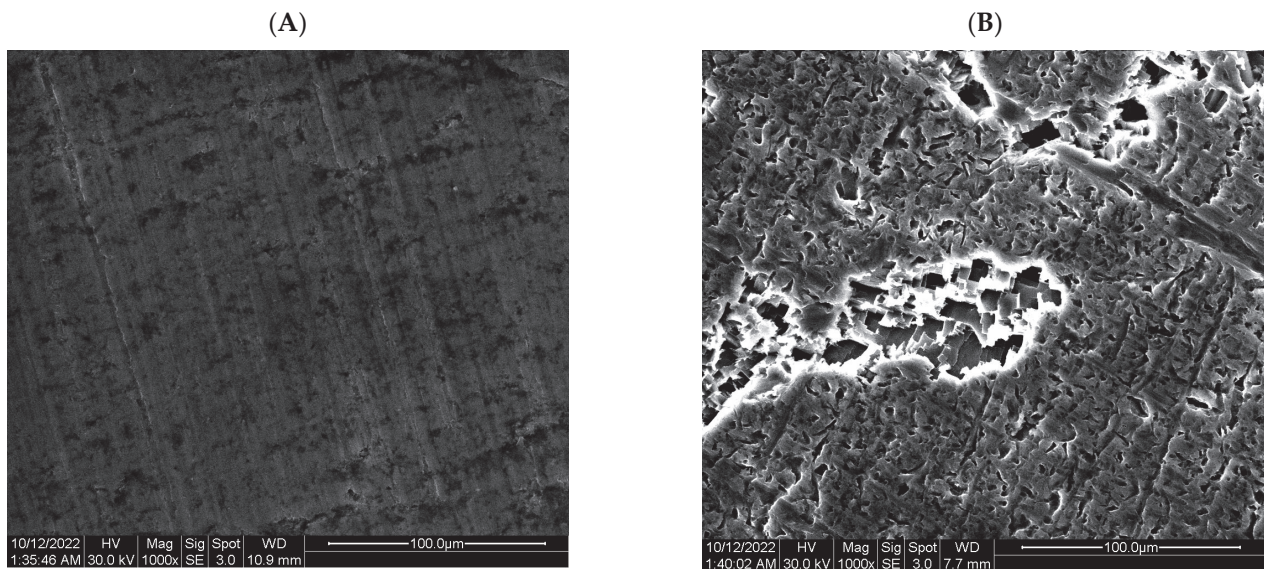


Figure 9. Cont.

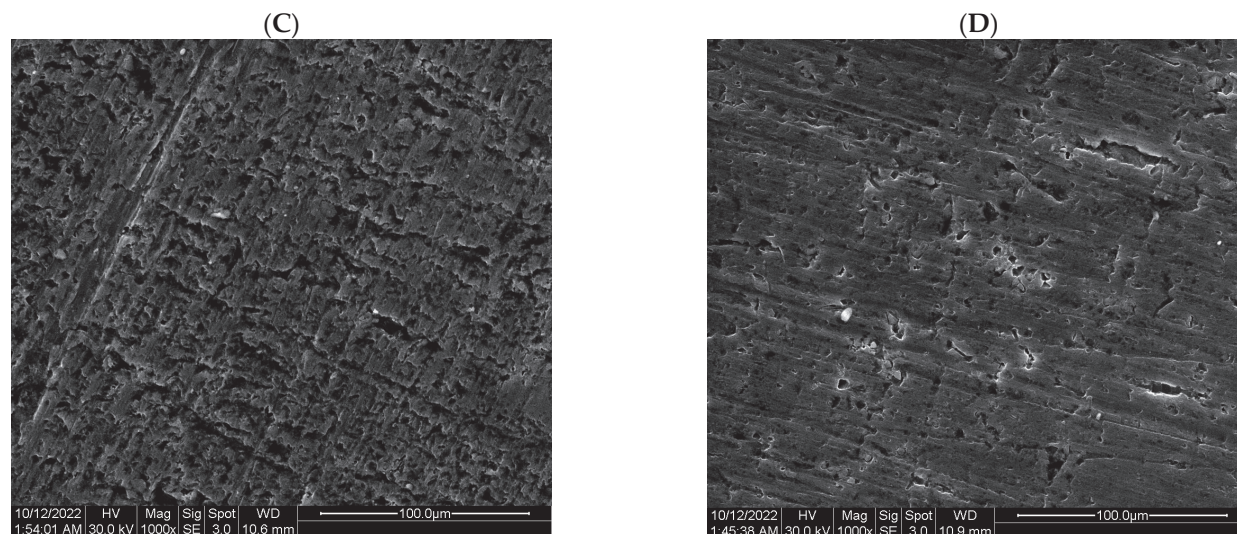


Figure 9. Scanning electron micrographs of plain Al in an acidic medium: (A) Al polished with emery paper; (B) Al in 1.0 M of HCl at 30 °C; (C) Al in 1.0 M of HCl in the presence of 80 ppm AO at 30 °C; (D) Al in 1.0 M of HCl in the presence of 300 ppm AO at 30 °C.

The metal surface is only partially covered with the inhibitor, providing it with a decent amount of protection, according to the SEM results for aluminum in the presence of the inhibitor. In the presence of hydrochloric acid, it is also obvious that the surface is covered with the inhibitor (Figure 9B–D). The efficiency of AO as an inhibitor in acidic environments is demonstrated by scanning electron micrographs, which reveal that increasing the inhibitor concentration induces an increase in the quantity of an adsorbed protective coating of the inhibitor molecules on the aluminum surface.

3.8. Quantum Chemical Calculation

The Frontier molecular orbital theory (FMO) provides an explanation for the adsorption ability of molecules on metal surfaces and their chemical reactivity. The interaction between the molecules' HOMO and LUMO levels is what primarily determines this reactivity [49]. In this study, DFT calculations were conducted for the main compounds (1, 2, 3, 4, and 5) found in the methanol extract of AO. Both gas phase and acidic solution (HCl) conditions were considered. Figure 10 illustrates the optimized geometry of these major compounds, as well as the characteristics of their molecular orbitals (HOMO and LUMO).

The reactivity of a molecule toward adsorption on an Al-metallic surface can be assessed using ΔE_{gap} . A decrease in ΔE_{gap} indicates increased reactivity and a higher inhibitor efficiency, as it enhances the stability of the formed complex between the major organic compound and the surface [50,51]. The concepts of σ and η are also introduced based on ΔE_{gap} . σ is closely associated with the molecule's polarizability, where a softer molecule with a smaller ΔE_{gap} is more easily polarized, and thus more reactive [21,26,51]. Quantum chemical and molecular dynamics parameters, such as ΔE_{gap} , σ , η , X , ΔN , and ω , were calculated for the identified major compounds (1, 2, 3, 4, and 5), as presented in Table 7.

Table 7. Calculated quantum parameters for main components of methanol extract of AO ($X_{\text{Al}} = 3.209$, $\eta_{\text{Al}} = 2.776$ [18,48]).

Quantum Parameters	1		2		3		4		5	
	Gas	Acidic	Gas	Acidic	Gas	Acidic	Gas	Acidic	Gas	Acidic
E_{HOMO} (eV)	−7.874	−7.891	−5.960	−6.086	−6.454	−6.549	−6.088	−6.113	−5.874	−6.068
E_{LUMO} (eV)	−0.583	−0.527	−0.385	−0.434	−0.605	−0.414	−1.935	−2.082	−1.649	−1.921
ΔE_{gap} (eV)	7.291	7.364	5.575	5.652	5.849	6.135	4.153	4.031	4.225	4.147
σ	0.274	0.271	0.358	0.353	0.341	0.325	0.481	0.496	0.473	0.482

Table 7. Cont.

Quantum Parameters	1		2		3		4		5	
	Gas	Acidic	Gas	Acidic	Gas	Acidic	Gas	Acidic	Gas	Acidic
η	3.645	3.682	2.787	2.826	2.924	3.067	2.076	2.015	2.112	2.073
X	4.228	4.209	3.172	3.26	3.529	3.481	4.011	4.097	3.761	3.994
ω	1.412	1.398	1.847	1.821	1.76	1.678	2.479	2.554	2.437	2.483
ΔN	0.079	0.077	0.003	0.004	0.0281	0.023	0.082	0.0927	0.056	0.08
Dipole moment μ (Debye)	0.0117	0.015	1.447	1.91	7.376	9.658	6.021	8.317	7.421	10.833

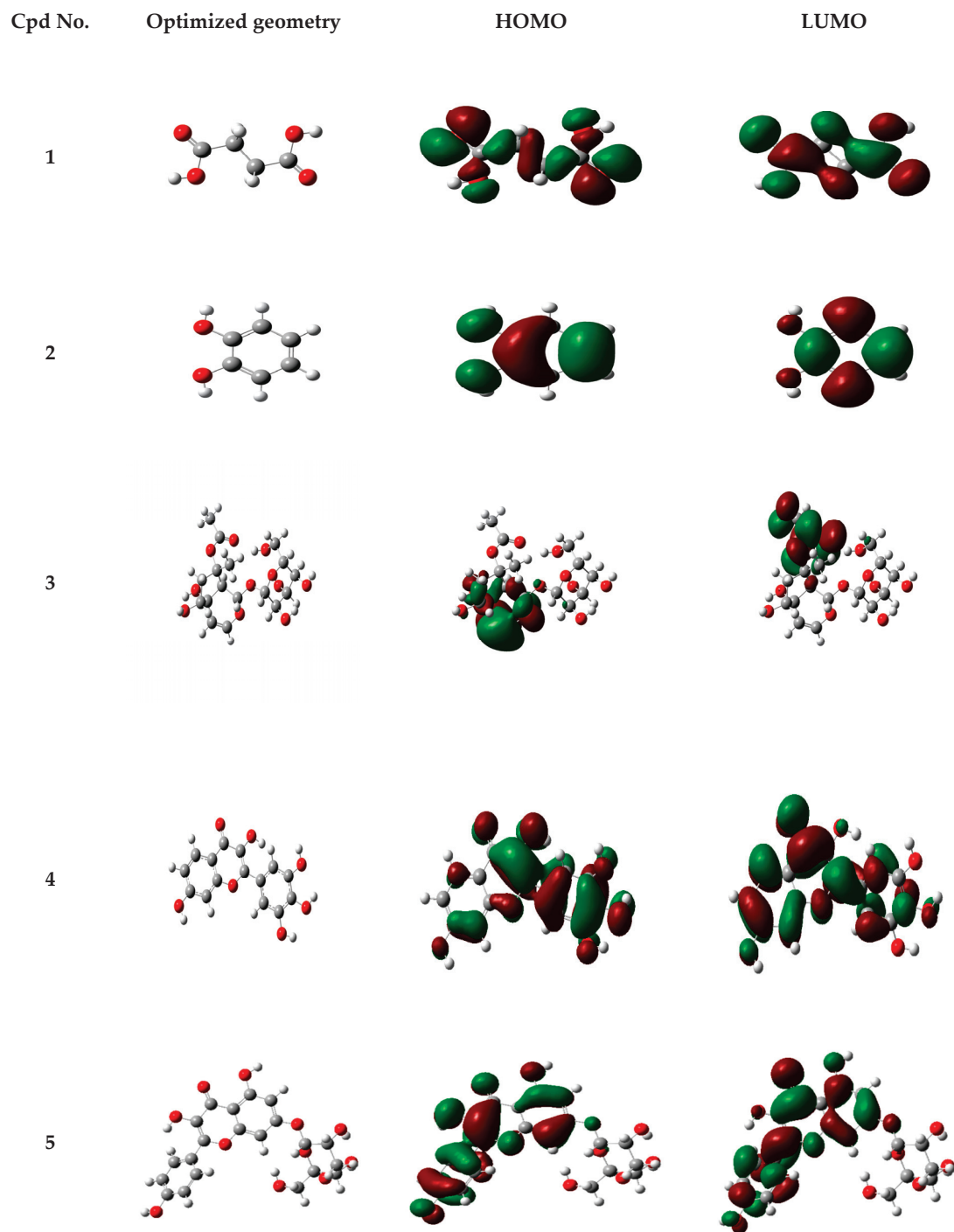


Figure 10. Optimized molecular geometry, HOMO and LUMO, of the studied compounds (1, 2, 3, 4 and 5).

The order of the ΔE_{gap} values for the five major components of the AO extract, both in gas and acidic solutions, follows the pattern $4 < 5 < 2 < 3 < 1$. Among these compounds, Compound 4 stands out with the highest σ value and the smallest η value. Additionally, it exhibits the highest ω value compared to the other inhibitors in both gas and acidic solutions. The ω value is an indicator of the inhibitor's electron-accepting ability from metal surfaces. In the case of Compound 4, its high ω value signifies its strong capability to accept electrons from aluminum (Al). This is further supported by its elevated ELUMO value, which reflects its high electron-accepting capacity from Al. Moreover, the ΔN values reveal that most of the electrons transferred to the Al surface originate from Compound 4 molecules. With ΔN values of 0.082 in the gas phase and 0.0927 in the presence of HCl, Compound 4 surpasses the other compounds in this regard. As a general trend, the inhibition efficiency of organic inhibitors tends to increase with a higher electron-donating ability at the metal's surface, particularly when ΔN is less than 3.6 [52]. In this context, all the examined compounds can be classified as green inhibitors due to their ΔN values falling below 3.6. However, Compound 4 emerges as the most effective inhibitor across all phases. In summary, the major components of AO extract exhibit varying ΔE_{gap} values, with Compound 4 demonstrating superior characteristics, such as high σ and ω values. It is also the primary source of electron transfer to the Al surface, making it the most efficient inhibitor among the studied compounds in both gas and acidic environments.

3.9. Mechanism of Inhibition

These N, O, and S atoms and aromatic rings are found in a lot of green rust inhibitors that come from plant extracts, amino acids, or natural oils. They are often chosen because they are non-toxic and biodegradable, which means they protect well while causing little harm to the Earth [12–20]. The findings suggest that compounds 1, 2, 3, 4, and 5 can adhere to the surface by donating electrons from electron-rich regions to the vacant d orbitals of Al. Additionally, they can accept electrons from the Al surface, forming a back-donating bond, which depends on the optimized structure's orientation of the inhibitor in space. Notably, Compound 4 exhibits the highest adsorption ability on the Al surface by donating the unshared pair of electrons from O atoms to the vacant d-orbitals of Al. Consequently, it is expected that the inhibition efficiency of the AO extract primarily arises from the adsorption of Compound 4 on the Al surface.

Furthermore, there are two adsorption modes for inhibitors on the Al surface in gas and acidic environments: physisorption and chemisorption. The extent of adsorption depends on the difference between the chemical potential of the Al metal and the inhibitors. The calculated ΔG_{ads} for Compound 4 is -18.517 in the gas phase and -20.50 in the acidic medium. The ΔG_{ads} value is higher than that of typical physical adsorption, but lower than that of typical chemical adsorption. This indicates the likelihood of both physical and chemical adsorption occurring, and the negative ΔG_{ads} values confirm that the adsorption process is spontaneous. These values fall within the range of zero to -40 kJ/mol, indicating the favorable nature of the adsorption process [21,26,52].

4. Conclusions

From the current investigation, the following primary conclusions may be drawn:

1. The findings of weight loss experiments and polarization techniques suggest that *A. orientalis* crude (AO) is useful as a green corrosion inhibitor for aluminum in an acidic medium.
2. The efficiency in an acidic medium decreases with an increasing temperature, until the temperature of 40°C is attained, and then increases until the temperature of 50°C is reached. The efficiency increases with increasing concentrations of *A. orientalis* crude (AO) to reach a maximum value of 300 ppm at 50°C .
3. It was discovered that the activation energy (E_a) for the dissolution of pure aluminum in solution is higher in the absence of an inhibitor than it is in the presence of an inhibitor in an acidic medium.

4. The widely used isotherm models (Freundlich, Temkin, El Awady, and Redlich–Peterson (R-P) adsorption isotherm models) were used to investigate the equilibrium isotherms for the adsorption of AO on aluminum in HCl at different temperatures.
5. The free Gibbs energy (ΔG_{ads}) value demonstrates that the inhibitory mechanism could be attributed to comprehensive physical and chemical adsorption in an acidic medium (1.0 M of HCl), and the sign of the free energy of adsorption suggests that the process is spontaneous.
6. Polarization tests revealed that the inhibitor (AO) is an anodic and cathodic mixed-type inhibitor.
7. EIS plots indicated that the charge transfer resistances increase with increasing the concentration of the extract.
8. The SEM findings reveal that the inhibitor (AO) partially covers the metal surface, providing it with a respectable level of protection.
9. Compound **4** demonstrates the best corrosion inhibition on the Al metal surface.
10. Experimental and DFT calculations show an excellent agreement, validating the accuracy of the theoretical predictions.

Author Contributions: Conceptualization, F.M.A.O., T.T.B. and M.A.A.-Q.; Data curation, F.K.A., T.T.B. and M.A.A.-Q.; Formal analysis, F.K.A., A.M.M.R. and M.A.A.-Q.; Funding acquisition, F.M.A.O. and M.A.A.-Q.; Investigation, S.T.A.-O. and M.A.A.-Q.; Methodology, F.M.A.O., O.A.F., A.M.M.R., T.T.B., G.M.A.-M. and M.A.A.-Q.; Project administration, M.A.A.-Q.; Resources, M.A.A.-Q.; Software, O.A.F., A.M.M.R., G.M.A.-M. and M.A.A.-Q.; Supervision, M.A.A.-Q.; Validation, M.A.A.-Q.; Visualization, S.T.A.-O. and M.A.A.-Q.; Writing—original draft, F.M.A.O., G.M.A.-M. and M.A.A.-Q.; Writing—review and editing, S.T.A.-O., F.K.A. and M.A.A.-Q. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Deanship of Scientific Research and Graduate Studies at Yarmouk University (103/2023).

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author/s.

Acknowledgments: The authors extend their appreciation to the Deanship of Scientific Research at Yarmouk University for funding this work. The authors also extend their appreciation to the Deanship of Scientific Research at the World Islamic Sciences and Education University.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Ali, A.; Foad, N. Inhibition of aluminum corrosion in hydrochloric acid solution using black mulberry extract. *J. Mater. Environ. Sci.* **2012**, *3*, 917–924.
2. Davis, J. (Ed.) *Corrosion: Understanding the Basics*; ASM International: Almere, The Netherlands, 2000.
3. Bastidas, D. Corrosion and protection of metals. *Metals* **2020**, *10*, 458. [CrossRef]
4. Ghali, E.; Sastri, V.; Elboujdaini, M. *Corrosion Prevention and Protection: Practical Solutions*; John Wiley & Sons: Hoboken, NJ, USA, 2007.
5. Jones, D. Principles and prevention. *Corrosion* **1996**, *2*, 168.
6. Berradja, A. Electrochemical techniques for corrosion and tribocorrosion monitoring: Methods for the assessment of corrosion rates. In *Corrosion Inhibitors*; IntechOpen: London, UK, 2019; pp. 1–26.
7. Uhlig, H.; Revie, R. *Corrosion and Corrosion Control*; U.S. Department of Energy Office of Scientific and Technical Information: Oak Ridge, TN, USA, 1985.
8. Romhanji, E.; Popovic, M. Problems and prospect of Al-Mg alloys application in marine constructions. *Metalurgija* **2006**, *12*, 297–307.
9. Foley, R.; Nguyen, T. The chemical nature of aluminum corrosion: V. Energy transfer in aluminum dissolution. *J. Electrochem. Soc.* **1982**, *129*, 464. [CrossRef]
10. Aramide, F.O. Corrosion inhibition of AISI/SAE steel in a marine environment. *Leonardo J. Sci.* **2009**, *15*, 47–52.
11. de Souza, F.S.; Spinelli, A. Caffeic acid as a green corrosion inhibitor for mild steel. *Corros. Sci.* **2009**, *51*, 642–649. [CrossRef]
12. Noor, E.A. Potential of aqueous extract of *Hibiscus sabdariffa* leaves for inhibiting the corrosion of aluminum in alkaline solutions. *J. Appl. Electrochem.* **2009**, *39*, 1465–1475. [CrossRef]
13. Bataineh, T.; Al-Qudah, M.; Nawafleh, E.; Al-Rawashdeh, N. *Sinapis alba* extract as green corrosion inhibitor for aluminum in alkaline media. *Int. J. Electrochem.* **2014**, *9*, 3543–3557. [CrossRef]

14. Bataineh, T.; Al-Qudah, M.; Nawafleh, E.; Ajlouni, A. Corrosion Control of Aluminium Alloy in Alkaline Solution Using Leave Extract of *Plumbago Europaea*. *Jordan J. Chem.* **2021**, *8*, 169–178. [CrossRef]
15. Miralrio, A.; Espinoza Vázquez, A. Plant extracts as green corrosion inhibitors for different metal surfaces and corrosive media: A review. *Processes* **2020**, *8*, 942. [CrossRef]
16. Rodrigues, S.; Dalmoro, V.; dos Santos, J. An evaluation of *Acacia mearnsii* tannin as an aluminum corrosion inhibitor in acid, alkaline, and neutral media. *Mater. Corros.* **2020**, *71*, 1160–1174. [CrossRef]
17. Al-Qudah, M.; Hamaideh, R.; Al-Momani, I.; Al-Bataineh, N. *Capparis decidua*: A green inhibitor for pure aluminum corrosion in basic media. *J. Surf. Sci. Technol.* **2020**, *36*, 109. [CrossRef]
18. Al-Qudah, M.A.; Algethami, F.K.; Fodeh, O.A.; Al-Momani, I.F.; Bataineh, T.T.; Alakhras, A.I.; Al-Mazaideh, G.M. Eco-friendly methanolic *Ajuga orientalis* extract as corrosion inhibitor for aluminium in 1.0 M NaOH. *Corros. Eng. Sci. Technol.* **2024**, *59*, 297–310. [CrossRef]
19. Al-Qudah, M.; Al-Keifi, H.; Al-Momani, I.; Abu-Orabi, S. *Capparis aegyptia* as a green inhibitor for aluminum corrosion in alkaline media. *Int. J. Corros. Scale Inhib.* **2020**, *9*, 201–218.
20. Al-Qudah, M. Inhibition of Copper Corrosion by Flavonoids in Nitric Acid. *J. Chem.* **2011**, *8*, 326–332. [CrossRef]
21. Udunwa, D.I.; Onukwuli, O.D.; Menkiti, M.C.; Nwanonyi, S.C.; Ezekannagha, C.B.; Aniagor, C.O. Experimental, computational, and theoretical studies on the corrosion inhibition potential of green *Gongronema latifolium* extract as corrosion inhibitor for aluminum alloy in HCl solutions. *J. Mol. Struct.* **2024**, *1302*, 137508. [CrossRef]
22. Boussalah, N.; Ghalem, S.; El Kadiri, S.; Hammouti, B.; Touzani, R. Theoretical study of the corrosion inhibition of some bipyrazolic derivatives: A conceptual DFT investigation. *Res. Chem. Intermed.* **2012**, *38*, 2009–2023. [CrossRef]
23. Obot, A.S.; BoEkom, E.J.; Ituen, E.B.; Ugi, B.U.; Essien, K.E.; Jonah, N.B. Thermodynamic investigation and quantum chemical evaluation of n-hexane extracts of *Costus lucanusianus* as corrosion inhibitors for mild steel and aluminum in 1 M HCl solution. *J. Appl. Phys. Sci. Int.* **2021**, *13*, 6–27.
24. Al-Qudah, M.; Al-Smadi, Z.; Al-Jaber, H.; Tashtoush, H.; Alkhatib, R.; Bataineh, T.; Al-Dalahmeh, Y.; Abu-Orabi, S. GC/MS and LC-MS/MS phytochemical evaluation of the essential oil and selected secondary metabolites of *Ajuga orientalis* from Jordan and its antioxidant activity. *Arab. J. Chem.* **2023**, *16*, 104641. [CrossRef]
25. Frisch, M.J.E.A.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.P.G.A.; Mennucci, B.; Petersson, G.A.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, USA, 2009.
26. Amin, M.; Abd El-Rehim, S.; El-Sherbini, E.; Hazzazi, O.; Abbas, M. Polyacrylic acid as a corrosion inhibitor for aluminium in weakly alkaline solutions. Part I: Weight loss, polarization, impedance EFM and EDX studies. *Corros. Sci.* **2009**, *51*, 658–667. [CrossRef]
27. Sherif, E.; Erasmus, R.; Comins, J. Inhibition of copper corrosion in acidic chloride pickling solutions by 5-(3-aminophenyl)-tetrazole as a corrosion inhibitor. *Corros. Sci.* **2008**, *50*, 3439–3445. [CrossRef]
28. Rajalakshmi, R.; Subhashini, S.; Nanthini, M.; Srimathi, M. Inhibiting effect of seed extract of *Abrus precatorius* on corrosion of aluminium in sodium hydroxide. *Orient. J. Chem.* **2009**, *25*, 313.
29. Raghavendra, N. Latest exploration on natural corrosion inhibitors for industrial important metals in hostile fluid environments: A comprehensive overview. *J. Bio- Tribo-Corros.* **2019**, *5*, 54. [CrossRef]
30. Nnanna, L.; Onwuagba, B.; Mejeha, I.; Okeoma, K. Inhibition effects of some plant extracts on the acid corrosion of aluminum alloy. *Afr. J. Pure Appl. Chem.* **2010**, *4*, 11–16.
31. Refaey, S.; Taha, F.; Abd El-Malak, A. Corrosion and Inhibition of 316L stainless steel in neutral medium by 2-Mercaptobenzimidazole. *Int. J. Electrochem. Sci.* **2006**, *1*, 80–91. [CrossRef]
32. Jung, J.; Oh, S.; Kwon, H. Effects of environmental factors on corrosion behavior of aluminum. *Mater. Corros.* **2021**, *72*, 557–563. [CrossRef]
33. Oguzie, E.; Onuoha, G.; Onuchukwu, A. Inhibitory mechanism of mild steel corrosion in 2 M sulphuric acid solution by methylene blue dye. *Mater. Chem. Phys.* **2005**, *89*, 305–311. [CrossRef]
34. Mu, G.; Li, X.; Liu, G. Synergistic inhibition between tween 60 and NaCl on the corrosion of cold rolled steel in 0.5 M sulfuric acid. *Corros. Sci.* **2005**, *47*, 1932–1952. [CrossRef]
35. Abd El Rehim, S.; Ibrahim, M.; Khalid, K. The inhibition of 4-(2'-amino-5'-methylphenylazo) antipyrine on corrosion of mild steel in HCl solution. *Mater. Chem. Phys.* **2001**, *70*, 268–273. [CrossRef]
36. Benabdellah, M.; Ousslim, A.; Hammouti, B.; Elidrissi, A.; Aouniti, A.; Dafali, A.; Bekkouch, k.; Benkaddour, M. The effect of poly (vinyl caprolactone-co-vinyl pyridine) and poly (vinyl imidazol-co-vinyl pyridine) on the corrosion of steel in H₃PO₄ media. *J. Appl. Electrochem.* **2007**, *37*, 819–826. [CrossRef]
37. Hamdy, A.; El-Gendy, N. Thermodynamic, adsorption and electrochemical studies for corrosion inhibition of carbon steel by henna extract in acid medium. *Egypt. J. Pet.* **2013**, *22*, 17–25. [CrossRef]
38. Ituen, E.; Akaranta, O.; James, A. Evaluation of performance of corrosion inhibitors using adsorption isotherm models: An overview. *Chem. Sci. Int. J.* **2017**, *18*, 1–34. [CrossRef]
39. Kokalj, A. Corrosion inhibitors: Physisorbed or chemisorbed? *Corros. Sci.* **2022**, *196*, 109939. [CrossRef]
40. Eddy, N.; Momoh-Yahaya, H.; Oguzie, E. Theoretical and experimental studies on the corrosion inhibition potentials of some purines for aluminum in 0.1 M HCl. *J. Adv. Res.* **2015**, *6*, 203–217. [CrossRef]
41. Mehra, R.; Soni, A. Cast iron deterioration with time in various aqueous salt solutions. *Bull. Mater. Sci.* **2002**, *25*, 53–58. [CrossRef]

42. Stern, M.; Geary, A.L. Electrochemical polarization: I. A theoretical analysis of the shape of polarization curves. *J. Electrochem. Soc.* **1957**, *104*, 56. [CrossRef]
43. Yan, Y.; Li, W.; Cai, L.; Hou, B. Electrochemical and quantum chemical study of purines as corrosion inhibitors for mild steel in 1 M HCl solution. *Electrochim. Acta* **2008**, *53*, 5953–5960. [CrossRef]
44. Ali, A. Melia azedarach L as eco-friendly corrosion inhibitor for Aluminum in 2M HCl. *J. Mater. Environ. Sci.* **2014**, *5*, 793–802.
45. Quraishi, M.; Singh, A.; Singh, V.; Yadav, D.; Singh, A. Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of *Murraya koenigii* leaves. *Mater. Chem. Phys.* **2010**, *122*, 114–122. [CrossRef]
46. Lebrini, M.; Robert, F.; Lecante, A.; Roos, C. Corrosion inhibition of C38 steel in 1 M hydrochloric acid medium by alkaloids extract from *Oxandra asbeckii* plant. *Corros. Sci.* **2011**, *53*, 687–695. [CrossRef]
47. Kamal, C.; Sethuraman, M. Spirulina platensis—A novel green inhibitor for acid corrosion of mild steel Arab. *J. Chem.* **2012**, *5*, 155–161.
48. Santhini, N.; Jeyaraj, T. The inhibition effect of [3-(4-hydroxy-3-methoxy-phenyl)-1-phenyl-propenone] on the corrosion of the aluminium in alkaline medium. *J. Chem. Pharm. Res.* **2012**, *4*, 3550–3556.
49. Lewis, D.; Ioannides, C.; Parke, D. Interaction of a series of nitriles with the alcohol-inducible isoform of P450: Computer analysis of structure—Activity relationships. *Xenobiotica* **1994**, *24*, 401–408. [CrossRef] [PubMed]
50. Zhou, Z.; Parr, R. Activation hardness: New index for describing the orientation of electrophilic aromatic substitution. *J. Am. Chem. Soc.* **1990**, *112*, 5720–5724. [CrossRef]
51. Adejoro, I.; Ibeji, C.; Akintayo, D. Quantum descriptors and corrosion inhibition potentials of Amodaquine and Nivaquine. *Chem. Sci. J.* **2017**, *8*, 149.
52. Fang, J.; Li, J. Quantum chemistry study on the relationship between molecular structure and corrosion inhibition efficiency of amides. *J. Mol. Struct.* **2002**, *593*, 179–185. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Effects of CTAB (Cetyltrimethylammonium Bromide) and Betaine as Corrosion Inhibitors on the Galvanic Corrosion of Cu Coupled with Au on Print Circuit Board in Etching Solution

HeeKwon Shin and SeKwon Oh *

Industrial Components R&D Department, Korea Institute of Industrial Technology,
Incheon 21999, Republic of Korea

* Correspondence: sk0514@kitech.re.kr; Tel.: +82-32-850-0238; Fax: +82-31-200-2467

Abstract: This study investigates the suppression of galvanic corrosion between copper and gold using cetyltrimethylammonium bromide (CTAB) and betaine as inhibitors. When copper is electrically connected to gold in PCB etching solutions, the substantial difference in their electrochemical potentials leads to the accelerated corrosion of copper, posing severe reliability risks. To mitigate this, we systematically investigated the galvanic corrosion inhibition properties of CTAB and betaine. Through comprehensive electrochemical analyses, it was found that the galvanic corrosion current density of copper, initially at 3.26 mA/cm², decreased significantly to 0.251 mA/cm² with 0.9 mM CTAB, indicating an inhibition efficiency of 92.3%. Furthermore, betaine, at a concentration of 0.1 mM, demonstrated an even higher inhibition efficiency, reducing the corrosion current to 0.03 mA/cm², achieving a 99.1% inhibition rate. These findings provide strong evidence that CTAB and betaine are highly effective in suppressing galvanic corrosion in copper–gold systems, thereby enhancing the long-term performance and reliability of PCBs in electronic applications.

Keywords: galvanic corrosion; Cu; Au; print circuit board; CTAB; betaine

1. Introduction

Copper is extensively used in industries such as electronics, construction, cooling systems, and alloys due to its malleability and ductility [1,2]. Its high electrical and thermal conductivity make it particularly suited for use in wires and pads for electrical connections in printed circuit boards (PCBs). PCBs typically consist of copper circuits and pads, with gold pads applied to enhance adhesion between the solder ball and copper pad [3–5]. The substrate of PCBs generally undergoes etching in acidic solutions to remove contaminants and improve the surface roughness of the metal pads. While etching is typically designed for uncoupled copper, during the process, electrically coupled copper–gold systems can experience over-etching, leading to reliability concerns. This occurs due to the significant electrochemical potential difference between copper ($E^\circ \text{Cu}^{2+}/\text{Cu} = +0.34 \text{ V}$) and gold ($E^\circ \text{Au}^+/\text{Au} = +1.7 \text{ V}$), which results in galvanic corrosion. Copper, being the more active metal, corrodes more rapidly when in contact with gold in the same electrolyte solution [6,7]. The over-etching of copper is caused by this galvanic corrosion, driven by the potential difference between copper ($E^\circ \text{Cu}^{2+}/\text{Cu} = +0.34 \text{ V}$) and gold ($E^\circ \text{Au}^+/\text{Au} = +1.7 \text{ V}$). When two dissimilar metals are placed in the same electrolyte, galvanic corrosion occurs on the metal with more active electrical potential, accelerating copper corrosion [8–10]. To mitigate galvanic corrosion, numerous corrosion inhibitors have been explored. These inhibitors form protective films by adsorbing onto the metal surface [11–22]. Hualiang Huang [23] evaluated copper corrosion inhibition in a NaCl solution using benzimidazole (BI), 2-mercaptobenzimidazole (MBI), and benzotriazole (BTA), with BTA showing the highest inhibition efficiency. Similarly, Shenghua [24] utilized 1-phenyl-3-methyl-5-pyrazolone (PMP) and BTA to inhibit galvanic corrosion between copper and cobalt in H₂O₂ solutions,

achieving a significant reduction in corrosion. The combination of PMP and BTA strongly mitigated galvanic corrosion. Caroline M. Murira [25] reported that CTAB effectively inhibited the galvanic corrosion of copper coupled with gold in a microreactor system, suppressing the corrosion by 99.5% by inhibiting the cathodic reaction on the gold surface. Additionally, Houyi Ma [26] demonstrated that CTAB inhibits copper corrosion in aerated H_2SO_4 solutions via the chemisorption of the n-cetyl group onto the copper surface. The inhibition efficiency varied depending on CTAB concentration and immersion time. Ma proposed an adsorption model, where horizontal binding occurs at low concentrations, transitioning to perpendicular adsorption at higher concentrations. M. El Bakri [27] studied the effects of triazole (TR), 3-amino-1,2,4-triazole (ATA), and CTAB on brass corrosion in a simulated cooling water system using electrochemical methods, SEM, and EDX analysis. ATA proved to be the most effective inhibitor, with improved inhibition efficiency under conditions of increased pH, immersion time, and temperature. The study revealed mixed-type inhibition, dependent on the nitrogen content in the inhibitor's structure. Chaodang Wu [28] investigated the effects of sodium lauryl ether sulfate and betaine as corrosion inhibitors on carbon steel in a NaCl solution, reporting inhibition efficiencies of 82% and 78%, respectively. While studies on corrosion inhibitors such as CTAB and betaine for various metals have been conducted [25–29], research specifically focusing on the galvanic corrosion inhibition of copper coupled with gold in PCB etching solutions remains limited.

In this study, we investigate the effects of CTAB and betaine as corrosion inhibitors on the galvanic corrosion of copper coupled with gold in PCB etching solutions through electrochemical experiments. Additionally, we explore the inhibition mechanisms of these inhibitors on the galvanic corrosion of copper in copper–gold systems.

2. Experimental

For the copper specimen, a copper foil on a copper-clad laminate (CCL) was used to simulate an actual printed circuit board system, and the exposed working area of the copper specimen was 0.2826 cm^2 (diameter 0.5 cm, circular shape).

For the gold specimen, to prevent the formation of an intermetallic compound between copper and gold, nickel was electroplated onto the copper substrate. Nickel electrodeposition was conducted for 15 min at 40°C using a cathodic current density of 100 mA/cm^2 from a solution containing $0.45 \text{ M NiSO}_4 \cdot 6\text{H}_2\text{O}$, $0.126 \text{ M NiCl}_2 \cdot 6\text{H}_2\text{O}$, and $0.8 \text{ M H}_3\text{BO}_3$. Then, gold was electroplated onto the nickel substrate for 10 min and 30 s at 50°C using a cathodic current density of 1.5 mA/cm^2 from a solution containing 50 mM KAu(CN)_2 . The exposed working area of the gold specimen was 0.2826 cm^2 (diameter 0.5 cm, circular shape), with the exposed area ratio of copper to gold being 1:1. The PCB etching solution was prepared by mixing $0.28 \text{ M H}_2\text{SO}_4$, $0.42 \text{ M H}_2\text{O}_2$, $0.28 \text{ M CuCl}_2 \cdot 2\text{H}_2\text{O}$, and deionized water. The pH of the etching solution was 0.47. These were directly added to the etching solution at varying concentrations. Electrochemical experiments were performed at an ambient temperature of $25 \pm 1^\circ\text{C}$ using a Versastat4 electrochemical workstation (Ametek). To investigate the corrosion behavior of copper and gold, a potentiodynamic polarization test was performed using a conventional three-electrode system, with the test specimens (Cu, Au) serving as the working electrode (WE), Pt as the counter electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode (RE) [30]. The open circuit potential (OCP) of the working electrode was measured until it stabilized sufficiently in the solution for 30 min, after which polarization testing was conducted. Once the OCP stabilized, the polarization test was performed with a scan rate of 1 mV/s , with a scan potential range from -200 mV to $+400 \text{ mV}$ relative to the OCP. To study the galvanic current density (i_{couple}) between the copper and gold electrodes in the etching solution, a galvanic corrosion test (zero resistance ammeter test) was conducted using a two-electrode system. The copper specimen was used as the working electrode (WE), and the gold specimen as both the counter electrode (CE) and the reference electrode (RE). The galvanic corrosion test was conducted according to the type and concentration of the corrosion inhibitor, lasting for 600 s.

3. Results and Discussion

Figure 1a illustrates the polarization curves of copper and gold to assess their corrosion behavior in the PCB etching solution. When the polarization curve test was conducted in the PCB etching solution, the corrosion potential of copper was $-7.01 \text{ mV}_{\text{SCE}}$, and the corrosion rate was determined to be $0.49 \text{ mA}/\text{cm}^2$. The polarization behavior of gold in the PCB etching solution is also indicated as a red line in Figure 2.

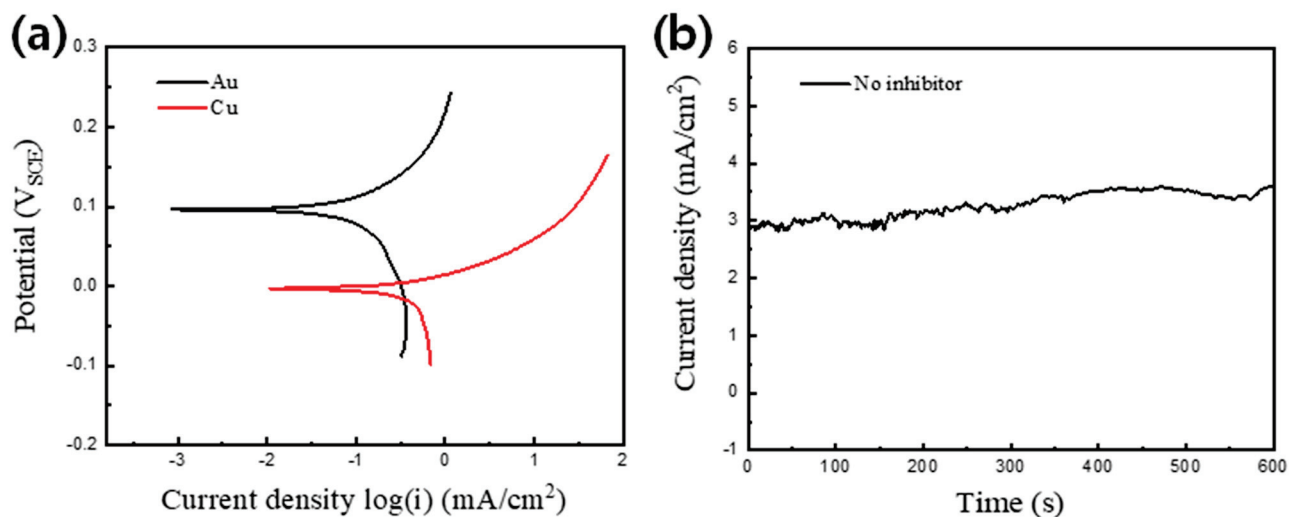


Figure 1. (a) Polarization behaviors of Cu and Au and (b) ZRA test results of Cu coupled with Au in PCB etching solution.

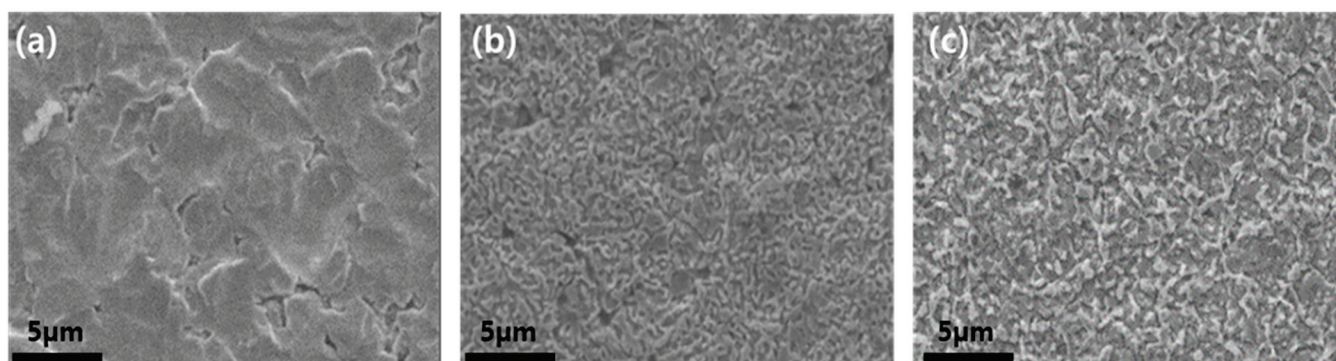


Figure 2. Surface images of (a) single Cu bare sample and (b) after etching of single Cu and (c) galvanic coupled Cu with Au in PCB etching solution.

The E_{corr} and i_{corr} were $91 \text{ mV}_{\text{SCE}}$ and $0.09 \text{ mA}/\text{cm}^2$, respectively. The polarization curve test showed a significant difference in corrosion potential between gold and copper. When these two metals are electrically connected, copper assumes the role of the anode, while gold takes on the role of the cathode, leading to an acceleration in copper corrosion due to galvanic corrosion, primarily because of copper's lower corrosion potential. Figure 1b represents the results of the zero-resistance ammeter (ZRA) test conducted on electrically connected copper and gold in the PCB etching solution. The ZRA test revealed that galvanic corrosion occurs due to the difference in corrosion potential between copper and gold in the PCB etching solution. During this process, the galvanic corrosion current ($i_{\text{couple, (Cu-Au)}}$) flowing between copper and gold was measured at $3.26 \text{ mA}/\text{cm}^2$. Comparing this with the corrosion current of isolated copper measured through the polarization curve test ($i_{\text{corr, Cu}}$) at $0.49 \text{ mA}/\text{cm}^2$, it was found that the galvanic corrosion current increased by 6.6 times. This confirms that in the presence of an electrical connection between copper and gold in the PCB etching solution, the corrosion rate of copper coupled with gold increases 6.6 times compared with single copper. Figure 2a–c shows the surface morphology of single

copper and copper coupled with gold before and after PCB etching. Figure 2a presents the surface morphology of copper before etching, revealing a smooth surface morphology. Figure 2b illustrates the surface morphology of single copper and electrically connected copper to Au (Figure 2c) after etching in the PCB solution. The specimen connected to gold exhibits a rougher surface due to the galvanic corrosion phenomenon. Figure 3a–c reveals the surface morphology measured using atomic force microscopy (AFM).

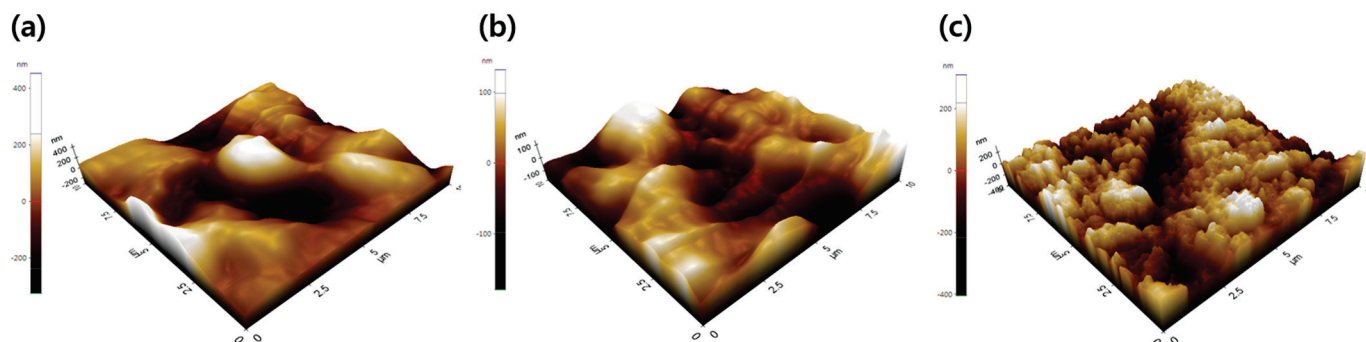


Figure 3. AFM images of (a) single Cu bare sample and (b) after etching of single Cu and (c) galvanic coupled Cu with Au in PCB etching solution.

The surface roughness of copper before etching measures $0.499\ \mu\text{m}$. When treated with the etching solution, the surface roughness of a single copper is measured at $0.527\ \mu\text{m}$, while electrically connected copper exhibits a surface roughness of $0.538\ \mu\text{m}$. This confirms that galvanic corrosion accelerates copper corrosion when it is electrically connected to gold. Figure 4 and Table 1 illustrate the results of ZRA tests conducted to assess the galvanic corrosion inhibition effect of CTAB when copper and gold are electrically connected in the PCB etching solution.

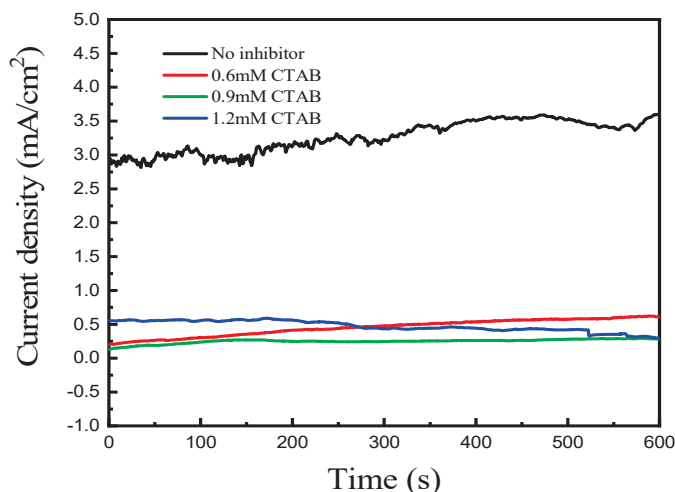


Figure 4. Effects of CTAB concentration on the galvanic corrosion rate of Cu coupled with Au at $25\ ^\circ\text{C}$ in PCB etching solution.

Different concentrations of CTAB, specifically $0.6\ \text{mM}$, $0.9\ \text{mM}$, and $1.2\ \text{mM}$, were introduced into the PCB etching solution. Subsequently, ZRA tests were carried out to measure the galvanic corrosion current, and the galvanic corrosion inhibition effect (IE) for each concentration was compared. Previously, the galvanic corrosion current of Cu coupled with gold in the PCB etching solution was $3.26\ \text{mA}/\text{cm}^2$. However, when $0.6\ \text{mM}$ CTAB was introduced, the corrosion current decreased to $0.453\ \text{mA}/\text{cm}^2$, resulting in an 86.1% corrosion inhibition effect compared with the results without the corrosion inhibitor. At $0.9\ \text{mM}$ CTAB, the current decreased further to $0.251\ \text{mA}/\text{cm}^2$, yielding a 92.3% inhibition effect. In the case of $1.2\ \text{mM}$ CTAB, the corrosion current measured at $0.474\ \text{mA}/\text{cm}^2$,

signifying an 85.5% corrosion inhibition effect. The results of comparing the galvanic corrosion inhibition effect of copper with varying CTAB concentrations revealed that the IE value increased up to 0.9 mM CTAB concentration, indicating an increasing corrosion inhibition effect. Indeed, when the CTAB concentration surpasses 0.9 mM, there is a noticeable reduction in the IE value. This behavior is attributed to the nature of CTAB as a surfactant with amphiphilic character. CTAB effectively inhibits copper corrosion with a hydrophobic tail binding to the metal surface and a hydrophilic head exposed to the solution. This results in the formation of a thin protective film on the metal surface, which prevents direct contact between the metal surface and the corrosive environment, thereby inhibiting the corrosion reaction. At lower concentrations (~0.6 mM), CTAB adsorbs onto metal through a combination of chemisorption of the n-cetyl chain and electrostatic interactions between the $C_{16}H_{33}N(CH_3)^{3+}$ ions and pre-adsorbed bromide ions on the metal surface. This creates a protective layer that minimizes corrosion by preventing direct contact with the corrosive medium [26]. The concentration at which a surfactant begins to form micelles and its corrosion inhibition effect diminishes is known as the critical micelle concentration (CMC). At this concentration, the adsorption behavior shifts as the hydrophobic chains of CTAB molecules interact through van der Waals forces, creating a compact and densely packed barrier that enhances the corrosion inhibition effect. However, as CTAB concentrations exceed 0.9 mM, excessive surface coverage can slightly decrease the inhibition efficiency due to changes in adsorption dynamics, as more molecules are adsorbed, but the effective surface area covered may be reduced. To compare the galvanic corrosion inhibition effects at different betaine concentrations, ZRA tests were conducted using concentrations of 0.05 mM, 0.1 mM, and 0.2 mM, as shown in Figure 5 and Table 2.

Table 1. Galvanic corrosion rate and inhibitor efficiency of Cu coupled with Au with the change in concentration of CTAB.

Concentration of CTAB (mM)	$i_{\text{couple}} \text{ (Cu-Au)}$ (mA/cm ²)	Inhibitor Efficiency
No inhibitor	3.26	
0.6	0.453	86.1%
0.9	0.251	92.3%
1.2	0.474	85.5%

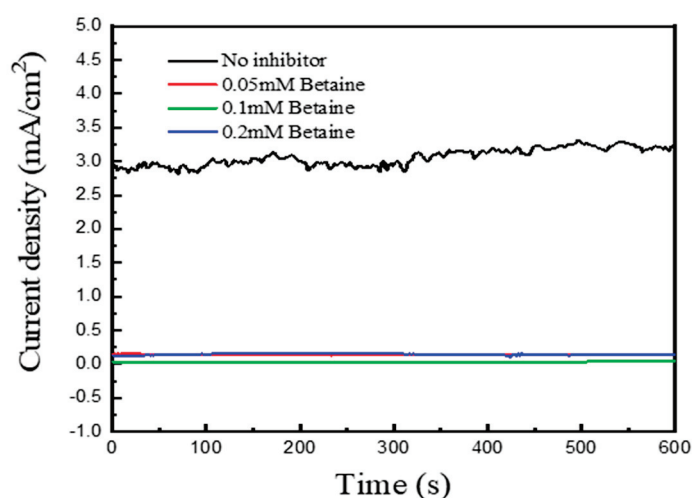
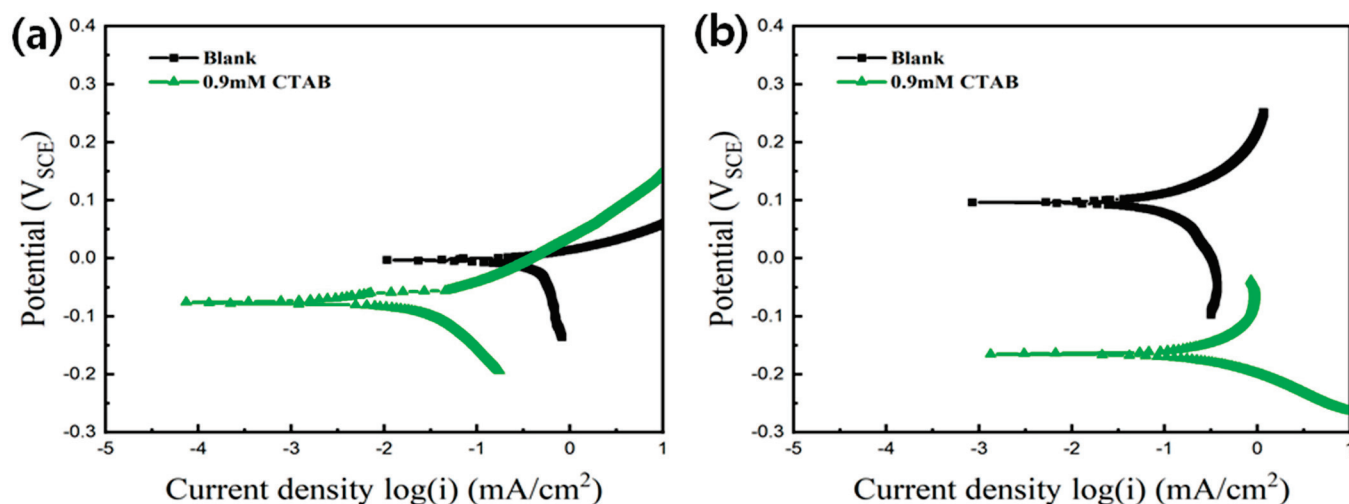


Figure 5. Effects of betaine concentration on the galvanic corrosion rate of Cu coupled with Au at 25 °C in PCB etching solution.

Table 2. Galvanic corrosion rate and inhibitor efficiency of Cu coupled with Au with the change in concentration of betaine.

Concentration of Betaine (mM)	$i_{\text{couple (Cu-Au)}}$ (mA/cm ²)	Inhibitor Efficiency
No inhibitor	3.26	
0.05	0.14	95.7%
0.1	0.03	99.1%
0.2	0.146	95.5%

In the PCB etching solution, the ZRA test results showed that at a betaine concentration of 0.05 mM, the galvanic corrosion current measured 0.14 mA/cm². This represents a 95.7% reduction in galvanic corrosion current compared with the solution without the corrosion inhibitor. When the betaine concentration was increased to 0.1 mM, the galvanic corrosion current dropped to 0.03 mA/cm², demonstrating a corrosion inhibition efficiency of 99.1%. However, at 0.2 mM betaine, the galvanic corrosion current increased slightly to 0.146 mA/cm², resulting in a 95.5% inhibition effect. The comparison of corrosion inhibition effects based on betaine concentration revealed an increase in the IE value up to a concentration of 0.1 mM, indicating an escalating corrosion inhibition effect. However, at concentrations exceeding 0.1 mM, a decrease in the IE value was observed as betaine concentration increased. This phenomenon is attributed to the CMC of betaine, which is 0.1 mM. The hydrophilic head of betaine with polar properties adsorbs to the copper surface and effectively inhibits copper corrosion until the betaine concentration reaches 0.1 mM. However, exceeding concentrations of 0.1 mM, betaine forms micellar structures, leading to a reduction in its corrosion inhibition effect. Figure 6 illustrates the results of the potentiodynamic polarization test, which was conducted to evaluate the effect of CTAB on the corrosion behavior of copper and gold in the PCB etching solution at 25 °C. The test was conducted by adding the most effective concentration of CTAB, which was determined through ZRA testing to be 0.9 mM.

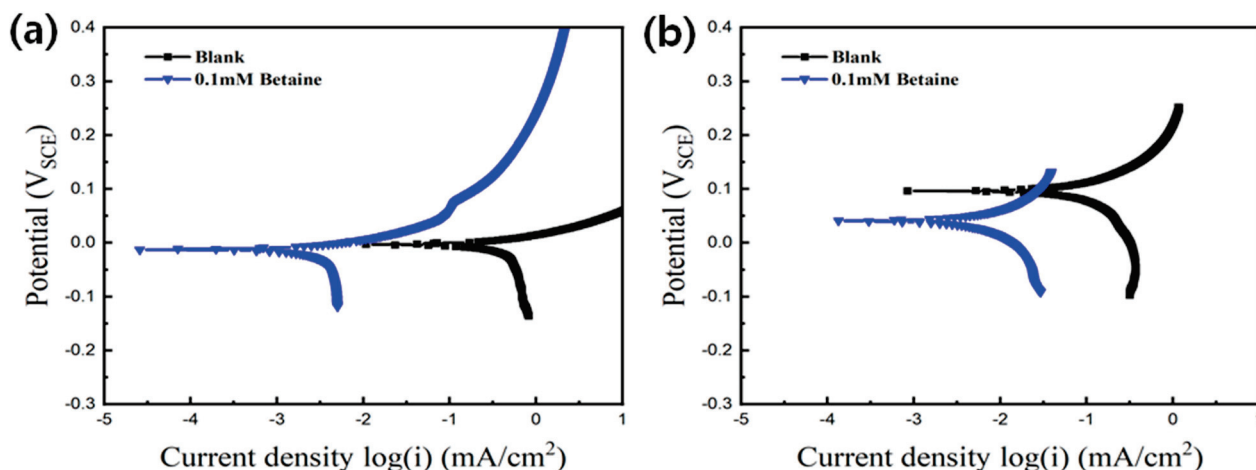
**Figure 6.** Polarization behaviors of (a) single Cu and (b) Au at 25 °C, depending on the presence or 0.9 mM CTAB in PCB etching solution.

The changes in corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were confirmed during this test. The addition of CTAB in the solution significantly decreases both the anodic and cathodic current density of copper; although, the corrosion potential was shifted negatively. The addition of CTAB resulted in a significant decrease in the corrosion potential of copper, from -7.01 mV to -84 mV, and a substantial reduction in the corrosion current density, from 0.49 mA to 0.0281 mA/cm² (Table 3).

Table 3. Corrosion rate and corrosion potential of copper and gold with and without CTAB and betaine.

	Cu		Au	
	i_{corr} (mA/cm ²)	E_{corr} (mV)	i_{corr} (mA/cm ²)	E_{corr} (mV)
Bare	0.49	−7.01	0.09	91
CTAB	0.028	−84	0.386	−172
Betaine	0.0051	−12	0.007	42

The calculated corrosion inhibition effect of CTAB showed a reduction of approximately 94% compared with the solution without the inhibitor. For Au with the addition of CTAB, the corrosion potential value decreased to −172 mV. However, the corrosion current actually increased from 0.007 to 0.386 mA/cm². The CTAB, a cationic surfactant, has a negatively charged head group. It adsorbs well onto the copper surface in the etching solution, inhibiting the corrosion rate. However, it does not affect the corrosion rate of gold due to poor adsorption. This confirms that CTAB adsorbs to the copper surface rather than Au in the PCB etching solution, leading to a corrosion inhibition effect and a significant decrease in corrosion rate. To investigate the influence of betaine as a corrosion inhibitor on the corrosion inhibition of copper and gold, a potentiodynamic polarization test was conducted in a solution containing 0.1 mM betaine (Figure 7).

**Figure 7.** Polarization behaviors of (a) single Cu and (b) Au at 25 °C, depending on the presence or 0.1 mM betaine in PCB etching solution.

The potentiodynamic polarization test results for copper exhibited negligible variation in the corrosion potential (E_{corr}), which consistently fell within the range of −7.01 mV to −12 mV. However, the corrosion current of copper significantly decreased from 0.49 mA/cm² to 0.0051 mA/cm² with the addition of betaine, demonstrating a substantial decrease in corrosion current by the addition of betaine, as shown in Table 3. The potentiodynamic polarization test results for gold specimens revealed that the addition of betaine led to a decrease in the corrosion potential, reducing it from 91 mV to 42 mV. Additionally, the corrosion current of gold specimens decreased from 0.09 mA/cm² to 0.007 mA/cm² with the addition of betaine. These observations confirm that betaine not only adsorbs onto copper specimens, reducing their corrosion rate, but also exhibits a similar protective effect on gold specimens, effectively slowing down their corrosion rate. Betaine (BTA), as a zwitterionic surfactant with both positive and negative charges in its head group, inhibits the corrosion of both copper and gold by adsorbing onto both surfaces, unlike CTAB, which selectively adsorbs only onto copper. Comparing the galvanic corrosion evaluation results in Figures 5 and 6, the galvanic corrosion inhibition effect of betaine was 99.1%, and CTAB had a relatively high galvanic corrosion inhibition rate of 92.3%. These results suggest that betaine, functioning as an amphoteric surfactant, effectively adsorbs onto both copper and gold surfaces, thereby reducing the galvanic corrosion rate.

4. Conclusions

In this study, the inhibiting effects of CTAB and betaine as corrosion inhibitors on the galvanic corrosion of Cu coupled with gold in a PCB etching solution were investigated using electrochemical techniques. The polarization test results demonstrated that copper acts as the anode with a corrosion potential of $-7.01 \text{ mV}_{\text{SCE}}$, while gold functions as the cathode with a corrosion potential of $91 \text{ mV}_{\text{SCE}}$. The substantial difference in corrosion potentials between copper and gold facilitates galvanic corrosion in the etching solution, leading to the accelerated corrosion of copper when the metals are electrically connected. Both CTAB and betaine were evaluated for their effectiveness as corrosion inhibitors. CTAB, at an optimal concentration of 0.9 mM , reduced the galvanic corrosion current density from 3.26 mA/cm^2 to 0.251 mA/cm^2 , corresponding to a corrosion inhibition efficiency of approximately 92.3%. In comparison, betaine showed superior performance as a corrosion inhibitor, with concentrations up to 0.1 mM reducing the corrosion current to 0.03 mA/cm^2 , corresponding to an inhibition efficiency of approximately 99.1%. The differences in inhibition effectiveness are attributed to the interaction of the surfactants with the metal surfaces. CTAB adsorbs preferentially on copper surfaces, effectively reducing corrosion rates by inhibiting anodic processes, whereas betaine exhibits adsorption on both copper and gold surfaces, mitigating galvanic corrosion by blocking both anodic and cathodic reactions. These findings enhance the understanding of surfactants' roles in mitigating galvanic corrosion in PCB manufacturing processes, demonstrating that CTAB and betaine are effective inhibitors under specific conditions.

Author Contributions: Conceptualization, S.O.; methodology, S.O.; software, H.S.; formal analysis, H.S.; investigation, H.S.; resources, S.O.; data curation, H.S.; writing—original draft preparation, S.O.; writing—review and editing, S.O.; visualization, H.S.; supervision, S.O.; project administration, S.O.; funding acquisition, S.O. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Ministry of Trade, Industry and Energy (MOTIE) of Republic of Korea (No. 20019192).

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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

References

1. Miura, S.; Honma, H. Advanced copper electroplating for application of electronics. *Surf. Coat. Technol.* **2003**, *169*, 91. [CrossRef]
2. Li, Z.; Chang, S.; Khuje, S.; Ren, S. Recent Advancement of Emerging Nano Copper-Based Printable Flexible Hybrid Electronics. *ACS Nano* **2021**, *15*, 6211. [CrossRef] [PubMed]
3. Julian, Y.; Hon, C.; Cotterell, B.; Chai, T.C. The mechanics of the solder ball shear test and the effect of shear rate. *Mater. Sci. Eng. A* **2006**, *417*, 259.
4. Wang, J.; Lim, H.K.; Lew, H.S.; Saw, W.T.; Tan, C.H. A testing method for assessing solder joint reliability of FCBGA packages. *Microelectron. Reliab.* **2004**, *44*, 833. [CrossRef]
5. Doranga, S.; Schuldt, M.; Khanal, M. Effect of Stiffening the Printed Circuit Board in the Fatigue Life of the Solder Joint. *Materials* **2022**, *15*, 6208. [CrossRef]
6. Murira, M.C.; Punckt, C.; Schniepp, H.C.; Khusid, B.; Aksay, I.A. Inhibition and Promotion of Copper Corrosion by CTAB in a Microreactor System. *Langmuir* **2008**, *24*, 14269. [CrossRef]
7. Oh, S.; Kim, Y.; Jung, K.; Kim, J.; Shon, M.; Kwon, H. Effects of Temperature and Operation Parameters on the Galvanic Corrosion of Cu Coupled to Au in Organic Solderability Preservatives Process. *Met. Mater. Int.* **2017**, *23*, 290. [CrossRef]
8. Xiao-qing, D.; Yang, Q.; Chen, Y.; Yang, Y.; Zhao, Z. Galvanic corrosion behavior of copper/titanium galvanic couple in artificial seawater. *Trans. Nonferrous Met. Soc. China* **2014**, *24*, 570.
9. Idrac, J.; Mankowski, G.; Thompson, G.; Skeldon, P.; Kihn, Y.; Blan, C. Galvanic corrosion of aluminium–copper model alloys. *Electrochim. Acta* **2007**, *52*, 7626. [CrossRef]
10. Huh, M.; Yu, Y.; Kahn, H.; Payer, J.H.; Heuer, A.H. Galvanic Corrosion during Processing of Polysilicon Microelectromechanical Systems. *J. Electrochem. Soc.* **2006**, *153*, 644. [CrossRef]
11. Oh, S.; Kim, Y.; Shon, M.; Kwon, H. Galvanic Corrosion of Cu Coupled to Au on a Printed Circuit Board; Effects of Pretreatment Solution and Etchant Concentration in Organic Solderability Preservatives Soft Etching Solution. *Met. Mater. Int.* **2016**, *22*, 781. [CrossRef]

12. Huang, H.; Guo, X.; Zhang, G.; Dong, Z. The effects of temperature and electric field on atmospheric corrosion behaviour of PCB-Cu under absorbed thin electrolyte layer. *Corros. Sci.* **2011**, *53*, 1700. [CrossRef]
13. Oh, S.; Kim, Y.; Jung, K.; Park, M.; Shon, M.; Kwon, H. Galvanic Corrosion Behaviors of Cu Connected to Au on a Printed Circuit Board in Ammonia Solution. *Met. Mater. Int.* **2018**, *24*, 67. [CrossRef]
14. Khadom, A.A.; Abod, B.M.; Mahood, H.B.; Kadhum, A.A.H. Galvanic Corrosion of Steel–Brass Couple in Petroleum Waste Water in Presence of a Green Corrosion Inhibitor: Electrochemical, Kinetics, and Mathematical View. *J. Fail. Anal. Preven.* **2018**, *18*, 1300–1310. [CrossRef]
15. Wang, X.; Liu, S.; Yan, J.; Zhang, J.; Zhang, Q.; Yan, Y. Recent Progress of Polymeric Corrosion Inhibitors: Structure and Application. *Materials* **2023**, *16*, 2954. [CrossRef]
16. Samarawickrama, C.; Pöhlker, S.; White, P.; Cole, I.; Keil, P. Corrosion Inhibitor Screening for AA6014 Aluminum Alloy Under Different Ambient Conditions Using a Novel Multielectrode Methodology. *Mol. Syst. Des. Eng.* **2024**, *9*, 518–531. [CrossRef]
17. Kamburova, K.; Boshkova, N.; Radeva, T.; Shipochka, M.; Boshkov, N. Chitosan–Alginate Nanocontainers with Caffeine as Green Corrosion Inhibitors for Protection of Galvanized Steel. *Crystals* **2024**, *14*, 660. [CrossRef]
18. Shwetha, K.M.; Praveen, B.M.; Devendra, B.K. A Review on Corrosion Inhibitors: Types, Mechanisms, Electrochemical Analysis, Corrosion Rate and Efficiency of Corrosion Inhibitors on Mild Steel in an Acidic Environment. *Results Surf. Interfaces* **2024**, *16*, 100258–100277.
19. Wulandari, M.; Nofrizal, N.; Impey, S.; Georgarakis, K.; Raja, P.B.; Hussin, M.H. The Effect of Corrosion Inhibitor on X-65 Steel Weldment in High Flow Rate Conditions. *Case Stud. Chem. Environ. Eng.* **2024**, *10*, 100868–100876. [CrossRef]
20. Hussein, S.A.; Khadom, A.A. Okra Leaves Extract as Green Corrosion Inhibitor for Steel in Sulfuric Acid: Gravimetric, Electrochemical, and Surface Morphological Investigations. *Results Chem.* **2024**, *8*, 101566–101577. [CrossRef]
21. Farh, H.M.H.; Ben Seghier, M.E.A.; Zayed, T. A Comprehensive Review of Corrosion Protection and Control Techniques for Metallic Pipelines. *Eng. Fail. Anal.* **2023**, *143*, 106885–106907. [CrossRef]
22. Xu, Z.; Cao, X.; Wang, P.; Jiang, J.; Zhang, H.; Slaný, M.; Bian, J. Shielding against Erosion: Exploring the Effectiveness of Pre-Erosion Surface Corrosion Inhibitors. *J. Colloid. Interface Sci.* **2024**, *675*, 1130–1148. [CrossRef] [PubMed]
23. Huang, H.; Bu, F. Correlations between the inhibition performances and the inhibitor structures of some azoles on the galvanic corrosion of copper coupled with silver in artificial seawater. *Corros. Sci.* **2020**, *165*, 108413. [CrossRef]
24. Yang, S.; Zhang, B.; Zhang, Q.; Wang, R.; Yu, X.; Wang, C.; Liu, Y. A Study of Cobalt Galvanic and Pitting Corrosion with combination of BTA and PMP. *ECS J. Solid State Sci. Technol.* **2019**, *8*, 416. [CrossRef]
25. Sargolzaei, B.; Arab, A. Synergism of CTAB and NLS surfactants on the corrosion inhibition of mild steel in sodium chloride solution. *Mater. Today Commun.* **2021**, *29*, 102809. [CrossRef]
26. Ma, H.; Chen, S.; Zhao, S.; Liu, X.; Li, D. A Study of Corrosion Behavior of Copper in Acidic Solutions Containing Cetyltrimethylammonium Bromide. *J. Electrochem. Soc.* **2001**, *148*, 482–488. [CrossRef]
27. El Bakri, M.; Touir, R.; Tazouti, A.; Dkhireche, N.; Ebn Touhami, M.; Rochdi, A.; Zarrouk, A. Corrosion Inhibition Study of Brass in Simulated Cooling Water by Triazole Derivatives, Cetyltrimethylammonium Bromide and Their Mixture. *Arab. J. Sci. Eng.* **2016**, *41*, 75–88. [CrossRef]
28. Wu, C.; Yang, H.; Zhang, S.; Han, P.; Sun, H.; Sheng, Z.; Yu, H.; Ma, X. The inhibition performance of anionic surfactant and zwitterionic surfactant toward the corrosion of carbon steel in NaCl solution. *Int. J. Chem. Kinet.* **2023**, *55*, 537. [CrossRef]
29. Arkhipushkin, I.A.; Shikhaliev, K.S.; Potapov, A.Y.; Sapronova, L.V.; Kazansky, L.P. Inhibition of Brass (80/20) by 5-Mercaptopentyl-3-Amino-1,2,4-Triazole in Neutral Solutions. *Metals* **2017**, *488*, 3390. [CrossRef]
30. Tkacz, J.; Slouková, K.; Minda, J.; Drábiková, J.; Fintová, S.; Doležal, P.; Wasserbauer, J. Influence of the Composition of the Hank's Balanced Salt Solution on the Corrosion Behavior of AZ31 and AZ61 Magnesium Alloys. *Metals* **2017**, *7*, 465. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Effective Corrosion Inhibition of Galvanic Corrosion of Cu Coupled to Au by Sodium Dodecyl Sulfate (SDS) and Polyethylene Glycol (PEG) in Acid Solution

HeeKwon Shin and SeKwon Oh *

Research Institute of Intelligent Manufacturing & Materials Technology, Korea Institute of Industrial Technology, Incheon 21999, Republic of Korea

* Correspondence: sk0514@kitech.re.kr; Tel.: +82-32-850-0238; Fax: +82-31-200-2467

Abstract: This study investigates the effects of sodium dodecyl sulfate (SDS) and polyethylene glycol (PEG) on the galvanic corrosion behavior of copper (Cu) coupled to gold (Au) in a printed circuit board (PCB) etching solution. Galvanic corrosion tests using ZRA (zero resistance ammeter) were performed to determine the optimal SDS concentration for corrosion inhibition. The corrosion current between Cu and Au decreased significantly with the addition of SDS, from 3.26 mA/cm² to 0.248 mA/cm² at 4 mM SDS, achieving an inhibitor efficiency (IE) of 92.3%. However, at 15 mM SDS, the corrosion current increased, and IE decreased to 80.5%. This phenomenon is attributed to the critical micelle concentration (CMC) of SDS, where surfactant molecules aggregate and reduce surface adsorption properties. Similarly, ZRA tests were conducted to analyze the effects of PEG on galvanic corrosion. The corrosion current significantly decreased with PEG addition, achieving 98.1% IE at 1 g/L and 99.5% IE at 2 g/L. Beyond this concentration, no significant change in IE was observed, indicating saturation. Potentiodynamic polarization tests were also conducted to study the individual effects of SDS and PEG on Cu and Au. The results showed that SDS effectively inhibited Cu corrosion but had a minimal impact on Au. In contrast, PEG significantly reduced the corrosion current density for both Cu and Au, with reductions of 99.5% and 95.1%, respectively.

Keywords: galvanic corrosion; SDS; PEG; PCB; Cu; Au

1. Introduction

Printed Circuit Boards (PCBs) are utilized as substrates in various electronic devices. These PCBs consist of a multilayer structure composed of copper, nickel, gold, and other metals [1–4]. During the PCB manufacturing process, including an etching process, galvanic corrosion occurs due to the electrochemical potential differences between the metals. In particular, significant galvanic corrosion occurs in patterns where copper and gold are electrically connected, which leads to an over-etching problem of copper pads [5–8]. To prevent galvanic corrosion problems, researchers investigated corrosion inhibitors such as organic surfactants, which function by physically and/or chemically adsorbing onto the metal surface to form a protective film [9–18]. Sodium dodecyl sulfate (SDS) functions effectively as a corrosion inhibitor due to its ability to adsorb onto metal surfaces, forming a protective layer that impedes oxidative and reductive processes. This surfactant's adsorption mechanism enhances its capacity to shield metals from corrosive environments, making it highly effective in diverse applications [19–22]. Honggun Song's research group [19] explored the use of SDS as a corrosion inhibitor for Mg alloys in NaCl environments, achieving a corrosion inhibition efficiency of 89.1% with the addition of 0.06 M SDS. X. Lu [22] and colleagues demonstrated that sodium dodecyl sulfate (SDS) serves as an effective corrosion inhibitor for AZ91 magnesium alloys. Their findings showed that when the alloy was immersed in a 3.5 wt.% NaCl solution with 0.05 M SDS for 48 h, the volume of hydrogen

generated decreased from 9.1 to 0.3 mL/cm². Ali Yousefi [20] employed SDS as a corrosion inhibitor for mild steel in hydrochloric acid solutions. They conducted experiments using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, atomic force microscopy (AFM), and dynamic light scattering, and compared the results with DFT calculations. Jianhong Tan [21] investigated the synergistic inhibition of carbon steel corrosion in acidic media by the combined addition of sodium dodecyl sulfonate (SDS) and potassium iodide (KI). The results indicated that adding 5 mM KI achieved approximately 75% corrosion inhibition, which was significantly enhanced to 96.9% with the inclusion of SDS, demonstrating the effective maximization of corrosion inhibition through the synergistic action of these two inhibitors. Polyethylene glycol (PEG) is also an effective corrosion inhibitor, as it forms a stable protective film on metal surfaces, significantly reducing corrosion rates [22–26]. Its versatility allows it to perform well in various acidic, alkaline, and neutral environments. Inhibition of PEG is further enhanced when combined with other inhibitors, such as cerium nitrate, providing robust protection for metals [27,28]. Fouda et al. examined the effectiveness of polyethylene glycol (PEG) in inhibiting the corrosion of α -brass alloy in a 1 M nitric acid solution, noting that higher concentrations of PEG resulted in greater protection efficiency [23]. H. Boudelloua [24] investigated the impact of polyethylene glycol (PEG) on the corrosion inhibition of mild steel using cerium nitrate in a 0.1 M NaCl solution. They discovered that adding PEG to the cerium nitrate solution improved protection by forming stable corrosion products and reducing cracks in the protective film on the mild steel surface. Jwahr M. AlGhamdi [25] achieved a 97.6% corrosion inhibition efficiency for mild steel in a 1 M HCl environment using PEG-BEC as an inhibitor. The efficiency increased with the rising inhibitor concentration but decreased with increasing temperature (25 °C to 65 °C) and under hydrodynamic conditions. The research group of X.Y. Wang [27] improved the corrosion resistance of aluminum in an alkaline zincate solution by adding PEG. The optimal electrolyte composition, containing 0.2 M ZnO and 2.0 mM PEG, exhibited the highest corrosion inhibition efficiency at 98.8%. Studies on the use of corrosion inhibitors such as SDS and PEG to prevent galvanic corrosion between copper and various dissimilar metals have been published, and there remains a gap in the research specifically examining the inhibition of galvanic corrosion in copper–gold pairs within PCB etching solutions using these inhibitors. This study examined the effectiveness of SDS and PEG as corrosion inhibitors of the galvanic corrosion of copper coupled with gold in PCB etching solutions through electrochemical experiments to elucidate the inhibition mechanisms.

2. Experimental Specimen Preparation

Copper foil on a copper-clad laminate (CCL) was utilized for the copper specimen to mimic a typical printed circuit board configuration. To avert the formation of an inter-metallic compound between copper and gold, nickel was plated onto the copper substrate. Nickel electroplating was performed for 15 min at 40 °C using a cathodic current density of 100 mA/cm² from a solution consisting of 0.45 M NiSO₄·6H₂O, 0.126 M NiCl₂·6H₂O, and 0.8 M H₃BO₃. Subsequently, gold was electroplated on the nickel substrate for 10 min and 30 s at 50 °C with a cathodic current density of 1.5 mA/cm² from a solution containing 50 mM KAu(CN)₂. The working area exposed on the gold specimen was 0.196 cm² (diameter of 0.5 cm, circular shape), maintaining a 1:1 ratio of exposed areas between copper and gold. The etching solution for the PCB was formulated with 0.28 M H₂SO₄, 0.42 M H₂O₂, 0.28 M CuCl₂·2H₂O, and deionized water, with a resultant pH of 0.47. These compounds were directly incorporated into the etching solution at varying concentrations.

Electrochemical Experiments

Electrochemical tests were conducted at 25 °C using a Versastat4 electrochemical workstation (Ametek). To examine the corrosion behavior of copper and gold, a potentiodynamic polarization test was executed, with a three-electrode system comprising the test specimens (Cu, Au) as the working electrode (WE), Pt as the counter electrode (CE), and a

saturated calomel electrode (SCE) as the reference electrode (RE). The open circuit of the working electrode was measured until it sufficiently stabilized in the solution for 30 min, after which polarization testing was conducted. After the open circuit potential (OCP) was stabilized, the polarization test was conducted. The polarization test was measured with a scan rate of 1 mV/s and the scan potential range was from -200 mV to $+400$ mV (OCP). To investigate the galvanic current density ($i_{\text{couple, (Cu-Au)}}$) between the copper and gold electrodes in the etching solution, a galvanic corrosion test (zero resistance ammeter test) was performed using a two-electrode system. The copper specimen served as the working electrode, while the gold specimen functioned as both the counter and reference electrode. The test was carried out for 600 s, varying the type and concentration of the corrosion inhibitor.

3. Results and Discussion

Figure 1 shows the effects of SDS contents on the galvanic corrosion behavior of Cu coupled to Au through the ZRA test. The contents of SDS were verified from 4 mM to 15 mM to confirm the optimum contents for the corrosion inhibition of Cu coupled to Au.

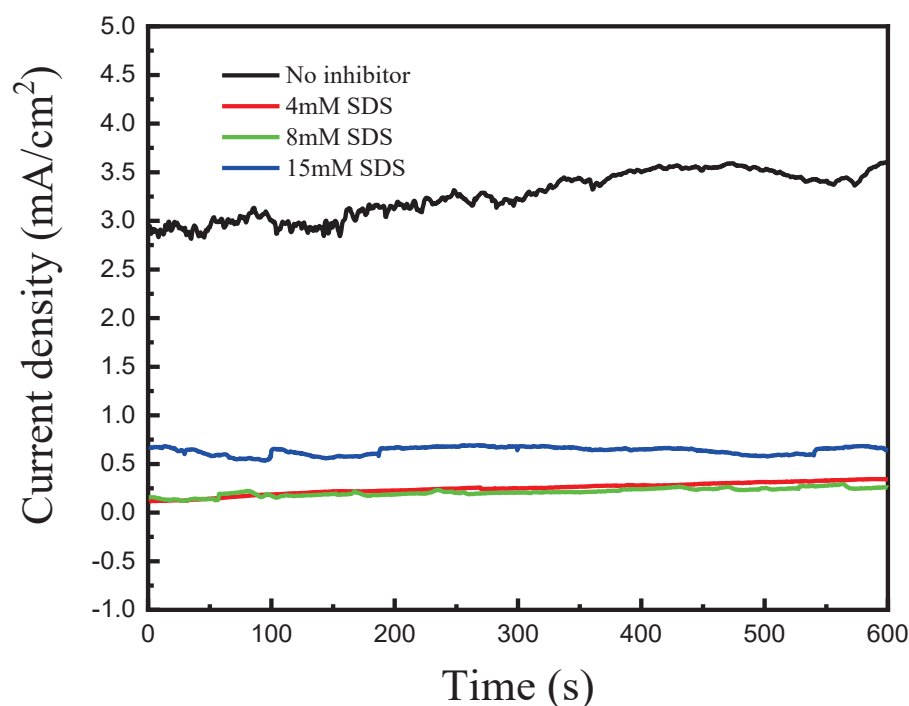


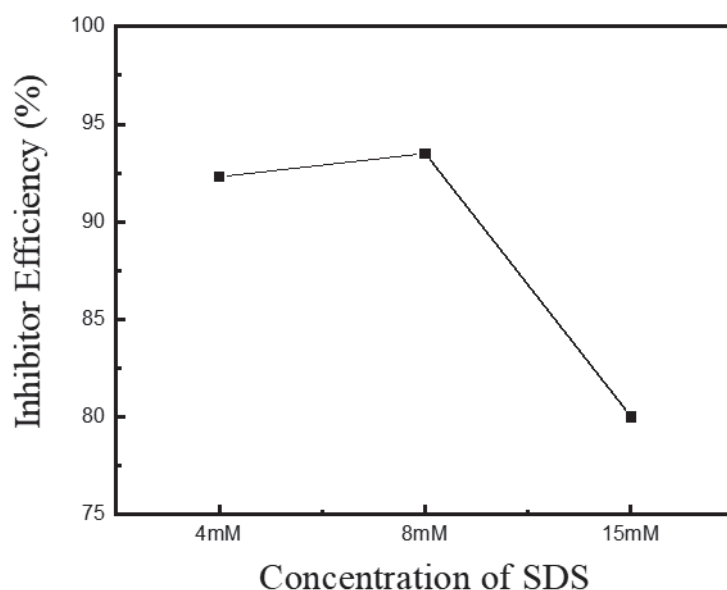
Figure 1. Effects of SDS concentration on the galvanic corrosion rate of Cu coupled to Au at 25°C in PCB etching solution.

Table 1 presents the corrosion current values according to the SDS and PEG concentration and the inhibitor efficiency (IE) calculated from these values. The galvanic corrosion test results indicated that the galvanic corrosion current between Cu and Au significantly decreased with the addition of SDS in etching solution. The galvanic corrosion current ($i_{\text{couple, (Cu-Au)}}$) was decreased from 3.26 mA/cm^2 to 0.248 mA/cm^2 with the addition of 4 mM SDS. The corrosion inhibitor efficiency of the 4 mM SDS was calculated to be 92.3%. With the increase in SDS contents to 8 mM, the galvanic corrosion current was decreased to 0.211 mA/cm^2 and the corrosion inhibitor efficiency was increased to 93.5%.

Table 1. Galvanic corrosion rate and inhibitor efficiency of Cu coupled to Au with the change in concentration of SDS and PEG.

	Concentration (g/L)	$i_{\text{couple, (Cu-Au)}}$ (mA/cm ²)	Inhibitor Efficiency (%)
No inhibitor	-	3.26	
SDS	4	0.248	92.3
	8	0.211	93.5
	15	0.636	80.5
PEG	1	0.06	98.1
	2	0.017	99.5
	4	0.02	99.4

With further increase in the SDS contents to 15 mM, the galvanic corrosion current was measured to be 0.636 mA/cm², which is an increased value compared with the contents under 8 mM SDS. The inhibitor efficiency was also decreased to 80.5% compared with the results of contents under 8 mM SDS. Figure 2 depicts the IE values according to SDS concentration. The comparison of the inhibitor efficiency with varying SDS concentrations reveals that the IE increased up to 8 mM but decreased beyond this concentration.

**Figure 2.** Correlation between corrosion inhibitor efficiency and concentration of SDS.

Upon the addition of SDS to a solution, the molecules initially disperse and adsorb individually onto metal surfaces. As the concentration of SDS increases and exceeds the critical micelle concentration (CMC), self-aggregation occurs, resulting in the formation of micelles. In these micellar structures, the hydrophobic tails converge within the core, while the hydrophilic heads orient outward, interacting with the aqueous environment. This self-assembly plays a crucial role in SDS's behavior as a corrosion inhibitor [17]. The CMC of SDS is known to be 8.2 mM. Below 8.2 mM of SDS, SDS molecules effectively inhibit corrosion reactions by adsorption on metal surfaces. Beyond the CMC, the molecules begin to form micelles rather than adsorbing directly onto the metal surface. While micelle formation helps in surfactant stabilization in solution, it can reduce the availability of individual SDS molecules for surface adsorption [24]. Additionally, micelles may act as a barrier, altering the surface chemistry and reducing the effectiveness of the protective layer, which can re-expose the metal to corrosive agents, resulting in diminished inhibition [29,30].

To compare the galvanic corrosion inhibition effects of polyethylene glycol (PEG) content on copper coupled to gold, ZRA tests were conducted. The PEG concentrations ranged from 1 g/L to 4 g/L and were added to the etching solution to observe the effect on the galvanic corrosion inhibition of copper coupled to gold. Figure 3 shows a significant decrease in the copper galvanic corrosion current when PEG is added to the etching solution.

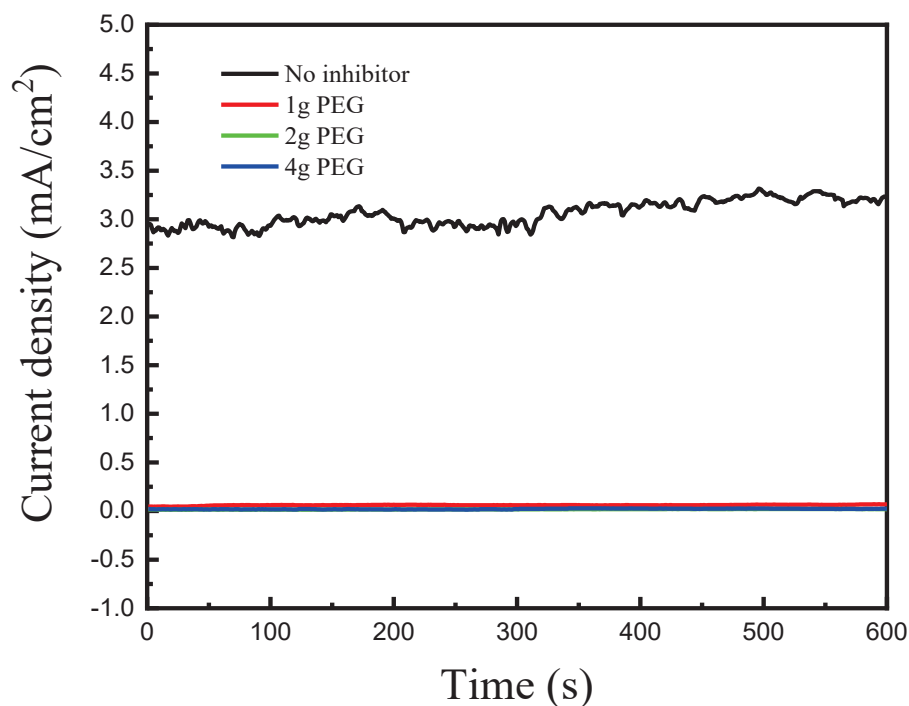


Figure 3. Effects of PEG concentration on the galvanic corrosion rate of Cu coupled to Au at 25 °C in PCB etching solution.

Table 1 presents the corrosion current values and the inhibitor efficiency calculated from the corrosion current for different PEG concentrations. In the galvanic test without any corrosion inhibitor, the galvanic corrosion current of copper and gold was 3.26 mA/cm². With 1 g/L PEG, the corrosion current decreased to 0.06 mA/cm², showing a 98.1% inhibition efficiency compared to the solution without the inhibitor. For 2 g/L PEG, the corrosion current was 0.017 mA/cm², with an inhibition efficiency of 99.5%. At 4 g/L PEG, the corrosion current measured 0.02 mA/cm², resulting in a 99.4% inhibition efficiency. The comparison of inhibitor efficiency with PEG content indicated an increase in IE values up to 2 g/L, enhancing the corrosion inhibition effect. However, beyond 2 g/L, the IE values showed no significant change, indicating saturation. Figure 4 illustrates the IE values with varying PEG concentrations. This phenomenon suggests that PEG, due to its non-polar molecular structure, anchors through physical adsorption or weak chemical interactions, reducing the active area available for corrosion reactions.

This adsorption creates a protective film that isolates the metal, thus inhibiting both the anodic and cathodic reactions responsible for corrosion. To study the influence of SDS as a corrosion inhibitor on the corrosion inhibition behavior of single copper and gold, a potentiodynamic polarization test was conducted in a PCB etching solution containing 8 mM SDS (Figure 5).

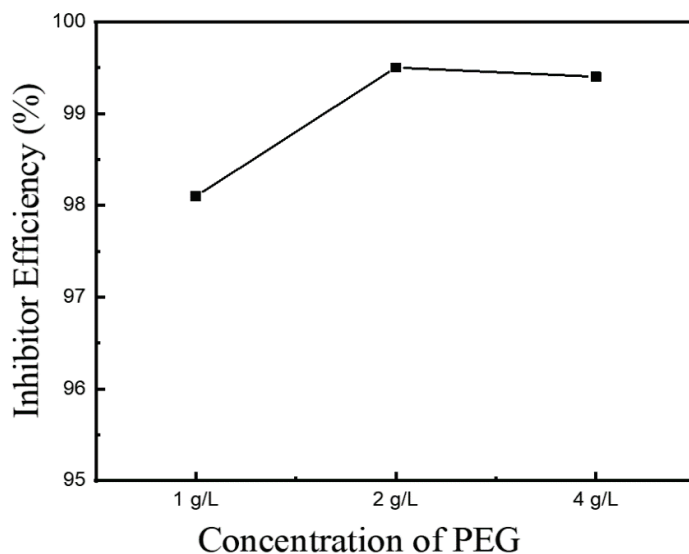


Figure 4. Correlation between corrosion inhibitor efficiency and concentration of PEG.

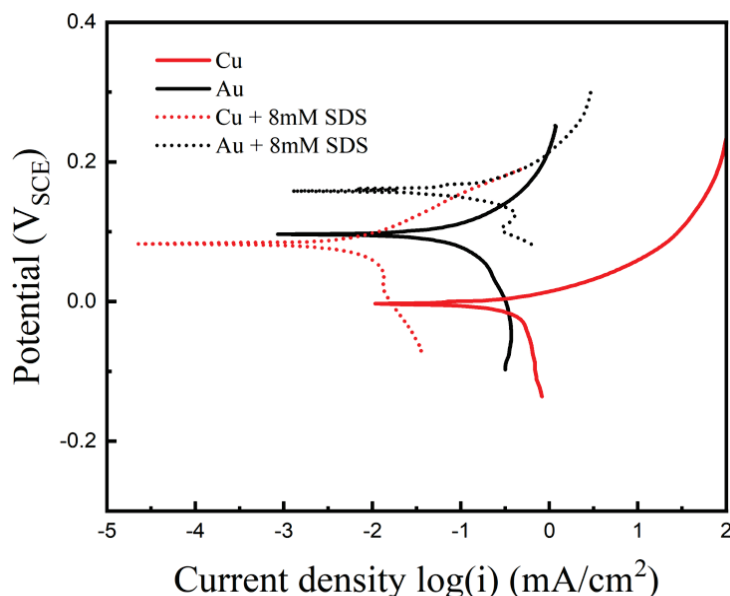


Figure 5. Polarization behaviors of single Cu and Au at 25 °C in the presence and absence of 8 mM SDS of in PCB etching solution.

The potentiodynamic polarization test results for copper exhibit a corrosion potential of -7.01 mV and a corrosion current of 0.49 mA mA/cm^2 . When SDS was added at its critical micelle concentration of 0.8 mM, the corrosion potential of copper increased to 89 mV, and the corrosion current density decreased to 0.0178 mA mA/cm^2 , showing a significant reduction of approximately 96%. This result indicates that the addition of SDS as a corrosion inhibitor substantially decreased the corrosion potential of copper by acting on the copper surface. To investigate the effect of SDS on the corrosion behavior of gold, polarization tests were conducted on gold specimens in an 8 mM SDS solution. The results showed that, in the absence of SDS, the corrosion current density of gold was 0.0992 mA mA/cm^2 , whereas with SDS, it was 0.114 mA mA/cm^2 , indicating no significant change in corrosion current density. However, the corrosion potential increased from 91 mV to 168 mV upon SDS addition. This indicates that the adsorption of SDS onto copper specimens effectively inhibits corrosion, leading to an increase in the corrosion potential and a corresponding decrease in the corrosion rate. Conversely, for gold, the

addition of SDS resulted in a relatively smaller increase in corrosion potential compared to copper, and the corrosion current values remained almost unchanged before and after the SDS treatment. These results indicate that SDS adsorbs less effectively onto gold than on copper, demonstrating its relatively lower efficacy as a corrosion inhibitor for gold. Figure 6 shows that a potentiodynamic polarization test was performed in a PCB etching solution with 2 g/L PEG to investigate the effect of PEG on the corrosion inhibition properties of individual copper and gold. The results of the polarization test demonstrated that the corrosion current density of copper without the addition of PEG measured to be 0.49 mA/cm^2 . However, when 2 g/L of PEG was introduced into the solution, the corrosion current density dramatically decreased to 0.0022 mA/cm^2 . This significant reduction of approximately 99.5% indicates the effectiveness of PEG as a corrosion inhibitor for copper. Furthermore, the addition of PEG resulted in a slight increase in the corrosion potential of copper from -7.01 mV to 31 mV .

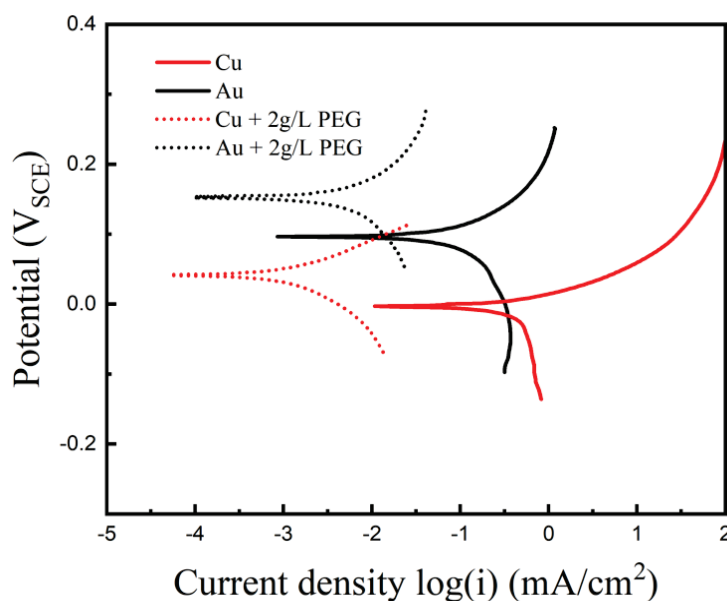


Figure 6. Polarization behaviors of single Cu and Au at 25°C in the presence and absence of 2 g/L PEG of in PCB etching solution.

These observations suggest that PEG adsorbs onto the copper surface in the etching solution, thereby reducing the reaction surface area and slowing down the corrosion rate, while having a minimal impact on the corrosion potential. To further investigate the impact of PEG on the corrosion behavior of gold, polarization tests were conducted on gold specimens in a solution containing 2 g/L of PEG. The results revealed that the corrosion current density of gold without PEG was 0.0992 mA/cm^2 . In contrast, with the addition of PEG, the corrosion current density decreased to 0.0048 mA/cm^2 , indicating a reduction of about 95.1%. Moreover, the corrosion potential of gold increased from 91 mV to 159 mV upon the addition of PEG. These findings clearly indicate that PEG effectively adsorbs onto both copper and gold specimens, enhancing their corrosion resistance. The non-polar molecular structure of PEG allows it to adhere to the surfaces of both copper and gold, thereby improving their corrosion resistance. The ability of PEG to reduce the corrosion current density and slightly alter the corrosion potential demonstrates its potential as an effective corrosion inhibitor in various applications. The adsorption of PEG onto the metal surfaces reduces the available reaction area, thus slowing down the overall corrosion process. This dual functionality of PEG in enhancing corrosion resistance without significantly affecting the corrosion potential is particularly beneficial in environments where both copper and gold are used.

4. Conclusions

This study evaluated the corrosion inhibition performance of SDS (sodium dodecyl sulfate) and PEG (polyethylene glycol) on copper coupled with gold, focusing on their galvanic corrosion behavior. Experimental results from ZRA tests and potentiodynamic polarization revealed clear trends in inhibitor efficiency with varying concentrations of SDS and PEG. For SDS, the galvanic corrosion current between copper and gold significantly decreased with increasing SDS concentration, reaching a maximum inhibitor efficiency (IE) of 93.5% at 8 mM. However, further increasing the concentration to 15 mM resulted in a decrease in IE due to micelle formation, as indicated by the reduction in surface adsorption properties. This behavior aligns with the critical micelle concentration (CMC) of SDS at 8.2 mM, where surfactant molecules begin to self-aggregate, reducing the direct interaction with the copper surface, as evidenced by the increase in galvanic corrosion current. PEG exhibited a different inhibition behavior. The galvanic corrosion current dropped significantly with the increasing PEG concentration, achieving a maximum IE of 99.5% at 2 g/L. Beyond this concentration, no further significant improvement in IE was observed, indicating surface saturation. The potentiodynamic polarization tests further validated these findings, showing that PEG effectively reduced the corrosion current density in both copper and gold, with reductions of 99.5% and 95.1%, respectively, confirming its broad efficacy across both metals.

Author Contributions: Conceptualization, S.O.; Methodology, S.O.; Software, H.S.; Formal analysis, H.S.; Investigation, H.S.; Resources, S.O.; Data curation, H.S.; Writing—original draft, S.O.; Writing—review & editing, S.O.; Visualization, H.S.; Supervision, S.O.; Project administration, S.O.; Funding acquisition, S.O. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Ministry of Trade, Industry and Energy (MOTIE) of Korea (No. 20019192).

Data Availability Statement: Data is contained within the article.

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

References

1. Dorang, S.; Schuldt, M.; Khanal, M. Effect of Stiffening the Printed Circuit Board in the Fatigue Life of the Solder Joint. *Materials* **2022**, *15*, 6208. [CrossRef] [PubMed]
2. Wang, J.; Bai, Z.; Xiao, K.; Gao, X.; Yi, P.; Dong, C.; Wu, J.; Wei, D. Influence of atmospheric particulates on initial corrosion behavior of printed circuit board in pollution environments. *Appl. Surf. Sci.* **2019**, *467*, 889. [CrossRef]
3. Wang, J.; Lim, H.K.; Lew, H.S.; Saw, W.T.; Tan, C.H. A testing method for assessing solder joint reliability of FCBGA packages. *Microelectron. Reliab.* **2004**, *44*, 833. [CrossRef]
4. Julian, Y.; Hon, C.; Cotterell, B.; Chai, T.C. The mechanics of the solder ball shear test and the effect of shear rate. *Mater. Sci. Eng. A* **2006**, *417*, 259.
5. Huh, M.; Yu, Y.; Kahn, H.; Payer, J.H.; Heuer, A.H. Galvanic Corrosion during Processing of Polysilicon Microelectromechanical Systems. *J. Electrochem. Soc.* **2006**, *153*, 644. [CrossRef]
6. Oh, S.; Kim, Y.; Jung, K.; Kim, J.; Shon, M.; Kwon, H. Effects of Temperature and Operation Parameters on the Galvanic Corrosion of Cu Coupled to Au in Organic Solderability Preservatives Process. *Met. Mater. Int.* **2017**, *23*, 290. [CrossRef]
7. Oh, S.; Kim, Y.; Jung, K.; Park, M.; Shon, M.; Kwon, H. Galvanic Corrosion Behaviors of Cu Coupled to Au on a Printed Circuit Board in Ammonia Solution. *Met. Mater. Int.* **2018**, *24*, 67. [CrossRef]
8. Oh, S.; Kim, Y.; Shon, M.; Kwon, H. Galvanic Corrosion of Cu Coupled to Au on a Print Circuit Board: Effects of Pretreatment Solution and Etchant Concentration in Organic Solderability Preservatives Soft Etching Solution. *Met. Mater. Int.* **2016**, *22*, 781. [CrossRef]
9. Idrac, J.; Mankowski, G.; Thompson, G.; Skeldon, P.; Kihn, Y.; Blan, C. Galvanic corrosion of aluminium–copper model alloys. *Electrochim. Acta* **2007**, *52*, 7626. [CrossRef]
10. Murira, M.C.; Punckt, C.; Schniepp, H.C.; Khusid, B.; Aksay, I.A. Inhibition and Promotion of Copper Corrosion by CTAB in a Microreactor System. *Langmuir* **2008**, *24*, 14269. [CrossRef]
11. Arkhipushkin, I.A.; Shikhaliev, K.S.; Potapov, A.Y.; Sapronova, L.V.; Kazansky, L.P. Inhibition of Brass (80/20) by 5-Mercaptopentyl-3-Amino-1,2,4-Triazole in Neutral Solutions. *Metals* **2017**, *488*, 3390. [CrossRef]

12. Koundal, M.; Singh, A.K.; Sharma, C. Study on the effect of imidazolium ionic liquid as a modulator of corrosion inhibition of anionic surfactant sodium dodecyl sulfate (SDS) on mild steel in sodium chloride solution. *J. Mol. Liq.* **2022**, *350*, 118561. [CrossRef]
13. Umorena, S.A.; Solomon, M.M. Synergistic corrosion inhibition effect of metal cations and mixtures of organic compounds: A Review. *J. Environ. Chem. Eng.* **2017**, *5*, 246. [CrossRef]
14. Farahmanda, R.; Sohrabi, B.; Ghaffarinejad, A.; Meymiand, M.R.Z. Synergistic effect of molybdenum coating and SDS surfactant on corrosion inhibition of mild steel in presence of 3.5% NaCl. *Corros. Sci.* **2018**, *136*, 393. [CrossRef]
15. Hussein, S.A.; Khadom, A.A. Okra Leaves Extract as Green Corrosion Inhibitor for Steel in Sulfuric Acid: Gravimetric, Electrochemical, and Surface Morphological Investigations. *Results Chem.* **2024**, *8*, 101566. [CrossRef]
16. Kamburova, K.; Boshkova, N.; Radeva, T.; Shipochka, M.; Boshkov, N. Chitosan–Alginate Nanocontainers with Caffeine as Green Corrosion Inhibitors for Protection of Galvanized Steel. *Crystals* **2024**, *14*, 660. [CrossRef]
17. Wang, X.; Liu, S.; Yan, J.; Zhang, J.; Zhang, Q.; Yan, Y. Recent Progress of Polymeric Corrosion Inhibitors: Structure and Application. *Materials* **2023**, *16*, 2954. [CrossRef]
18. Xu, Z.; Cao, X.; Wang, P.; Jiang, J.; Zhang, H.; Slaný, M.; Bian, J. Shielding against Erosion: Exploring the Effectiveness of Pre-Erosion Surface Corrosion Inhibitors. *J. Colloid Interface Sci.* **2024**, *675*, 1130. [CrossRef] [PubMed]
19. Song, H.; Xu, Z.; Benabou, L.; Yin, Z.; Guan, H.; Ya, H.; Chao, L.; Hu, Z.; Wa, X. Sodium dodecyl sulfate (SDS) as an effective corrosion inhibitor for Mg-8Li-3Al alloy in aqueous NaCl: A combined experimental and theoretical investigation. *J. Magnes. Alloy.* **2023**, *11*, 287. [CrossRef]
20. Yousefi, A.; Javadian, S.; Dalir, N.; Kakemam, J.; Akbari, J. Imidazolium-based ionic liquids as modulators of corrosion inhibition of SDS on mild steel in hydrochloric acid solutions: Experimental and theoretical studies. *RSC Adv.* **2015**, *5*, 11697. [CrossRef]
21. Tan, J.; Guo, L.; Yang, H.; Zhang, F.; Bakri, Y.E. Synergistic effect of potassium iodide and sodium dodecyl sulfonate on the corrosion inhibition of carbon steel in HCl medium: A combined experimental and theoretical investigation. *RSC Adv.* **2020**, *10*, 15163. [CrossRef] [PubMed]
22. Lu, X.L.; Li, Y.; Ju, P.; Chen, Y.; Yang, J.; Qiane, K.; Zhanga, T.; Wang, F. Unveiling the inhibition mechanism of an effective inhibitor for AZ91 Mg alloy. *Corros. Sci.* **2019**, *148*, 264. [CrossRef]
23. Fouda, A.S.; El-Dossoki, F.I.; Shady, I.A. Adsorption and corrosion inhibition behavior of polyethylene glycol on α -brass alloy in nitric acid solution. *Green Chem. Lett. Rev.* **2018**, *11*, 67. [CrossRef]
24. Boudelloua, H.; Hamlaoui, Y.; Tifoutia, L.; Pedrazac, F. Effects of polyethylene glycol (PEG) on the corrosion inhibition of mild steel by cerium nitrate in chloride solution. *Appl. Surf. Sci.* **2019**, *473*, 449. [CrossRef]
25. AlGhamdi, J.M.; Haladu, S.A.; Mu'azu, N.D.; Alqahtani, H.A.; Zubair, M.; Manzar, M.S.; Alkhawildi, F.A.; Kuban, R.Z.M.; AlSubaie, N.F. Polyethyleneglycol bisphenol A epichlorohydrin copolymer (PEG-BEC) as a highly efficient inhibitor for mild steel corrosion in 1M HCl solutions. *S. Afr. J. Chem. Eng.* **2024**, *49*, 326. [CrossRef]
26. Vaidya, N.R.; Aklujkar, P.; Rao, A.R. Modification of natural gums for application as corrosion inhibitor: A review. *J. Coat. Technol. Res.* **2022**, *19*, 223. [CrossRef]
27. Wang, X.Y.; Wang, J.M.; Wang, Q.L.; Shao, H.B.; Zhang, J.Q. The effects of polyethylene glycol(PEG) as an electrolyte additive on the corrosion behavior and electrochemical performances of pure aluminum in an alkaline zincate solution. *Mater. Corros.* **2011**, *62*, 1149. [CrossRef]
28. Umoren, S.A.; Abdullahi, M.T.; Solomon, M.M. An overview on the use of corrosion inhibitors for the corrosion control of Mg and its alloys in diverse media. *J. Mater. Res.* **2022**, *20*, 2060. [CrossRef]
29. Ma, I.A.W.; Ammar, S.; Kumar, S.S.A.; Ramesh, K.; Ramesh, S. A concise review on corrosion inhibitors: Types, mechanisms and electrochemical evaluation studies. *J. Coat. Technol. Res.* **2022**, *19*, 241–268. [CrossRef]
30. Bijapur, K.; Molahalli, V.; Shetty, A.; Toghan, A.; De Padova, P.; Hegde, G. Recent trends and progress in corrosion inhibitors and electrochemical evaluation. *Appl. Sci.* **2023**, *13*, 10107. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Corrosion Properties and Surface Chemistry of Graphene Oxide-Coated AZ91D Magnesium Alloy in Sodium Chloride Solution

Nathalia Sartori da Silva, Aila Cossovan Alves, Jaine Aparecida da Silva Pereira, Leandro Antonio de Oliveira, Mara Cristina Lopes de Oliveira and Renato Altobelli Antunes *

Center for Engineering, Modeling and Applied Social Sciences (CECS), Federal University of the ABC (UFABC), Santo André 09210-580, SP, Brazil; nathalia.sartori@ufabc.edu.br (N.S.d.S.); aila.cossovan@ufabc.edu.br (A.C.A.); jaine.pereira@ufabc.edu.br (J.A.d.S.P.); leandro.oliveira@ufabc.edu.br (L.A.d.O.); mara.oliveira@ufabc.edu.br (M.C.L.d.O.)

* Correspondence: renato.antunes@ufabc.edu.br

Abstract: In the present work, the corrosion properties and the surface chemistry of a graphene oxide-coated AZ91D alloy were investigated. The coatings were deposited on the substrate specimens by immersion in solutions with GO concentrations of 0.05% and 0.1% (*m/v*). An intermediate silane layer was firstly obtained to improve adhesion between the GO films and the AZ91D substrate. The electrochemical behavior of the coated specimens was assessed using electrochemical impedance spectroscopy and potentiodynamic polarization curves in 3.5 wt.% NaCl solution. The surface chemistry was assessed using X-ray photoelectron spectroscopy (XPS). The GO films consisted of a mixture of carbon-based bonds (C-C, C-OH, C=O, and O-C=O). The surface morphology of the coated specimens was examined using scanning electron microscopy. The results revealed that the compactness of the GO films was dependent on the deposition conditions. The corrosion resistance was affected by the surface morphology.

Keywords: AZ91D magnesium alloy; graphene oxide; coating; surface chemistry; corrosion

1. Introduction

The AZ series of magnesium alloys has found applications in the automotive and aircraft industries. The lightweight AZ91D alloy, for instance, is especially employed for use in structural components in the automotive industry due to its excellent castability and suitable mechanical strength [1–3]. Nonetheless, the well-known intrinsic low corrosion resistance of magnesium alloys is a major drawback for large-scale applications [4,5].

In order to take advantage of the attractive engineering properties of magnesium alloys, such as high strength-to-weight ratio and good formability and weldability, it is imperative to employ corrosion protection methods [6–8]. Traditional methods rely on microstructural and compositional control [9,10] combined with suitable surface treatments such as anodization or plasma electrolytic oxidation, conversion coatings, and so on [11–15].

Graphene-related materials have gained importance in several fields owing to an impressive set of attributes, such as high mechanical strength, surface functionalization, wear resistance, self-lubrication, and impermeability [16–20]. The chemical inertness of graphene materials has been advantageously explored for corrosion protection applications, either as additive for organic coatings or as a topcoat itself [21–23].

Graphene oxide (GO) has been used as corrosion-protective coating for magnesium alloys instead of pure graphene sheets. This is due to its stronger interaction with the metal's surface [24,25]. GO contains carbonyl, epoxide, and hydroxyl groups, which account for its hydrophilic nature that makes it readily dispersible in water or polar solvents. As a consequence, stable aqueous solutions of GO in water can be prepared [26]. Neupane

et al. [27] successfully obtained GO coatings on the surface of pure magnesium. The GO layer was formed on aqueous solutions of dispersed GO particles over previously silanized samples. Silanization was employed to promote the formation of silanol groups (Si-OH) from reactions of silane and water. The silanol groups can attach to the metal surface after a proper hydration treatment, enabling the formation of Si-O-metal bonds [28]. The combined silanization pre-treatment and GO coating increased the corrosion resistance of the magnesium surface. The beneficial effect of GO coating on the corrosion properties of bulk metallic surfaces was also observed by Prasai et al. [29]. Copper and nickel substrates were coated by graphene layers obtained using chemical vapor deposition or which were mechanically transferred onto the substrates. They observed the corrosion rate decreased one order of magnitude for the graphene-coated surfaces with respect to the pristine materials. Recently, Chu et al. [30] employed an innovative concept to obtain hybrid graphene oxide-polyvinyl alcohol (GO-PVA) coatings on Mg-Zn-Ca alloy substrates. They aimed to improve the interaction of GO with the magnesium surface by means of an organic medium that promotes a crosslinking effect, such as PVA. Effective barrier properties of the hybrid GO-PVA layer decreased the corrosion rate of the Mg alloy by one order of magnitude with respect to the bare substrate. By contrast, a single GO layer did not increase the corrosion resistance due to its poor interaction with the bulk metallic surface.

It is, therefore, imperative that chemical interaction exists between the graphene oxide layer and the metallic substrate in order to consolidate the corrosion protection ability of the graphene-based topcoat. In this respect, X-ray photoelectron spectroscopy (XPS) can be regarded as a powerful technique to assess such interactions. Lin et al. [31] studied the corrosion behavior of nickel–aluminum–bronze substrates with GO coatings. XPS was employed to examine the formation of chemical bonds between the metallic substrate and the GO layer. They were capable of identifying the main carbon chemical states and correlate them with the GO/metallic alloy interfacial bonding. Furthermore, they observed the dependence of corrosion resistance of the coated substrates with the presence of these chemical interactions.

In spite of the knowledge accumulated so far, the literature is still scarce on the relationship between the surface chemistry and the corrosion-protective properties of GO-coated magnesium alloys. In this work, we shed additional light on this subject by studying the electrochemical behavior of a GO-treated AZ91D magnesium alloy and its connections to the surface morphology and chemical composition. Silanization pre-treatment was combined with GO deposition to promote suitable bonding between the bulk metal surface and the topcoat. XPS analysis was employed to assess the surface chemical's states. The corrosion behavior was evaluated using electrochemical impedance spectroscopy and potentiodynamic polarization.

2. Materials and Methods

2.1. Materials and Sample Preparation

AZ91D magnesium alloy (nominal chemical composition in wt.%: Al 8.3–9.7%; Mn 0.15%; Zn 0.35–1.00%; Si 0.1%; Fe 0.005%; Cu 0.3%; Ni 0.002%; Mg balance) was kindly provided by Rima Industrial Magnésio S/A (Belo Horizonte, Brazil) as a die-cast ingot. The as-received material was cut into small pieces with approximate dimensions of $1.8 \times 1.8 \times 0.5$ cm using silicon carbide disks in a conventional cut-off machine. Next, samples were ground using waterproof silicon carbide papers up to grit 2000. After grinding, samples were carefully rinsed with ethanol, washed with distilled water, and dried in a warm air stream provided by a conventional heat gun.

In order to increase the number of OH^- groups on the surface of the AZ91D, an initial pretreatment was undertaken by immersing the ground samples in a 3 M NaOH solution at room temperature for 1 h. The hydrolyzed surface was washed with distilled water and let to naturally dry in the air. After the NaOH-based treatment, samples were silanized in a solution consisting of a mixture of 5 vol% 3-Aminopropyltriethoxysilane (APTES), 5 vol%

water, and 90 vol% ethanol at room temperature for 1 h. Right after, the samples were cured at 100 °C for 1 h in a laboratory oven.

GO was purchased from Graphenea Inc. (Cambridge, MA, USA) as an aqueous suspension. Different GO-based solutions were prepared from the GO suspensions in order to achieve distinct GO contents. The different samples are described in Table 1. The as-received (AR) and silanized conditions (without GO coating) were also tested for comparison. The GO coating was prepared by immersing the silanized specimens in the GO solutions under soft magnetic stirring for different times, as described in Table 1. After deposition, the specimens were rinsed with distilled water and dried in open air.

Table 1. Samples tested in the present work.

Sample	Pretreatment	GO Concentration (wt.%)	Time (h)
AR	----	----	----
Silanized	Immersion in 3 M NaOH solution for 1 h + silanization with APTES	----	----
0.05% 2 h	Immersion in 3 M NaOH solution for 1 h + silanization with APTES	0.05	2
0.05% 4 h	Immersion in 3 M NaOH solution for 1 h + silanization with APTES	0.05	4
0.1% 2 h	Immersion in 3 M NaOH solution for 1 h + silanization with APTES	0.1	2
0.1% 4 h	Immersion in 3 M NaOH solution for 1 h + silanization with APTES	0.1	4

2.2. Characterization

The surface morphology of the different GO coatings was examined using scanning electron microscopy (Jeol 6010 LA, Tokyo, Japan). The surface chemical states were analyzed with XPS using a Thermo VG K-alpha+ spectrometer operating with Al-K α radiation source (1486.6 eV). The pressure in the analysis chamber was approximately 10^{-7} Pa. High-resolution spectra were fitted using a combination of Lorentzian–Gaussian functions in the Advantage[®] software (version 5.976) and Smart algorithm for background subtraction. Complementary analysis of the functional groups of the silane and GO layers was carried out by Fourier Transform Infrared spectroscopy (FTIR, Varian 660-IR, Santa Clara, CA, USA) in the attenuated total reflection (ATR) mode in the wavenumber range of 600 to 4000 cm⁻¹. Baseline correction was carried out using a second derivative method. Smoothing was also applied to reduce noise with the Savitsky–Golay (SG) function with a polynomial order of 2.

The electrochemical behavior of the different samples was assessed in an Autolab M101 potentiostat/galvanostat. A conventional three-electrode cell configuration was used for the measurements with a platinum wire as the auxiliary electrode, Ag/AgCl (KCl, 3 M) as reference, and the AZ91-D alloy in the AR and treated states as the working electrodes. The open circuit potential (OCP) was monitored for 1 h. Next, electrochemical impedance spectroscopy (EIS) measurements were made at the OCP in the frequency range of 100 kHz to 0.01 Hz using a sinusoidal perturbation signal with an amplitude of ± 10 mV (rms) and an acquisition rate of 10 points per frequency decade. Potentiodynamic polarization curves were obtained right after the EIS measurements. The potential was swept from -300 mV versus the OCP up to 0 V_{Ag/AgCl} or up to a current of 10 mA was achieved. The sweep rate was 1 mV·s⁻¹. The tests were conducted in quadruplicate. All measurements were carried out in 3.5 wt.% NaCl solution at room temperature. The working electrode area exposed to solution was 2 cm².

3. Results

3.1. Morphological Examination

Figure 1 shows macroscopic images of the AR, silanized, and GO-coated samples. The visual aspects of the AR and silanized samples were quite similar, whereas the GO coating can be promptly seen in the other samples with its typical black surface. No distinguishable features could be seen on the GO-coated surfaces by only visually inspecting them.

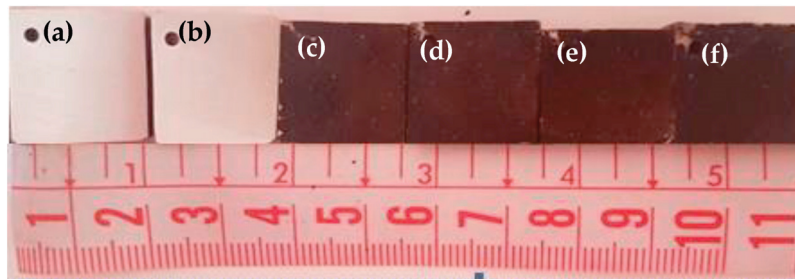


Figure 1. Macroscopic images of the different AZ91D samples: (a) AR; (b) silanized; (c) 0.05% 2 h; (d) 0.05% 4 h; (e) 0.1% 2 h; (f) 0.1% 4 h.

SEM analysis was carried out in order to gain further understanding on the morphological aspects of the different samples. Figure 2 shows the SEM micrographs of the AZ91D samples.

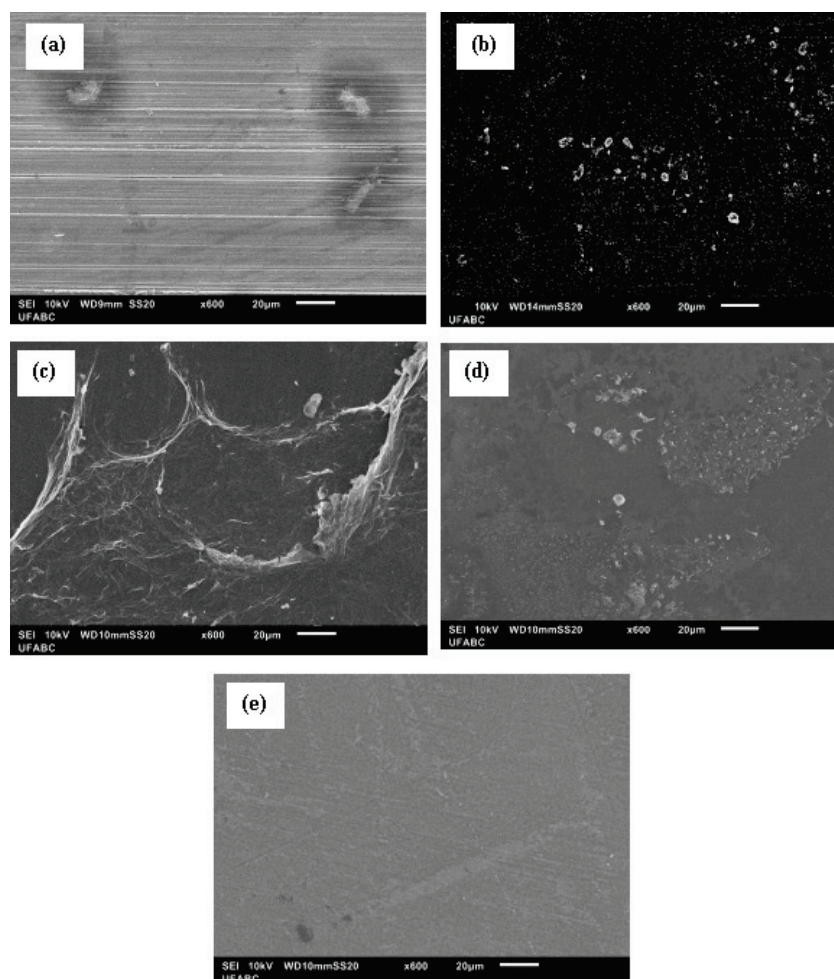


Figure 2. SEM micrographs of the AZ91D alloy samples: (a) AR; (b) 0.05% 2 h; (c) 0.05% 4 h; (d) 0.1% 2 h; (e) 0.1% 4 h.

The morphology of the AR condition (Figure 2a) exhibited the ground markings of the surface preparation procedure. The surface aspect of the coated samples is completely different. The ground markings are no longer visible, as the GO coating covers the whole surface. The coatings obtained in both solutions at 2 h displayed a granular aspect (Figure 2b,d) with an irregular morphology, especially in the solution with a GO concentration of 0.05 wt.% (Figure 2b). By increasing the immersion time to 4 h, the coatings became smoother and fewer defects were observed. Sample 0.05% 4 h (Figure 2c) spread over the surface, showing a layered structure. Sample 0.1% 4 h (Figure 2e), in turn, displayed a uniform surface aspect.

3.2. Spectroscopic Analyses

The surface chemical states of the different AZ91D samples were assessed using XPS. Figure 3 shows the survey spectra of AR, silanized, and 0.1% 4 h samples. The spectra of the pure GO and the other GO-coated samples are shown as Supplementary Materials (Figure S1). In the AR condition, the main photoelectron lines were assigned to magnesium and oxygen. Carbon was found as surface contamination (adventitious carbon), as observed by other authors for the air-formed surface oxide of magnesium alloys [32,33]. In the silanized sample, in addition to these species, a small silicon peak appears, as well as nitrogen. These elements are part of the APTES molecule. The spectrum of the 0.1% 4 h sample, in turn, exhibited a stronger C 1s peak and the magnesium signal was attenuated due to the presence of the GO film.

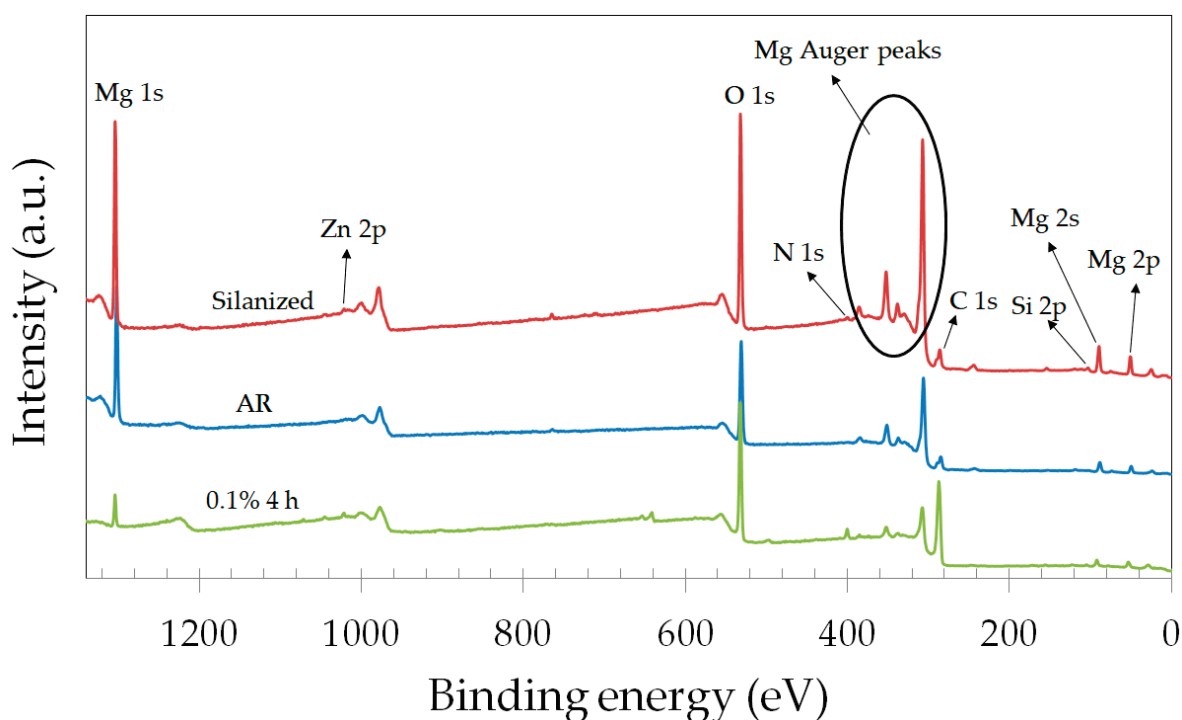
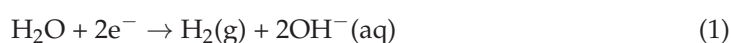
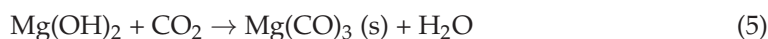
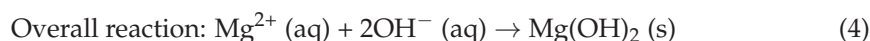
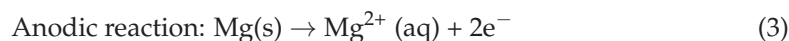
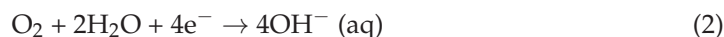


Figure 3. Representative XPS survey spectra AZ91D samples.

Figure 4 shows the high-resolution spectra for the Mg 1s, O 1s, Al 2p, and Zn 2p photoelectron lines of the AR sample. The Mg 1s spectrum (Figure 4a) was fitted with three peaks centered at 1303.7, 1304.7, and 1305.6 eV, which were assigned to metallic magnesium, $\text{Mg}(\text{OH})_2$, and MgCO_3 , respectively, in accordance with other reports [34,35]. The naturally formed oxide film on magnesium and its alloys is mainly comprised of $\text{Mg}(\text{OH})_2$ which, in turn, reacts with the CO_2 in the atmosphere, forming MgCO_3 , as shown in the sequence of reactions (1)–(5) [36].

Cathodic reaction:





The O 1s spectrum (Figure 4b) was deconvoluted with three peaks, which were assigned to oxide-type bonds (O^{2-}), hydroxide-type bonds (OH^-), and adsorbed water ($\text{H}_2\text{O}_{\text{ads}}$), in agreement with the literature [37,38]. Hydroxide bonds predominate over oxide ones, likely due to the relatively large amount of Mg(OH)_2 formed on the AZ91D surface, as Mg is the main constituent of the alloy.

Figure 4c shows the Al 2p high-resolution spectrum of the AR sample. One single peak was observed. It was centered at 74.1 eV, which is typically assigned to Al^{3+} species such as AlOOH , Al(OH)_3 , and Al_2O_3 , as reported by other authors [39,40]. The signal of Zn 2p was very weak, as seen in Figure 4d. This is likely due to the relatively small amount of zinc in the AZ91D alloy (less than 1.0 wt.%). Thus, it is not one of the main constituents of the native oxide film, which is mainly comprised of magnesium and aluminum oxidized species.

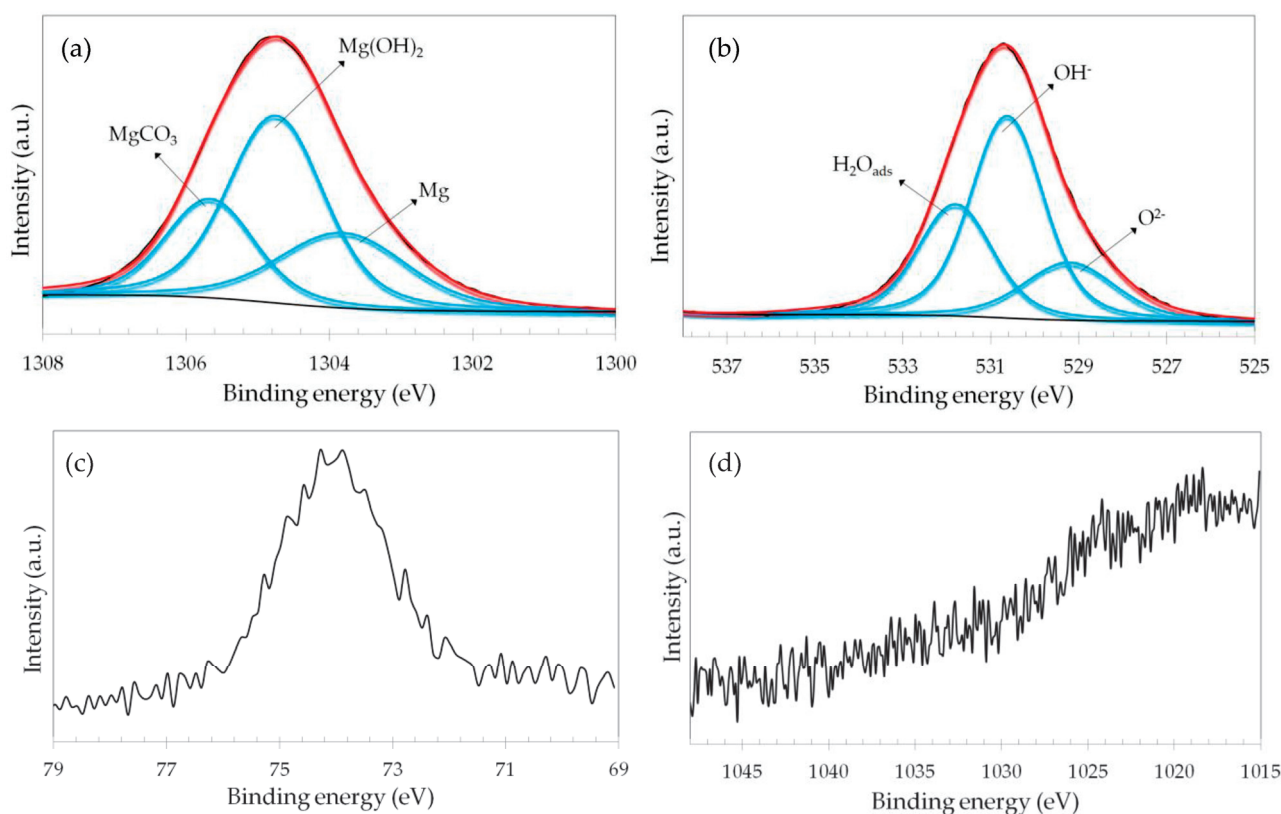


Figure 4. XPS high-resolution spectra of the AR sample (uncoated AZ91D alloy): (a) Mg 1s; (b) O 1s; (c) Al 2p; (d) Zn 2p.

Figure 5 shows the XPS high-resolution spectra of the silanized sample (without GO coating). The C 1s peak (Figure 5a) was deconvoluted with five peaks. The lowest-binding energy component was assigned to C-Si bonds (284.2 eV). The second component (at approximately 285 eV) was assigned to C-C/C-H bonds. The peak at 286 eV was assigned to C-N, where the higher-binding energy components were due to C-O and C=O bonds. These peaks are in good agreement with the literature [41]. The O 1s spectrum (Figure 5b) was fitted with three peaks. The lowest-binding energy component was assigned to C-O-Si/C-O bonds. The intermediate component was assigned to C-O-C/C-OH bonds, whereas

the highest-binding energy component was due to siloxane-type bonds of the APTES molecule (Si-O-Si), as reported in the literature [42,43].

The Si 2p spectrum of the silanized sample is presented in Figure 5c. It was deconvoluted with two peaks that were assigned to Si-O-Mg and Si-O-Si bonds, in accordance with other published results [44,45]. The presence of Si-O-Mg bonds gives unequivocal evidence of the interaction between the APTES molecule and the AZ91D substrate. The N 1s spectrum is shown in Figure 5d. It was fitted with two components. The first peak is centered at 339.6 eV and was assigned to primary amine bonds (NH₂). The highest-binding energy peak (at approximately 402 eV) was due to secondary amine bonds, in good agreement with the literature [45].

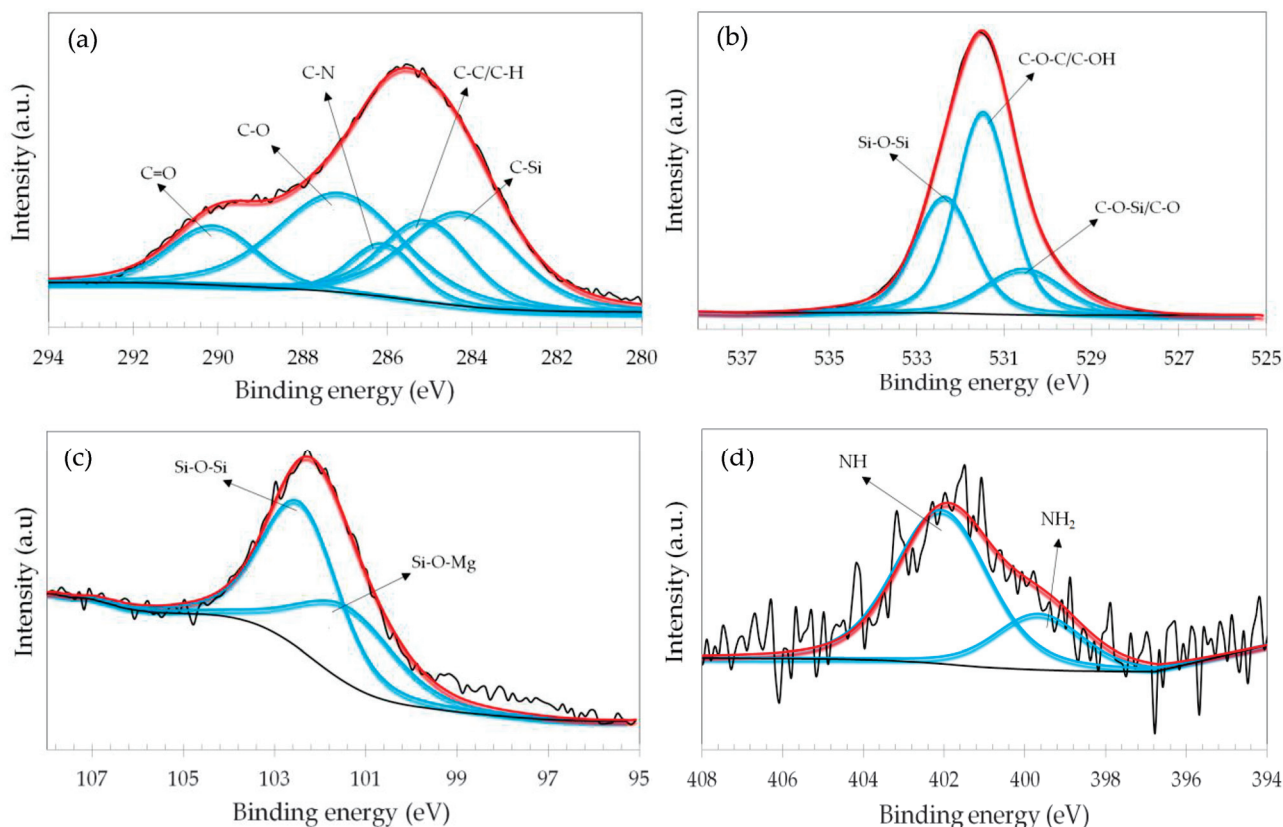


Figure 5. XPS high-resolution spectra of the silanized sample (without GO coating): (a) C 1s; (b) O 1s; (c) Si 2p; (d) N 1s.

Figure 6 shows the XPS high-resolution spectra of the 0.1% 4 h sample for the C 1s, O 1s, N 1s, and Si 2p photoelectron lines. This sample was chosen as representative of all GO-coated samples due to its high corrosion resistance, as will be discussed in Section 3.3. The C 1s, N 1s, and Si 2p spectra of the other GO-coated samples are very similar to those of 0.1% 4 h. They are presented as Supplementary Materials. The O 1s high-resolution spectra of the other GO-coated samples exhibited one additional feature that is not encountered in the spectrum of the 0.1% 4 h sample. They are shown in Figure 7.

The C 1s spectrum of the 0.1% 4 h sample (Figure 6a) was deconvoluted with five peaks, in accordance with the literature for the XPS results of graphene oxide, showing its typical functional groups [46–48]. The same components were also observed for the C 1s photoelectron lines of the other GO-coated samples, as shown in Figure S2 (Supplementary Materials). A pure GO sample was also analyzed using XPS, and its C 1s spectrum is shown in Figure 8a. The same components were also observed. They were assigned to C=C (284.4 eV), C-C (285.4 eV), C-OH (286.4 eV), C=O (288.0 eV), and O-C=O (290.0 eV) bonds of the GO coating on the surface of the AZ91D substrate.

The O 1s spectrum of the 0.1% 4 h sample is displayed in Figure 6b. It was deconvoluted with three components assigned to O=C/O=C-OH, C-OH, and C-O-C bonds, in good agreement with other reports for the O 1s photoelectron line of graphene oxide [49,50]. The O 1s spectrum of the GO sample (Figure 8b) exhibited the same components. However, if one considers the other GO-coated samples, one additional feature was observed. As shown in Figure 7, besides the three components already mentioned above for the pure GO and 0.1% 4 h samples, one additional peak was encountered at approximately 535 eV. This peak was due to an Auger peak of sodium (Na KLL), as reported in the literature [51]. Sodium species originate from the NaOH pretreatment of the AZ91D substrate to enhance its interaction with the intermediate APTES layer before GO deposition. Thus, the presence of such a peak in the O 1s spectrum suggests that the GO layer is less defective on the 0.1% 4 h sample when compared to the other GO-coated samples, as it did not display the Na KLL peak. In fact, the surface morphology of 0.1% 4 h (Figure 2e) indicated that it exhibited the best surface coverage and less-defective topography among the GO-coated samples. Yet, it is interesting to note that the intensity of the Na KLL peak decreases as the GO concentration and deposition time increased (see the evolution of the Na KLL intensity from Figure 7c to Figure 7a), thus indicating that the coverage of the NaOH-treated AZ91D substrate was gradually improved. Furthermore, as evident in Figure 7, the relative area of the peak assigned to hydroxyl bonds (C-OH) increased with the GO concentration and immersion time. These bonds are typical functional groups present in the basal planes of GO [52]. Hence, its increased relative fraction in the 0.1% 2 h sample (Figure 7a) with respect to the samples obtained at a GO concentration of 0.05% (Figure 7b,c) suggests an increased coverage of the substrate with the GO film.

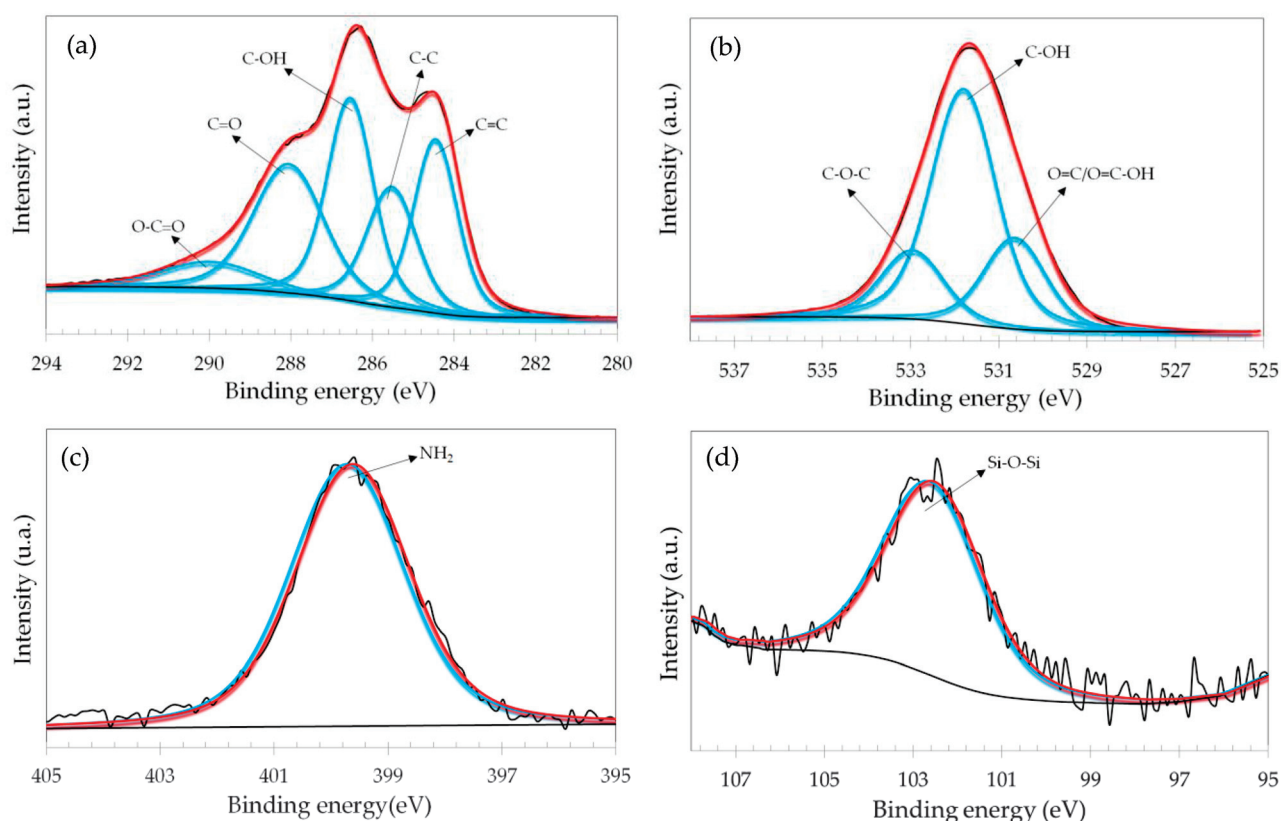


Figure 6. XPS high-resolution spectra of the 0.1% 4 h sample: (a) C 1s; (b) O 1s; (c) N 1s; (d) Si 2p.

The N 1s and Si 2p signals (Figure 6c,d) are due to the intermediate APTES layer. The N 1s spectrum exhibited one single peak centered at 399.6 eV that was assigned to NH₂ bonds in the APTES molecule, in agreement with other authors [53]. The Si 2p spectrum also displayed one single peak. This peak was assigned to Si-O-Si bonds formed during

the silanization treatment, indicating that APTES was chemically bonded to the AZ91D surface [54]. The N 1s and Si 2p spectra of the other GO-coated samples are very similar, and are displayed as Supplementary Materials (Figures S3 and S4 for the N 1s and Si 2p spectra, respectively).

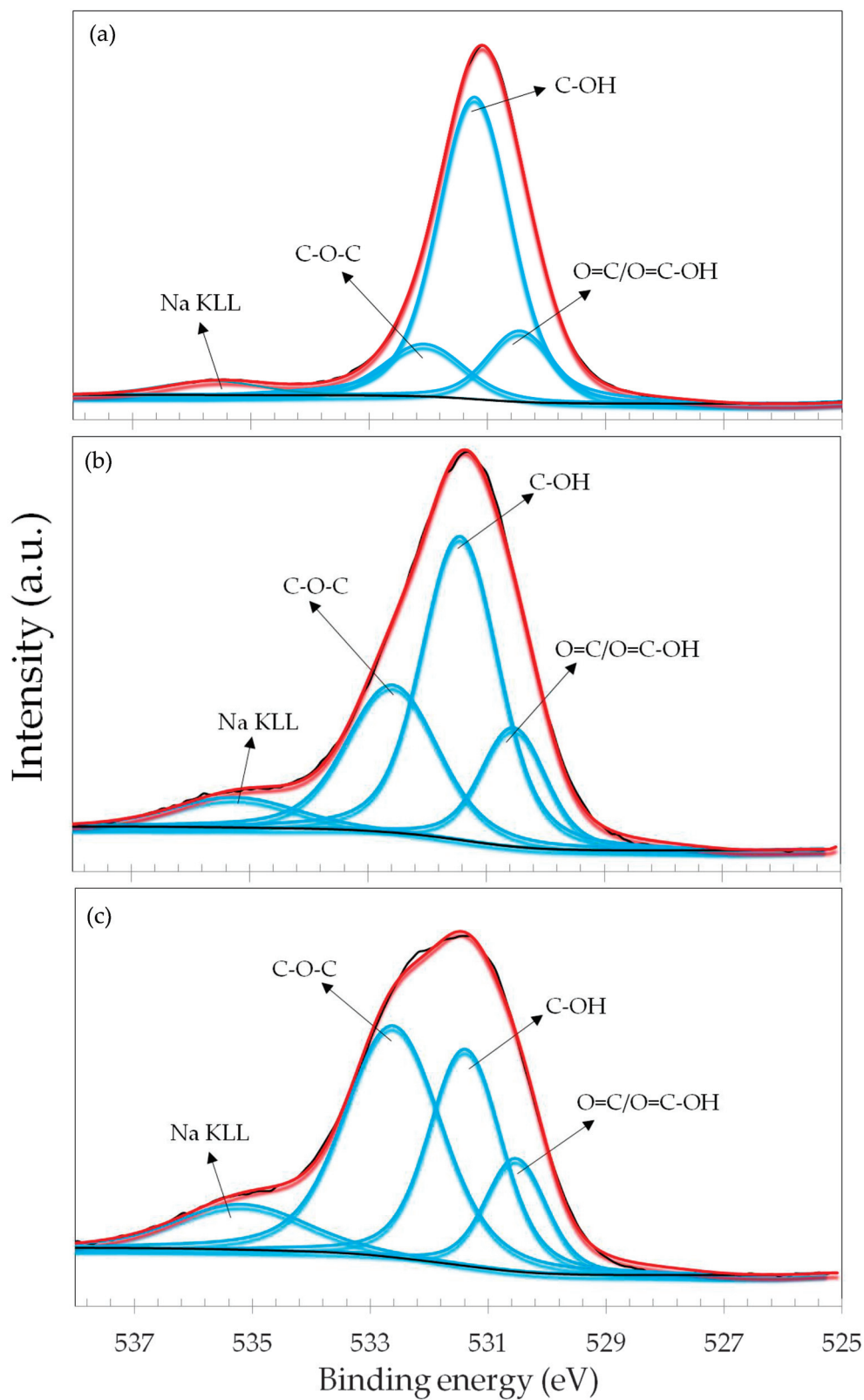


Figure 7. O 1s high-resolution spectra of GO-coated samples: (a) 0.1% 2 h; (b) 0.05% 4 h; (c) 0.05% 2 h.

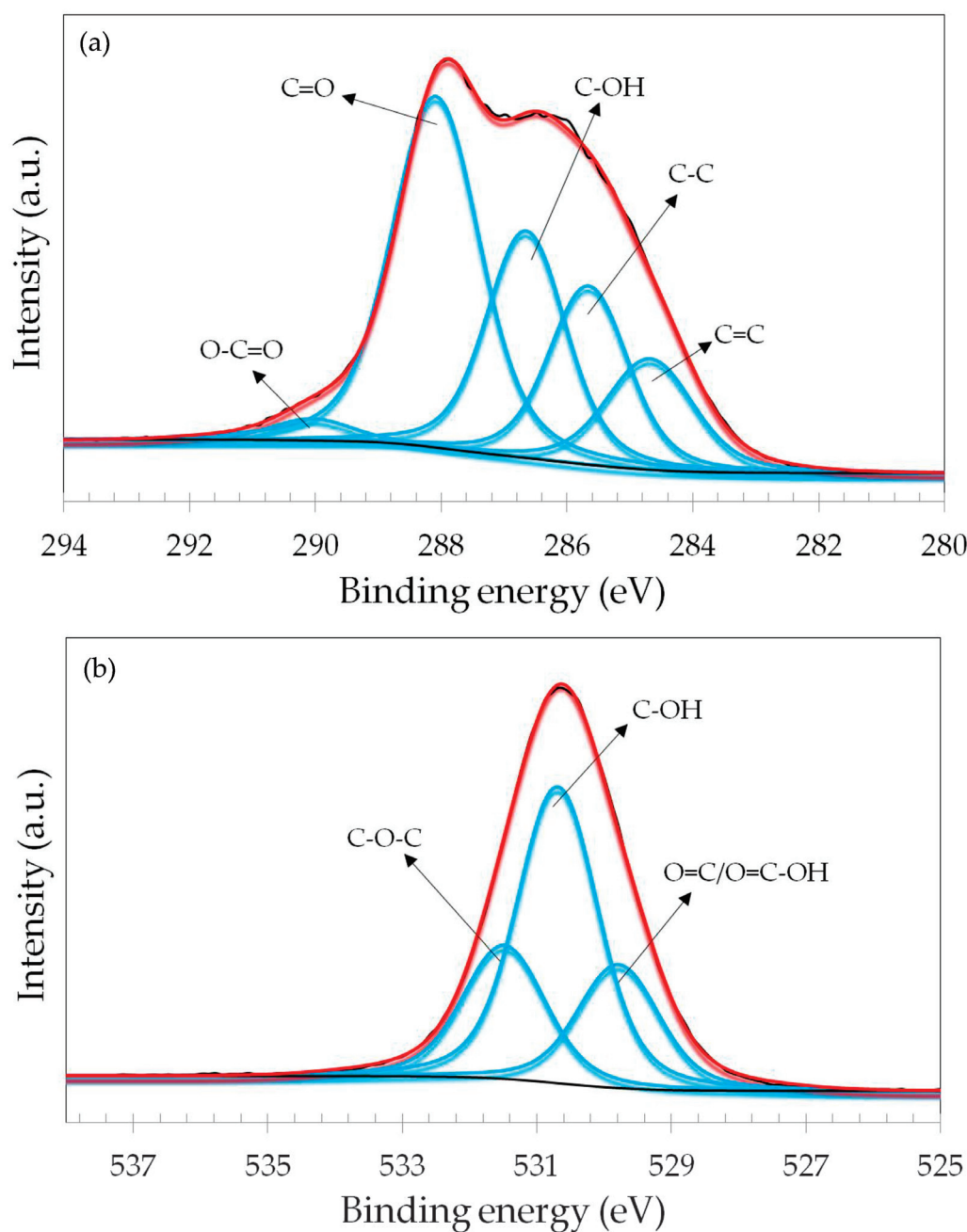


Figure 8. XPS high-resolution spectra of the graphene oxide sample: (a) C 1s; (b) O 1s.

Further assessment of the functional groups was carried out using FTIR. The silanized sample was analyzed to help understand its interaction with the AZ91D substrate. The 0.1% 4 h sample was chosen as a representative of the GO-coated samples. The spectra are shown in Figure 9.

The spectrum of the silanized sample exhibited the characteristic band of –OH groups at 3700 cm^{-1} , indicating the formation of hydroxyl groups in the NaOH pretreatment step and humidity. Characteristic bands of N–H groups were encountered at 3500 cm^{-1} , between 2800 and 3000 cm^{-1} and 1580 – 1650 cm^{-1} , followed by the band at 1020 – 1250 cm^{-1} that is typical of C–N groups, both due to amino groups of the APTES structure. The bands in the region 1580 – 1650 cm^{-1} indicate the presence of aminosilane bonds (Si–NH). Furthermore, bands of Si–O groups (Si–O–Si and O–Si–O) appear in the region 1000 – 1150 cm^{-1} . The presence of these bands is an evidence of the bonding between the APTES layer and the magnesium alloy substrate [27].

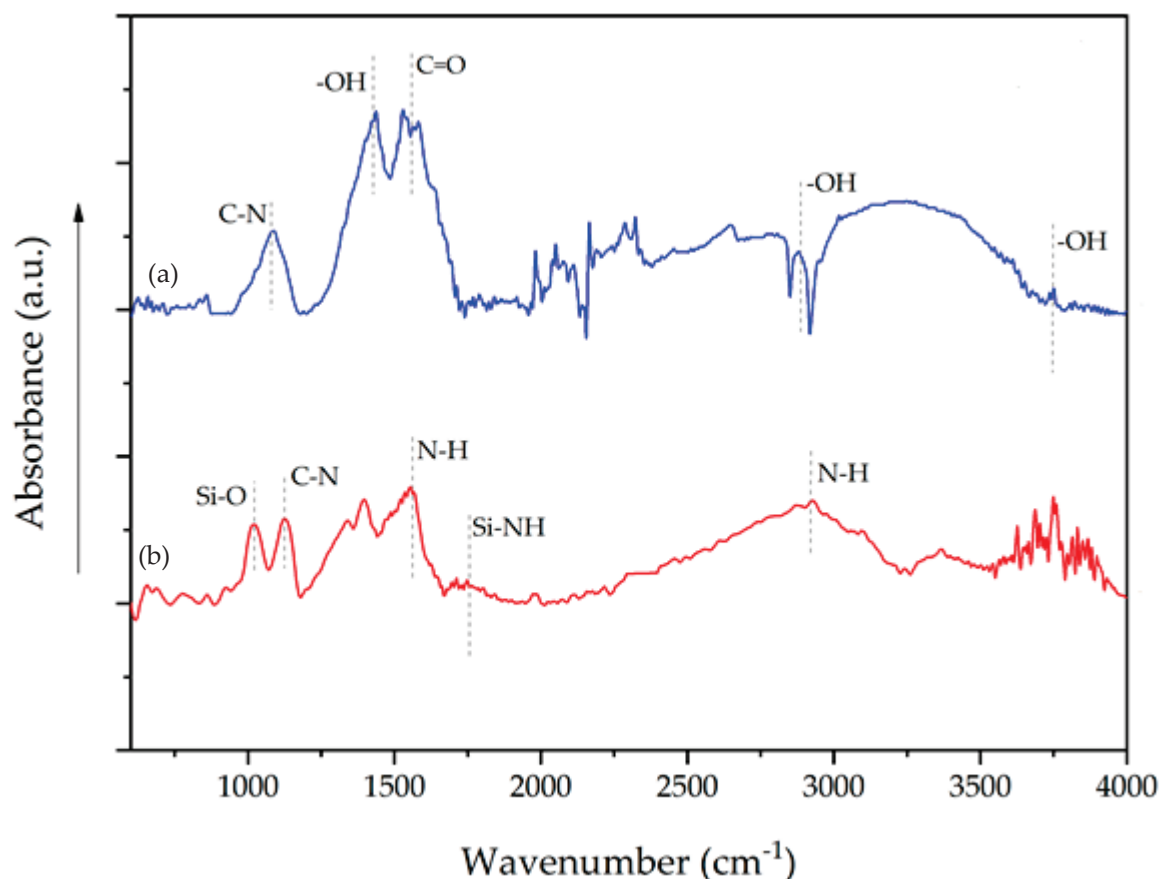


Figure 9. FTIR spectra of the: (a) 0.1% 4 h and (b) silanized samples.

In the spectrum of the 0.1% 4 h sample, the peak at 3700 cm^{-1} is due to -OH groups in the GO structure and also likely due to humidity in the sample. The bands around $2500\text{--}3300\text{ cm}^{-1}$ and $1440\text{--}1395\text{ cm}^{-1}$ correspond to -OH bonds in carboxyl groups. The absorption peaks around $1650\text{--}2000\text{ cm}^{-1}$ correspond to C-H in the structure of the graphene oxide. The band at 1590 cm^{-1} indicates the presence of C=O groups in amide groups, indicating that an amidation reaction occurred between the intermediate silane layer and the GO top film [26,27]. The spectrum of the GO-coated sample also exhibits the C-N band at $1020\text{--}1250\text{ cm}^{-1}$, characteristic of the silane layer, but with a lower intensity when compared to the silanized sample.

3.3. Corrosion Behavior

3.3.1. Open Circuit Potential (OCP) and Electrochemical Impedance Spectroscopy (EIS)

Before the EIS measurements, the open circuit potential (OCP) was monitored for 3600 s. The results are shown in Figure 10. The AR condition presented a gradual decrease in the OCP with time, which is likely associated with the non-protective nature of the naturally formed corrosion film on the surface of the AZ91D electrode [55]. When compared to the AR condition, the silanized sample exhibited a sharp increase in the very beginning of the monitoring period, followed by a gradual ascending trend up to the end of the test, without significant fluctuations. All GO-coated samples also showed an ascending trend, which was less pronounced for the 0.05% 2 h condition. The OCP was shifted to nobler values for the other GO-coated samples [56], suggesting a decrease in the electrochemical activity of the AZ91D substrate, depending on the GO concentration.

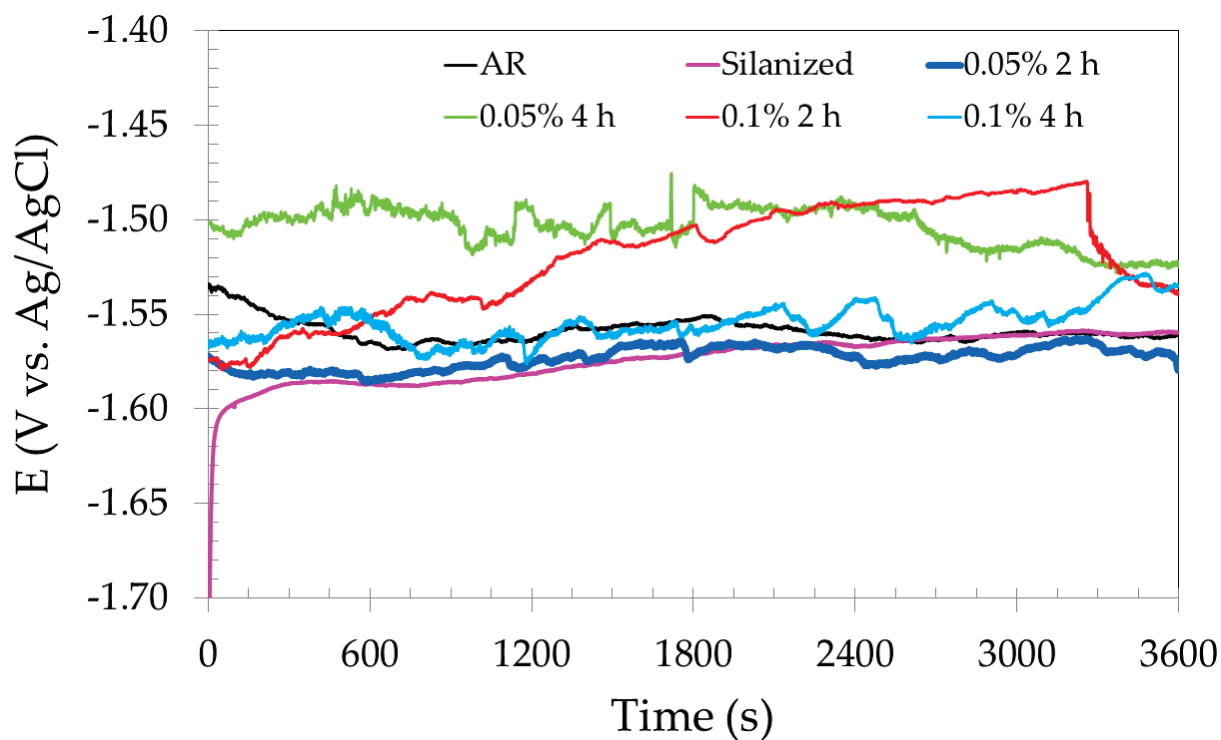


Figure 10. Open circuit potential curves of the AZ91D samples after 3600 s of immersion in 3.5 wt.% NaCl solution at room temperature.

Nyquist plots of the AR, silanized, and GO-coated AZ91D samples are shown in Figure 11. The results were obtained after 1 h of immersion in 3.5 wt.% NaCl solution at room temperature. The AR sample (uncoated AZ91D) exhibited a depressed capacitive loop in the high- to medium-frequency domain, followed by an inductive loop at the lowest frequencies. The silanized (without GO coating) and GO-coated samples displayed similar behavior. The smallest capacitive loop diameter was observed for the uncoated AZ91D alloy. The diameter of the capacitive loop is associated with the corrosion resistance of the electrode surface, being related to its charge transfer resistance [57,58]. The best corrosion resistance was, therefore, observed for the 0.01% 4 h sample, which displayed the highest impedance values and the largest capacitive loop. Furthermore, two additional features can be noticed from Figure 11. The first one is related to the deposition time: (i) the corrosion resistance was gradually decreased when the deposition time was reduced at the same GO concentration. The second one refers to the effect of GO concentration: (ii) the corrosion resistance increased, as the GO concentration was raised from 0.05% to 0.1% at the same deposition time.

The origin of the low-frequency inductive behavior is due to localized corrosion and relaxation processes of adsorbed corrosion species such as Mg^+_{ads} and $\text{Mg}(\text{OH})^+_{\text{ads}}$ [59,60]. This is frequently reported for Mg alloys, being associated with the onset of corrosion processes for uncoated alloys and for coated alloys at the interface between the coating and the substrate [61,62]. Nie et al. [63], for instance, observed that the AZ91D alloy exhibited a low-frequency inductive behavior when exposed to 3.5 wt.% NaCl solution. The authors considered that this behavior was due to the adsorbed Mg^+_{ads} during corrosion.

The EIS response of the AZ91D samples can be further evaluated from the Bode plots shown in Figure 12. As seen in Figure 12a, the phase angle plot of the AR condition is characterized by one peak, whose maximum reaches an angle of approximately -71° . The phase angle dropped off below 100 Hz, indicating the onset of corrosion processes. The capacitive response was improved for the silanized sample, as the phase angle peak was shifted to a slightly higher value and dropped off only at lower frequencies. The GO-coated samples displayed more capacitive response with respect to the silanized one,

as inferred from the increase in the maximum phase angle that reached up to -80° for the 0.1% 4 h sample. Furthermore, the peak plateau widened for the GO-coated samples when compared to AR, suggesting that one additional time constant can be superimposed. One additional feature is that the phase angles dropped off at lower frequencies for the GO-coated samples, indicating its superior capacitive response and higher corrosion resistance. This is confirmed by the results shown in the $|Z|$ vs. $\log f$ plots in Figure 12b. The impedance magnitude at 0.01 Hz is often employed as a measure of the corrosion resistance of the electrode [64,65].

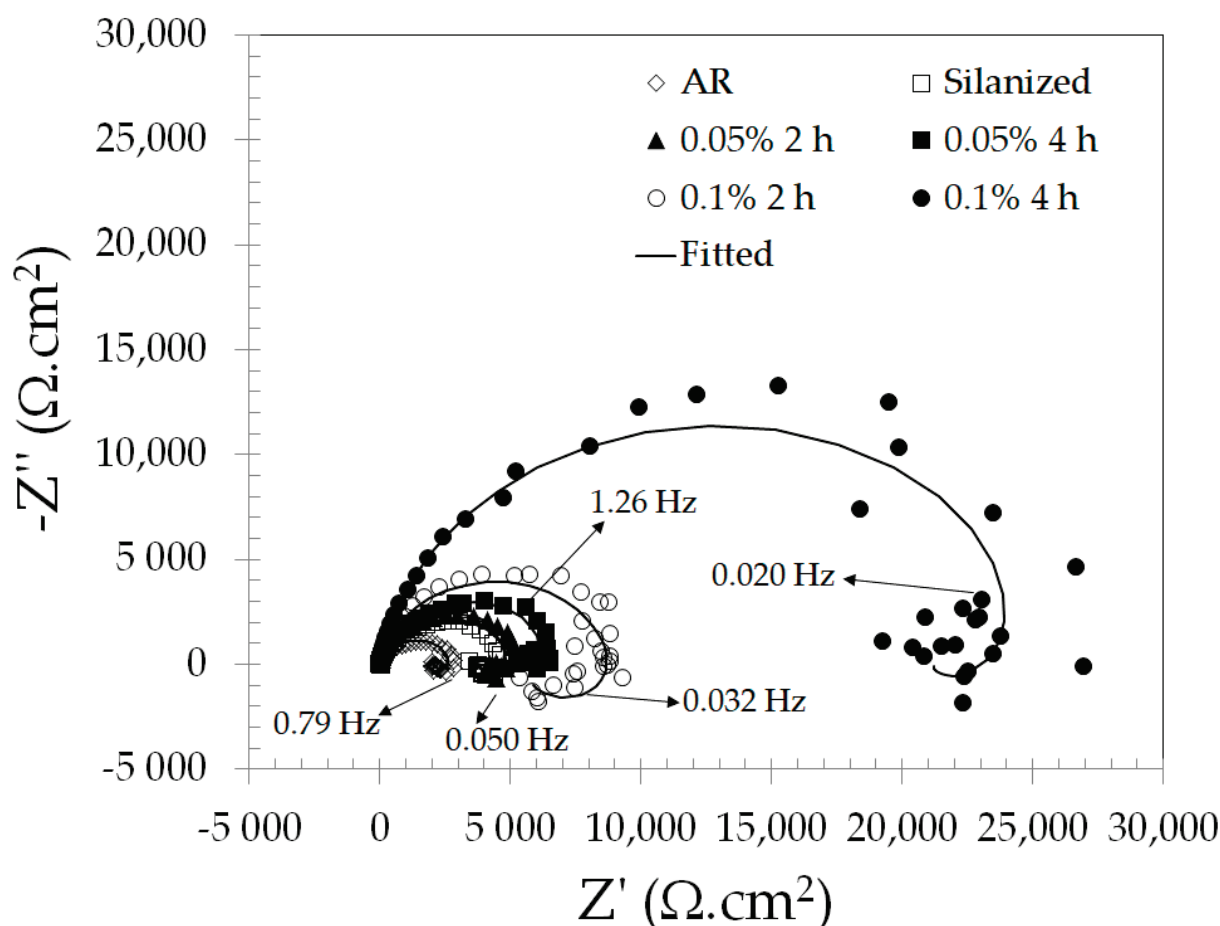


Figure 11. Nyquist plots of the uncoated and GO-coated AZ91D samples after 1 h of immersion in 3.5 wt.% NaCl solution at room temperature.

The corrosion protection ability of the GO coating can, therefore, be associated with the results exhibited in Figure 12b. The best corrosion resistance was shown by 0.1% 4 h. In light of the results obtained using EIS, it is possible to correlate the electrochemical behavior of the GO-coated samples with the morphological aspects described in Section 3.1. Based on the SEM micrographs displayed in Figure 2, the GO coating became less defective and more homogeneously spread over the surface as the deposition time and GO concentration increased. In this respect, the 0.1% 4 h sample (Figure 2e) exhibited the best surface morphology, with few defects. According to the EIS results (Figures 11 and 12), it also exhibited the best corrosion resistance. The barrier properties of the GO coating were, therefore, enhanced for this sample, thus improving its corrosion protection ability.

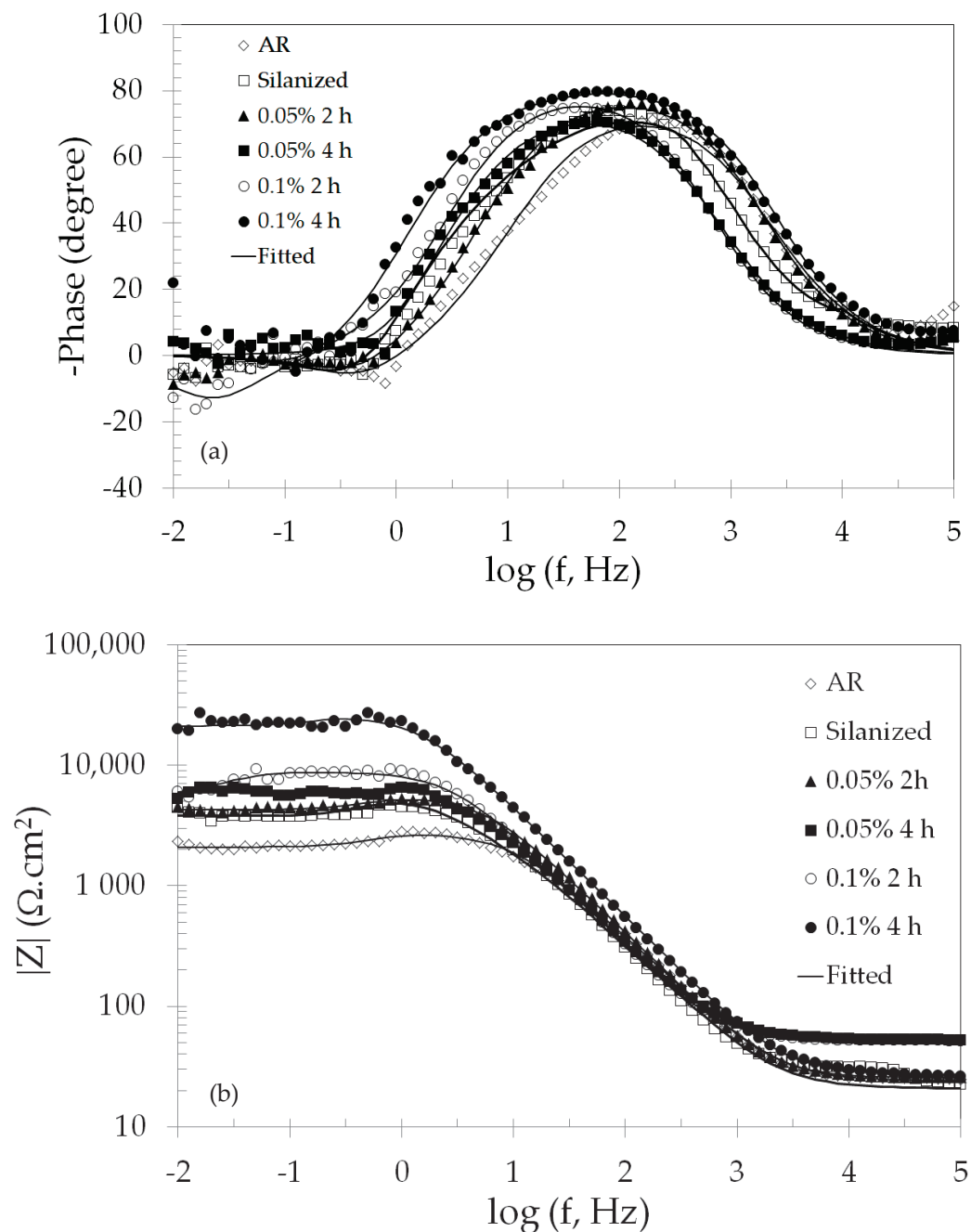


Figure 12. Bode plots of the uncoated and GO-coated AZ91D samples after 1 h of immersion in 3.5 wt.% NaCl solution at room temperature: (a) phase angle plots; (b) impedance modulus plots.

In order to give a quantitative interpretation of the EIS results, equivalent electrical circuits (EECs) were employed to simulate the experimental data. Two different EECs were used to fit the experimental results, as seen in Figure 13. Constant phase elements (CPE) were used instead of pure capacitors due to the heterogeneous nature of the electrode surface [66]. The impedance of a CPE (Z_{CPE}) is expressed as shown in Equation (6), where Q is the CPE magnitude, j is the complex operator, ω is the angular frequency, and n is the CPE exponent (varies between 0 and 1, depending on the capacitive response) [67,68].

$$Z_{CPE} = \frac{1}{Q(j\omega)^n} \quad (6)$$

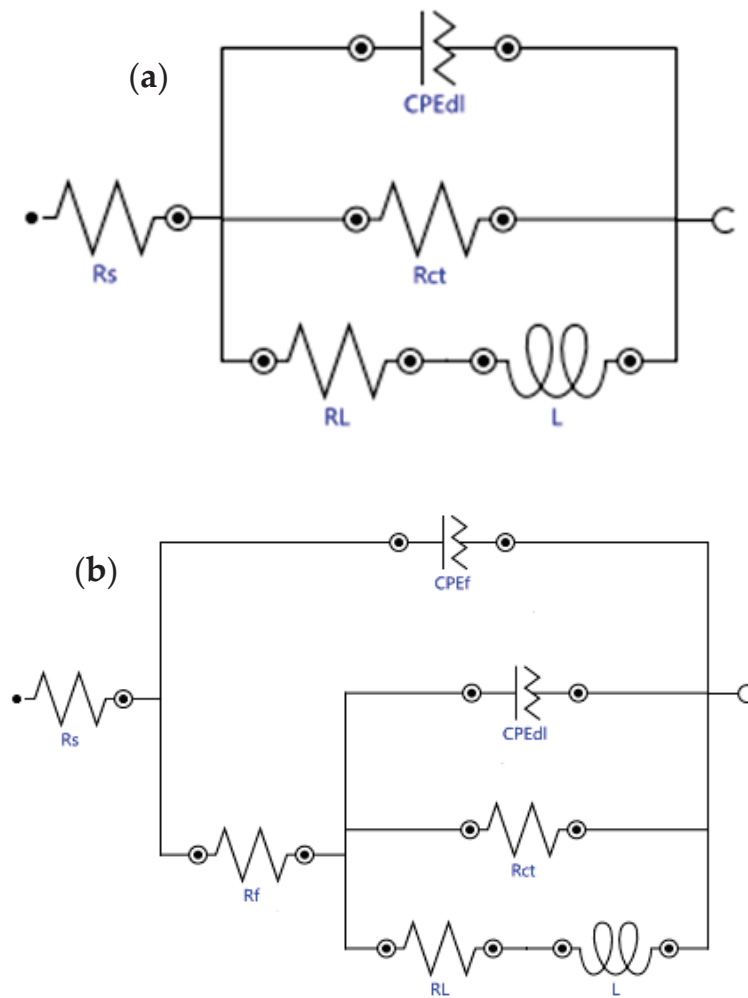


Figure 13. Fitted EECs used to simulate the EIS response of the AZ91D samples: (a) AR sample; (b) GO-coated samples.

The EEC shown in Figure 13a was used to simulate the EIS response of the AR sample. It consists of the solution resistance (R_s), one high-frequency time constant related to the capacitance of the electrical double layer (CPE_{dl}) and the charge transfer resistance (R_{ct}), and one time constant to model the inductive behavior of the electrode at low frequencies, with the inductive component (L) and its corresponding resistance (R_L). This EEC was also proposed by other authors to fit the EIS response of uncoated magnesium alloys in sodium chloride solution [69,70]. One additional time constant was incorporated into the EEC model of the silanized and GO-coated samples (Figure 13b), with its capacitance (CPE_f) and corresponding resistance (R_f). The other elements have the same physical meaning of those in Figure 13a. This circuit was also employed by other authors to simulate the EIS data of coated Mg alloys [71,72]. The fitted data are displayed in Table 2. The corrosion resistance of the GO-coated samples is mainly due to the resistance of the GO film itself (R_f). The highest R_f value was obtained for the 0.1% 4 h sample, confirming its superior corrosion protection ability, as qualitatively inferred from the Nyquist and Bode plots (Figures 6 and 7). The R_f value of approximately $20 \text{ k}\Omega \cdot \text{cm}^2$ is more than three times higher than that of the second best sample (0.1% 2 h).

Table 2. EIS fitting results using the EECs shown in Figure 13 for the uncoated AZ91D substrate and the silanized and GO-coated samples.

Sample	R_s ($\Omega \cdot \text{cm}^2$)	CPE_f ($10^{-6} \Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	R_f ($\Omega \cdot \text{cm}^2$)	n_f	CPE_{dl} ($10^{-6} \Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	R_{ct} ($\Omega \cdot \text{cm}^2$)	n_{dl}	R_L ($\Omega \cdot \text{cm}^2$)	L ($\text{H} \cdot \text{cm}^2$)	χ^2
AR	24	----	----	----	8.9	8700	0.88	2761	660	0.34
Silanized	21	27.1	3232	0.78	5.8	2210	0.88	709	803	0.44
0.05% 2 h	25	6.6	3426	0.92	0.2	2086	0.69	1344	856	0.14
0.05% 4 h	52	10.2	5147	0.88	4.1	2356	0.68	1146	634	0.21
0.1% 2 h	50	8.2	6323	0.92	2.1	3189	0.70	810	737	0.31
0.1% 4 h	27	4.7	20,224	0.92	4.1	5617	0.87	1130	6027	0.56

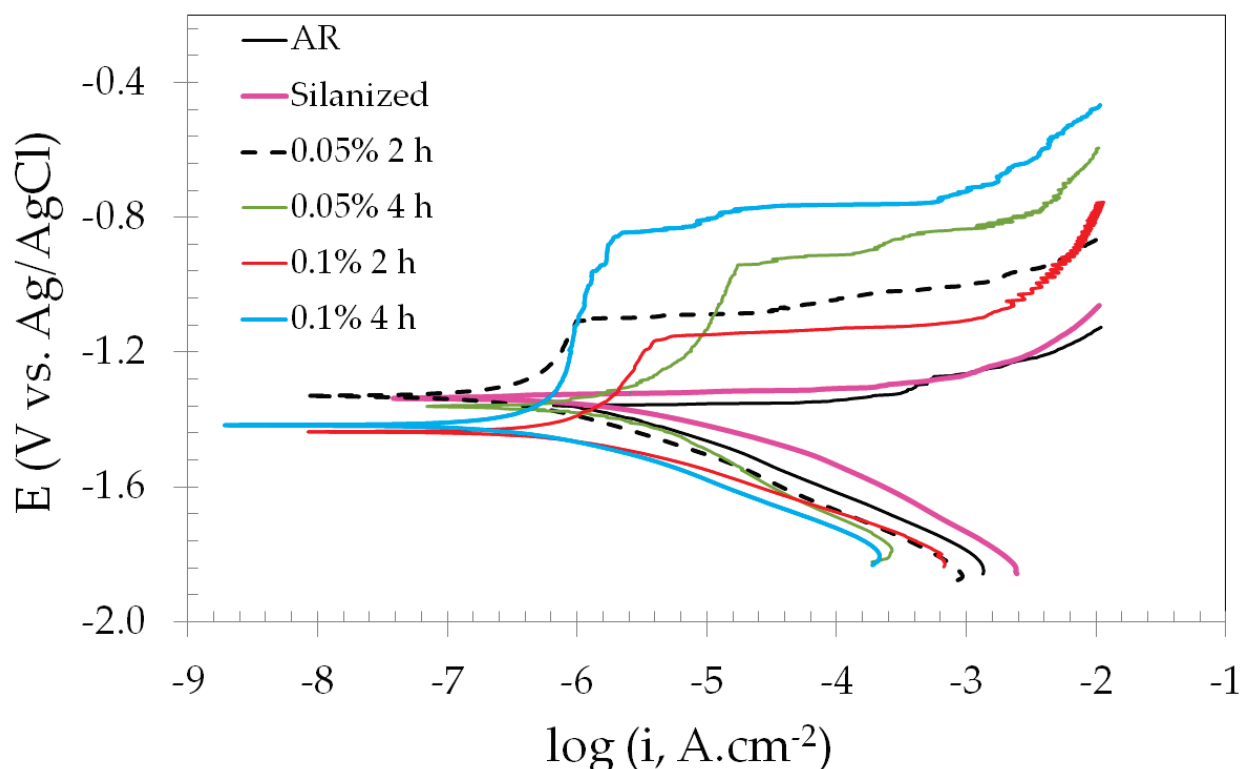
3.3.2. Potentiodynamic Polarization Curves

Figure 14 shows the potentiodynamic polarization curves of the different AZ91D samples after 1 h of immersion in 3.5 wt.% NaCl solution at room temperature. The electrochemical parameters determined from these curves are displayed in Table 3. The alloy in the AR condition exhibited active behavior, as denoted by the continuous increase in the current density with the applied potential. The silanized sample also displayed an active behavior, but the polarization curve was shifted to lower current densities, indicating a beneficial role of the APTES layer to slow down the uniform corrosion kinetics of the AZ91D substrate. In these cases, the active dissolution is governed by the corrosion current density (i_{corr}), which was determined by the Tafel extrapolation method, considering only the cathodic branch, as proposed in the literature for Mg alloys [73]. Conversely, all of the GO-coated samples exhibited passive behavior. For these samples, the anodic dissolution is governed by the passive current density (i_{pass}). These values are shown in Table 3, along with the corrosion potential (E_{corr}), pitting potential (E_{pit}), and passive range ($\Delta E = E_{\text{pit}} - E_{\text{corr}}$). The values of E_{corr} are related to the electrochemical activity of the electrode surface. The pitting potential is associated with the onset of localized corrosion spots. Higher values of E_{pit} denote increased resistance to pitting corrosion, reflecting the stability of the surface film facing chloride-induced localized attack [74]. In the same regard, the passive range (ΔE) is also an indication of the stability of the surface against localized corrosion. High values of ΔE express surface enhancement against the penetration of corrosive species through the coating layer, such as Cl^- ions [75].

The values of E_{corr} varied between $-1436 \text{ mV}_{\text{Ag}/\text{AgCl}}$ and $-1330 \text{ mV}_{\text{Ag}/\text{AgCl}}$, depending on the deposition parameters, which are compatible with other published results for GO-coated Mg alloys and for the uncoated AZ91D alloy in sodium chloride solution [27,71]. Although the E_{corr} values were not significantly improved by the GO films, the results shown in Table 3 reveal an evident decrease in the corrosion kinetics of the AZ91D alloy after deposition, as denoted by the lower values of i_{corr} and the passive character of the GO-coated samples. The i_{corr} of the AR condition was found to be $5.6 \mu\text{A} \cdot \text{cm}^{-2}$, which is in the same order of magnitude as the results published by Jiang et al. [76] and Peng et al. [77] for the bare AZ91D alloy in 3.5 wt.% NaCl solution. The corrosion current density was decreased by one order of magnitude after deposition of the GO film. Neupane et al. [27] obtained an i_{corr} of $2.7 \mu\text{A} \cdot \text{cm}^{-2}$ for GO-coated pure Mg. Tong et al. [26], in turn, obtained an i_{corr} of $8.4 \mu\text{A} \cdot \text{cm}^{-2}$ for a Mg-Zn-Ca coated with a GO film combined with an intermediate coupling silane layer. Thus, the results obtained in the present work point to a further improvement with respect to other published data. Moreover, the anodic dissolution was slowed down, as the coated samples exhibited passive behavior. As shown in Table 3, the highest E_{pit} and widest passive range were obtained for the 0.1% 4 h sample. This result is consistent with the EIS data discussed in Section 3.3.1, confirming that the 0.1% 4 h sample maximized the barrier properties of the GO film.

Table 3. Electrochemical parameters obtained from the potentiodynamic polarization curves shown in Figure 14.

Sample	E_{corr} (mV vs. Ag/AgCl)	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	E_{pit} (mV vs. Ag/AgCl)	ΔE (mV)	i_{pass} ($\mu\text{A}\cdot\text{cm}^{-2}$)
AR	-1523 ± 55	4.9 ± 0.4	----	----	----
Silanized	-1380 ± 81	2.7 ± 0.3	----	----	----
0.05% 2 h	-1335 ± 91	----	-1170 ± 65	211 ± 61	0.8 ± 0.2
0.05% 4 h	-1332 ± 52	----	-980 ± 140	425 ± 24	6.2 ± 0.7
0.1% 2 h	-1408 ± 50	----	-1151 ± 83	259 ± 63	1.6 ± 0.5
0.1% 4 h	-1424 ± 30	----	-970 ± 101	538 ± 52	0.7 ± 0.2

**Figure 14.** Potentiodynamic polarization curves of the different AZ91D samples after 1 h of immersion in 3.5 wt.% NaCl solution at room temperature.

4. Discussion

The corrosion protection mechanism of the GO-coated samples can be derived based on the results described in the previous sections, as illustrated in Figure 15.

As inferred from the XPS and FTIR spectra, the silanized sample adhered to the AZ91D substrate through Si-O bonds, forming the intermediate layer. However, the corrosion protection ability of this layer, in spite of showing increased impedance and lower corrosion current density than the magnesium alloy substrate, was relatively weak due to intrinsic defects such as microcracks in the silane layer, as illustrated in Figure 15a.

The GO topcoat increased the diffusion path of the corrosive electrolyte by forming an additional layer over the APTES intermediate film (Figure 15b). The bonding between the silane film and the GO topcoat was observed using FTIR (Section 3.2), as indicating by the presence of amide-type groups arising from the amidation reaction between APTES and GO [26]. As a consequence, the corrosion resistance of the GO-coated samples was improved with respect to either the AZ91D substrate or the silanized layer. The corrosion protection ability of the GO films was higher depending on the compactness of the GO topcoat.

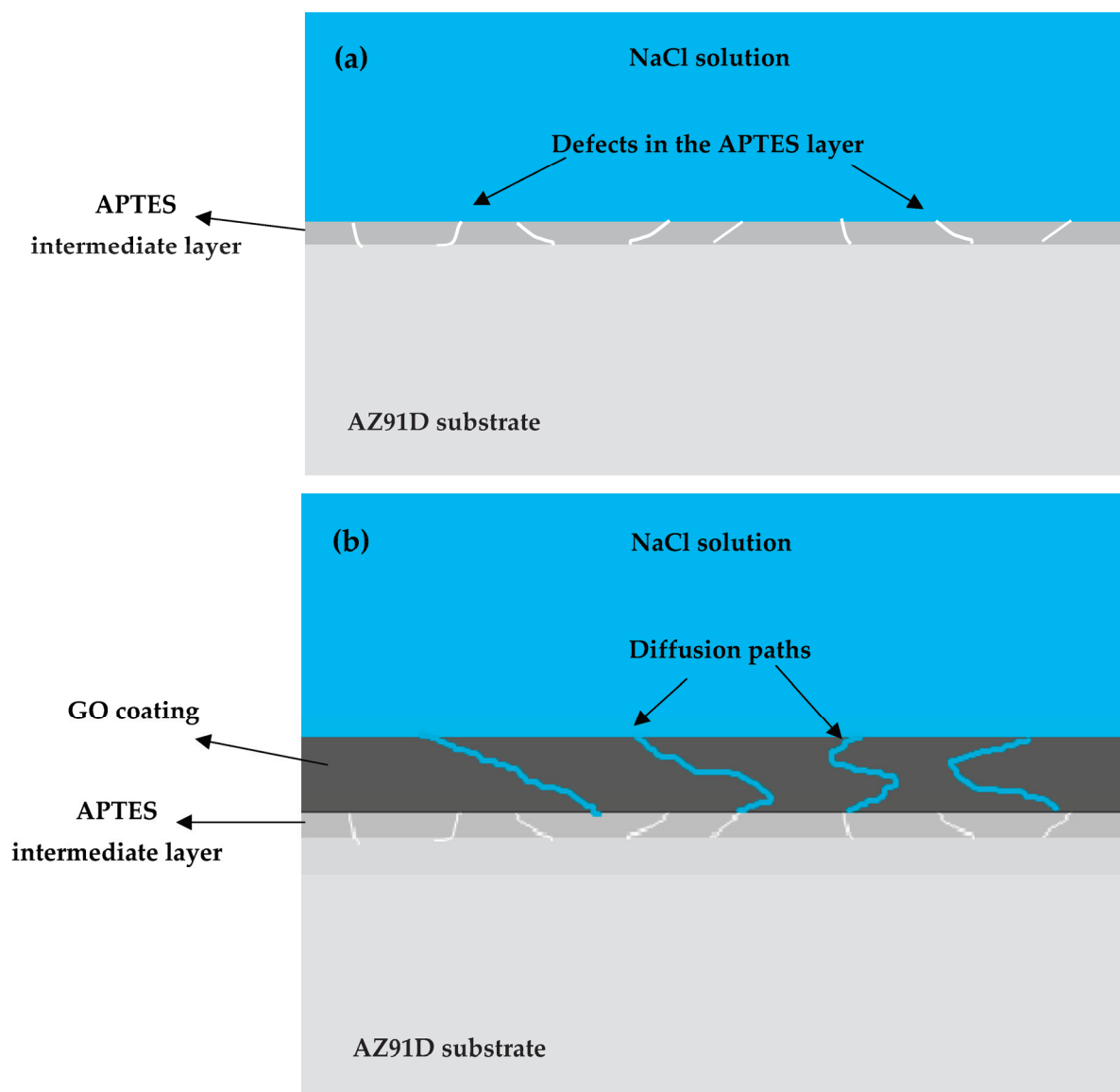


Figure 15. Illustration of the corrosion protection mechanism of the AZ91D samples: (a) silanized; (b) GO-coated samples.

The role of the GO coating was to act a physical separation between the corrosive environment and the AZ91D substrate. Based on the SEM micrographs shown in Section 3.1, the surface morphology of the GO films was enhanced for the 0.1% 4 h sample, as denoted by its smooth and homogeneous topography (Figure 2e). The XPS results discussed in Section 3.2 have also confirmed this result, as suggested by the absence of the NaKLL Auger peak in the O 1s high-resolution spectrum of the 0.1% 4 h sample (Figure 6b) and its presence in the corresponding spectra of the other GO-coated samples (Figure 7). As mentioned before, this peak is due to the initial NaOH surface pretreatment conducted before silanization. Hence, as the deposition time and GO concentration increased, this peak was no longer observed, indicating that the GO film more homogeneously spread over the surface. This is also an indirect indication that coating thickness increased with the deposition time, which also influenced the corrosion resistance of the GO-coated samples. Because of the enhanced surface topography, the corrosion resistance was improved, as the barrier properties of the GO film were optimized.

5. Conclusions

In the present work, graphene oxide (GO) coatings were effectively deposited on the surface of a silanized AZ91D Mg alloy substrate by immersion in aqueous solutions with 0.05 wt.% and 0.1 wt.% of the carbon-based nanometer material. The effects of deposition time and GO concentration on the coating morphology, surface chemistry, and corrosion behavior were investigated.

The surface morphology was improved as the deposition time and GO concentration increased, obtaining less defective and more homogeneously distributed films. The film formed in the solution with a GO concentration of 0.1 wt.% for 4 h exhibited the more compact surface morphology.

The GO films consisted of C=C, C-C, C-OH, C=O, and O-C=O bonds. The O 1s XPS high-resolution spectra were useful to confirm the integrity of the GO coatings. The presence of a NaKLL Auger peak in the O 1s spectrum, which was due to the signal originated from the NaOH pretreatment of the AZ91D substrate, was not observed for the 0.1% 4 h sample, while it was present in the O 1s spectra of all of the other GO-coated samples.

Due to the best surface coverage and film integrity, the 0.1% 4 h sample displayed the best corrosion resistance, as indicated by its high impedance, low corrosion current density, and wide passive range.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met14091019/s1>, Figure S1: XPS survey spectra of pure GO (a) and GO-coated samples: (b) 0.1% 2 h; (c) 0.05% 4 h; (d) 0.05% 2 h. Figure S2: C 1s high resolution spectra of GO-coated samples: (a) 0.1% 2 h; (b) 0.05% 4 h; (c) 0.05% 2 h. Figure S3: N 1s high resolution spectra of GO-coated samples: (a) 0.1% 2 h; (b) 0.05% 4 h; (c) 0.05% 2 h. Figure S4: Si 2p high resolution spectra of GO-coated samples: (a) 0.1% 2 h; (b) 0.05% 4 h; (c) 0.05% 2 h.

Author Contributions: Conceptualization, R.A.A.; methodology, N.S.d.S., L.A.d.O., A.C.A., J.A.d.S.P. and R.A.A.; validation, N.S.d.S. and R.A.A.; investigation, N.S.d.S., A.C.A., J.A.d.S.P., L.A.d.O. and M.C.L.d.O.; writing—original draft preparation, M.C.L.d.O. and R.A.A.; writing—review and editing, M.C.L.d.O. and R.A.A.; supervision, R.A.A.; project administration, R.A.A. All authors have read and agreed to the published version of the manuscript.

Funding: Brazilian Agency CAPES (Finance Code 001).

Data Availability Statement: The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Acknowledgments: The authors are grateful to the Multiuser Experimental Facilities (CEM) of the Federal University of the ABC for the infrastructure necessary to develop this work. Rima Industrial Magnésio S/A (Belo Horizonte, Brazil) is acknowledged for kindly providing the AZ91D alloy used in this study.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Castellanos, A.; Altube, A.; Veja, J.M.; García-Lecina, E.; Díez, J.A.; Grande, H.J. Effect of different post-treatments on the corrosion resistance and tribological properties of AZ91D magnesium alloy coated PEO. *Surf. Coat. Technol.* **2015**, *278*, 99–107. [CrossRef]
2. Liu, B.; Yang, J.; Zhang, X.; Yang, Q.; Zhang, J.; Li, X. Development and application of magnesium alloy partis for automotive OEMs: A review. *J. Magnes. Alloys* **2023**, *11*, 15–47. [CrossRef]
3. Jouini, N.; Ruslan, M.S.M.; Ghani, J.A.; Haron, C.H.C. Sustainable high-speed milling of magnesium alloy AZ91D in dry and cryogenic conditions. *Sustainability* **2023**, *15*, 3760. [CrossRef]
4. Gobara, M.; Shamekh, M.; Akid, R. Improving the corrosion resistance of AZ91D magnesium alloy through reinforcement with titanium carbides and borides. *J. Magnes. Alloys* **2015**, *3*, 112–120. [CrossRef]
5. Wu, T.; Zhang, K. Corrosion and protection of magnesium alloys: Recent advances and future perspectives. *Coatings* **2023**, *13*, 1533. [CrossRef]
6. Jiang, M.; Wu, J.; Zhu, J. One-step preparation of silicate coatings on AZ91D magnesium alloy surface for boosting its corrosion resistance. *Silicon* **2024**, *16*, 1147–1159. [CrossRef]

7. Zeng, R.-C.; Zhang, F.; Lan, Z.-D.; Cui, H.-Z.; Han, E.-H. Corrosion resistance of calcium-modified zinc phosphate conversion coatings on magnesium-aluminium alloys. *Corros. Sci.* **2014**, *88*, 452–459. [CrossRef]
8. Ashassi-Sorkhabi, H.; Moradi-Alavian, S.; Kazempour, A. Salt-nanoparticle systems incorporated into sol-gel coatings for corrosion protection of AZ91 magnesium alloy. *Prog. Org. Coat.* **2019**, *135*, 475–482. [CrossRef]
9. Grimm, M.; Lohmüller, A.; Singer, R.F.; Virtanen, S. Influence of the microstructure on the corrosion behavior of cast Mg-Al alloys. *Corros. Sci.* **2019**, *155*, 195–208. [CrossRef]
10. Su, Y.; Lin, J.; Su, Y.; Zai, W.; Li, G.; Wen, C. Investigation on composition, mechanical properties, and corrosion resistance of Mg-0.5Ca-X (Sr, Zr, Sn) biological alloy. *Scanning* **2018**, *2018*, 6519310. [CrossRef]
11. Pezzato, L.; Coelho, L.B.; Bertolini, R.; Settimi, A.G.; Brunelli, K.; Olivier, M.; Dabalà, M. Corrosion and mechanical properties of plasma electrolytic oxidation-coated AZ80 magnesium alloy. *Mater. Corros.* **2019**, *70*, 2103–2112. [CrossRef]
12. Murakami, K.; Hino, M.; Nakai, K.; Kobayashi, S.; Saijo, A.; Kanadani, T. Mechanism of corrosion protection of anodized magnesium alloys. *Mater. Trans.* **2008**, *49*, 1057–1064. [CrossRef]
13. Chen, X.B.; Birbilis, N.; Abbott, T.B. Review of corrosion-resistant conversion coatings for magnesium and its alloys. *Corrosion* **2011**, *67*, 035005-1–035005-16. [CrossRef]
14. Khiabani, A.B.; Ghanbari, A.; Yarmand, B.; Zamanian, A.; Mozafari, M. Improving corrosion behavior and in vitro bioactivity of plasma electrolytic oxidized AZ91 magnesium alloy using calcium fluoride containing electrolyte. *Mater. Lett.* **2018**, *212*, 98–102. [CrossRef]
15. Hoche, H.; Groß, S.; Oechsner, M. Development of new PVD coatings for magnesium alloys with improved corrosion properties. *Surf. Coat. Technol.* **2014**, *259*, 102–108. [CrossRef]
16. Ding, R.; Li, W.; Wang, X.; Gui, T.; Li, B.; Han, P.; Tian, H.; Liu, A.; Wang, X.; Liu, X.; et al. A brief review of corrosion protective films and coatings based on graphene and graphene oxide. *J. Alloys Compd.* **2018**, *764*, 1019–1055. [CrossRef]
17. Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J.W.; Potts, J.R.; Ruoff, R.S. Graphene and graphene oxide: Synthesis, properties and applications. *Adv. Mater.* **2010**, *22*, 3906–3924. [CrossRef]
18. Torrisi, L.; Sliipigni, L.; Cutroneo, M. Radiation effects of IR laser on graphene oxide irradiated in vacuum and in air. *Vacuum* **2018**, *153*, 122–131. [CrossRef]
19. Kang, D.; Kwon, J.Y.; Cho, H.; Sim, J.; Hwang, H.S.; Kim, C.S.; Kim, Y.J.; Ruoff, R.S.; Shin, H.S. Oxidation resistance of iron and copper foils coated with reduced graphene oxide multilayers. *ACS Nano* **2012**, *6*, 7763–7769. [CrossRef]
20. Medelienė, V.; Stankevič, V.; Griguševičienė, A.; Selskienė, A.; Bikulcius, G. The study of corrosion and wear resistance of copper composite coatings with inclusion of carbon nanomaterials in the copper metal matrix. *Mater. Sci.* **2011**, *17*, 132–139. [CrossRef]
21. Mahato, N.; Cho, M.W. Graphene integrated polyaniline nanostructured composite coating for protecting steels from corrosion: Synthesis, characterization, and protection mechanism of the coating material in acidic environment. *Constr. Build Mater.* **2016**, *115*, 618–633. [CrossRef]
22. Bakhsheshi-Rad, H.R.; Hamzah, E.; Kasiri-Asgarani, M.; Saud, S.N.; Yaghoubidoust, F.; Akbari, E. Structure, corrosion behavior, and antibacterial properties of nano-silica/graphene oxide coating on biodegradable magnesium alloy for biomedical applications. *Vacuum* **2016**, *131*, 106–110. [CrossRef]
23. Ho, C.-H.; Huang, S.-M.; Lee, S.-T.; Chang, Y.-J. Evaluation of synthesized graphene oxide as corrosion protection film coating on steel substrate by electrophoretic deposition. *Appl. Surf. Sci.* **2019**, *477*, 226–231. [CrossRef]
24. Li, P.F.; Zhou, H.; Cheng, X.-H. Nano/micro tribological behaviors of a self-assembled graphene oxide nanolayer on Ti/titanium alloy substrates. *Appl. Surf. Sci.* **2013**, *285*, 937–944. [CrossRef]
25. Li, P.F.; Zhou, H.; Cheng, X. Investigation of a hydrothermal reduced graphene oxide nano coating on Ti substrate and its nano-tribological behavior. *Surf. Coat. Technol.* **2014**, *254*, 298–304. [CrossRef]
26. Tong, L.B.; Zhang, J.B.; Xu, C.; Wang, X.; Song, S.Y.; Jiang, Z.H.; Kamado, S.; Cheng, L.R.; Zhang, H.J. Enhanced corrosion and wear resistances by graphene oxide coating on the surface of Mg-Zn-Ca alloy. *Carbon* **2016**, *109*, 340–351. [CrossRef]
27. Neupane, M.P.; Lee, S.J.; Kang, J.Y.; Park, I.S.; Bae, T.S.; Lee, M.H. Surface characterization and corrosion behavior of silanized magnesium coated with graphene for biomedical application. *Mater. Chem. Phys.* **2015**, *163*, 229–235. [CrossRef]
28. Sakeye, M.; Smatt, J.-H. Comparison of different amino-functionalization procedures on a selection of metal oxide microparticles: Degree of modification and hydrolytic stability. *Langmuir* **2012**, *28*, 16491–16950. [CrossRef]
29. Prasai, D.; Tuberquia, J.C.; Harl, R.R.; Jennings, G.K.; Bolotin, K.I. Graphene: Corrosion-inhibiting coating. *ACS Nano* **2012**, *6*, 1102–1108. [CrossRef]
30. Chu, J.H.; Tong, L.B.; Zhang, J.B.; Kamado, S.; Jiang, Z.H.; Zhang, H.J.; Sun, G.X. Bio-inspired graphene-based coatings on Mg alloy surfaces and their integrations of anti-corrosive/wearable performances. *Carbon* **2019**, *141*, 154–168. [CrossRef]
31. Lin, L.; Wu, H.; Green, S.J.; Crompton, J.; Zhang, S.; Horsell, W. Formation of tunable graphene oxide coating with high adhesion. *Phys. Chem. Chem. Phys.* **2016**, *18*, 5086–5090. [CrossRef] [PubMed]
32. Xu, R.; Yang, X.; Zhang, X.; Wang, M.; Li, P.; Zhao, Y.; Wu, G.; Chu, P.K. Effects of carbon dioxide plasma immersion ion implantation on the electrochemical properties of AZ31 magnesium alloy in physiological environment. *Appl. Surf. Sci.* **2013**, *286*, 257–260. [CrossRef]
33. Pan, C.-J.; Pang, L.-Q.; Hou, Y.; Lin, Y.-B.; Gong, T.; Liu, T.; Ye, W.; Ding, H.-Y. Improving corrosion resistance and biocompatibility of magnesium alloy by sodium hydroxide and hydrofluoric acid treatments. *Appl. Sci.* **2017**, *7*, 33. [CrossRef]

34. Man, C.; Dong, C.; Fang, Y.; Xiao, K.; Guo, C.; He, G.; Li, X. The corrosion behavior of magnesium alloy AZ31 in hot and dry atmospheric environment in Turpan, China. *Int. J. Electrochem. Sci.* **2015**, *10*, 8691–8705. [CrossRef]
35. Santamaria, M.; Di Quarto, F.; Zanna, S.; Marcus, P. Initial surface film on magnesium metal: A characterization by X-ray photoelectron spectroscopy (XPS) and photocurrent spectroscopy (PCS). *Electrochim. Acta* **2007**, *53*, 1314–1324. [CrossRef]
36. Jönsson, M.; Persson, D.; Thierry, D. Corrosion product formation during NaCl induced atmospheric corrosion of magnesium alloy AZ91D. *Corros. Sci.* **2007**, *49*, 1540–1558. [CrossRef]
37. Feliu, S., Jr.; Galván, J.C.; Pardo, A.; Merino, M.C.; Arrabal, R. Native air-formed oxide film and its effect on magnesium alloys corrosion. *Open Corros. J.* **2010**, *3*, 80–91. [CrossRef]
38. Lakshimi, R.V.; Aruna, S.T.; Anandan, C.; Bera, P.; Sampath, S. EIS and XPS studies on the self-healing properties of Ce-modified silica-alumina hybrid coatings: Evidence for Ce(III) migration. *Surf. Coat. Technol.* **2017**, *309*, 363–370. [CrossRef]
39. López, A.D.F.; Lehr, I.L.; Saidman, S.B. Anodisation of AZ91D magnesium alloy in molybdate solution for corrosion protection. *J. Alloys Compd.* **2017**, *702*, 338–345. [CrossRef]
40. Wang, H.; Li, Y.; Wang, F. Influence of cerium on passivity behavior of wrought AZ91 alloy. *Electrochim. Acta* **2008**, *54*, 706–713. [CrossRef]
41. Rao, X.; Hassan, A.A.; Guyon, C.; Zhang, M.; Ognier, S.; Tatouliau, M. Plasma polymer layers with primary amino groups for immobilization of nano and microparticles. *Plasma Chem. Plasma Process.* **2020**, *40*, 589–606. [CrossRef]
42. Liu, J.; Xi, T. Enhanced anti-corrosion ability and biocompatibility of PLGA coatings on MgZnYNd alloy by BTSE-APTES pretreatment for cardiovascular stent. *J. Mater. Sci. Technol.* **2016**, *32*, 845–857. [CrossRef]
43. Lavorgna, M.; Romeo, V.; Martone, A.; Zarrelli, M.; Giordano, M.; Buonocore, G.G.; Qu, M.Z.; Fei, G.X.; Xia, H.S. Silanization and silica enrichment of multiwalled carbon nanotubes: Synergistic effects on the thermal-mechanical properties of epoxy nanocomposites. *Eur. Polym. J.* **2013**, *49*, 428–438. [CrossRef]
44. Zhang, Z.-Q.; Zeng, R.-C.; Lin, C.-G.; Wang, L.; Chen, X.-B.; Chen, D.-C. Corrosion resistance of self-cleaning silane/polypropylene composite coatings on magnesium alloy AZ31. *J. Mater. Sci. Technol.* **2020**, *41*, 43–55. [CrossRef]
45. Sánchez-López, L.; Chico, B.; Llorente, I.; Escudero, M.L.; Lozano, R.M.; García-Alonso, M.C. Covalent immobilization of graphene oxide on biomedical grade CoCr alloy by an improved multilayer system assembly via silane/GO bonding. *Mater. Chem. Phys.* **2022**, *287*, 126296. [CrossRef]
46. Hu, H.; Zhao, S.; Sun, G.; Zhong, Y.; You, B. Evaluation of scratch resistance of functionalized graphene oxide/polysiloxane nanocomposite coatings. *Prog. Org. Coat.* **2018**, *117*, 118–129. [CrossRef]
47. Pei, S.; Meng, H.-M. The reduction of graphene oxide. *Carbon* **2012**, *50*, 3210–3228. [CrossRef]
48. Ferrari, I.; Motta, A.; Zanoni, R.; Scaramuzzo, F.A.; Amato, F.; Dalchiele, E.A.; Marrani, A.G. Understanding the nature of graphene oxide functional groups by modulation of the electrochemical reduction: A combined experimental and theoretical approach. *Carbon* **2023**, *203*, 29–38. [CrossRef]
49. Lee, Y.S.; Ji, B.C.; Seo, J.-W.; Jeon, D.I.; Kwon, S.B.; Yoo, J.H.; Kang, B.G.; Song, Y.H.; Yang, W.S.; Kang, B.K.; et al. Facile recyclable process of high-quality single layer graphene oxide via waste graphite anode scrap. *Ceram. Int.* **2023**, *49*, 34774–34779. [CrossRef]
50. Gnanaseelan, N.; Marasamy, L.; Mantilla, A.; Kamaraj, S.K.; Espinosa-Faller, F.J.; Caballero-Briones, F. Exploring the impact of doping and co-doping with B and N on the properties of graphene oxide and its photocatalytic generation of hydrogen. *Int. J. Hydrogen Energy* **2022**, *47*, 40905–40919. [CrossRef]
51. Oliveira, L.A.; Silva, R.M.P.; Rodas, A.C.D.; Souto, R.M.; Antunes, R.A. Surface chemistry, film morphology, local electrochemical behavior and cytotoxic response of anodized AZ31B magnesium alloy. *J. Mater. Res. Technol.* **2020**, *9*, 14754–14770. [CrossRef]
52. Guo, S.; Garaj, S.; Bianco, A.; Ménard-Moyon, C. Controlling covalent chemistry on graphene oxide. *Nat. Rev. Phys.* **2022**, *4*, 247–262. [CrossRef]
53. Zhong, Y.; Gu, Y.; Yu, L.; Cheng, G.; Yang, X.; Sun, M.; He, B. APTES-functionalized Fe₃O₄ microspheres supported Cu atom-clusters with superior catalytic activity towards 4-nitrophenol reduction. *Colloids Surf. A* **2018**, *547*, 28–36. [CrossRef]
54. Li, L.; Chen, D.; Long, Y.; Wang, F.; Kang, Z. Silane modification of semi-curing epoxy surface: High interfacial adhesion for conductive coatings. *Prog. Org. Coat.* **2023**, *174*, 107228. [CrossRef]
55. Iranshahi, F.; Nasiri, M.B.; Warchomicka, F.G.; Sommitsch, C. Corrosion behavior of electron beam processed AZ91 magnesium alloy. *J. Magnes. Alloys* **2020**, *8*, 1314–1327. [CrossRef]
56. Liu, W.; Cao, F.; Zhong, L.; Zheng, L.; Jia, B.; Zhang, Z.; Zhang, J. Influence of rare earth element Ce and La addition on corrosion behavior of AZ91 magnesium alloy. *Mater. Corros.* **2009**, *60*, 795–803. [CrossRef]
57. Osipenko, M.A.; Kasach, A.A.; Adamiec, J.; Zimowska, M.; Kurilo, I.I.; Kharytonau, D.S. Corrosion inhibition of magnesium alloy AZ31 in chloride-containing solutions by aqueous permanganate. *J. Solid State Electrochem.* **2023**, *27*, 1847–1860. [CrossRef]
58. Tang, J.; Chen, L.; Li, Z.; Zhao, G.; Zhang, C. Formation of abnormal coarse grains and its effects on corrosion behaviors of solution treated ZK60 Mg alloy. *Corros. Sci.* **2021**, *180*, 109201. [CrossRef]
59. Song, Y.; Shan, D.; Chen, R.; Han, E.-H. Corrosion characterization of Mg-8Li alloy in NaCl solution. *Corros. Sci.* **2009**, *51*, 1087–1094. [CrossRef]
60. Feliu, S., Jr. Electrochemical impedance spectroscopy for the measurement of the corrosion rate of magnesium alloys: Brief review and challenges. *Metals* **2020**, *10*, 775. [CrossRef]
61. Torbati-Sarraf, H.; Torbati-Sarraf, S.A.; Poursaee, A.; Langdon, T.G. Electrochemical behavior of a magnesium ZK60 alloy processed by high-pressure torsion. *Corros. Sci.* **2019**, *154*, 90–100. [CrossRef]

62. Jiao, Z.-J.; Yu, C.; Wang, X.-M.; Zhou, Y.-F.; Guo, L.; Xia, Y.; Zhang, B.-C.; Zeng, R.-C. Corrosion resistance enhanced by an atomic layer deposited Al_2O_3 /micro-arc oxidation coating on magnesium alloy AZ31. *Ceram. Int.* **2024**, *50*, 5541–5551. [CrossRef]
63. Nie, L.; Xia, Y.; Zhou, Y.; Zhang, J.; Cao, F.; Zhang, J. Investigation of AZ91D magnesium alloy corrosion behavior under thin electrolyte layer using nondestructive electrochemical techniques. *Int. J. Electrochem. Sci.* **2016**, *11*, 259–276. [CrossRef]
64. Guo, C.; Liu, L.; Liu, H.; Qian, F.; Zhou, Y.; Wang, L.; Li, J.; Wang, J. Effect of indium and yttrium on the corrosion behavior of AZ63 magnesium alloy. *J. Alloys Compd.* **2024**, *985*, 174068. [CrossRef]
65. Chen, Y.; Li, J.; Wu, L.; Zhang, Y.; Deng, J.; Yao, W.; Wu, J.; Yuan, Y.; Xie, Z.; Atrens, A.; et al. Effect of solution pH value on the corrosion resistance of Co-Fe LDHs coating developed on MAO treated magnesium alloy AZ31. *Colloids Surf. A* **2024**, *694*, 134220. [CrossRef]
66. Zhao, X.; Jin, Z.; Zhang, B.; Zhai, X.; Liu, S.; Sun, X.; Zhu, Q.; Hou, B. Effect of graphene oxide on anticorrosion performance of polyelectrolyte multilayer for 2A12 aluminum alloy substrates. *Rsc Adv.* **2017**, *7*, 33764. [CrossRef]
67. Samadianfard, R.; Seifzadeh, D.; Dikici, B. Smart sol-gel nanocomposite containing inhibitor-stabilized g-C₃N₄ nanoplates for corrosion protection of magnesium alloy. *Surf. Coat. Technol.* **2024**, *484*, 130764. [CrossRef]
68. Liu, S.; Huang, H.; Huang, G.; Qu, J. Influence of oxalic acid on the corrosion behavior of AZ91D magnesium alloy in deionized water. *Vacuum* **2023**, *215*, 112351. [CrossRef]
69. Zhang, W.; Zhang, R.; Xu, D.; Wu, L.; Xie, Z.-H.; Yu, G. Growth mechanism and corrosion resistance of layered double hydroxide film on magnesium alloy without external addition of magnesium and aluminum salts. *Colloids Surf. A* **2024**, *689*, 133677. [CrossRef]
70. Bahrapour, S.; Bordbar-Khiabani, A.; Siadati, M.H.; Gasik, M.; Mozafari, M. Improving the inflammatory-associated corrosion behavior of magnesium alloys by Mn₃O₄ incorporated plasma electrolytic oxidation coatings. *Chem. Eng. J.* **2024**, *483*, 149016. [CrossRef]
71. Xu, X.; Qu, J.; Huang, H. Synthesis of a dibenzimidazole compound and its corrosion inhibition behavior on AZ91D Mg alloy in 3.5 wt.% NaCl solution. *J. Mol. Struct.* **2023**, *1291*, 136065. [CrossRef]
72. Zhang, Y.; Dai, J.Y.; Zhao, L.; Wu, L.P. Corrosion resistance and biocompatibility of the KMgF₃ coated AZ31 magnesium alloy. *J. Alloys Compd.* **2023**, *968*, 172210. [CrossRef]
73. Curioni, M. The behaviour of magnesium during free corrosion and potentiodynamic polarization investigated by real-time hydrogen measurement and optical imaging. *Electrochim. Acta* **2014**, *120*, 284–292. [CrossRef]
74. Chen, Y.; Ying, T.; Yang, Y.; Wang, J.; Zeng, X. Regulating corrosion resistance of Mg alloys via promoting precipitation with trace Zr alloying. *Corros. Sci.* **2023**, *216*, 111106. [CrossRef]
75. Daroonparvar, M.; Helmer, A.; Ralls, A.M.; Khan, M.U.F.; Kasar, A.K.; Gupta, R.K.; Misra, M.; Shao, S.; Menezes, P.L.; Shamsaei, N. Pitting corrosion behavior and corrosion protection performance of cold sprayed double layered noble barrier coating on magnesium-based alloy in chloride containing solutions. *J. Magnes. Alloys* **2023**, *11*, 3099–3119. [CrossRef]
76. Jian, S.-Y.; Liu, Y.-C.; Chang, C.-J. Novel green and ecofriendly route for fabricating a robust corrosion protection coating on AZ91D magnesium alloy. *Electrochem. Commun.* **2024**, *160*, 107667. [CrossRef]
77. Peng, Y.; Wan, S.; Liao, B.; Guo, X. Preparation and properties of multi-function composite coating on AZ91D magnesium alloy with wave-assimilation and anti-corrosion performance. *Surf. Coat. Technol.* **2024**, *478*, 130464. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

A Study on the Influence of Different Defect Types on the Corrosion Behavior of Q235/TA2 Composite Plates in a Marine Environment

Jianbo Jiang ^{1,2,†}, Nannan Li ^{3,†}, Bingqin Wang ^{3,*}, Fangfang Liu ^{1,2}, Chao Liu ³ and Xuequn Cheng ³

¹ State Key Laboratory of Metal Material for Marine Equipment and Application, Anshan 114009, China; jiangjianbo@ansteel.com.cn (J.J.); liufangfang@ansteel.com.cn (F.L.)

² Ansteel Beijing Research Institute Co., Ltd., Beijing 102209, China

³ Institute for Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, China; m202121375@xs.ustb.edu.cn (N.L.); liuchao@ustb.edu.cn (C.L.); chengxuequn@ustb.edu.cn (X.C.)

* Correspondence: d202110692@xs.ustb.edu.cn

† These authors contributed equally to this work.

Abstract: The structural design of steel–titanium composite plates significantly affects their corrosion resistance. To investigate the impact of defects of different shapes and sizes on the corrosion behavior of steel–titanium composite plates, this study designed six types of defects and conducted a series of characterization tests. The results showed that due to the galvanic interaction between carbon steel and titanium alloy, small defects initially accelerate corrosion, resulting in 50% to 200% more corrosion weight loss compared to large defects. However, in the later stages of immersion, the corrosion rate of small defects decreased by up to 35%, which was attributed to the accumulation of protective corrosion products. Additionally, there is an inverse relationship between the corrosion rate and the thickness ratio of the composite plate. The reduction in the area of Q345B also results in additional corrosion loss of up to 32%.

Keywords: titanium/steel composite plates; defect morphology; marine environment; corrosion dynamics; thickness ratio

1. Introduction

Steel–titanium composite plate plates [1–4], as an emerging class of composite materials, capitalize on the synergistic benefits of carbon steel’s superior mechanical properties and cost-effectiveness, coupled with the corrosion resistance of titanium alloys [5,6]. This combination has led to their extensive application in various large-scale infrastructure projects, such as bridges, pipelines, and offshore platforms, offering significant advantages in terms of cost-effectiveness and corrosion resistance. However, due to their unique structure and inevitable defects, steel–titanium composite plates still face significant corrosion challenges in harsh marine environments characterized by high humidity, high temperatures, and corrosive ions [7–10].

Previous studies have extensively explored the corrosion behavior of these composite plates in marine environments [11–13], focusing on aspects such as surface corrosion, electrochemical behavior, and long-term stability. Li et al. investigated the performance of 316L stainless steel and A6 carbon steel composite plates under neutral salt spray tests, observing significant elemental overlap at the composite interface [12]. Patnaik et al. indicated that the coupling of titanium with steel accelerates the corrosion of steel due to titanium’s more noble position in the electrochemical series [13]. Prolonged exposure led to accelerated corrosion along the interface of A6 carbon steel components, surpassing the corrosion rate of the carbon steel matrix. Li et al.’s results indicate that the corrosion of titanium–steel composite plates is influenced by various corrosion behaviors in both the

near-interface and far-interface regions [5,6]. In regions far from the interface unaffected by galvanic effects, the corrosion reaction begins with localized corrosion, which then transitions to uniform corrosion. At the interface, carbon steel experiences accelerated corrosion through galvanic effects in the early stages. In the later stages, once the corrosion at the interface reaches a certain level, it transitions to a combined action of galvanic corrosion and crevice corrosion.

In marine environments, various factors significantly influence the corrosion of titanium-clad steel plates. Salinity, temperature, pH levels, and oxygen concentrations are pivotal in determining the rate and nature of corrosion [14–19]. These environmental variables can either accelerate corrosive processes or, in some instances, help form protective barriers on the materials [20,21]. Liu et al. studied the corrosion behavior of steel–titanium composite plates in different marine environments [22]. The composite interface area has a complex, layered structure and can be divided into five areas. Among them, areas III and IV have higher electrochemical activity and are corrosion-inducing areas. The microcurrent in zone III is twice that of carbon steel and titanium. At the same time, the accumulation of Cr in the corrosion product layer promotes the generation of α -FeOOH, further improving the protection of the corrosion product layer. Furthermore, effective strategies for corrosion prevention are essential in extending the lifespan of these composite materials. Techniques such as applying protective coatings, implementing cathodic protection, or modifying the alloy composition are commonly employed. However, the effectiveness of these strategies varies based on environmental conditions and the specific application of the material. Additionally, the long-term durability and maintenance of titanium-clad steel plates in harsh marine environments remain a critical concern. Regular maintenance practices, proactive inspection schedules, and timely repairs play a crucial role in ensuring the structural integrity and performance of these materials over time.

The presence of surface defects has been identified as a critical factor exacerbating corrosion in composite plates. Hu et al. examined the galvanic corrosion behavior of Titanium-Clad Steel Plates (TCSP) with defects penetrating the titanium layer from the side and underside [11]. The galvanic corrosion on the TCSP side resulted in extensive pitting corrosion, with pits distributed differently across splash zones, tidal zones, and submerged areas. Severe corrosion occurred beneath TCSP titanium layer defects, with the size of the defect impacting the density of corrosion products. Zhao et al.'s research showed that defects increased the corrosion rate, and while welds did not alter the structure of the corrosion product film, defects led to a lack of protective corrosion products [23]. Additionally, defects invariably increase the corrosion rate. Under flowing systems, samples with shallow defects tended to deepen radially, and under high shear rates [24], the upper and rear edges of defects showed tendencies to deepen and expand the affected area. However, existing studies lack a comprehensive understanding of the corrosion mechanisms and influencing factors of various sizes and types of defects, leaving knowledge gaps that require further exploration to address practical engineering challenges.

To deepen the understanding of the corrosion behavior of titanium–steel composite plates in marine environments, this study focuses on pinpointing corrosion mechanisms in simulated marine solutions, examining point defects [25–27], surface defects, and samples with varying thickness ratios [28]. Through systematic experimental investigations, this research aims to enhance the understanding of the corrosion mechanisms of titanium–steel composite plates in marine settings, providing crucial insights for the design of more corrosion-resistant engineering materials.

2. Materials and Methods

2.1. Immersion Test

This study conducts a comprehensive examination of the corrosion resistance of titanium–steel composite plates, specifically focusing on different types of surface defects and varying thickness ratios. The experimental design was structured into four distinct periods: 7, 15, 30, and 45 days. The simulated marine environment for these experiments

was using Xisha simulated solution, comprising 0.1 wt% NaCl, 0.05 wt% Na₂SO₄, and 0.05 wt% CaCl₂, with a pH maintained at 4.9.

The experimental samples were categorized into three distinct groups based on their defect types and thickness ratios, as illustrated in Figure 1a–c. The first two groups comprised three sets of point defect samples and three sets of line defect samples, respectively. In these groups, the titanium plates were consistently 2 mm thick, while the Q345B steel plates were 4 mm thick. The third group consisted of two types of titanium–steel composite plates with varying thickness ratios. The specific thicknesses of the titanium and Q345B steel in this group are depicted in Figure 1(c1,c2), designed with ratios of 1:4 and 1:1, respectively. The sample size and structural design of three types of point defects and three types of line defects are shown in Figure 1e,f. The chemical compositions of titanium alloy plate and carbon steel are shown in Tables 1 and 2, respectively.

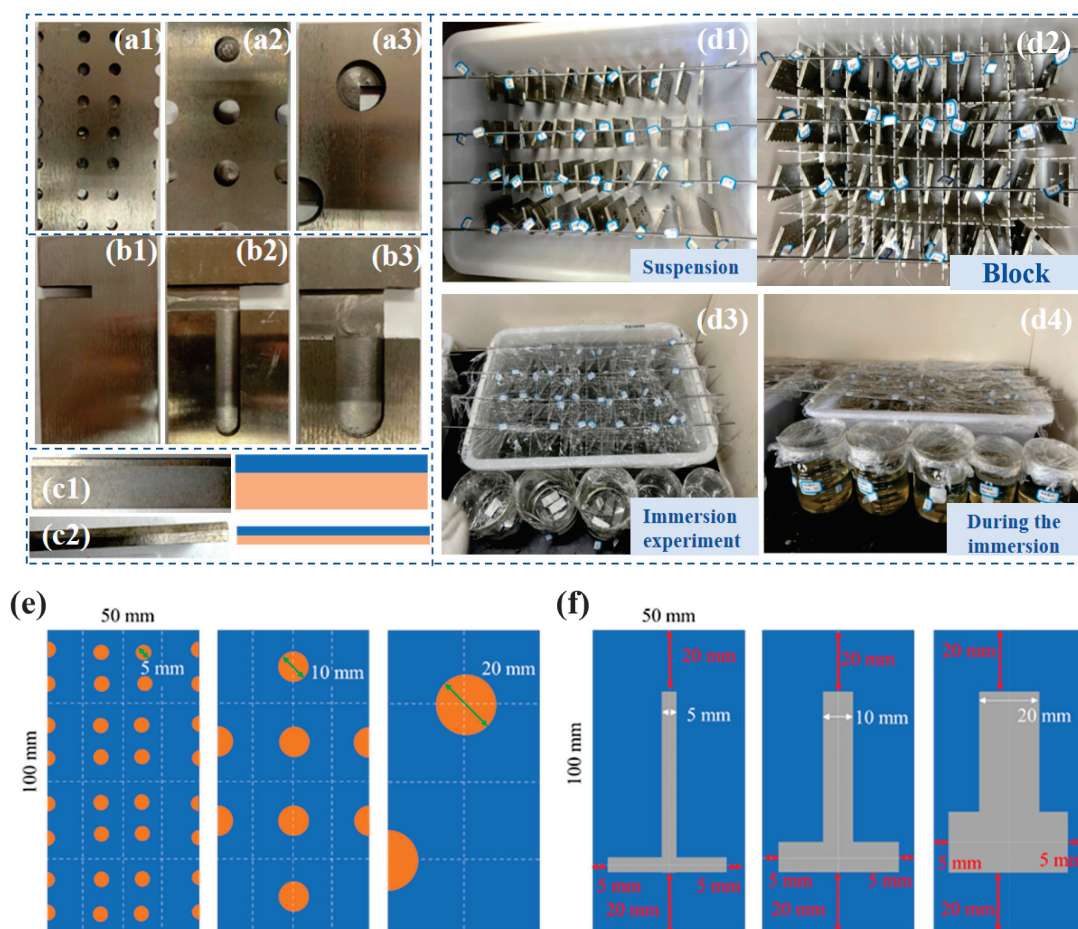


Figure 1. Preparation process for specimen immersion and initial state after immersion. (a1–a3) are samples with three types of point defects, (b1–b3) are samples with three types of point defects, (c1,c2) are samples with two different thickness ratios, (d1–d4) show the four main steps of the immersion experiment, (e) is the design drawing of three point defect samples, (f) is the design drawing of three line defect samples.

Table 1. Chemical composition of titanium (wt%).

H	C	N	O	Si	Fe	Ti
0.002	0.03	0.01	0.01	0.04	0.18	Bal.

Table 2. Chemical composition of Q345B low alloy steel (wt%).

C	Si	Mn	P	S	Fe	C
0.16	0.35	1.34	0.22	0.11	Bal.	0.16

2.2. Weight Loss Measurement

In this investigation, eight carbon steel specimens were methodically prepared, each exhibiting varying exposed areas from 5.598 cm² to 17.6 cm². The initial preparation of each sample involved a standard procedure of polishing, followed by degreasing using acetone and subsequent cleansing with anhydrous ethanol. Upon drying, their initial weights were meticulously recorded. The samples were then subjected to a series of four immersion cycles, during which the non-experimental areas were carefully sealed. After each cycle, the corrosion morphology was documented to track progressive changes.

The removal of rust was carried out in accordance with the GB/T16545-1996 standards [29], employing a designated solution and conducting the procedure within a fume hood to ensure safety and accuracy. Following this, each specimen underwent ultrasonic cleaning and was extensively rinsed with distilled water and anhydrous ethanol, after which they were dried, and their post-corrosion weights were accurately measured. To avoid errors, all measurements were performed three times and averaged in the final results.

To elucidate the influence of surface defects on the corrosion resistance of the specimens, a detailed examination of their surface micromorphology post-rust removal was conducted using a scanning electron microscope (SEM, ZEISS Gemini SEM 500, Jena, Germany).

2.3. Electrochemical Testing

Electrochemical measurement is carried out in PARSTAT4000A (AMETEK, San Diego, CA, USA) electrochemical workstation. A standard three-electrode system comprising a saturated calomel electrode (SCE) as the reference electrode, a Pt plate as the counter electrode (CE), and specimens as the working electrode (WE) were hired in the electrochemical test. Before the electrochemical experiment, the open circuit potential was measured for 60 min until it reached a stable state. When the dynamic polarization curve is measured, the scanning rate is 0.5 mV/s, and the scanning potential ranges from 0.5V_{vs}OCP to 0.5V_{vs}OCP. EIS tests were performed over the frequency range of 100 kHz to 0.01 Hz at open-circuit potential (OCP) with a 10 mV sinusoidal amplitude. The EIS data were analyzed using the ZsimpWin 3.1 software. The test solution was consistent with the soaking experiment. The displayed results are selected based on tests conducted three times or more to ensure the reproducibility of the experiment.

3. Results

3.1. The Impact of Point Defects

In Figure 2a, the first type of point defects shows these trends: After 7 days, slight corrosion products accumulate around the through-hole, while noticeable corrosion, indicated by red rust traces, appears in the non-through-hole area. At 15 days, rust layers significantly increase in both regions, with noticeable corrosion products at the hole and exposed carbon steel edges. By 30 days, surface rust flow is significantly enhanced for both defect types. After 45 days, despite a slight increase in corrosion products and rust flow, the corrosion rate slows, with minimal changes from the 30-day mark. The titanium plate remains uncorroded, while the carbon steel surface shows progressively deepening corrosion over time. In Figure 2b, the second type of point defect shows limited rust layer accumulation in both through-hole and non-through-hole regions after 7 days of immersion testing, with red rust streaks on the titanium plate surface. With increased immersion time, corrosion products continue to accumulate in the through-hole area and gradually increase in the non-through-hole area, filling the holes and accumulating externally. The proportion of loose, easily detached red rust decreases, while dense rust layers significantly

accumulate in the hole defect area, and red rust streaks on the titanium plate deepen. After rust removal, corrosion traces inside the holes are slight at early stages but become more pronounced with time, forming corrosion pits on the hole surfaces. In Figure 2c, the third type of point defect shows more pronounced corrosion in both the through-hole and surrounding non-through-hole areas. With prolonged immersion, corrosion products gradually cover the entire exposed carbon steel surface, and red rust streaks become more prominent. After rust removal, the dissolution of the steel matrix at the hole-like defect areas is evident, with corrosion traces deepening over time.

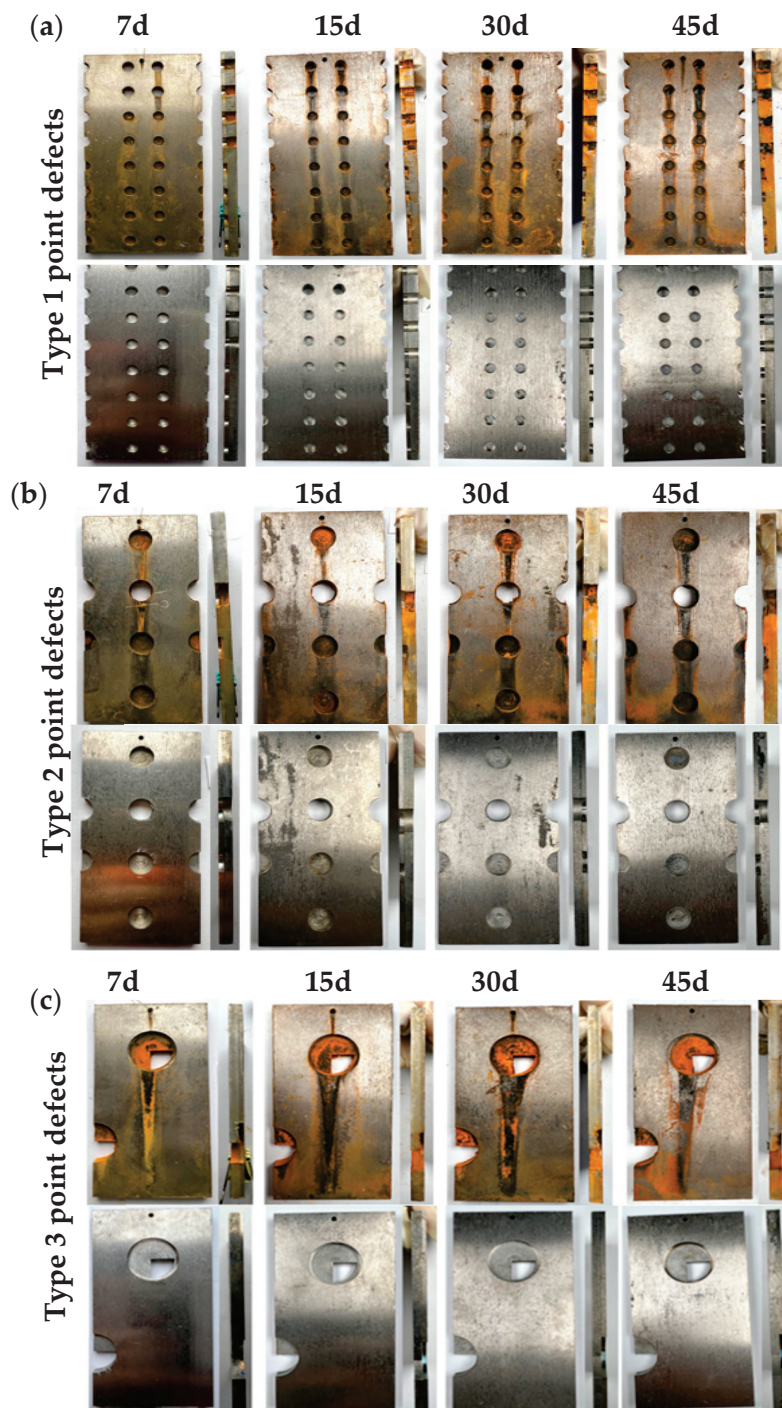


Figure 2. Macroscopic corrosion morphologies of different point-defect samples in simulated marine solution after various immersion durations: (a) type I point defects; (b) type II point defects; (c) type III point defects.

After 45 days of immersion in a simulated marine solution, detailed observations were made on the corrosion behavior of three types of point-defect titanium–steel composite plates. As shown in Figure 3, the carbon steel surface with type I point defects exhibited significant longitudinal corrosion, especially in areas far from the composite plate (Figure 3a). Type II point defects displayed dense pitting on the carbon steel longitudinal surface, particularly in regions distant from the composite plate, with small, deep pits at the composite interface (Figure 3b). Type III point defects exhibited uniform longitudinal corrosion in the titanium–steel composite plates, with smaller and shallower pits (Figure 3c).

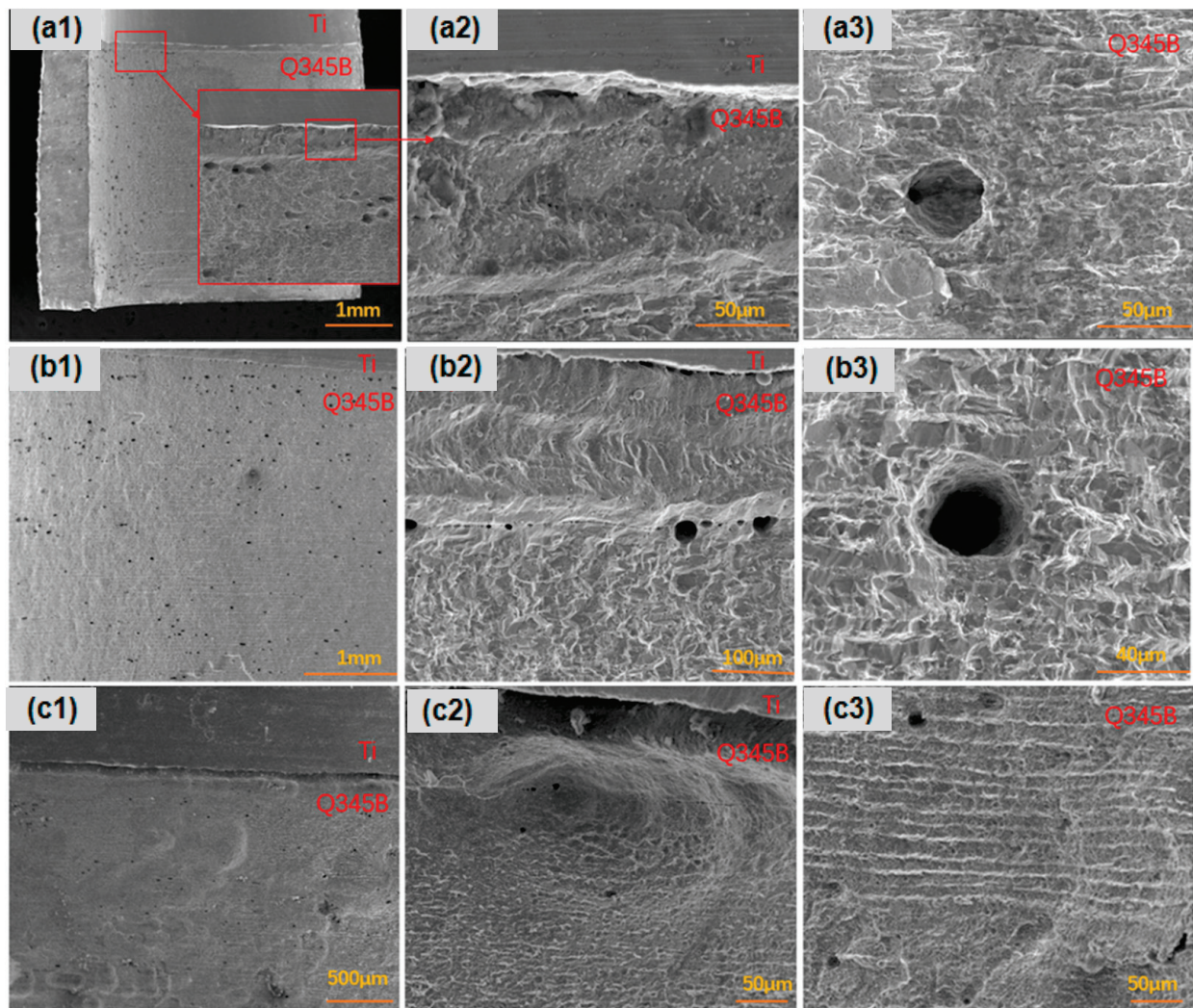


Figure 3. Longitudinal corrosion morphologies of point-defect samples after 45-day marine immersion. (a1–a3) are type I point defects; (b1–b3) are type II point defects; (c1–c3) are type III point defects.

In contrast, focusing on surface corrosion, as shown in Figure 4, the titanium–steel composite plate with type I point defects exhibited uniform surface corrosion, with larger corrosion pits and notable pitting. Longitudinal galvanic corrosion of titanium–steel was more pronounced (Figure 4a). Type II point defects also showed uniform surface corrosion, but the pits were smaller and shallower, with more evident accelerated longitudinal galvanic corrosion (Figure 4b). Lastly, the titanium–steel composite plate with type III point defects exhibited uniform surface corrosion (Figure 4c). Due to the differences between ferrite and pearlite, deeper surface corrosion mainly occurred in ferrite areas, with less accelerated galvanic corrosion.

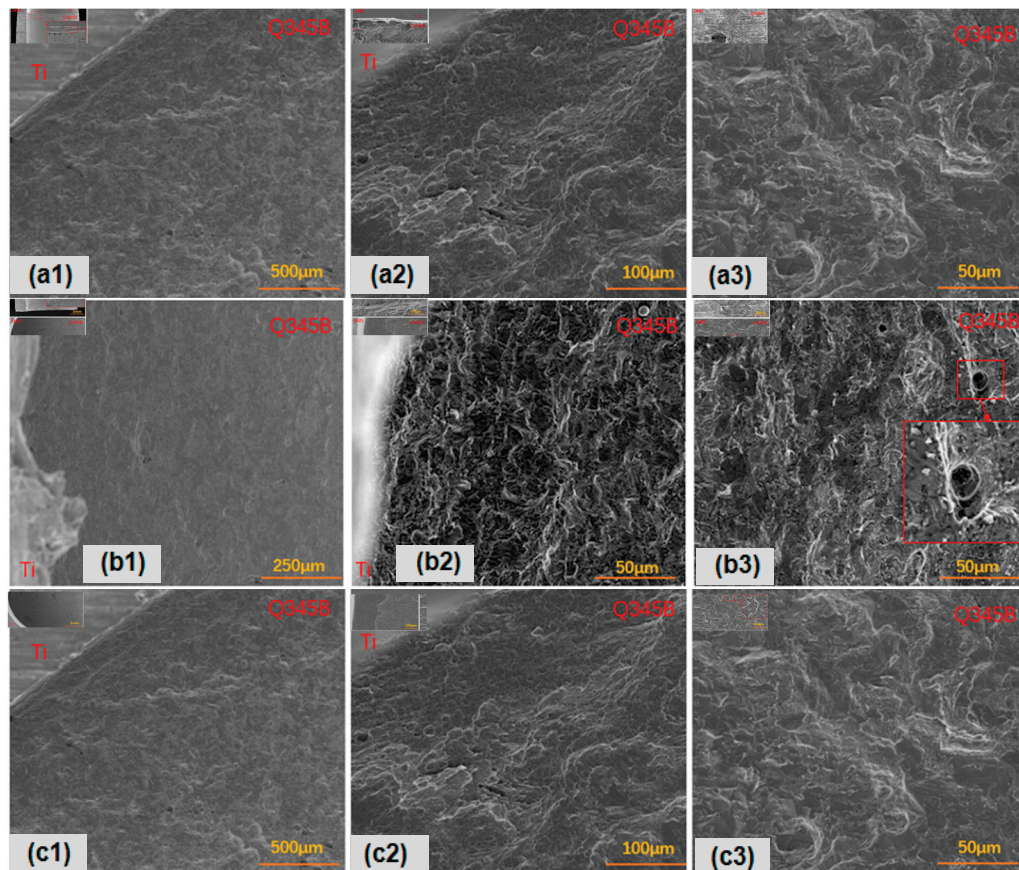


Figure 4. Transverse corrosion morphologies of point-defect samples after 45-day marine immersion: (a1–a3) are type I point defects; (b1–b3) are type II point defects; (c1–c3) are type III point defects.

Figure 5 shows the weight loss and corrosion rate of the three types of point-defect samples in the simulated marine solution after various immersion durations. The increasing weight loss for all three types of point defects indicates an intensifying degree of corrosion. The corrosion rate increased in the first three cycles and decreased in the fourth cycle (45 days) due to the early formation of loose, easily detachable corrosion products. Among them, the corrosion rate of point defect 1 dropped by 35%, and the corrosion rate of point defect 2 dropped by 16%.

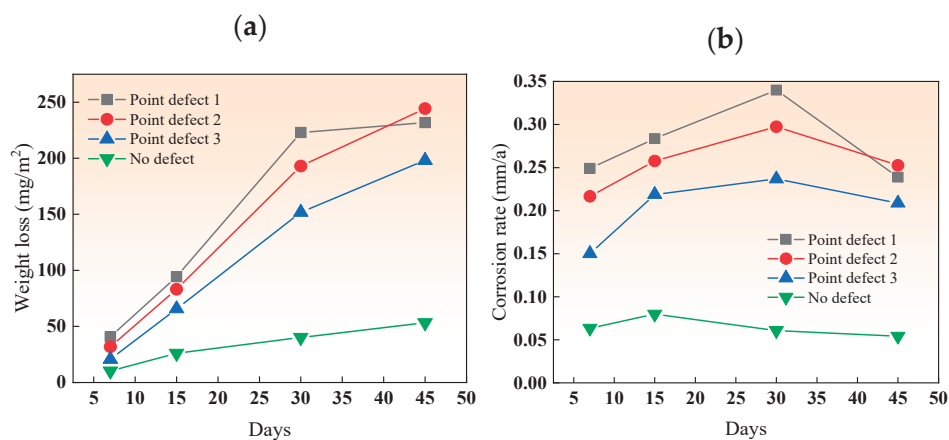


Figure 5. (a) Weight loss and (b) corrosion rate of different point-defect samples in simulated marine solution after various immersion durations.

Over time, these products accumulated and became denser and harder to detach, forming a protective layer and reducing the corrosion rate of carbon steel. In the simulated marine solution, the period of increased corrosion rate for the three types of point defects was longer than in a neutral salt spray environment. This is because the titanium–steel composite plates corroded more severely in the salt spray environment, forming a dense corrosion product film more quickly, hence the reduction in corrosion rate starting in the third cycle. The decrease in corrosion rate with increasing defect size is due to the significant effect of galvanic acceleration in small-sized defects. In the fourth cycle, the accumulation of corrosion products in type I point defects provided some protection to the carbon steel, leading to a reduced corrosion rate. The delay in the onset of the decrease in the rate of type I point defects, compared to salt spray, is due to the overall lower corrosion rate in the simulated marine solution, making it difficult to accumulate enough products to fill the entire defect hole early on.

It can be seen from Figure 6a that the potentials of composite plates with three different point defects are very close to the self-corrosion potential of carbon steel. As the size of point defects increases, the potential shifts slightly positively. The galvanic current shifts slightly negatively with increasing point defect size. The galvanic potential and galvanic current change slightly with the size of point defects, and the corrosion rate of titanium/steel galvanic pairs with small-size point defects is slightly larger, which is consistent with the weight loss and characterization results.

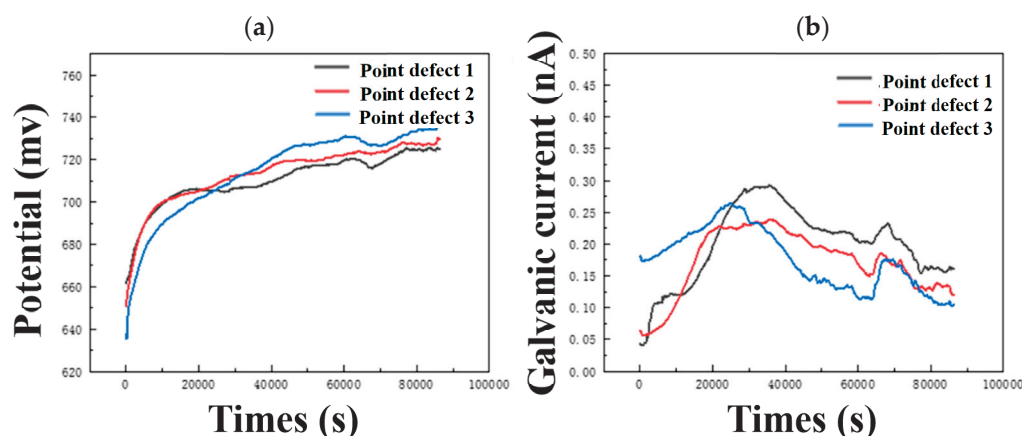


Figure 6. Continuous monitoring results of (a) open circuit potential and (b) galvanic current of three different point defect samples.

3.2. The Impact of Linear Defects

As shown in Figure 7a, with increasing immersion time, significant corrosion occurred inside the linear defects, with corrosion products accumulating within these defects. After an initial 7-day immersion, the exposed carbon steel areas were filled with easily detachable red rust due to the narrowness of type I linear defects and the ease of filling these defects with galvanic corrosion when in contact with titanium. With time, the corrosion intensified, and the rust layer became denser and continued to accumulate. After derusting, the titanium alloy surface of the titanium–steel composite plate was visibly uncorroded, with a metallic luster, while the carbon steel surface inside the linear defects became rougher and showed clear signs of corrosion, which deepened over time. Figure 7b shows the corrosion morphology of type II linear defect samples after various immersion durations. After 7 days of immersion, the entire surface of the linear defect was covered with an orange-yellow rust layer, which, after 15 days, transformed into a denser corrosion product in about 80% of the area, with continuous accumulation and formation of more dense rust layers over time. After derusting, the titanium alloy surface was uncorroded, but the carbon steel surface inside the linear defects became increasingly rough, showing clear signs of deepening corrosion. Figure 7c shows the corrosion morphology of type III linear

defect samples in a simulated marine environment after various immersion durations. The exposed carbon steel areas inside the linear defects were uniformly covered with corrosion products, which were not very dense initially, exposing the carbon steel substrate. As immersion time increased, more corrosion products accumulated, increasing their density. After 45 days, all exposed carbon steel substrates were covered with corrosion products. After derusting, the exposed carbon steel areas showed uniform corrosion, which deepened over time.

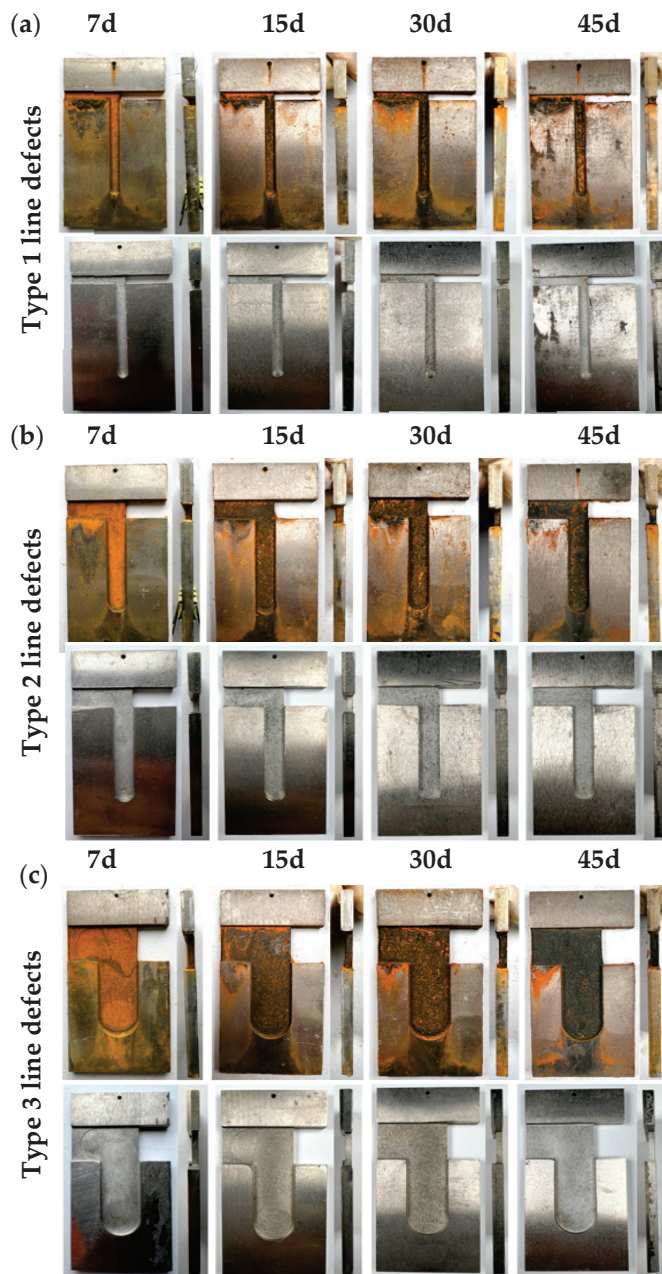


Figure 7. Macroscopic corrosion morphologies of linear-defect samples post various immersion durations: (a) type I linear defects; (b) type II linear defects; (c) type III linear defects.

After 45 days of immersion in the simulated marine solution, the titanium–steel composite plates with three types of linear defects showed unique characteristics in terms of longitudinal corrosion. As shown in Figure 8, for type I linear defects, the surface point defects of the titanium–steel composite plate exhibited uniform corrosion, but the corrosion depth was slightly greater in areas closer to the titanium. Type II linear defects showed a

difference in the density of pitting pits along the longitudinal direction of the carbon steel, especially with denser pits near the composite interface, accompanied by deeper pits and slight delamination. Additionally, longitudinal corrugated corrosion morphologies were observed due to sample processing. Lastly, the situation with type III linear defects was that the carbon steel had more and larger pitting pits near the composite interface, deeper in depth, while areas farther from the interface exhibited uniform corrosion.

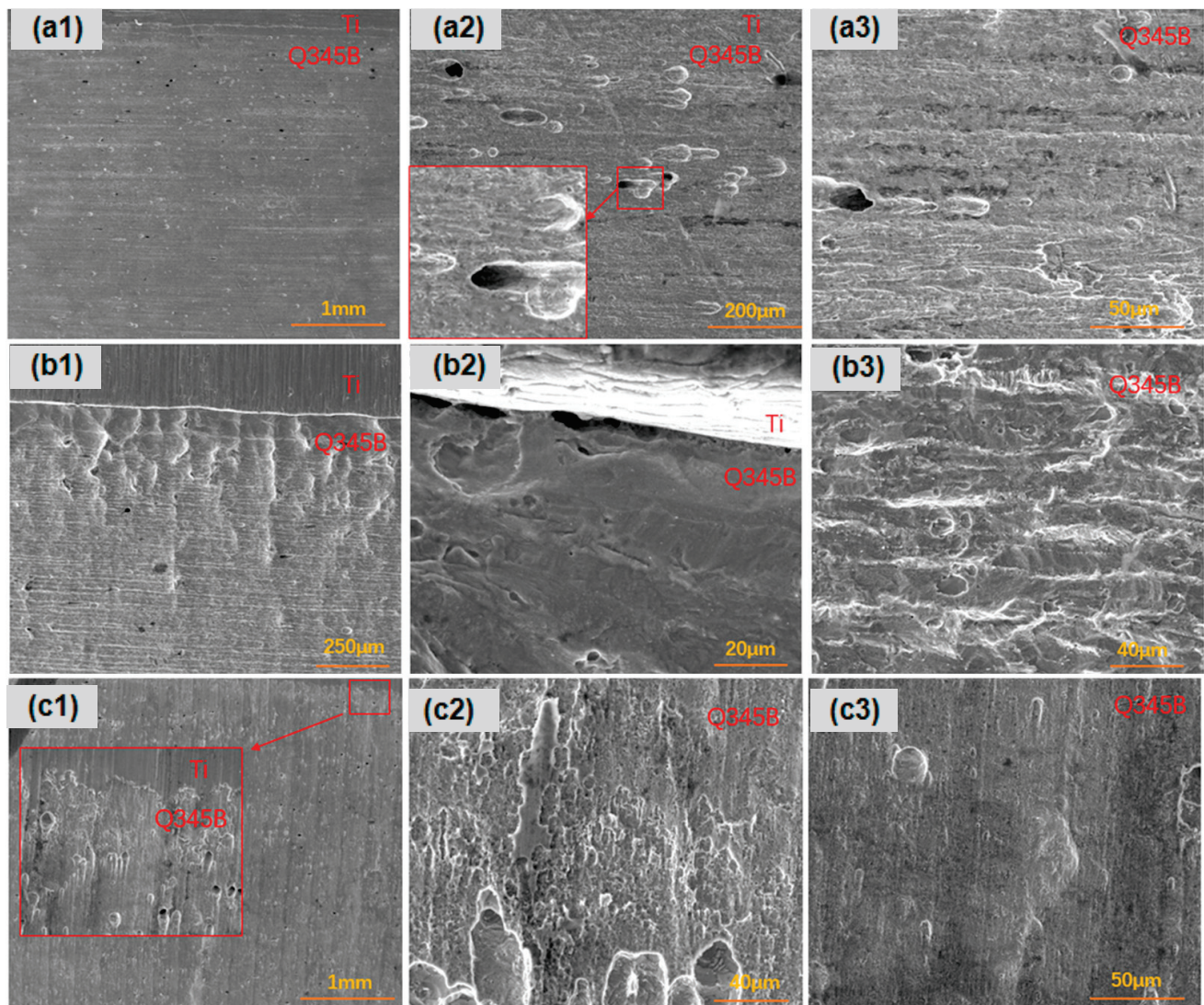


Figure 8. Longitudinal corrosion morphologies of linear-defect samples after 45-day marine immersion: (a1–a3) are type I linear defects; (b1–b3) are type II linear defects; (c1–c3) are type III linear defects.

Regarding surface corrosion, the titanium–steel composite plates with three types of linear defects exhibited distinct characteristics. As shown in Figure 9, for type I linear defects, the titanium–steel composite plate displayed uniform corrosion at the surface defect sites, with varying depths, particularly near the titanium. This type also showed pronounced longitudinal galvanic corrosion effects. In type II linear defects, pitting was present, but overall surface corrosion was uniform, with smaller and shallower pits. Longitudinal galvanic corrosion effects were also observed. Lastly, for type III linear defects, the titanium–steel composite plate had dense pitting near the titanium but uniform corrosion in areas farther away, with less pronounced longitudinal galvanic corrosion effects compared to the other types.

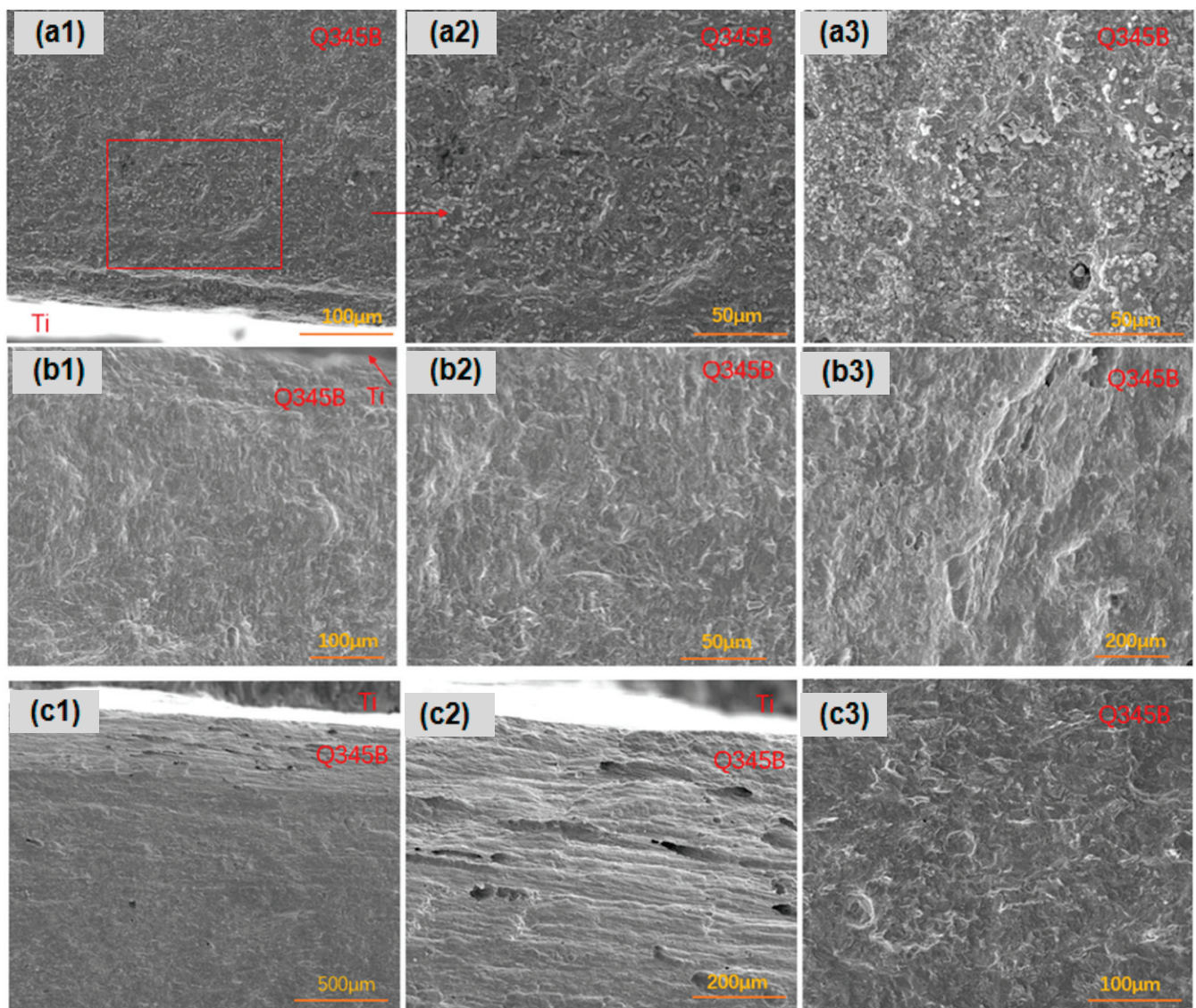


Figure 9. Transverse corrosion morphologies of linear-defect samples after 45-day marine immersion: (a1–a3) are type I linear defects; (b1–b3) are type II linear defects; (c1–c3) are type III linear defects.

In the simulated marine solution, the weight loss and corrosion rate of the three types of linear defects after various immersion durations are shown in Figure 10. The corrosion rate pattern for all three types of linear defects was relatively uniform, increasing initially and then decreasing due to the early formation of loose, easily detachable corrosion products. With time, the products accumulated and became denser and harder to detach, forming a protective layer on the substrate and reducing the corrosion rate. The corrosion rate of the composite plates with linear defects decreased from type I to type III as the size of the linear defects increased, reducing the area affected by the galvanic acceleration of the titanium–steel couple. The reason for the difference in behavior compared to point defects is that, although linear defects have the same width as point defects, they are continuous along the length, making it harder for corrosion products to accumulate in linear defects than in point defects. Similar to point defects, the corrosion rate of smaller line defects (types 1 and 2) decreases more, about 20%, in the later stages of immersion.

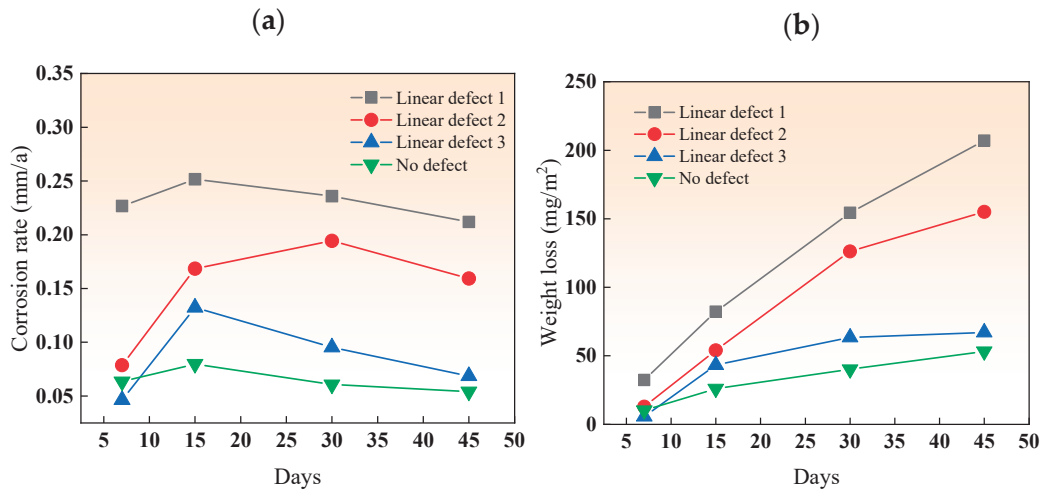


Figure 10. (a) Corrosion rate and (b) weight loss of linear-defect samples after various immersion durations.

It can be seen from Figure 11a that as the size of the linear defect increases, the potential shifts slightly positively. On the contrary, the galvanic current shifts negatively with the increase in line defect size, and when the line defect size increases to type 3, the negative shift of the curve is very large. This shows that increasing the size of line defects in composite plates can slow down corrosion to a certain extent, which is consistent with the weight loss and characterization results.

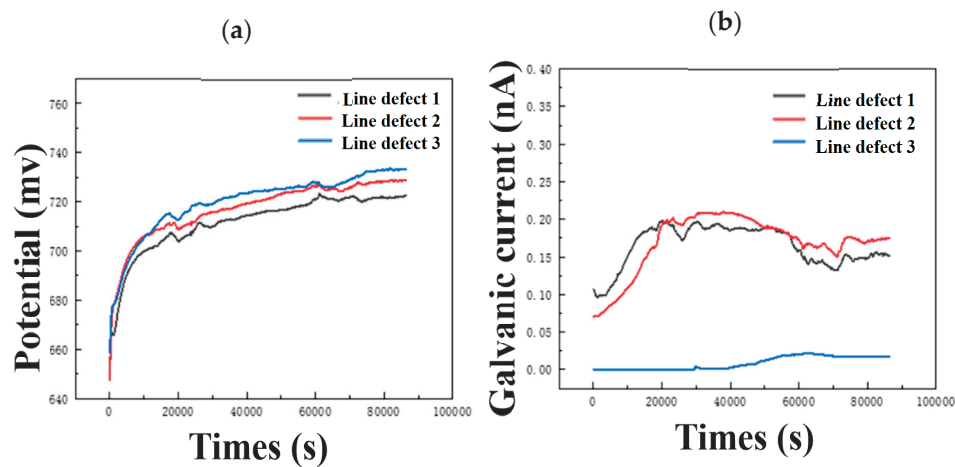


Figure 11. Continuous monitoring results of (a) open circuit potential and (b) galvanic current of three different line defect samples.

3.3. Impact of Different Thickness Ratios on the Corrosion of Titanium–Steel Composite Plates

Figure 12a reveals the corrosion patterns of 1:4 thickness ratio titanium–steel composite plates after varying immersion times in a simulated marine environment. The carbon steel on the titanium plate's reverse side corrodes, with corrosion deepening and product accumulation increasing over time. The side touching the titanium showed similar trends, with pronounced corrosion at the interface. Figure 12b displays similar findings for 1:1 thickness ratio plates, showing increased surface corrosion over time. After de-rusting, the carbon steel side shows severe corrosion, worsening with time. Initially, no holes were evident at the interface, but they appeared after 30 days.

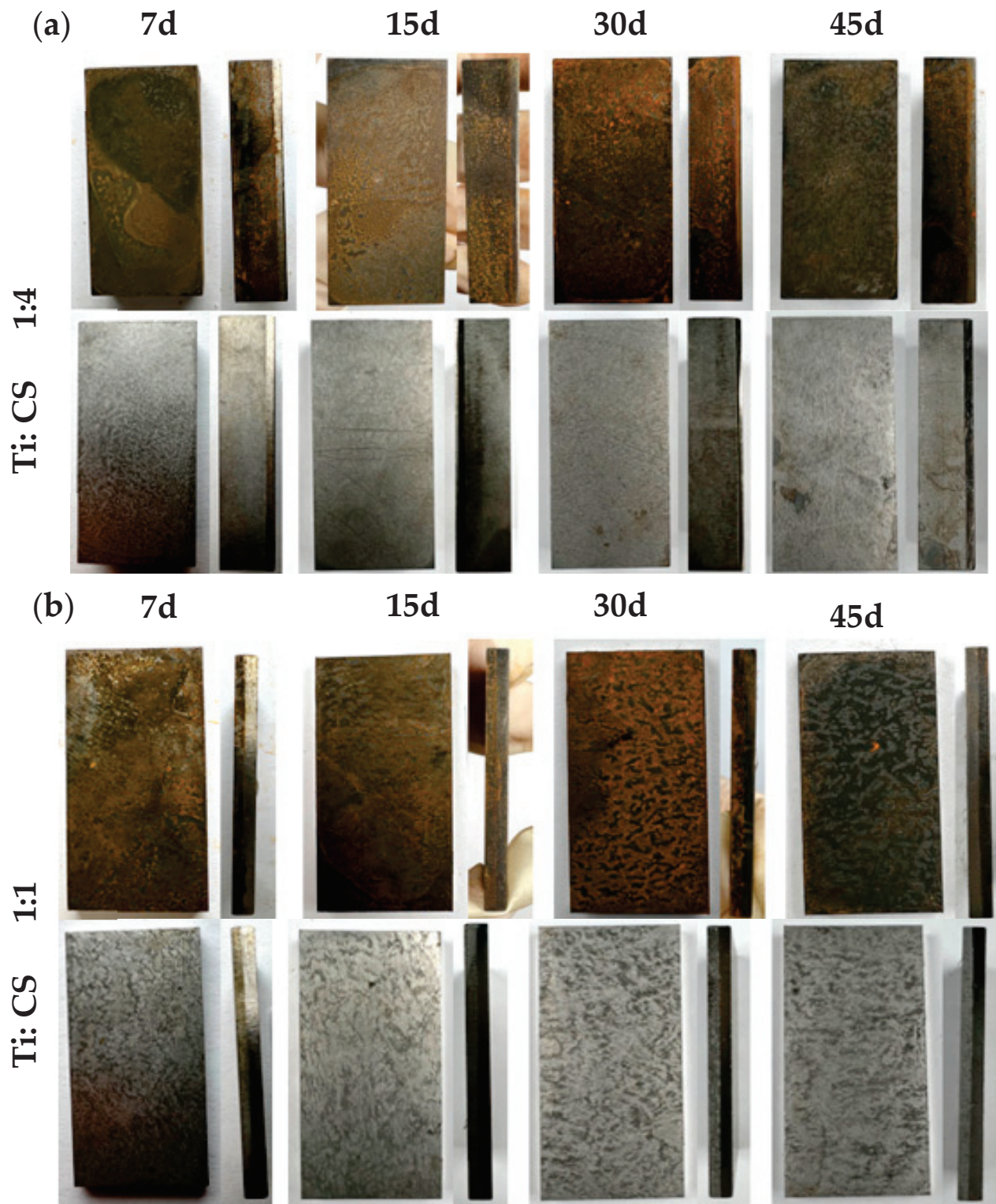


Figure 12. Compares the corrosion morphologies of composite plates with (a) 1:4 and (b) 1:1 thickness ratios after marine environment immersion tests.

For the titanium–steel composite plate with a thickness ratio of 1:4 immersed in a marine simulated solution for 45 days, as shown in Figure 13, the carbon steel along the longitudinal direction exhibited more numerous, larger, and deeper pitting near the composite interface compared to farther regions, where corrosion was more uniform. The carbon steel surface showed uniform corrosion with pit presence.

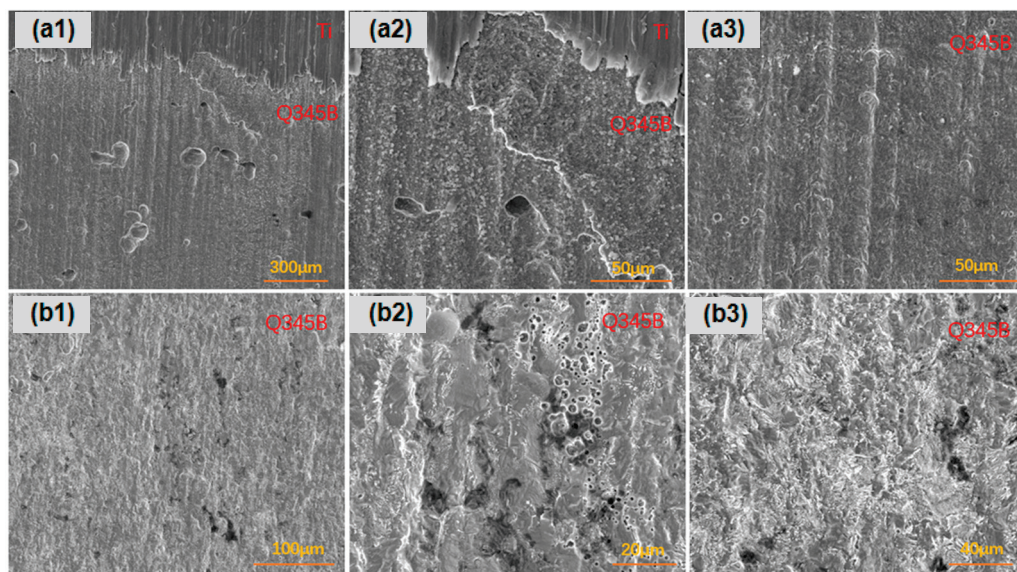


Figure 13. The corrosion morphology of the titanium–steel specimen with a thickness ratio of 1:4 after 45 days of immersion in a simulated marine solution, post-rust removal: (a1–a3) are longitudinally; (b1–b3) are laterally.

As shown in Figure 14, for the titanium–steel composite plate with a thickness ratio of 1:1 immersed for 45 days, the corrosion along the longitudinal direction was more severe near the composite interface, with more pits that were larger and deeper compared to farther regions. The overall corrosion severity was greater than that of the plate, with a thickness ratio of 1:4. The carbon steel surface showed uniform corrosion with pit presence.

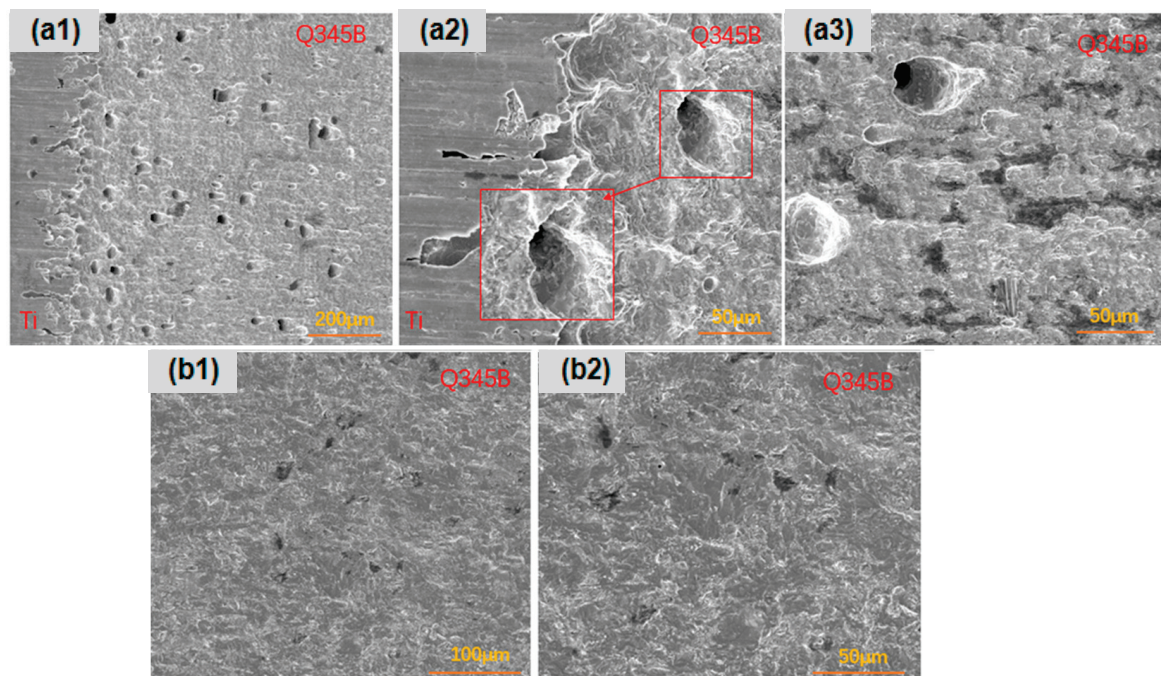


Figure 14. The corrosion morphology of the titanium–steel specimen with a thickness ratio of 1:1 after 45 days of immersion in a simulated marine solution, post-rust removal: (a1–a3) are longitudinally; (b1,b2) are laterally.

Figure 15 indicates that for both ratios, weight loss and corrosion severity increased over time. The corrosion rates showed an initial increase, followed by a decrease, suggesting

that corrosion products eventually form a protective layer. The corrosion rate per unit area was higher in the 1:1 ratio plate than in the 1:4 plate, mainly due to changes in the carbon steel component.

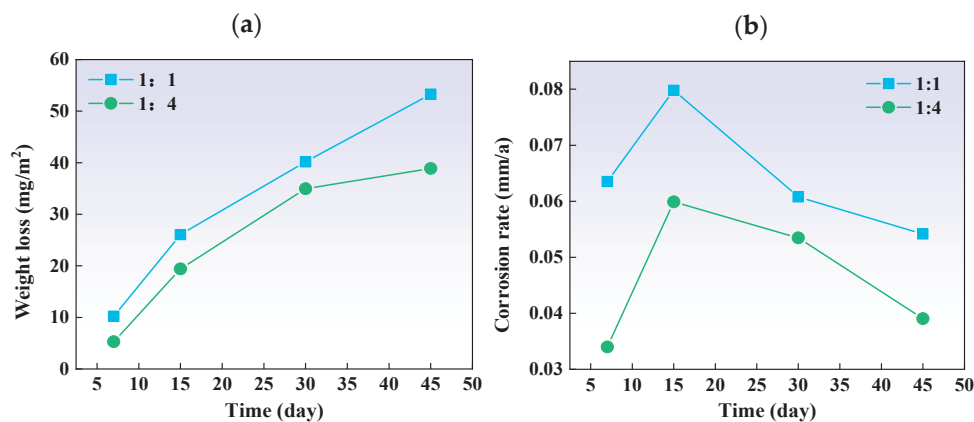


Figure 15. The (a) weight loss and (b) corrosion rate of different thickness ratio titanium–steel composite plate samples after immersion tests.

The polarization curves of two different titanium/carbon steel thickness ratio samples (1:1 and 1:4) in the simulated solution are shown in Figure 16. The cathodic process of all curves is clearly dominated by electron transfer, and their anodic process is controlled by the dissolution of the Q345B matrix. The fitting results show that the thicker the carbon steel, that is, the larger its area, the lower its corrosion current density (i_{corr}). This is consistent with the results of weight loss and microscopic characterization.

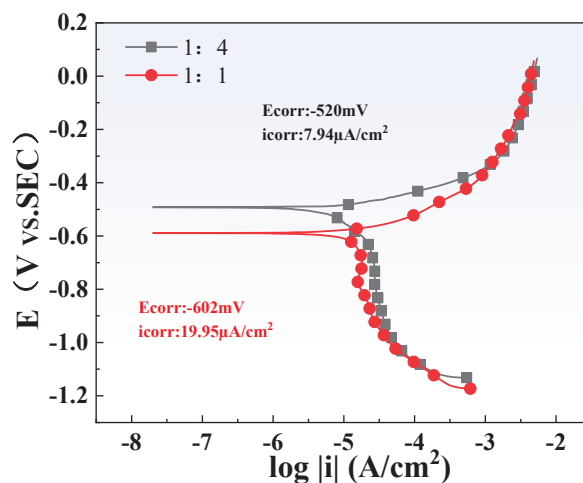


Figure 16. Electrochemical polarization curve test results of steel plates with different thickness ratios.

Figure 17 shows the results of electrochemical impedance spectroscopy testing. Both curves on the Nyquist plot exhibit a single semicircular arc, indicating that their electrochemical kinetics are controlled by charge transfer. It is worth noting that compared with the 1:1 titanium/carbon steel composite plate, the curve corresponding to the titanium alloy of the 1:4 titanium/carbon steel composite plate has a larger radius. R_s in the equivalent circuit diagram represents the solution resistance, R_f and CPE_f are the resistance and capacitance of the membrane, respectively, and R_{ct} represents the charge transfer resistance. Fitting results show that thicker carbon steel can provide composite plates with higher charge transfer resistance (Table 3), thereby slowing down corrosion.

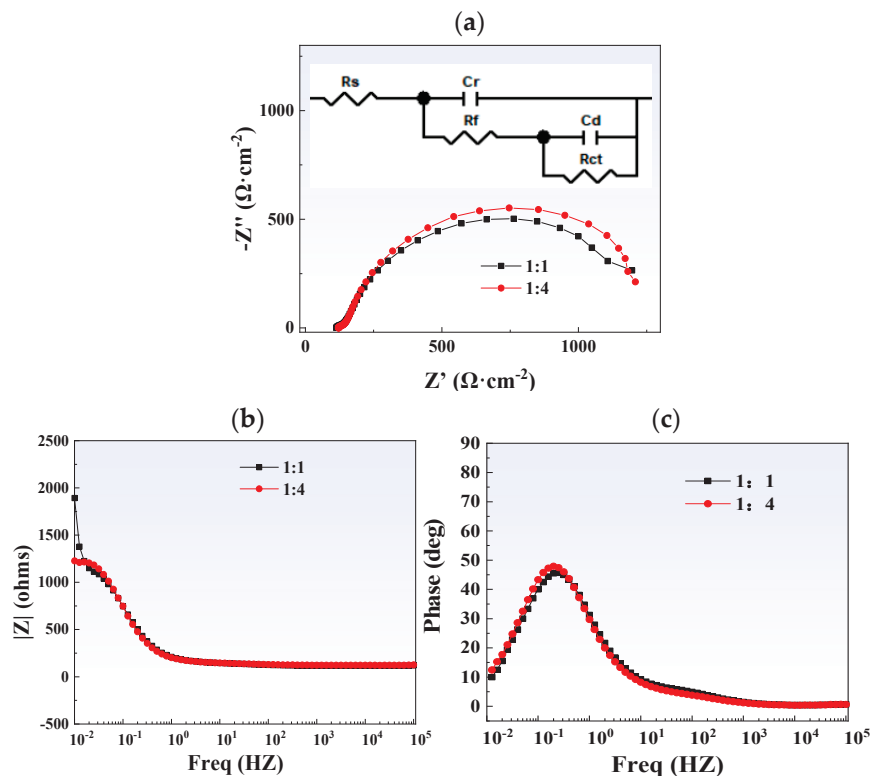


Figure 17. Electrochemical impedance spectroscopy test results of steel plates with different thickness ratios: (a) Nyquist plot (with the equivalent circuit shown as an inset); (b) Bode-phase plot; (c) Bode- $|Z|$ plot.

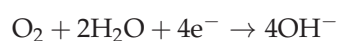
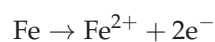
Table 3. EIS fitting parameters of steel plates with different thickness ratios.

Sample	R_s ($\Omega \cdot \text{cm}^2$)	n	R_f ($\Omega \cdot \text{cm}^2$)	n	R_{ct} ($\Omega \cdot \text{cm}^2$)	n
1:1	119.2	0.89	58.9	0.89	995	0.89
1:4	125.6	0.89	62.6	0.89	1072	0.89

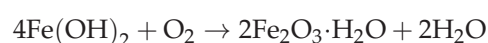
4. Discussion

4.1. Small-Scale Defects and Corrosion Dynamics

In the context of minor defects, the exposed carbon steel area, in conjunction with the adjacent titanium alloy, forms a galvanic couple [30–32]. This electrochemical interaction can be represented by the following reactions:



The galvanic coupling significantly accelerates the oxidation of iron, subsequently leading to a rapid accumulation of corrosion products, predominantly iron oxides and hydroxides [33–35]. These corrosion products, over time, obstruct the diffusion paths for oxygen and chloride ions [36,37], thus impeding further corrosion. This phenomenon can be described by the formation of a semi-permeable barrier [38,39]:



However, in larger defects, the localized galvanic effect is more pronounced at the defect edges, leading to preferential corrosion in these regions. The hypothesis is that the central areas of larger defects, being relatively isolated from the galvanic interaction, experience a slower corrosion rate. This observation suggests a non-uniform corrosion pattern influenced by defect size and distribution [40–42].

4.2. Impact of Thickness Ratio on Corrosion Rate

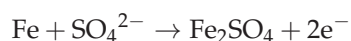
The corrosion rate per unit exposed area of titanium–steel composite plates increases as the thickness ratio decreases. This phenomenon can be primarily attributed to the variations in surface area ratios between the anodic and cathodic regions [43,44], influenced by the constant dimensions of the titanium alloy (cathode) and the variable dimensions of the carbon steel (anode). In detail, the titanium alloy maintains a consistent cathodic surface area, while the anodic area of carbon steel varies. This variation leads to a fluctuating anodic-to-cathodic area ratio, which is a crucial factor in galvanic corrosion [45–48]. The electrochemical principle that governs this behavior is based on the fact that the corrosion rate through the galvanic couple is a function of the surface area of both the anode and cathode.

As the anodic area decreases, the anodic current density increases. This increase in current density at the anode leads to a more rapid dissolution of the carbon steel, thereby accelerating the overall corrosion process. Moreover, this inverse relationship between anodic area and corrosion rate underlines the significance of balancing the thickness ratio in composite material design. A smaller anodic area concentrates the galvanic effect, intensifying the local corrosion [49]. Furthermore, the observed phenomenon suggests that the distribution of the galvanic current over the anodic surface is not uniform, especially in the case of varying thickness ratios. This non-uniform distribution can lead to localized areas of severe corrosion, which could compromise the structural integrity of the composite material.

Therefore, optimizing the thickness ratio in the design of titanium–steel composite materials is not only about achieving the desired mechanical properties but also about mitigating the corrosion rate. This optimization would involve a careful balance between the structural requirements and the corrosion resistance properties, possibly leading to innovative designs that extend the lifespan and enhance the durability of such materials in corrosive environments.

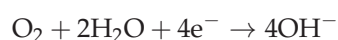
4.3. Corrosion Mechanisms of Defective Titanium/Steel Composite Plates

In simulated oceanic solutions, the corrosive attack on carbon steel involves a complex interaction of ions, primarily Cl^- [50–52], SO_4^{2-} [52,53], and Ca^{2+} [50,54]. The presence of Cl^- and SO_4^{2-} ions disrupts the passive layer of iron, potentially through the following reactions:



These reactions lead to the breakdown of passivity and acceleration of corrosion, often resulting in pitting corrosion [55,56]. On the other hand, Ca^{2+} ions are hypothesized to play a role in inhibiting corrosion by decreasing the porosity of the corrosion product film, although their limited concentration in this study resulted in a minimal protective effect.

At the anode, the dissolution of carbon steel, as previously mentioned, is coupled with the oxygen reduction reaction at the cathode, primarily occurring on the titanium alloy:



The proximity of carbon steel to titanium alloy exacerbates the corrosion at the interface, suggesting that the galvanic interaction plays a pivotal role in the localized corrosion dynamics (Figure 18).

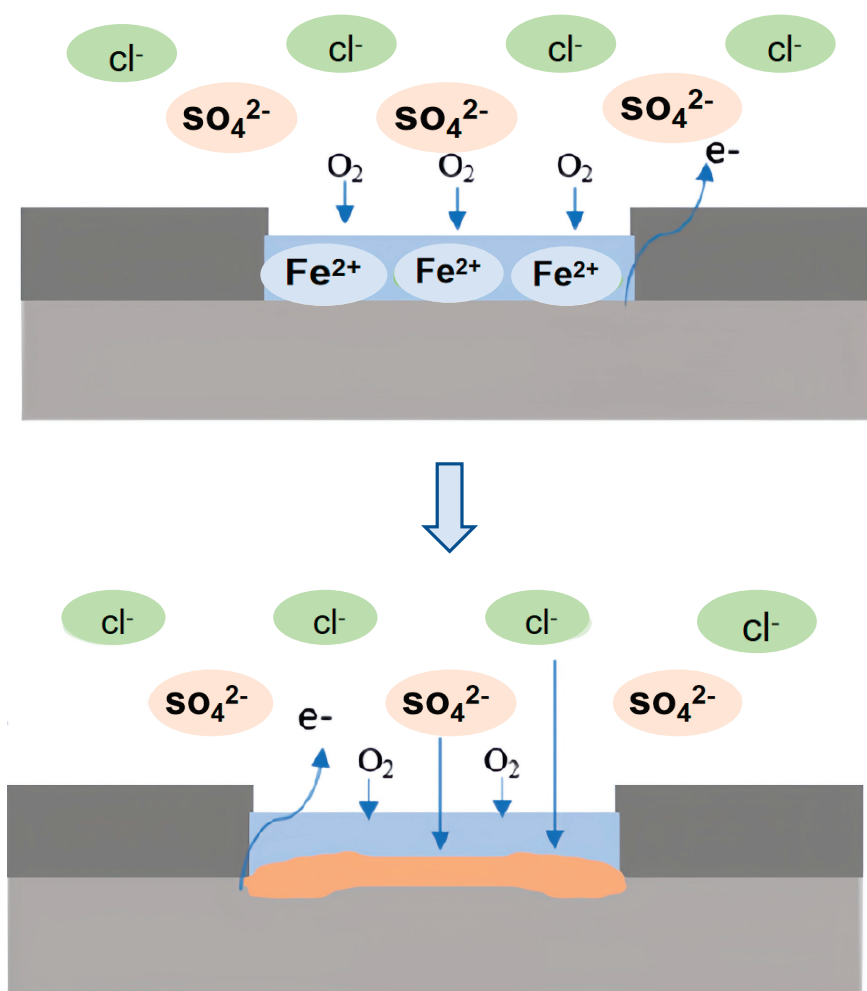


Figure 18. Corrosion mechanism diagram of titanium/steel composite plate in marine simulated environment.

5. Conclusions

In summary, our study reveals that the corrosion mechanism of titanium/steel composite plates in a simulated marine environment is complex and significantly influenced by defect size and thickness ratio:

- (1) Small-scale defects accelerate initial corrosion but eventually lead to a decrease in corrosion rate due to the buildup of protective corrosion products. Larger defects show a more localized corrosion impact.
- (2) The overall corrosion rate in a simulated marine environment has a distinct negative correlation with defect size.
- (3) When the thickness of the anode carbon steel in the composite plate increases, both RCT and RF increase and the corrosion loss is reduced by 32%, which can slow down the corrosion rate.

Author Contributions: Conceptualization, J.J. and F.L.; methodology, J.J., B.W. and X.C.; software, B.W.; validation, N.L.; formal analysis, N.L. and J.J.; investigation, C.L.; resources, C.L.; data curation, J.J. and F.L.; writing—original draft preparation, J.J.; writing—review and editing, B.W. and N.L.; visualization, F.L.; supervision, C.L. and X.C.; project administration, X.C. and C.L.; funding acquisition, C.L. and X.C. All authors have read and agreed to the published version of the manuscript.

Funding: The authors are grateful for the financial support from the National Key Research and Development Plan of China (2021YFB3701700) and the National Natural Science Foundation of China (No. 52374323).

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Conflicts of Interest: Authors Jianbo Jiang and Fangfang Liu were employed by the company Ansteel Beijing Research Institute Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Su, H.; Luo, X.B.; Chai, F.; Shen, J.C.; Sun, X.J.; Lu, F. Manufacturing technology and application trends of titanium clad steel plates. *J. Iron Steel Res. Int.* **2015**, *22*, 977–982. [CrossRef]
2. Yu, C.; Qi, Z.C.; Yu, H.; Xu, C.; Xiao, H. Microstructural and mechanical properties of hot roll bonded titanium alloy/low carbon steel plate. *J. Mater. Eng. Perform.* **2018**, *27*, 1664–1672. [CrossRef]
3. Atasoy, E.; Kahraman, N. Diffusion bonding of commercially pure titanium to low carbon steel using a silver interlayer. *Mater. Charact.* **2008**, *59*, 1481–1490. [CrossRef]
4. Kahraman, N.; Gülenç, B.; Findik, F. Joining of titanium/stainless steel by explosive welding and effect on interface. *J. Mater. Process. Technol.* **2005**, *169*, 127–133. [CrossRef]
5. Manikandan, P.; Hokamoto, K.; Deribas, A.A.; Raghukandan, K.; Tomoshige, R. Explosive welding of titanium/stainless steel by controlling energetic conditions. *Mater. Trans.* **2006**, *47*, 2049–2055. [CrossRef]
6. Hayes, J.; Richards, R. The use of titanium and stainless steel in fracture fixation. *Expert Rev. Med. Devices* **2010**, *7*, 843–853. [CrossRef] [PubMed]
7. Procópio, L. The role of biofilms in the corrosion of steel in marine environments. *World J. Microbiol. Biotechnol.* **2019**, *35*, 73. [CrossRef] [PubMed]
8. Madrid, F.M.G.; Soliz, A.; Cáceres, L.; Salazar-Avalos, S.; Guzmán, D.; Gálvez, E. Corrosion of Reinforced A630-420H Steel in Direct Contact with NaCl Solution. *Materials* **2023**, *16*, 6017. [CrossRef] [PubMed]
9. Vera, R.; Bagnara, M.; Henríquez, R.; Muñoz, L.; Rojas, P.; Díaz-Gómez, A. Performance of Anticorrosive Paint Systems for Carbon Steel in the Antarctic Marine Environment. *Materials* **2023**, *16*, 5713. [CrossRef]
10. Qiu, L.; Zhao, D.; Zheng, S.; Gong, A.; Liu, Z.; Su, Y.; Liu, Z. Inhibition Effect of *Pseudomonas stutzeri* on the Corrosion of X70 Pipeline Steel Caused by Sulfate-Reducing Bacteria. *Materials* **2023**, *16*, 2896. [CrossRef]
11. Hu, J.; Huang, H.; Deng, P.; Wang, G.; Wu, M.; Liu, W. Galvanic corrosion behavior of titanium-clad steel plate in the marine environment. *Mater. Corros.* **2022**, *73*, 887–896. [CrossRef]
12. Liu, Y.; Zheng, Z.; Long, J.; Xu, Z.; Jiao, S.; Qiao, Y.; Zheng, K.; Yin, F. Corrosion behaviour of hot-rolled 316L stainless steel-A6 carbon steel composite steel plate for marine environment. *J. Mater. Res. Technol.* **2023**, *26*, 556–570. [CrossRef]
13. Patnaik, A.; Shan, X.; Adams, M.; Srivatsan, T.S.; Menzemer, C.C.; Payer, J. Isolating Corrosion of Steel Plates Coupled with Titanium. *Adv. Steel Constr.* **2014**, *10*, 216–233.
14. El Ibrahim, B.; Jmami, A.; El Mouaden, K.; Baddouh, A.; El Issami, S.; Bazzi, L.; Hilali, M. Effect of solution's pH and molecular structure of three linear α -amino acids on the corrosion of tin in salt solution: A combined experimental and theoretical approach. *J. Mol. Struct.* **2019**, *1196*, 105–118. [CrossRef]
15. Abbas, M.; Shafiee, M. An overview of maintenance management strategies for corroded steel structures in extreme marine environments. *Mar. Struct.* **2020**, *71*, 102718. [CrossRef]
16. Islam, M.; Sakairi, M. Corrosion inhibition of mild steel by metal cations in high pH simulated fresh water at different temperatures. *Corros. Sci.* **2019**, *153*, 100–108. [CrossRef]
17. Alamri, A.H. Localized corrosion and mitigation approach of steel materials used in oil and gas pipelines—An overview. *Eng. Fail. Anal.* **2020**, *116*, 104735. [CrossRef]
18. Zhang, W.; Oswal, H.; Renew, J.; Ellison, K.; Huang, C.H. Removal of heavy metals by aged zero-valent iron from flue-gas-desulfurization brine under high salt and temperature conditions. *J. Hazard. Mater.* **2019**, *373*, 572–579. [CrossRef] [PubMed]
19. Zhi, Y.; Jin, Z.; Lu, L.; Yang, T.; Zhou, D.; Pei, Z.; Wu, D.; Fu, D.; Zhang, D.; Li, X. Improving atmospheric corrosion prediction through key environmental factor identification by random forest-based model. *Corros. Sci.* **2021**, *178*, 109084. [CrossRef]
20. Farh, H.; Seghier, M.; Zayed, T. A comprehensive review of corrosion protection and control techniques for metallic pipelines. *Eng. Fail. Anal.* **2023**, *143*, 106885. [CrossRef]
21. Ge, T.; Zhao, W.; Wu, X.; Lan, X.; Zhang, Y.; Qiang, Y.; He, Y. Incorporation of electroconductive carbon fibers to achieve enhanced anti-corrosion performance of zinc rich coatings. *J. Colloid Interface Sci.* **2020**, *567*, 113–125. [CrossRef] [PubMed]
22. Liu, Y.; Zheng, Z.; Xu, L.; Xu, Z.; Yin, F.; Zheng, K. Unraveling the interfacial structure of TA2 titanium-A36 steel composite plate and its corrosion behavior in marine environment. *Corros. Sci.* **2024**, *230*, 111923. [CrossRef]
23. Zhao, X.; Qi, Y.; Wang, J.; Peng, T.; Zhang, Z.; Li, K. Effect of Weld and Surface Defects on the Corrosion Behavior of Nickel Aluminum Bronze in 3.5% NaCl Solution. *Metals* **2020**, *10*, 1227. [CrossRef]
24. Zhang, D.; Yang, L.; Tan, Z.; Xing, S.; Bai, S.; Wei, E.; Tang, X.; Jin, Y. Corrosion behavior of X65 steel at different depths of pitting defects under local flow conditions. *Exp. Therm. Fluid Sci.* **2021**, *124*, 110333. [CrossRef]

25. Li, Y.; Macdonald, D.D.; Yang, J.; Qiu, J.; Wang, S. Point defect model for the corrosion of steels in supercritical water: Part I, film growth kinetics. *Corros. Sci.* **2020**, *163*, 108280. [CrossRef]
26. Macdonald, D. The history of the Point Defect Model for the passive state: A brief review of film growth aspects. *Electrochim. Acta* **2011**, *56*, 1761–1772. [CrossRef]
27. Cheung, G.S.P.; Peng, B.; Bian, Z.; Shen, Y.; Darvell, B.W. Defects in ProTaper S1 instruments after clinical use: Fractographic examination. *Int. Endod. J.* **2005**, *38*, 802–809. [CrossRef] [PubMed]
28. Silva, J.E.; Garbatov, Y.; Soares, C.G. Ultimate strength assessment of rectangular steel plates subjected to a random localised corrosion degradation. *Eng. Struct.* **2013**, *52*, 295–305. [CrossRef]
29. GB/T16545-1996; Corrosion of Metals and Alloys. Removal of Corrosion Products from Corrosion Specimens. National Steel Standardization Technical Committee: Beijing, China, 1996.
30. Rahimi, E.; Rafsanjani-Abbasi, A.; Imani, A.; Hosseinpour, S.; Davoodi, A. Insights into galvanic corrosion behavior of Ti-Cu dissimilar joint: Effect of microstructure and volta potential. *Materials* **2018**, *11*, 1820. [CrossRef]
31. Jadhav, N.; Gelling, V. The use of localized electrochemical techniques for corrosion studies. *J. Electrochem. Soc.* **2019**, *166*, C3461. [CrossRef]
32. De Oliveira, M.C.L.; Da Silva, R.M.P.; Souto, R.M.; Antunes, R.A. Investigating local corrosion processes of magnesium alloys with scanning probe electrochemical techniques: A review. *J. Magnes. Alloys* **2022**, *11*, 2997–3030. [CrossRef]
33. Chan, E. Magnetite and Its Galvanic Effect on the Corrosion of Carbon Steel under Carbon Dioxide Environments. Ph.D. Thesis, Curtin University, Bentley, Australia, 2011.
34. McMahon, M.E.; Santucci, R.J., Jr.; Glover, C.F.; Kannan, B.; Walsh, Z.R.; Scully, J.R. A review of modern assessment methods for metal and metal-oxide based primers for substrate corrosion protection. *Front. Mater.* **2019**, *6*, 190. [CrossRef]
35. AlAbbas, F.M.; Williamson, C.; Bhola, S.M.; Spear, J.R.; Olson, D.L.; Mishra, B.; Kakpovbia, A.E. Microbial corrosion in linepipe steel under the influence of a sulfate-reducing consortium isolated from an oil field. *J. Mater. Eng. Perform.* **2013**, *22*, 3517–3529. [CrossRef]
36. Liu, L.; Li, Y.; Wang, F. Electrochemical corrosion behavior of nanocrystalline materials—A review. *J. Mater. Sci. Technol.* **2010**, *26*, 1–14. [CrossRef]
37. Wong, H.S.; Zhao, Y.X.; Karimi, A.R.; Buenfeld, N.R.; Jin, W.L. On the penetration of corrosion products from reinforcing steel into concrete due to chloride-induced corrosion. *Corros. Sci.* **2010**, *52*, 2469–2480. [CrossRef]
38. Ding, Y.; Gutiérrez-Ariza, C.M.; Zheng, M.; Felgate, A.; Lawes, A.; Sainz-Díaz, C.I.; Cartwright, J.H.; Cardoso, S.S. Downward fingering accompanies upward tube growth in a chemical garden grown in a vertical confined geometry. *Phys. Chem. Chem. Phys.* **2022**, *24*, 17841–17851. [CrossRef] [PubMed]
39. Maj, M.; Ubysz, A. The reasons for the loss of polyurea coatings adhesion to the concrete substrate in chemically aggressive water tanks. *Eng. Fail. Anal.* **2022**, *142*, 106774. [CrossRef]
40. Zhang, X.; Jiang, C.; Chen, Y.; Memon, S.A.; Lun, P.; Sun, H.; Ren, J.; Wang, J. Study on the non-uniformity of rust layer and residual rebar caused by pitting corrosion in mortar. *Constr. Build. Mater.* **2023**, *406*, 133442. [CrossRef]
41. Luo, G.; Zhang, K.; Zhu, W.; Chen, T.; Yang, X.; Yang, S.; Xu, Y. Effect of non-uniform corrosion on the cracking propagation of the RC specimens. *Constr. Build. Mater.* **2021**, *270*, 121460. [CrossRef]
42. Wang, F.; Xue, X.; Hua, J.; Chen, Z.; Huang, L.; Wang, N.; Jin, J. Non-uniform corrosion influences on mechanical performances of stainless-clad bimetallic steel bars. *Mar. Struct.* **2022**, *86*, 103276. [CrossRef]
43. Ogle, K.; Baudu, V.; Garrigues, L.; Philippe, X. Localized electrochemical methods applied to cut edge corrosion. *J. Electrochem. Soc.* **2000**, *147*, 3654. [CrossRef]
44. Pasupuleti, S.B.; Srikanth, S.; Dominguez-Benetton, X.; Mohan, S.V.; Pant, D. Dual gas diffusion cathode design for microbial fuel cell (MFC): Optimizing the suitable mode of operation in terms of bioelectrochemical and bioelectro-kinetic evaluation. *J. Chem. Technol. Biotechnol.* **2016**, *91*, 624–639. [CrossRef]
45. Shi, L.; Song, Y.; Zhao, P.; Wang, H.; Dong, K.; Shan, D.; Han, E.H. Variations of galvanic currents and corrosion forms of 2024/Q235/304 tri-metallic couple with multivariable cathode/anode area ratios: Experiments and modeling. *Electrochim. Acta* **2020**, *359*, 136947. [CrossRef]
46. Okonkwo, B.O.; Ming, H.; Wang, J.; Han, E.H.; Rahimi, E.; Davoodi, A.; Hosseinpour, S. A new method to determine the synergistic effects of area ratio and microstructure on the galvanic corrosion of LAS A508/309 L/308 L SS dissimilar metals weld. *J. Mater. Sci. Technol.* **2021**, *78*, 38–50. [CrossRef]
47. Nakatsugawa, I.; Chino, Y. Effect of area ratio on the galvanic corrosion of AZX611 magnesium alloy / A6N01 aluminum alloy joint. *Mater. Trans.* **2021**, *62*, 1764–1770. [CrossRef]
48. Song, G.; Johannesson, B.; Hapugoda, S.; StJohn, D. Galvanic corrosion of magnesium alloy AZ91D in contact with an alu-minium alloy, steel and zinc. *Corros. Sci.* **2004**, *46*, 955–977. [CrossRef]
49. Yin, Z.; He, R.; Chen, Y.; Yin, Z.; Yan, K.; Wang, K.; Yan, H.; Song, H.; Yin, C.; Guan, H.; et al. Effects of surface micro-galvanic corrosion and corrosive film on the corrosion resistance of AZ91-xNd alloys. *Appl. Surf. Sci.* **2021**, *536*, 147761. [CrossRef]
50. Song, Q.; Nie, J.; Wu, D.; Hu, Y.; Chen, Y. Effect of SO_4^{2-} , Cl^- and Mg^{2+} on the system of CSH and $\text{Ca}(\text{OH})_2$. *Constr. Build. Mater.* **2021**, *285*, 122955. [CrossRef]
51. Krivenko, P.; Rudenko, I.; Konstantynovskiy, O.; Vaičiukynienė, D. Mitigation of corrosion initiated by Cl^- and SO_4^{2-} -ions in blast furnace cement concrete mixed with sea water. *Materials* **2022**, *15*, 3003. [CrossRef]

52. Feng, X.; Yan, Q.; Zhu, C.; Chen, Z.; Lu, X.; Lu, S. Corrosion Performance of 201 low-Nickel Stainless Steel Anchor in Cl^- Contaminated Underground Water with Various Concentrations of SO_4^{2-} and HCO_3^- . *J. Electrochem. Soc.* **2022**, *169*, 021507. [CrossRef]
53. Bonilla, A.; Argiz, C.; Moragues, A.; Gálvez, J.C. Effect of Sulfate Ions on Galvanized Post-Tensioned Steel Corrosion in Alkaline Solutions and the Interaction with Other Ions. *Materials* **2022**, *15*, 3950. [CrossRef] [PubMed]
54. Abd El Haleem, S.M.; Abd El Wanees, S.; Abd El Aal, E.E.; Diab, A. Environmental factors affecting the corrosion behavior of reinforcing steel II. Role of some anions in the initiation and inhibition of pitting corrosion of steel in $\text{Ca}(\text{OH})_2$ solutions. *Corros. Sci.* **2010**, *52*, 292–302. [CrossRef]
55. Ogunleye, D.; Odulanmi, A.; Fayomi, S. Corrosion Characteristics and Passive Behavioral Responses. *IOP Conf. Ser. Mater. Sci. Eng.* **2021**, *1107*, 012234. [CrossRef]
56. Green, W.K. Steel reinforcement corrosion in concrete—An overview of some fundamentals. *Corros. Eng. Sci. Technol.* **2020**, *55*, 289–302. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Effect of Graphene Oxide as an Anodizing Additive for the ZK60A Magnesium Alloy: Correlating Corrosion Resistance, Surface Chemistry and Film Morphology

Paula Lima Braga ¹, Denise Criado Pereira de Souza ², Mara Cristina Lopes de Oliveira ¹ and Renato Altobelli Antunes ^{1,*}

¹ Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas (CECS), Universidade Federal do ABC (UFABC), Santo André 09210-580, SP, Brazil; paula.braga@ufabc.edu.br (P.L.B.); mara.oliveira@ufabc.edu.br (M.C.L.d.O.)

² Centro de Ciências Naturais e Humanas (CCNH), Universidade Federal do ABC (UFABC), Santo André 09210-580, SP, Brazil; denise.criado@ufabc.edu.br

* Correspondence: renato.antunes@ufabc.edu.br

Abstract: The aim of the present work was to study the effect of graphene oxide as an additive in the anodization bath of the ZK60A magnesium alloy on the corrosion resistance, film morphology and surface chemical composition. The anodizing process was conducted at a constant current density of 30 mA.cm^{-2} in an electrolyte consisting of 3 M de KOH, 0.15 M de Na_2SiO_3 and 0.1 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. Graphene oxide was added to this bath at three different concentrations: 0.5 g.L^{-1} , 1.0 g.L^{-1} and 3.0 g.L^{-1} . The ability of the graphene oxide nanofiller to enhance the corrosion resistance of the ZK60A alloy was evaluated by electrochemical impedance spectroscopy and potentiodynamic polarization tests in 3.5 wt.% NaCl solution. The surface chemical composition was assessed by X-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) coupled with EDS analysis was employed to examine the anodized layer morphology and thickness. The results pointed to a beneficial effect of graphene oxide addition on the corrosion resistance of the anodized ZK60A which was dependent on the concentration of the nanofiller in the anodizing electrolyte.

Keywords: ZK60A magnesium alloy; anodization; graphene oxide; corrosion

1. Introduction

Magnesium alloys are increasingly attracting attention as structural materials in the transportation industry, especially for automotive and aircraft applications due to their high strength-to-weight ratio [1–3]. The ZK60A alloy belongs to the ZK series for which zinc and zirconium are the main alloying elements. It exhibits a good set of mechanical properties, mainly due to the grain refinement effect of zirconium in conjunction with solid solution strengthening and precipitation hardening due to the presence of zinc-rich precipitates [4,5].

One major concern in consolidating and expanding the engineering applications of magnesium alloys is their well-known high electrochemical activity, which makes them prone to corrosion in chloride-containing environments [6,7]. The ZK60A alloy has been shown to be susceptible to corrosion attack in sodium chloride solutions. For example, Li et al. [8] studied the effect of microstructure on the corrosion resistance of a commercial ZK60 alloy in 0.1 mol.L^{-1} NaCl solution at room temperature. A strong micro-galvanic effect was observed between the Mg- α and MgZn₂ second-phase particles precipitated at grain boundaries. Baek et al. [9] have also observed that intermetallic particles played a major role in the corrosion behavior of the ZK60 alloy in sodium chloride solution due to

microgalvanic effects between the anodic Mg- α matrix and precipitates containing zinc and zirconium.

In light of the examples depicted in the previous paragraph, intense research activity has been dedicated to improving the corrosion resistance of magnesium alloys. Several different methods have been reported based on microstructural control by proper heat treatments [10,11], deformation processes [12] and surface modification techniques, such as ion implantation [13], plasma electrolytic oxidation (PEO) [14,15], electrodeposition [16] and anodization [17]. Anodization is a common protective method for enhancing the corrosion properties of magnesium alloys. The process is based on the electrolytic anodic oxidation of the metallic surface, converting it into an oxide layer in an electrolyte with controlled composition [18–20]. Species from the electrolyte are incorporated into the anodized layer, providing it with functional properties [21,22]. Silicate-based electrolytes have been extensively employed as environmentally friendly solutions to conduct the anodizing of magnesium alloys, giving satisfactory corrosion protection to the underlying substrate. As previously reported [23], silicate may enhance the compactness and increase the thickness of the anodized film, thus improving its corrosion protection ability.

Due to the inherent porous structure of anodic films grown during anodization, several researchers have developed electrolytic baths containing inorganic nanoparticles as a strategy to enhance the barrier properties of the anodized layer [24–26]. For instance, Zhang et al. [27] observed that the corrosion resistance of an anodized AZ31 magnesium alloy was improved when Al_2O_3 nanoparticles were added to the anodizing electrolyte due to the enhanced compactness of the anodic film. Similarly to oxide nanoparticles, graphene and its derivatives may have a beneficial influence on the corrosion protection ability of either organic or inorganic coatings [28]. Such a positive effect is mainly due to an enhanced barrier effect as the presence of the graphene-based nanoparticles increases the diffusion path of corrosive species in the electrolyte [29,30]. Graphene oxide (GO) plays a central role in this scenario [31].

Among graphene derivatives, graphene oxide is often reported as having superior corrosion resistance either when used directly as a coating layer or as an additive to improve the barrier properties of organic and inorganic films [32–34]. Zhao et al. [35] employed GO as an additive in the electrolyte of a PEO-treated AZ31 magnesium alloy. They observed that, depending on the concentration of GO in the electrolyte, the corrosion resistance was increased due to the pore-blocking effect of GO particles.

While some reports can be found with regard to the use of GO as an additive for improving the corrosion protection ability of anodic oxide films obtained on magnesium alloys, this information is scarce if one considers the anodization process of the ZK60 alloy. Furthermore, the correlation between corrosion resistance and the surface chemistry of the GO-doped anodized layer is not reported in the current literature. The aim of the present work is to fill this gap by evaluating the effect of GO as an additive in the anodizing bath of the ZK60A alloy on the corrosion resistance, surface chemistry and film morphology. The anodizing bath consisted of an alkaline electrolyte containing sodium silicate. The correlation between corrosion resistance in sodium chloride solution, the surface chemistry of the anodized layer and its morphology is discussed.

2. Materials and Methods

2.1. Materials, Sample Preparation and Anodization

The substrate material used in the present work was an extruded bar (diameter of 90 mm) of the ZK60A alloy (nominal chemical composition in wt.%: Zn 4.8–6.2; Zr $\geq$ 0.45; Mg Balance), supplied by Xi'an Yuechen Metal Products Co. Ltd. (Xi'an, China). Initially, circular disks with a thickness of 3 mm were cut from the original bar using a cut-off instrument equipped with silicon carbide blades and water-refrigerated. Next, rectangular specimens were cut from these disks with dimensions of 10 mm $\times$ 10 mm $\times$ 3 mm.

The graphene oxide was a commercial product (UFMG, Belo Horizonte, Brazil) in the form of an aqueous suspension with a nominal concentration of 5 g.L⁻¹. All chemicals

used in the anodizing process were reagent-grade products. The specimens for anodizing were ground with silicon carbide waterproof papers up to grit 2000, followed by polishing with 0.5 μm alumina suspension.

The composition of the anodizing electrolyte consisted of a mixture of 3 M KOH, 0.15 M Na_2SiO_3 and 0.1 M de $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (pH = 13.5) with additions of three different concentrations of graphene oxide: 0.5 g.L^{-1} , 1.0 g.L^{-1} and 3.0 g.L^{-1} . The process was conducted using a D.C. power supply (MP5003D, Shenzhen, China) for 30 min at a constant current density of 30 mA.cm^{-2} , under magnetic stirring. A stainless steel vessel was used as the cathode. After anodizing, the specimens were washed with deionized water and dried in a warm air stream with a heat gun.

Samples designation throughout the text is as follows: 0-GO (anodized in the electrolyte without GO addition); 0.5-GO, 1.0-GO and 3.0 GO (samples anodized in the electrolytes with additions of 0.5 g.L^{-1} , 1.0 g.L^{-1} and 3.0 g.L^{-1} , respectively).

2.2. Characterization

2.2.1. Microstructural and Topographic Aspects

Surface and cross-sectional examination of the anodized samples were carried out by scanning electron microscopy (SEM, Leica, LEO 440i, Wetzlar, Germany). For surface topography examination, the micrographs were acquired in the secondary electrons mode (SEM-SE). For atomic number contrast, the images were obtained in the backscattered electrons mode (SEM-BSE). In the latter case, EDS (energy dispersive X-ray spectroscopy) analyses were carried out to map the elemental distribution on the surface of the samples. Surface roughness was measured by confocal laser scanning microscopy (Olympus Lext, OLS 4100, Waltham, MA, USA) in a non-contact mode. The roughness values are expressed as R_a (average roughness) and were obtained from an average value of 10 measurements.

2.2.2. Raman Spectroscopy and X-ray Photoelectron Spectroscopy (XPS)

Raman spectroscopy analysis (Horiba Scientific, T64000 dispersive Raman, Kyoto, Japan), equipped with a laser excitation source of a wavelength of 532 nm was employed to characterize the main structural aspects of the graphene oxide particles. Sample preparation consisted of dispersing a droplet of the as-received graphene oxide aqueous suspension on a glass plate and letting it dry overnight. After complete drying, the remaining graphene oxide particles were analyzed in the Raman spectrometer.

XPS analysis of the anodized layers was carried out to assess their surface chemical states. A ThermoFisher Scientific spectrometer (K-alpha, Waltham, MA, USA) was used, operating with an $\text{Al-K}\alpha$ radiation source (1486.6 eV) with a spot size of 400 μm and vacuum pressure of 10^{-7} Pa in the analysis chamber. Pass energies were 200 eV and 50 eV for the wide and narrow scan spectra, respectively. Peak fitting was carried out using the Smart algorithm for background subtraction in the Avantage 5.976© software, considering a mixture of Lorentzian and Gaussian functions (70/30).

2.2.3. Electrochemical Tests

As-received and anodized (with and without graphene oxide addition) ZK60A samples were subjected to electrochemical characterization using a conventional three-electrode cell setup. Autolab M101 potentiostat/galvanostat was employed for all measurements. The ZK60A samples were the working electrodes, a platinum wire was used as the auxiliary electrode and Ag/AgCl (KCl, 3 M) was the reference electrode. The electrolyte consisted of a 3.5 wt.% NaCl solution at room temperature. This electrolyte was chosen to assess the general corrosion properties of the different samples with regard to their potential engineering applications as structural materials, allowing their comparison with other published reports in the literature.

Initially, the open circuit potential (OCP) was monitored for 1 h. Next, electrochemical impedance spectroscopy (EIS) measurements were conducted at the OCP in the frequency range of 100 kHz to 10 mHz with an amplitude of the sinusoidal potential signal of ± 10 mV

(rms), and acquisition rate of 10 points per frequency decade. Potentiodynamic polarization tests were carried out right after the EIS measurements in the potential range of -300 mV versus the OCP up to -1.0 V_{Ag/AgCl}. The tests were conducted in triplicate.

3. Results and Discussion

3.1. Morphological and Topographic Aspects

SEM micrographs (secondary electrons mode) of the top surfaces of the anodized ZK60A alloy with and without the addition of graphene oxide are shown in Figure 1. The anodized layer without the incorporation of GO (Figure 1a) displays a flat surface, permeated by microcracks and pores with small diameters that can be more easily observed in the SEM-BSE micrographs (backscattered electrons mode) shown in Figure S1a (Supplementary Files). By adding 0.5 g.L⁻¹ of GO to the anodizing electrolyte, the number of pores in the anodic film was greatly increased, as well as the pore diameter, as seen in Figures 1b and S1b (0.5-GO). When the GO concentration was increased to 1.0 g.L⁻¹ (Figures 1c and S1c) and 3.0 g.L⁻¹ (Figures 1d and S1d), the surface morphology was remarkably affected, exhibiting a more compact character when compared to the sample obtained in the anodizing bath with the lowest GO concentration.

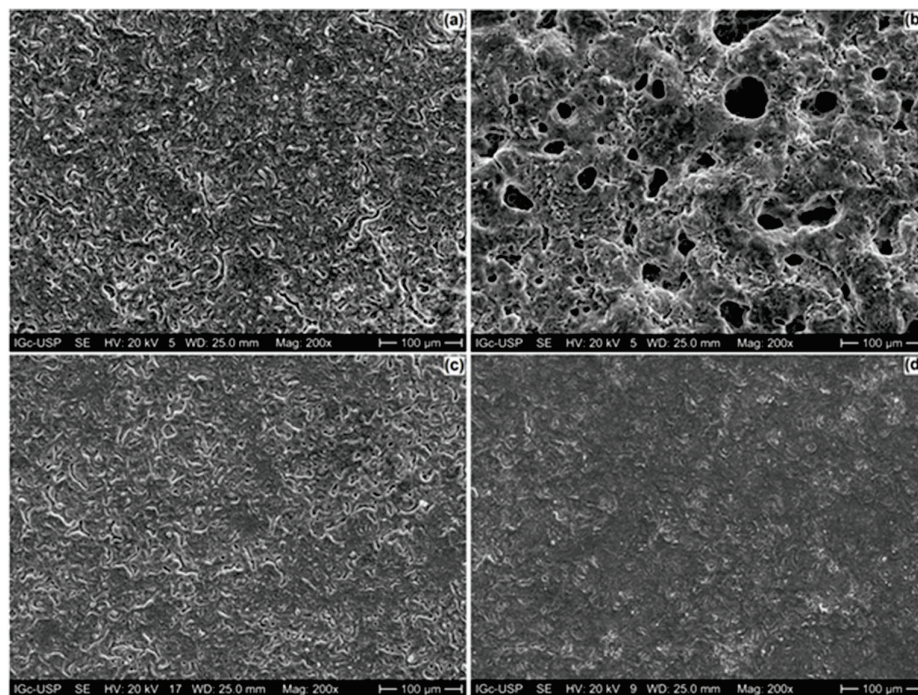


Figure 1. SEM micrographs (secondary electrons mode) of the anodized ZK60A alloy: (a) 0-GO; (b) 0.5-GO; (c) 1.0-GO; (d) 3.0-GO.

Elemental analysis for the 0-GO sample (anodized ZK60A without GO addition) was conducted over the surface displayed in the SEM-BSE image in Figure 2a. The distribution of the main constituents of the ZK60A substrate (Mg, Zn and Zr) and the anodized layer (Mg and Si) was examined by EDS mapping. Magnesium is distributed over the whole surface, as part of the anodized layer. The main alloying elements of the ZK60A alloy, Zn and Zr, displayed weak signals, confirming the good coverage of the underlying surface by the anodic film. The silicon signal is also detected. In fact, for sodium silicate-containing electrolytes, silicon-based species may be part of the anodic film, such as Mg₂SiO₄, as reported in the literature [36,37].

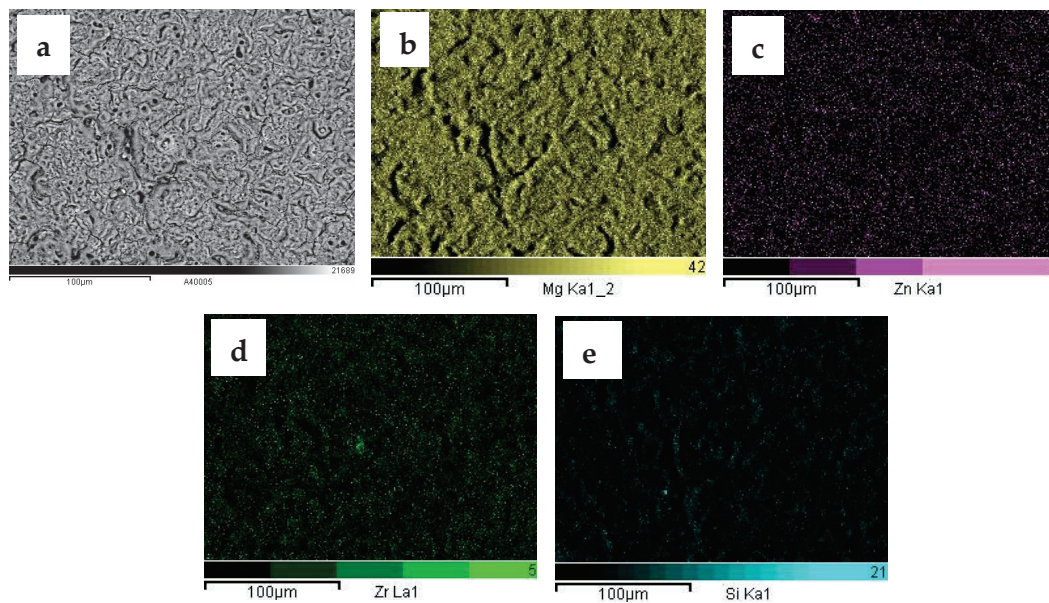


Figure 2. SEM-BSE micrograph (a) and corresponding EDS maps of the 0-GO sample: (b) Mg, (c) Zn, (d) Zr; (e) Si.

The EDS maps of the 3.0-GO sample are displayed in Figure 3. The SEM-BSE micrographs (Figure 3a) reveal its more compact surface when compared to the sample obtained in the electrolyte without GO addition (Figure 2a). EDS maps gave similar information with respect to those found in Figure 2. Magnesium is spread over the whole surface, whereas Zn and Zr (signals from the ZK60A substrate) can be barely seen. Additionally, the Si map (Figure 3e) confirms the incorporation of silicon species from the anodizing electrolyte. The maps obtained for the 0.5 GO and 1.0 GO present similar features and are available as Supplementary Materials (Figures S2 and S3, respectively).

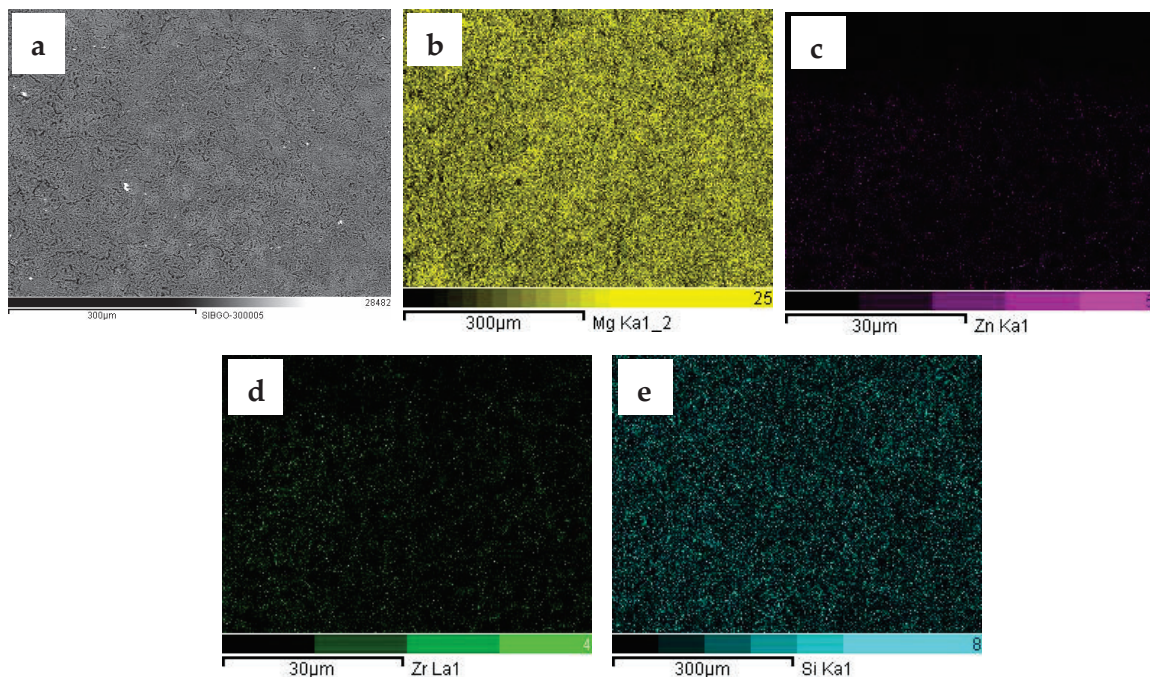


Figure 3. SEM-BSE micrograph (a) and corresponding EDS maps of the 3.0-GO sample: (b) Mg, (c) Zn, (d) Zr; (e) Si.

The morphological aspects of the anodized layers were further examined by SEM-BSE micrographs of the cross-sections. Figure 4 exhibits the SEM-BSE micrograph of the 0-GO sample and corresponding EDS maps for Mg, O, Zn, Zr and Si. The anodic film is indicated by a white arrow in Figure 4a. It is permeated by pores and cracks, reaching a maximum thickness of approximately 10 μm . The presence of Mg, O and Si is clearly seen in the anodic film.

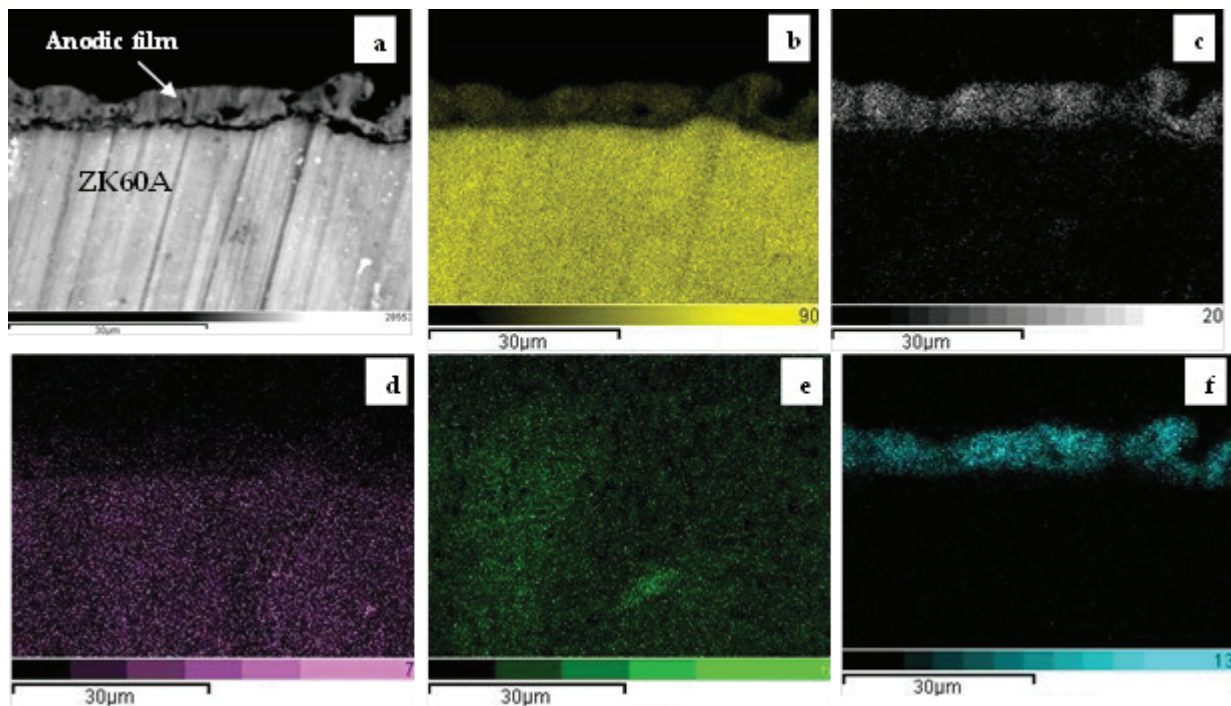


Figure 4. Cross-sectional SEM-BSE micrograph (a) and corresponding EDS maps of the 0-GO sample: (b) Mg, (c) O; (d) Zn, (e) Zr; (f) Si.

A representative EDS mapping of the cross-section of the anodized samples is given in Figure 5 for the 3.0-GO sample. When compared to the 0-GO sample (Figure 4a), the anodic film is much thinner, reaching only 5 μm . Additionally, it is more compact, being permeated by fewer pores and cracks. A possible explanation for the decrease in the anodic layer thickness with increasing GO concentration is related to the agglomeration of GO particles that reduce the growth rate of the anodic film or blocks discharge channels during the anodizing treatment, as suggested by Grigoriev et al. for a PEO/GO composite coating formed on the Ti-6Al-4V alloy [38]. The main elements that constitute the anodic film are also Mg, O and Si. Similar results were observed for the 0.5-GO and 1.0-GO samples with respect to the chemical composition of the anodic film, as shown in the cross-sectional EDS maps displayed in Figures S4 and S5, respectively (Supplementary Materials).

The roughness values (R_a) of the anodized ZK60A samples were determined using confocal laser scanning microscopy (CLSM), as displayed in Table 1. The polished ZK60A prior to anodizing is also included for comparison. As expected, after anodizing the values of R_a increased with respect to the uncoated substrate. Interestingly, roughness exhibited a remarkable increase for the 0.5-GO sample. As the GO concentration increased, the values of R_a progressively decreased. This is in accordance with the surface aspect observed in the top surface SEM micrographs (Figure 1). This finding may be due to the faster growth rate of the anodic film with low GO concentration, which also makes it thicker, as observed in the SEM micrographs, but more porous and cracked. As the GO concentration increased, and the corresponding growth rate of the anodic film decreased, a thinner and less rough oxide layer was formed.

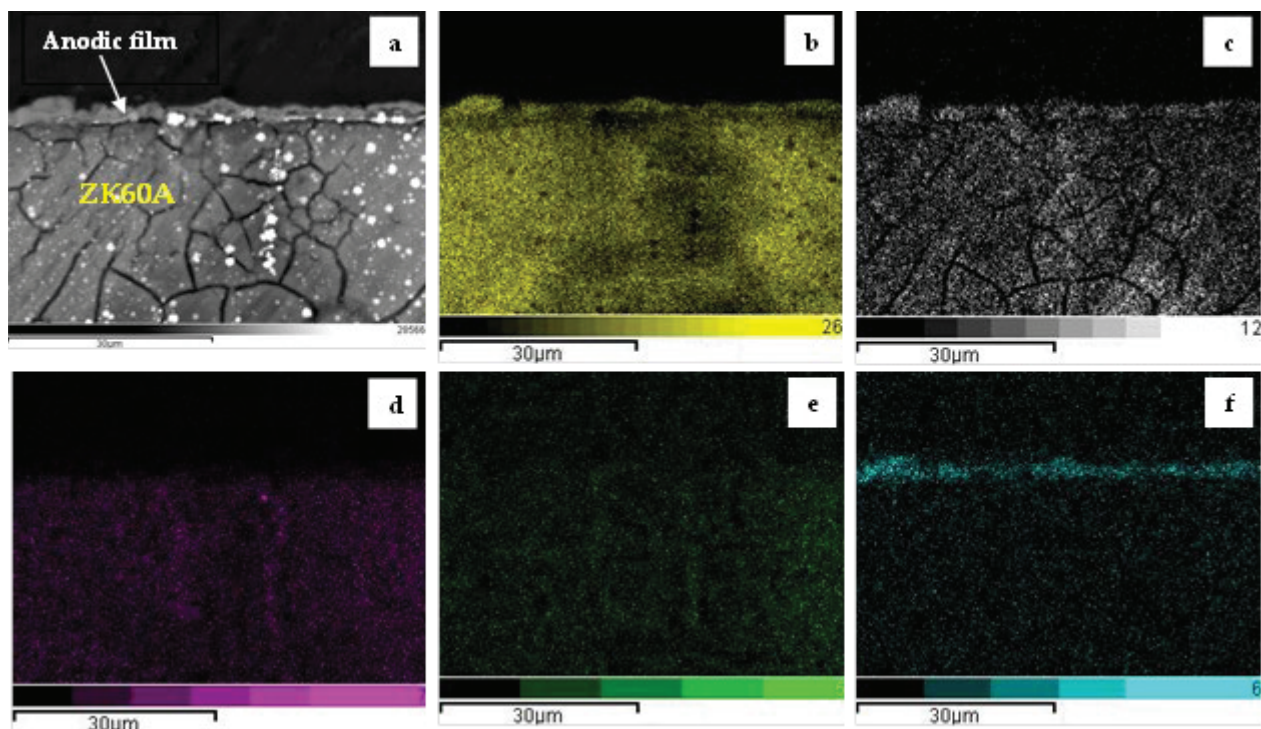


Figure 5. Cross-sectional SEM-BSE micrograph (a) and corresponding EDS maps of the 3.0-GO sample: (b) O, (c) Mg; (d) Zn, (e) Zr; (f) Si.

Table 1. Roughness values (Ra) of the anodized ZK60A samples.

Sample	Ra (μm)
Uncoated ZK60A	0.58
0-GO	1.91
0.5-GO	6.10
1.0-GO	2.74
3.0-GO	0.67

3.2. Raman Spectroscopy

The structural characteristics of the graphene oxide particles employed in the present work were obtained by Raman spectroscopy. Figure 6 shows the Raman spectrum of GO. The spectrum is characterized by two distinct bands, D and G bands, that are centered at 1352 cm^{-1} and 1606 cm^{-1} , respectively, in reasonable agreement with the literature [39].

The D band is due to vibrations of sp^3 hybridized carbon atoms and the G band is due to in-plane vibrations of sp^2 carbon atoms (graphitic carbons) [40]. The D band is associated with defects in the hexagonal carbon lattice with graphitic structure [41]. The ratio (I_D/I_G) between the intensities of the D (I_D) and G (I_G) bands is often used as a criterion to evaluate the defective character of graphene and its derivatives [42]. The higher the I_D/I_G ratio, the more defective the graphene structure. The I_D/I_G ratio obtained from the spectrum shown in Figure 6 was 1.02, which is typical of GO structure with a low degree of functionalization [43,44].

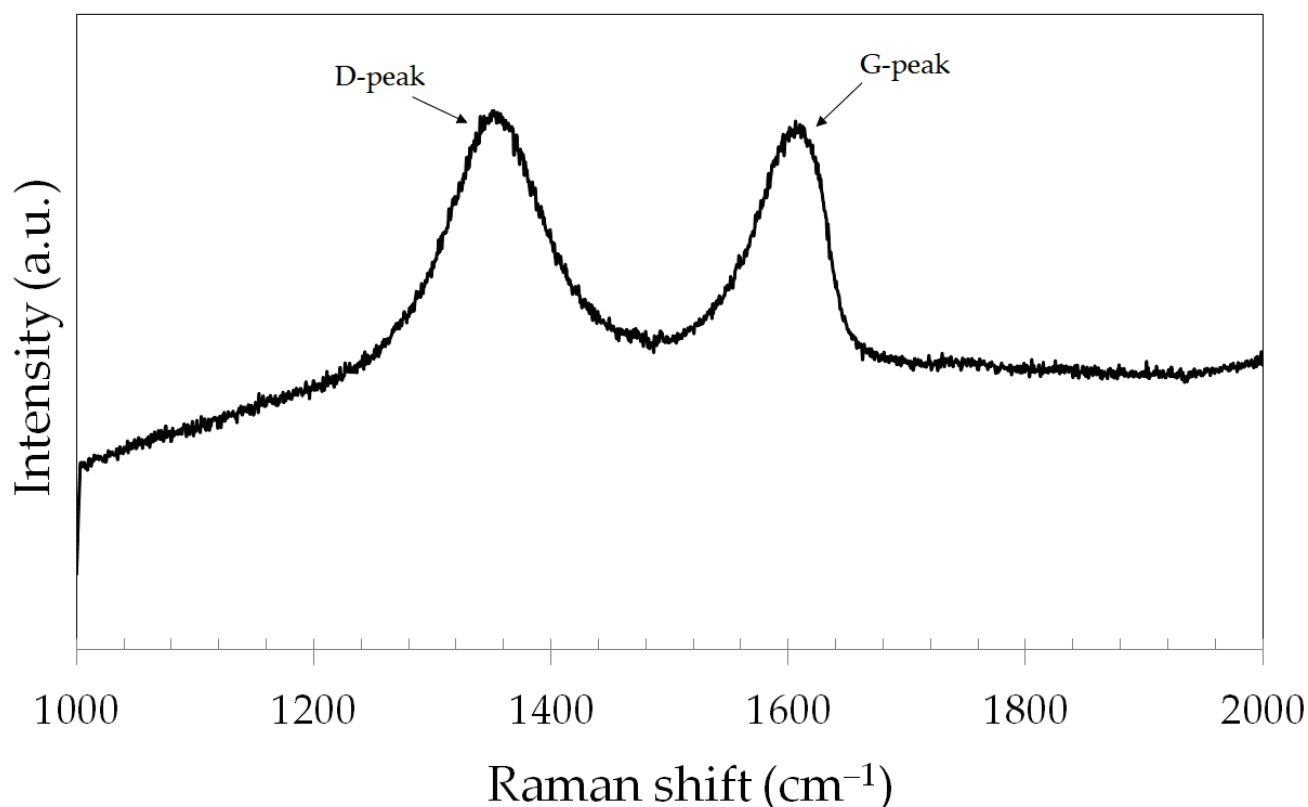


Figure 6. Raman spectrum of the GO particles.

3.3. X-ray Photoelectron Spectroscopy (XPS)

The GO particles were further characterized by XPS. Figure 7a displays the C 1s narrow scan spectrum of the GO particles. The spectrum was deconvoluted with four components that were assigned to C-C/C=C (284.7 eV), C-O (285.3 eV), C=O (286.4 eV) and O-C=O (288.8 eV) [45,46]. Figure 7b exhibits the O 1s narrow scan spectrum of the GO particles. The spectrum was deconvoluted with three components that were assigned to C-O, C=O and O-H bonds at 530.7 eV, 531.5 eV and 532.3 eV, respectively, in agreement with the literature [47,48].

The anodized films were also characterized by XPS. The Mg 1s, Si 2p, B 1s and O 1s narrow scan spectra of the 0-GO sample are shown in Figure 8. The Mg 1s spectrum was deconvoluted with three components that were assigned to Mg(OH)₂, MgO and Mg₂SiO₄, as reported by other authors [49,50]. The Si 2p spectrum (Figure 8b) displayed one single component assigned to silicate bonds due to the Mg₂SiO₄ compound in the anodized layer. The B 1s spectrum (Figure 8c) exhibited one single component assigned to B-O bonds, confirming that borate species are part of the anodized layer, as also observed by Okamoto et al. [49] and Ardelean et al. [51] for magnesium alloys anodized in borate-containing electrolytes. Oxygen species were identified from the O 1s narrow scan spectrum displayed in Figure 8d. The most intense peaks were assigned to O²⁻ (oxide) and OH⁻ (hydroxide) bonds. Adsorbed water (H₂O_{ads}) was also observed at higher binding energies, in good agreement with the literature [52,53].

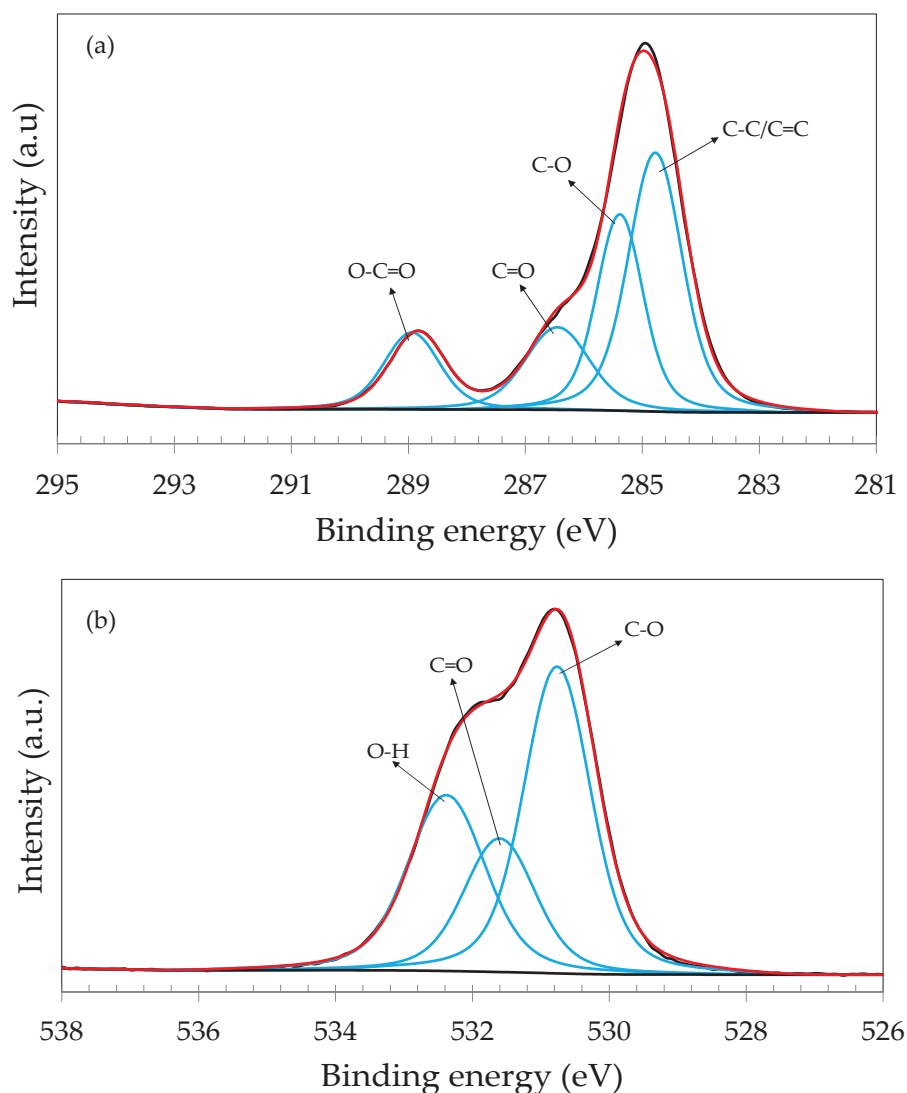


Figure 7. XPS narrow scan spectrum of the GO particles: (a) C 1s; (b) O 1s.

The Mg 1s, Si 2p and B 1s narrow scan spectra were not affected by GO addition. The same components were identified for 0.5-GO, 1.0-GO and 3.0-GO. The results are shown as Supplementary Materials (Figures S6–S8 for the Mg 1s, Si 2p and B 1s spectra, respectively).

The C 1s and O 1s narrow scan spectra of the GO-containing anodized samples, in turn, exhibited additional features when compared to the GO particles (Figure 7). Representative spectra are shown in Figure 9 for the 3.0-GO sample. Similar C 1s and O 1s spectra were obtained for the 0.5-GO and 1.0-GO samples (Supplementary Materials, Figures S9 and S10). As seen in the C 1s spectrum (Figure 9a) a strong π - π^* satellite was observed at the highest binding energy. This interaction has also been reported by other authors, being associated with the increase in the aromatic character of the GO structure that can originate from an oxidation process [48,54], such as the anodizing treatment of the ZK60A alloy. The O 1s spectrum (Figure 9b) was deconvoluted with four components, showing a mixture of bonds typical of the anodized layer (oxide and hydroxide bonds) and those of the GO structure (C-O, C=O, C-O-C). Both the C 1s and O 1s narrow scan spectra of the GO-containing samples show that GO was effectively incorporated into the anodic film during the anodization of the ZK60A alloy.

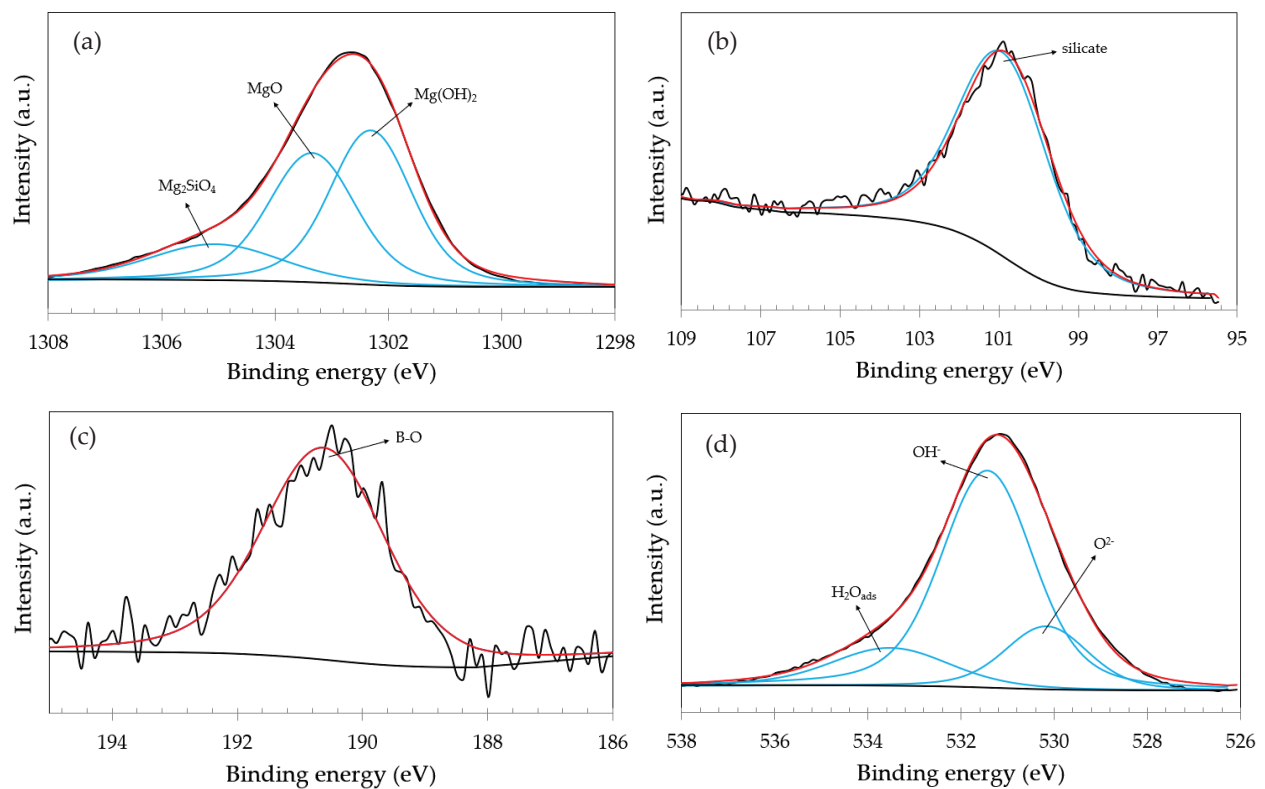


Figure 8. XPS narrow scan spectra of the 0-GO sample: (a) Mg 1s; (b) Si 2p; (c) B 1s; (d) O 1s.

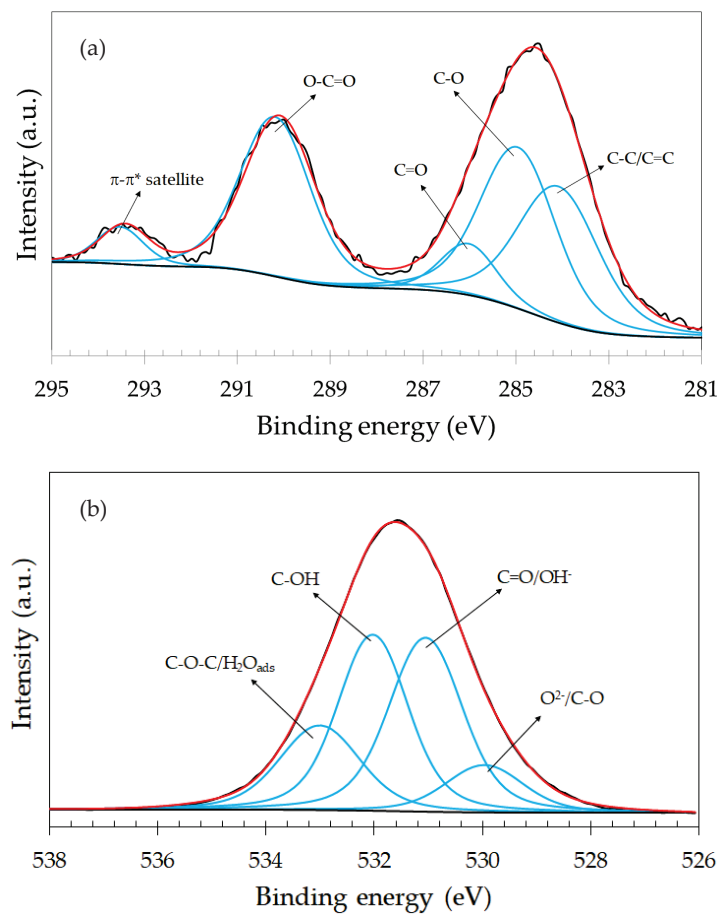


Figure 9. XPS narrow scan spectra of the 3.0-GO sample: (a) C 1s; (b) O 1s.

3.4. Corrosion Behavior

3.4.1. Electrochemical Impedance Spectroscopy (EIS)

Nyquist plots of the uncoated and anodized ZK60A alloy obtained in 3.5 wt.% NaCl solution at room temperature are shown in Figure 10a. The diameter of the semicircle is associated with the charge transfer resistance of the electrode surface [55,56]. The plot of the uncoated ZK60A alloy can be barely seen in Figure 10a, as it exhibits a capacitive loop whose diameter is much smaller than those of the anodized samples, thus indicating that the anodizing treatment greatly enhanced the corrosion resistance of the alloy. Figure 10b shows the Nyquist plots with expanded scales in order to allow one to visualize the result obtained for the uncoated ZK60A alloy.

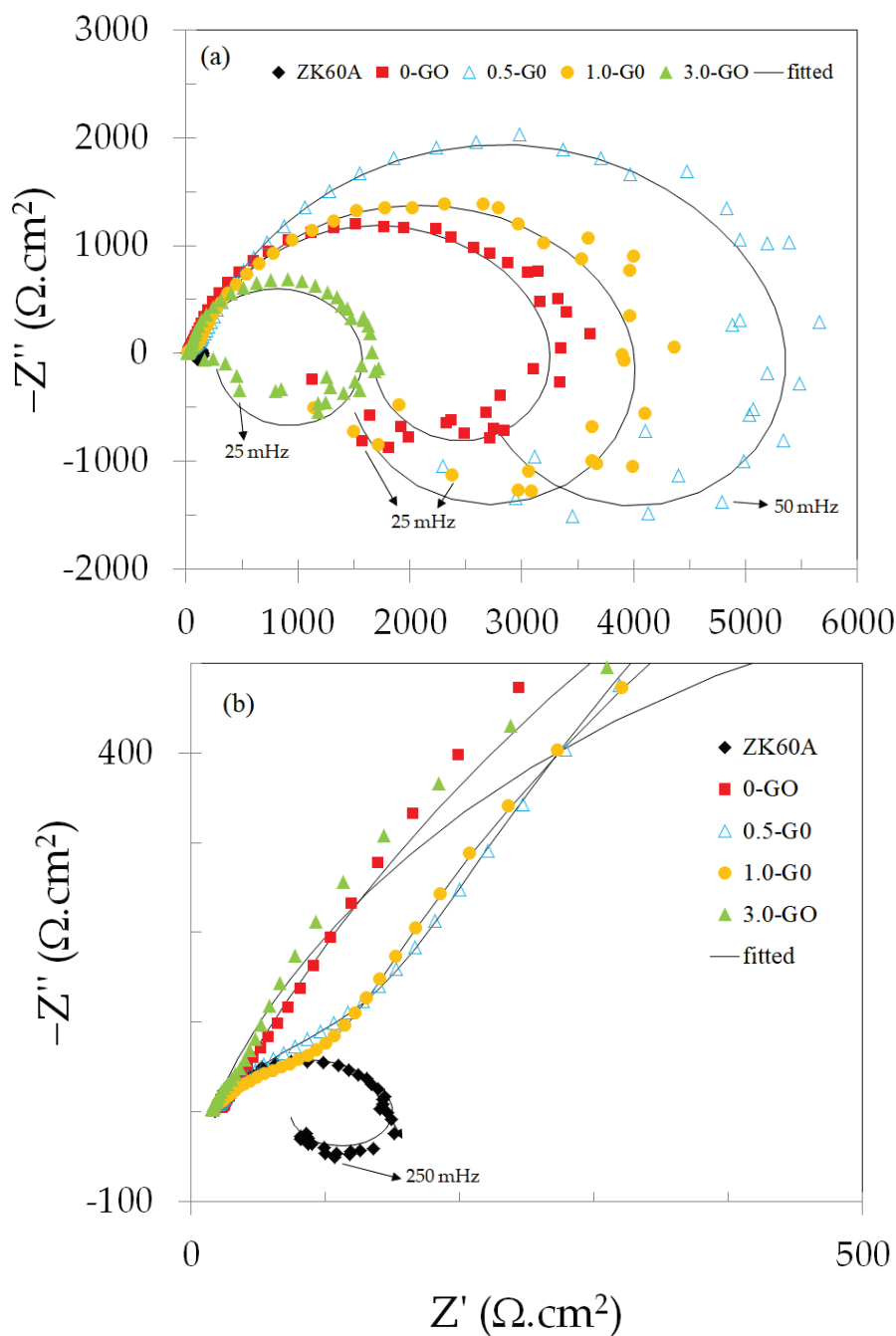


Figure 10. (a) Nyquist plots of the uncoated and anodized ZK60A alloy samples obtained in 3.5 wt.% NaCl solution at room temperature; (b) The same plots shown in (a) with expanded scales.

In addition to the capacitive loop that appears in the high-to-middle frequency range for all samples, another time constant is observed at low frequencies. It is characterized by an inductive loop. This behavior is typically found in magnesium alloys, being associated with the adsorption of ionized intermediate corrosion products such as $\text{Mg}(\text{OH})^+_{\text{ads}}$ [57,58].

The diameters of the capacitive loops were larger for the 0.5-GO and 1.0-GO samples when compared to the 0-GO (without GO addition). By increasing the GO concentration in the anodizing bath, the diameter of the capacitive loop decreased, as seen in Figure 10a for the 3.0-GO sample, which is even smaller than that of the sample without GO addition (0-GO). Electrical equivalent circuits (EECs) were used to fit the experimental EIS data, as shown in Figure 11. The EEC shown in Figure 11a was used to simulate the EIS response of the uncoated ZK60A substrate, whereas the one shown in Figure 11b simulated the responses of the anodized samples (with and without GO addition).

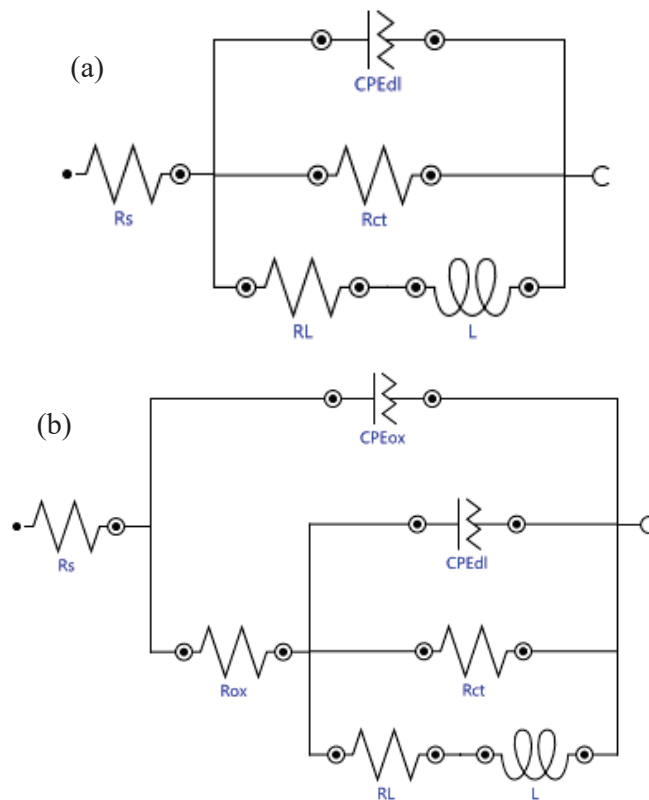


Figure 11. EECs used to fit the experimental EIS data: (a) uncoated ZK60A substrate; (b) anodized samples (with and without GO addition).

Constant phase elements (CPEs) were used instead of ideal capacitors to account for the heterogeneities of the electrode surface. The impedance of a CPE (Z_{CPE}) is given by Equation (1), where Q is associated with the CPE capacitance, j is the complex operator, ω is the angular frequency and n is the CPE exponent which varies from 0 for a pure resistor to 1 for an ideal capacitor [59,60]. The physical meaning of the EEC parameters are given as follows: R_s is the solution resistance; CPE_{ox} is the capacitance of the oxide layer and R_{ox} its resistance; CPE_{dl} is the double layer capacitance and R_{ct} is the charge transfer resistance. The local corrosion processes at the substrate are modeled by the inductive element (L) and its corresponding resistance (R_L) [61]. The fitted values of the circuit parameters are displayed in Table 2.

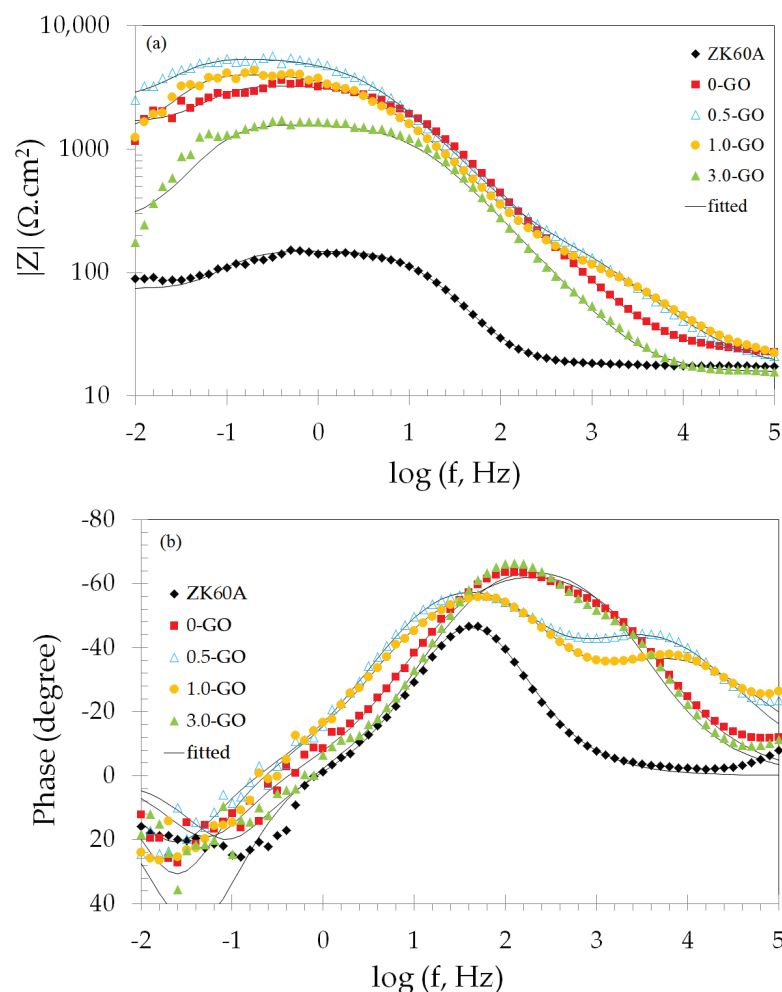
$$Z_{\text{CPE}} = \frac{1}{Q(j\omega)^n} \quad (1)$$

Table 2. EIS fitting results using the EECs shown in Figure 11 for the uncoated ZK60A substrate and the anodized samples.

Sample	R_s ($\Omega \cdot \text{cm}^2$)	$\text{CPE}_{\text{ox}} (10^{-6} \Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n)$	$R_{\text{ox}} (\Omega \cdot \text{cm}^2)$	n_{ox}	$\text{CPE}_{\text{dl}} (10^{-6} \Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n)$	$R_{\text{ct}} (\Omega \cdot \text{cm}^2)$	n_{dl}	$R_L (\Omega \cdot \text{cm}^2)$	L (H.cm ²)
Uncoated ZK60A	18	----	----	----	138.0	97	0.91	134	287
0-GO	22	13.8	3993	0.78	5.6	860	0.82	608	474
0.5-GO	16	5.2	4595	0.72	7.5	920	0.86	784	704
1.0-GO	15	6.8	5215	0.70	6.8	1032	0.85	459	74
3.0-GO	15	17.4	853	0.70	8.5	750	0.83	335	540

The uncoated ZK60A substrate exhibited one time constant ($\text{CPE}_{\text{dl}}\text{-}R_{\text{ct}}$) in connection with the inductive component ($R_L\text{-}L$), modeling the charge transfer reactions and adsorption of corrosive species on the surface of the electrode. After anodizing, a second time constant appeared due to the presence of the oxide layer ($\text{CPE}_{\text{ox}}\text{-}R_{\text{ox}}$) in addition to the charge transfer reactions and inductive components.

The higher impedance values of the 0.5-GO and 1.0-GO samples when compared to the 0-GO and 3.0-GO samples are also observed in the Bode magnitude plots ($\log |Z|$ vs. $\log f$) shown in Figure 12a. The value of the impedance magnitude at low frequencies can be used to express the corrosion resistance of the electrode surface [62,63]. This trend confirms the indication of the Nyquist plots, revealing the apparent higher corrosion resistance of the 0.5-GO and 1.0-GO samples.

**Figure 12.** Bode plots of the uncoated and anodized ZK60A alloy samples obtained in 3.5 wt.% NaCl solution at room temperature: (a) Impedance magnitude; (b) Phase angle.

The Bode phase angle plots are displayed in Figure 12b. All anodized samples present more capacitive phase angles than the uncoated ZK60A alloy over the whole frequency range, indicating the increase in corrosion resistance after the anodizing treatment. The samples lose their capacitive response at the lowest frequencies, as the phase angles drop off at frequencies below 10 Hz, indicating that corrosion processes are taking place (inductive response—positive phase angles). This feature corresponds to the inductive behavior also observed in the low-frequency domain of the Nyquist plots (Figure 10). One can also notice that the drop-off of the phase angles occurs at lower frequencies for the 0.5-GO and 1.0-GO when compared to the 0-GO and 3.0-GO samples. Hence, the onset of corrosion processes is shifted to lower frequencies for the 0.5-GO and 1.0-GO samples, suggesting their anodic films display improved corrosion protection ability. Moreover, these samples exhibit two well-separated time constants in the frequency range of 10^5 to 10^1 Hz. The time constant at the highest frequency may be associated with the EIS response of the anodic film, whereas that at the lowest one is due to the charge transfer resistance arising from the corrosion processes at the base of the defects of the anodized layer [64,65]. In this regard, it is also noticeable that the high-frequency time constant of the 0.5-GO sample exhibits a more capacitive phase angle than that of the 1.0-GO. This may be due to two distinct effects, either related to the resistance or the capacitance of the anodic film. The capacitance (C) of a coating layer depends on the area exposed to the electrolyte (A) and also on its thickness (d), as seen in Equation (2), where ϵ_0 is the vacuum permittivity and ϵ is the coating dielectric constant [66,67].

$$C = \epsilon\epsilon_0 \frac{A}{d} \quad (2)$$

Thus, based on Equation (2), the more capacitive phase angle of the 0.5-GO sample could be due to either an increase in the area exposed to the electrolyte or an increased resistance due to a high thickness of the anodic film, or a combination of both. In fact, the SEM cross-sectional micrographs (Supplementary Materials—Figure S4) confirmed that the thickness of the anodic film was increased for the 0.5-GO sample with respect to all other GO-containing anodized layers. Moreover, the porous nature of its top surface was also clearly seen in Figure 1b. As shown in Table 1, this was accompanied by a significant increase in surface roughness that was likely due to the faster growth rate of the anodic film for the 0.5-GO sample. This would lead to a reduced capacitance of the oxide layer (CPE_{ox}). Indeed, as shown in Table 2, this sample exhibited the lowest value of CPE_{ox} . As the GO concentration in the electrolyte increased, the surface roughness decreased, as well as the thickness of the anodic film, as shown in Section 2. On one hand, this led to an increase in the oxide film capacitance with respect to 0.5-GO, as can be seen in Table 2. On the other hand, the lower growth rate of the oxide film could also lead to the formation of a denser layer, thus increasing the corrosion protection ability, as observed for 1.0-GO. However, when GO concentration is excessive, in spite of the lower growth rate of the oxide film, agglomeration of GO particles may be detrimental to its corrosion resistance. This would explain the decreased value of the oxide film resistance (R_{ox}) for 3.0-GO, as observed in Table 2. In order to give further understanding of the corrosion behavior of the anodic films formed on the ZK60A alloy, and the effect of GO addition to the anodizing bath, potentiodynamic polarization tests were also conducted, as described in the next section.

3.4.2. Potentiodynamic Polarization Curves

Figure 13 shows the potentiodynamic polarization curves of the uncoated and anodized ZK60A alloy in 3.5 wt.% NaCl at room temperature. The electrochemical parameters obtained from these curves are presented in Table 3. The corrosion current density (i_{corr}) values were obtained by the Tafel extrapolation method, using the cathodic branches.

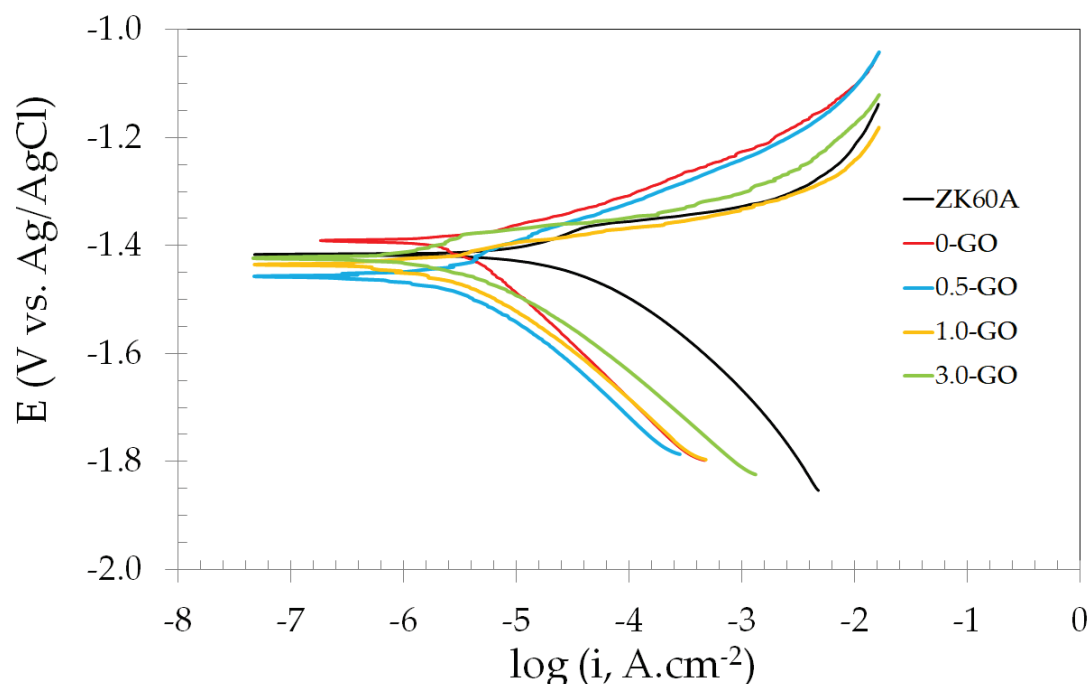


Figure 13. Potentiodynamic polarization curves of the uncoated and anodized ZK60A alloy samples obtained in 3.5 wt.% NaCl solution at room temperature.

Table 3. Electrochemical parameters obtained from the potentiodynamic polarization curves shown in Figure 13.

Sample	E_{corr} (mV vs. Ag/AgCl)	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)
Uncoated ZK60A	-1417 ± 20	24.5 ± 7.10
0-GO	-1390 ± 22	3.16 ± 0.58
0.5-GO	-1457 ± 7	2.40 ± 0.32
1.0-GO	-1435 ± 28	1.66 ± 0.23
3.0-GO	-1424 ± 10	2.75 ± 0.43

The corrosion potential (E_{corr}) was little affected by the anodization process, independently of the GO concentration in the anodizing electrolyte. Conversely, the corrosion current density (i_{corr}) was reduced by one order of magnitude after anodizing when compared to the uncoated ZK60A alloy. Interestingly, GO addition further decreased the values of i_{corr} . As shown in Table 2, the slowing down of the corrosion rate was dependent on the GO concentration in the anodizing electrolyte. The lowest i_{corr} was obtained for the 1.0-GO, which was reduced compared to 0.5-GO, suggesting that, by increasing the GO concentration from 0.5 g.L⁻¹ to 1.0 g.L⁻¹ in the anodizing electrolyte, the corrosion resistance was enhanced. Notwithstanding this beneficial effect, when the GO concentration was further increased to 3.0 g.L⁻¹ (3.0-GO) the value of i_{corr} was no longer reduced. This result is in agreement with the EIS results, showing that the GO concentration exhibits an optimum value in order to enhance the corrosion resistance of the anodized layer formed on the ZK60A alloy.

The explanation for such behavior can be derived from the following aspects. If one considers the roughness values (R_a) displayed in Table 1, there was a trend of increasing the roughness after anodization with respect to the uncoated ZK60A alloy. This trend was observed up to a GO concentration of 0.5 g.L⁻¹ (0.5-GO). For higher GO concentrations, the surface roughness decreased. Although the corrosion resistance displayed a similar trend, being favored after anodization, it does not follow the same trend as the surface roughness. This can be promptly seen if one notices that the sample with the lowest roughness (3.0-GO) is not that with the lowest value of i_{corr} (1.0-GO).

The XPS results (Section 3.3) revealed that the composition of the anodized layer was not significantly altered by GO addition with respect to the Mg 1s, Si 2p and B 1s spectra. As Mg, Si and B are incorporated into the anodizing electrolyte into the anodic film, it is reasonable to hypothesize that GO did not chemically interact with the main components of the anodized layer. Nevertheless, XPS unequivocally showed that GO was incorporated into the anodic film, as denoted by the C 1s and O 1s spectra of the anodized samples (Figures 9, S9 and S10). The corrosion behavior could not, therefore, be explained by differences between the surface chemical states of each sample.

As the compositional aspects and the surface topography were not the main factors influencing the electrochemical response of the anodized samples, one further aspect must be carefully examined. The morphology of the anodic films, as inferred from the SEM results presented in Section 3.1, was dependent on the GO concentration in the anodizing electrolyte. For example, when the GO was 0.5 g.L^{-1} (0.5-GO) the thickness of the anodic film was increased, as well as defects, such as microcracks and pores (Figures 1b and S4) when compared to 0-GO (Figures 1a and 4). The thick anodic film may be responsible for the increase in the impedance values, as shown in the Nyquist and Bode magnitude plots (Figures 10a and 12a). However, even though the thick anodized layer would imply an impedance increase, it does not form a sufficiently compact film to slow down the corrosion kinetics, as the defects in the anodic film would constitute a preferential pathway to corrosive species. As reported in the literature, the main effect of GO particles is related to the enhancement of the barrier properties of anodic films by increasing the diffusion pathway of corrosive species [35]. There is, therefore, a critical GO concentration that would give the necessary compactness and, hence, improve the corrosion resistance of the anodic film. In this respect, the 1.0-GO sample displayed a surface film that was thinner than that formed on 0.5-GO (Figure S5) but exhibited fewer defects. Hence, on one hand, its impedance values are lower due to the thinner oxide film, as observed in the Nyquist and Bode impedance plots (Figures 10a and 11a). On the other hand, it also displayed the lowest i_{corr} (Table 3), indicating the thin and compact oxide film provided a better barrier property than the thick and defective film formed on the 0.5-GO sample. By further increasing the GO concentration (3.0-GO) the impedance values decreased (Figures 10a and 12a) and i_{corr} increased (Table 3). As shown in Figure 5, the anodic film of this sample is as thin as that of 1.0-GO. Figure 1d points to the formation of a surface film that is more compact than that of the 0.5-GO as well. In spite of these apparently favorable morphological features, the loss of corrosion resistance when compared to 1.0-GO is evident. It is likely that the increase in GO concentration would cause an undesirable agglomeration effect, that hampers the distribution of GO within the anodized layer, thus diminishing the pore-blocking effect of GO, as reported by other authors for composite coatings containing GO [68–71].

4. Conclusions

Graphene oxide was effectively incorporated into the anodized layer when used as an additive to the anodizing electrolyte of the ZK60A magnesium alloy. XPS results showed that typical graphene oxide functional groups were observed in the anodized layers for all concentrations tested in the present work.

In spite of the GO incorporation into the anodic films, the corrosion resistance of GO-containing layers was dependent on the GO concentration in the anodizing bath. The optimum concentration was 1.0 g.L^{-1} , as denoted by the increase in impedance magnitude and decrease in corrosion current density obtained at this condition. Further increase in GO concentration to 3.0 g.L^{-1} reduced the corrosion resistance of the anodized layer.

The morphology of the anodic film was affected by GO concentration and influenced its corrosion properties. A thick and defective film was obtained for the anodizing bath containing a GO concentration of 0.5 g.L^{-1} , whereas a thin and more compact layer was formed when the GO concentration was raised to 1.0 g.L^{-1} .

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met14020210/s1>, Figure S1: SEM micrographs (secondary electrons mode) of the anodized ZK60A alloy: (a) 0-GO; (b) 0.5-GO; (c) 1.0-GO; (d) 3.0-GO. Figure S2. SEM-BSE micrograph (a) and corresponding EDS maps of the 0.5-GO sample: (b) Mg, (c) Zn, (d) Zr; (e) Si. Figure S3. SEM-BSE micrograph (a) and corresponding EDS maps of the 1.0-GO sample: (b) Mg, (c) Zn, (d) Zr; (e) Si. Figure S4. Cross-sectional SEM-BSE micrograph (a) and corresponding EDS maps of the 0.5-GO sample: (b) O; (c) Mg, (d) Zn, (e) Zr; (f) Si. Figure S5. Cross-sectional SEM-BSE micrograph (a) and corresponding EDS maps of the 1.0-GO sample: (b) Mg; (c) O; (d) Zn, (e) Zr; (f) Si. Figure S6. XPS Mg 1s narrow scan spectra: (a) 0.5-GO; (b) 1.0-GO; (c) 3.0-GO. Figure S7. XPS Si 2p narrow scan spectra: (a) 0.5-GO; (b) 1.0-GO; (c) 3.0-GO. Figure S8. XPS B 1s narrow scan spectra: (a) 0.5-GO; (b) 1.0-GO; (c) 3.0-GO. Figure S9. XPS C 1s narrow scan spectra: (a) 0.5-GO; (b) 1.0-GO. Figure S10. XPS O 1s narrow scan spectra: (a) 0.5-GO; (b) 1.0-GO.

Author Contributions: Conceptualization, P.L.B. and R.A.A.; methodology, P.L.B., D.C.P.d.S. and R.A.A.; validation, P.L.B. and R.A.A.; investigation, P.L.B., D.C.P.d.S. and M.C.L.d.O.; data curation, M.C.L.d.O., P.L.B. and R.A.A.; writing—original draft preparation, M.C.L.d.O. and R.A.A.; writing—review and editing, M.C.L.d.O. and R.A.A.; supervision, R.A.A.; project administration, R.A.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Brazilian Agency CAPES (Finance Code 001).

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

Acknowledgments: The authors are grateful to the Multiuser Experimental Facilities (CEM) of the Federal University of the ABC for the infrastructure necessary to develop this work.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Liu, B.; Yang, J.; Zhang, X.; Yang, Q.; Zhang, J.; Li, X. Development and application of magnesium alloy parts for automotive OEMs: A review. *J. Magnes. Alloys* **2023**, *11*, 15–47. [CrossRef]
2. Bai, J.; Yang, Y.; Wen, C.; Chen, J.; Zhou, G.; Jiang, B.; Peng, X.; Pan, F. Applications of magnesium alloys for aerospace: A review. *J. Magnes. Alloys* **2023**, *11*, 3609–3619. [CrossRef]
3. Tan, J.; Ramakrishna, S. Applications of magnesium and its alloys: A review. *Appl. Sci.* **2021**, *11*, 6861. [CrossRef]
4. Hort, N.; Vogt, C.; Cohen, S.; Kainer, K.U.; Willumeit, R.; Feyerabend, F. Degradable biomaterials based on magnesium corrosion. *Curr. Opin. Solid State Mater. Sci.* **2008**, *12*, 63–72.
5. Malik, A.; Wang, Y.; Cheng, H.; Nazeer, F.; Khan, M.A. Microstructure evolution of Mg-Zn-Zr magnesium alloy against soft steel core projectile. *J. Mater. Sci. Technol.* **2021**, *79*, 46–61. [CrossRef]
6. Wu, T.; Zhang, K. Corrosion and protection of magnesium alloys: Recent advances and future perspectives. *Coatings* **2023**, *13*, 1533. [CrossRef]
7. Talha, M.; Ma, Y.; Xu, M.; Wang, Q.; Lin, Y.; Kong, X. Recent advancements in corrosion protection of magnesium alloys by silane-based sol-gel coating. *Ind. Eng. Chem. Res.* **2020**, *59*, 19840–19857. [CrossRef]
8. Li, Z.; Peng, Z.; Qiu, Y.; Qi, K.; Chen, Z.; Guo, X. Study on heat treatment to improve the microstructure and corrosion behavior of ZK60 magnesium alloy. *J. Mater. Res. Technol.* **2020**, *9*, 11201–11219. [CrossRef]
9. Baek, S.-M.; Kim, B.; Park, S.S. Influence of intermetallic particles on the corrosion properties of extruded ZK60 Mg alloy containing Cu. *Metals* **2018**, *8*, 323. [CrossRef]
10. Chowdary, S.; Dumpala, R.; Kumar, A.S.; Kondaiah, V.V. Influence of heat treatment on the machinability and corrosion behavior of AZ91 Mg alloy. *J. Magnes. Alloys* **2018**, *6*, 52–58.
11. Balaji, V.; Raja, V.K.B.; Palanikumar, K.; Aditya, N.; Rohit, V. Effect of heat treatment on magnesium alloys used in automotive industry: A review. *Mater. Today. Proc.* **2021**, *46*, 3769–3771. [CrossRef]
12. Huang, S.-J.; Wang, C.-F.; Subramani, M.; Fan, F.-Y. Effect of ECAP on microstructure, mechanical properties, corrosion behavior, and biocompatibility of Mg-Ca alloy composite. *J. Comp. Sci.* **2023**, *7*, 292. [CrossRef]
13. Zheng, Y.; Ma, Y.; Zang, L.; Chen, Y. Microstructure, corrosion behavior, and surface mechanical properties of Fe oxide coatings on biomedical ZK60 Mg alloy. *Mater. Corros.* **2019**, *70*, 2292–2302. [CrossRef]
14. Darband, G.B.; Aliofkhazraei, M.; Hamghalam, P.; Valizade, N. Plasma electrolytic oxidation of magnesium and its alloys: Mechanism, properties and applications. *J. Magnes. Alloys* **2017**, *5*, 74–132. [CrossRef]
15. Strbak, M.; Kajánek, D.; Knap, V.; Florková, Z.; Pastorková, J.; Hadzima, B.; Goraus, M. Effect of plasma electrolytic oxidation on the short-term corrosion behaviour of AZ91 magnesium alloy in aggressive chloride environment. *Coatings* **2022**, *12*, 566. [CrossRef]

16. Yuan, J.; Dai, B.; Cui, X.; Li, P. The effects of electrodeposition temperature on morphology and corrosion resistance of calcium phosphorus coatings on magnesium alloy: Comparative experimental and molecular dynamics simulation studies. *RSC Adv.* **2023**, *13*, 34145–34156. [CrossRef]
17. Zaffora, A.; Di Franco, F.; Virtú, D.; Pavia, F.C.; Ghersi, G.; Virtanen, S.; Santamaria, M. Tuning of the Mg alloy AZ31 anodizing process for biodegradable implants. *ACS Appl. Mater. Interfaces* **2021**, *13*, 12866–12876. [CrossRef]
18. Blawert, C.; Dietzel, W.; Ghali, E.; Song, G. Anodizing treatments for magnesium alloys and their effect on corrosion resistance in various Environments. *Adv. Eng. Mater.* **2006**, *8*, 511–533. [CrossRef]
19. Pan, S.; Tu, X.; Yu, J.; Zhang, Y.; Miao, C.; Xu, Y.; Fu, R.; Li, J. Optimization of AZ31B magnesium alloy anodizing process in NaOH-Na₂SiO₃-Na₂B₄O₇ environmental-friendly electrolyte. *Coatings* **2022**, *12*, 578. [CrossRef]
20. Zhang, G.; Wu, L.; Tang, A.; Weng, B.; Atrens, A.; Ma, S.; Liu, L.; Pan, F. Sealing of anodized magnesium alloy AZ31 with MgAl layered double hydroxides layers. *Rsc Adv.* **2018**, *8*, 2248–2259. [CrossRef]
21. Santamaria, M.; Di Quarto, F.; Zanna, F.; Marcus, P. The influence of surface treatment on the anodizing of magnesium in alkaline solution. *Electrochim. Acta* **2011**, *56*, 10533–10542. [CrossRef]
22. Song, G.L.; Shi, Z. Corrosion mechanism and evaluation of anodized magnesium alloys. *Corros. Sci.* **2014**, *85*, 126–140. [CrossRef]
23. Fukuda, H.; Matsumoto, M. Effects of Na₂SiO₃ on anodization of Mg-Al-Zn alloy in 3 M KOH solution. *Corros. Sci.* **2004**, *46*, 2135–2142.
24. Zhang, P.; Zuo, Y.; Nie, G. The enhanced properties of anodic films on AZ91D magnesium alloy by addition of oxide nanoparticles. *J. Alloys Compd.* **2020**, *834*, 155041. [CrossRef]
25. Seyfi, M.; Fattah-alhosseini, A.; Pajohi-Alamoti, M.; Nikoomanzari, E. Effect of ZnO nanoparticles addition to PEO coatings on AZ31B Mg alloy: Antibacterial effect and corrosion behavior of coatings in Ringer's physiological solution. *J. Asian Ceramic Soc.* **2021**, *9*, 1114–1127. [CrossRef]
26. Gnedenkov, S.V.; Sinebryukhov, S.L.; Mashtalyar, D.V.; Imshinetskiy, I.M.; Samokhin, A.V.; Tsvetkov, Y.V. Fabrication of coatings on the surface of magnesium alloy by plasma electrolytic oxidation using ZrO₂ and SiO₂ nanoparticles. *J. Nanomat.* **2015**, *2015*, 154298. [CrossRef]
27. Zhang, D.; Gou, Y.; Liu, Y.; Guo, X. A composite anozing coating containing superfine Al₂O₃ particles on AZ31 magnesium alloy. *Surf. Coat. Technol.* **2013**, *236*, 52–57. [CrossRef]
28. Oliveira, M.C.L.; Antunes, R.A. Graphene-based coating for magnesium alloys: Exploring the correlation between coating architecture, deposition methods, corrosion resistance and materials selection. *Corros. Rev.* **2022**, *40*, 427–451. [CrossRef]
29. Askarnia, R.; Fardi, S.R.; Sobhani, M.; Staji, H. Ternary hydroxyapatite/chitosan/graphene oxide composite coating on AZ91D magnesium alloy by electrophoretic deposition. *Ceram. Int.* **2021**, *47*, 27071–27081. [CrossRef]
30. Cui, G.; Bi, Z.; Zhang, R.; Liu, J.; Yu, X.; Li, Z. A comprehensive review on graphene-based anti-corrosive coatings. *Chem. Eng. J.* **2019**, *373*, 104–121. [CrossRef]
31. Jena, G.; Philip, J. A review on recent advances in graphene oxide-based composite coatings for anticorrosion applications. *Prog. Org. Coat.* **2022**, *173*, 107208. [CrossRef]
32. Shang, W.; Wu, F.; Wang, Y.; Baboukani, A.R.; Wen, Y.; Jiang, J. Corrosion resistance of micro-arc oxidation/graphene oxide composite coatings on magnesium alloys. *ACS Omega* **2020**, *5*, 7262–7270. [CrossRef]
33. Wen, C.; Zhan, X.; Huang, X.; Xu, F.; Luo, L.; Xia, C. Characterization and corrosion properties of hydroxyapatite/graphene oxide bio-composite coating on magnesium alloy by one step micro-arc oxidation method. *Surf. Coat. Technol.* **2017**, *317*, 125–133. [CrossRef]
34. Ikhe, A.B.; Kale, A.B.; Jeong, J.; Reece, M.J.; Choi, S.-H.; Pyo, M. Perfluorinated polysiloxane hydridized with graphene oxide for corrosion inhibition of AZ31 magnesium alloy. *Corros. Sci.* **2016**, *109*, 238–245. [CrossRef]
35. Zhao, J.; Xie, X.; Zhang, C. Effect of graphene oxide additive on the corrosion resistance of the plasma electrolytic oxidation coating of the AZ31 magnesium alloy. *Corros. Sci.* **2017**, *114*, 146–155. [CrossRef]
36. Gao, H.; Zhang, M.; Yang, X.; Huang, P.; Xu, K. Effect of Na₂SiO₃ solution concentration of micro-arc oxidation process on lap-shear strength of adhesive-bonded magnesium. *Appl. Surf. Sci.* **2014**, *314*, 447–452. [CrossRef]
37. Ahn, B.H.; Song, J.I.; Koo, B.H. Effect of electrolyte on mechanical properties of AZ31B Mg alloy in electrolytic plasma processing. *Trans. Nonferrous Met. Soc. China* **2014**, *24*, s125–s128. [CrossRef]
38. Grigoriev, S.; Peretyagin, N.; Apelfeld, A.; Smirnov, A.; Morozov, A.; Torskaya, E.; Volosova, M.; Yanushevich, O.; Yarygin, N.; Krikheli, N.; et al. Investigation of tribological characteristics of PEO coatings formed on Ti6Al4V titanium alloy in electrolyte with graphene oxide additives. *Materials* **2023**, *16*, 3928. [CrossRef]
39. Zhou, X.; Zhang, S.; Song, Y.; Qin, H.; Xiong, C.; Wang, S.; Xie, D.; Fan, R.; Chen, D. A novel and green 3-amino-1,2,4-triazole modified graphene oxide nanomaterial for enhancing anti-corrosion performance of water-borne epoxy coatings on mild steel. *Prog. Org. Coat.* **2024**, *187*, 108106. [CrossRef]
40. Akbarzadeh, S.; Ramezanzaden, M.; Ramezanzadeh, B.; Bahlakeh, G. A green assisted route for the fabrication of a high-efficiency self-healing anti-corrosion coating through graphene oxide nanoplateform reduction by Tamarindus indica extract. *J. Hazard. Mater.* **2020**, *390*, 122147. [CrossRef]
41. Derelizade, K.; Venturi, F.; Wellman, R.G.; Khlobystov, A.; Hussain, T. Structural changes of thermal sprayed graphene nanoplatelets film into amorphous carbon under sliding wear. *Appl. Surf. Sci.* **2020**, *528*, 146315. [CrossRef]

42. Dresselhaus, M.S.; Jorio, A.; Hofmann, M.; Dresselhaus, G.; Saito, R. Perspectives on carbon nanotubes and graphene Raman spectroscopy. *Nano Lett.* **2010**, *10*, 751–758. [CrossRef]
43. Mulone, A.; Xia, Z.; Klement, U. Electrodeposition of FeW-graphene composites: Effect of graphene oxide concentration on microstructure, hardness and corrosion properties. *FlatChem* **2023**, *40*, 100525. [CrossRef]
44. Thoume, A.; Left, D.B.; Elmakssoudi, A.; Safi, Z.S.; Benzbiria, N.; Berisha, A.; Kellal, R.; Zertoubi, M. An in-depth on the high corrosion resistance of carbon steel in an acidic solution by a novel functionalized graphene oxide with oxide derivative via cutting-edge experimental characterization and computational modeling. *Mater. Chem. Phys.* **2023**, *310*, 128487. [CrossRef]
45. Zak, A.K.; Hashim, A.M. Synthesis, characterization and cytotoxicity studies of Au-decorated graphene oxide nanosheets. *Ceram. Int.* **2023**, *49*, 18577–18583.
46. Wang, T.; Dong, Y.; Xu, Y.; Li, G.; Guo, Y.; Lian, J.; Zhang, Z.; Ren, L. A calcium phosphate coating improving corrosion resistance of the biodegradable magnesium alloy with graphene oxide modifying the deposition. *Ceram. Int.* **2023**, *49*, 11926–11935. [CrossRef]
47. Zhang, W.; Li, B.; Mei, T.; Li, M.; Hong, M.; Yuan, Z.; Chu, H. Effects of graphene oxide and current density on structure and corrosion properties of nanocrystalline nickel coating fabricated by electrodeposition. *Colloids Surf. A* **2022**, *648*, 129220. [CrossRef]
48. Haubner, K.; Murawski, J.; Olk, P.; Eng, L.M.; Ziegler, C.; Adolph, B.; Jaehne, E. The route to functional graphene oxide. *ChemPhysChem* **2010**, *11*, 2131–2139. [CrossRef]
49. Qiu, Z.; Wang, R.; Zhang, Y.; Qu, Y.; Wu, X. Study of coating growth behavior during the plasma electrolytic oxidation of magnesium alloy ZK60. *J. Mater. Eng. Perform.* **2015**, *24*, 1483–1491. [CrossRef]
50. Okamoto, F.; Oliveira, M.C.L.; Silva, A.A.; Droppa, R., Jr.; Antunes, R.A. Effect of anodization on the stress corrosion cracking behavior of the AZ61 magnesium alloy in 0.1 M NaCl solution. *Mater. Res.* **2023**, *26*, e20220357.
51. Ardelean, H.; Frateur, I.; Zanna, S.; Atrous, A.; Marcus, P. Corrosion protection of AZ91 magnesium alloy by anodizing in niobium and zirconium-containing electrolytes. *Corros. Sci.* **2009**, *51*, 3030–3038. [CrossRef]
52. Lakshmi, R.V.; Aruna, S.T.; Anandan, C.; Bera, P.; Sampath, S. EIS and XPS studies on the self-healing properties of Ce-modified silica-alumina hybrid coatings: Evidence for Ce(III) migration. *Surf. Coat. Technol.* **2017**, *309*, 363–370. [CrossRef]
53. Oliveira, L.A.; Silva, R.M.P.; Rodas, A.C.D.; Souto, R.M.; Antunes, R.A. Surface chemistry, film morphology, local electrochemical behavior and cytotoxic response of anodized AZ31B magnesium alloy. *J. Mater. Res. Technol.* **2020**, *9*, 14754–14770. [CrossRef]
54. Hortigüela, M.J.; Machado, D.; Bdiqin, I.; Neto, V.; Otero-Irurueta, G. Chemical changes of graphene oxide thin films induced by thermal treatment under vacuum conditions. *Coatings* **2020**, *10*, 113. [CrossRef]
55. Choi, H.Y.; Kim, W.J. Development of the highly corrosion resistant AZ31 magnesium alloy by the addition of a trace amount of Ti. *J. Alloys Compd.* **2016**, *664*, 25–37. [CrossRef]
56. Osipenko, M.A.; Kasach, A.A.; Adamiec, J.; Zimowska, M.; Kurilo, I.I.; Kharytonau, D.S. Corrosion inhibition of magnesium alloy AZ31 in chloride-containing solutions by aqueous permanganate. *J. Solid State Electrochem.* **2023**, *27*, 1847–1860. [CrossRef]
57. Kharitonov, D.S.; Zimowska, M.; Ryl, J.; Zielinski, A.; Osipenko, M.A.; Adamiec, J.; Wrzesinska, A.; Claesson, P.M.; Kurilo, I.I. Aqueous molybdate provides effective corrosion inhibition on WE43 corrosion inhibition of WE43 magnesium alloy in sodium chloride solutions. *Corros. Sci.* **2021**, *190*, 109664. [CrossRef]
58. King, A.D.; Birbilis, N.; Scully, J.R. Accurate electrochemical measurement of magnesium corrosion rates: A combined impedance, mass-loss and hydrogen collection study. *Electrochim. Acta* **2014**, *121*, 394–406. [CrossRef]
59. Gu, J.-L.; Lu, S.-Y.; Shao, Y.; Yao, K.-F. Segregating the homogeneous passive film and understanding the passivation mechanism of Ti-based metallic glasses. *Corros. Sci.* **2021**, *178*, 109078. [CrossRef]
60. Qiao, X.Y.; Zheng, Y.G.; Ke, W.; Okafor, P.C. Electrochemical behaviour of high nitrogen stainless steel in acid solution. *Corros. Sci.* **2009**, *51*, 979–986. [CrossRef]
61. Jiao, Z.-J.; Yu, C.; Wang, X.-M.; Zhou, Y.-F.; Guo, L.; Xia, Y.; Zhang, B.-C.; Zeng, R.-C. Corrosion resistance enhanced by an atomic layer deposited Al₂O₃/micro-arc oxidation coating on magnesium alloy AZ31. *Ceram. Int.* **2024**, *50*, 5541–5551. [CrossRef]
62. Zhang, S.; Bi, Y.; Li, J.; Wang, Z.; Yan, J.; Song, J.; Sheng, H.; Guo, H.; Li, Y. Biodegradation behavior of magnesium and ZK60 alloy in artificial urine and rat models. *Bioact. Mater.* **2017**, *2*, 53–62. [CrossRef]
63. Heidari, E.; Atapour, M.; Obeydavi, A. The effect of Cr-content on the corrosion behavior of Ti_{0.5}Mo_{0.5}CoNiMnCr_x high-entropy alloy thin films deposited by direct current magnetron sputtering. *J. Alloys Compd.* **2024**, *976*, 173265.
64. Han, H.; Wang, R.; Wu, Y.; Zhang, X.; Wang, D.; Yang, Z.; Su, Y.; Shen, D.; Nash, P. An investigation of plasma electrolytic oxidation coatings on crevice surface of AZ31 magnesium alloy. *J. Alloys Compd.* **2019**, *811*, 152010. [CrossRef]
65. Guo, X.; An, M.; Yang, P.; Li, H.; Su, C. Effects of benzotriazole on Anodized film formed on AZ31B magnesium alloy in environmental-friendly electrolyte. *J. Alloys Compd.* **2009**, *482*, 487–497. [CrossRef]
66. Akbarzadeh, S.; Naderi, R.; Mahdavian, M. Fabrication of a highly protective silane composite coating with limited water uptake utilizing functionalized carbon nanotubes. *Compos. Part B* **2019**, *175*, 107109. [CrossRef]
67. Calderon-Gutierrez, J.A.; Bedoya-Lora, F.E. Barrier property determination and lifetime prediction by electrochemical impedance spectroscopy of a high performance organic coating. *Dyna* **2014**, *81*, 97–106. [CrossRef]
68. Jyotheender, K.S.; Srivastava, C. Ni-graphene oxide Composite coatings: Optimum graphene oxide for enhanced corrosion resistance. *Compos. Part B* **2019**, *175*, 107145. [CrossRef]

69. Calovi, M.; Rossi, S.; Deflorian, F.; Dirè, S.; Ceccato, R. Effect of functionalized graphene oxide concentration on the corrosion resistance properties provided by cathodic acrylic coating. *Mater. Chem. Phys.* **2020**, *239*, 121984. [CrossRef]
70. Zhang, Y.; Chen, F.; Zhang, Y.; Du, C. Influence of graphene oxide additive on the tribological and electrochemical corrosion properties of a PEO coating prepared on AZ31 magnesium alloy. *Tribol. Int.* **2020**, *146*, 106135. [CrossRef]
71. Guo, Z.; Wang, N.; Chen, Y.; Xu, Y.; Zhao, Q.; Zhang, Y.; Bai, X.; Yu, Y.; Zhao, Y. Regulation the graphene oxide concentration for the low energy consumption ceramic coating. *Prog. Org. Coat.* **2024**, *188*, 108200. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Corrosion Behavior of Titanium Alloys (Ti CP2, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-4V and Ti Beta-C) with Anodized and Exposed in NaCl and H₂SO₄ Solutions

Citlalli Gaona-Tiburcio ¹, Jesús Manuel Jáquez-Muñoz ^{1,2,*}, Demetrio Nieves-Mendoza ³, Erick Maldonado-Bandala ³, Maria Lara-Banda ¹, Manuel Alejandro Lira-Martinez ², Hortensia Reyes-Blas ², Miguel Ángel Baltazar-Zamora ³, Laura Landa-Ruiz ³, Luis Daimir Lopez-Leon ⁴ and Facundo Almeraya-Calderon ^{1,*}

¹ FIME, Centro de Investigación e Innovación en Ingeniería Aeronáutica (CIIA), Universidad Autónoma de Nuevo León, San Nicolás de los Garza 66455, Mexico; citlalli.gaonatbr@uanl.edu.mx (C.G.-T.); maria.laraba@uanl.edu.mx (M.L.-B.)

² Instituto de Ingeniería y Tecnología, Universidad Autónoma de Ciudad Juárez, Ciudad Juárez 32310, Mexico; manuel.lira@uacj.mx (M.A.L.-M.); hortensia.reyes@uacj.mx or hortensia.reyes@uv.mx (H.R.-B.)

³ Facultad de Ingeniería Civil, Universidad Veracruzana, Xalapa 91000, Mexico; dnieves@uv.mx (D.N.-M.); erimaldonado@uv.mx (E.M.-B.); mbaltazar@uv.mx (M.Á.B.-Z.); lalanda@uv.mx (L.L.-R.)

⁴ Área Académica de Ingeniería y Arquitectura, Universidad Autónoma del Estado de Hidalgo, Carretera Pachuca-Tulancingo, Km 4.5, Pachuca 42082, Mexico; olguinc@uaeh.edu.mx or luis_lopez@uaeh.edu.mx

* Correspondence: jesus.jaquezmn@uanl.edu.mx (J.M.J.-M.); facundo.almerayacl@uanl.edu.mx (F.A.-C.)

Abstract: Nowadays, different industries, such as the aerospace and biomedical industries, prefer using Ti alloys due to their excellent anti-corrosion properties and ability to generate a TiO₂ oxide layer; this induces the use of anodization to increase the useful life of components. The aim of this work is to characterize the electrochemical effect of anodizing treatment on titanium alloys (Ti CP2, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-4V, and Ti Beta-C) in NaOH and KOH at 1 M, applying a current density of 0.0025 A/cm². The electrochemical techniques employed were electrochemical noise (EN) and electrochemical impedance spectroscopy (EIS), supported by ASTM G199 and ASTM G106 in electrolytes of NaCl and H₂SO₄ at 3.5 wt. % as a simulation of marine and industrial atmospheres. Also, the anodized transversal section and surface morphology were characterized by a scanning electron microscope (SEM). The results of both electrochemical techniques indicated that Ti-6Al-2Sn-4Zr-2Mo anodized in NaOH presented the best properties against corrosion, and the thickness of the oxide was the biggest.

Keywords: titanium; anodized; alkaline; electrochemical noise; Hilbert–Huang recurrence plots; electrochemical impedance spectroscopy

1. Introduction

The aerospace, biomedical, chemical, naval, and automotive industries need materials with special anti-corrosion properties due to their high performance. Therefore, titanium and its alloys have been considered an option for those industries [1–3].

Considering that titanium is a very reactive material, even when exposed to oxygen, it generates an oxide layer, mostly of TiO₂, depending on the alloying element. The generation of the oxide layer increases the resistance against alloy corrosion. However, the quality of the oxide layer will depend on the chemical composition of the alloy and factors such as area, roughness, and material porosity. Other important factors are the oxygen in the system, the humidity, and the environmental composition [4–9].

A good generation of a passive layer has many variables; for that reason, titanium and its alloys are susceptible to attacks in different electrolytes because of irregular passive layer formation. The predisposition of titanium to generate a natural oxide layer makes

it perfect for being anodized. Authors have reported that anodized titanium generates a bigger oxide layer than passivated titanium, making it more corrosion-resistant. Also, they reported a homogeneous morphology, good thermodynamic stability, low conductivity, and low ion formation [10–14].

The anodized process consists of two different stages. The first is generating a constant oxide layer, which occurs quickly when applying a current. The next stages consist of the porous layer generation, increasing the thickness of the coating. The anodization process occurs due to a diffusion of oxygen and titanium on the surface; metal ions move to the interface of anodization through oxygen adsorption, generating TiO_2 on the surface [15,16].

However, the homogeneity of the oxide layer will depend on anodization factors such as pH, current, oxygen in the system, electrolytes, and the chemical composition of the Ti alloy. Usually, acid electrolytes are employed as anodizing bath solutions; however, authors such as Hugot-Le Goff [17] report that anodizing in basic media generates good oxide layers. Afshar and Veazi [18] reported an anodizing thickness from 0.4 to 1.5 μm when a Ti CP1 was anodized in NaOH, varying the anodizing time. In both cases, the corrosion resistance increased and was related to the high concentration of NaOH with a compact and homogenous coating. Also, they reported differences between anodized alloys obtained by acid media, mainly H_2SO_4 and H_3PO_4 [19].

It is important to mention that anodizing has several advantages compared to other coating methods. Thermal oxidation, sputtering, passivation, electrodeposition, and sol-gel generate an oxide layer in Ti and Ti alloys. Still, this method presents disadvantages such as high costs, difficult application for complex geometries, and the lack of homogeneous oxide generated.

The aim of this work is to characterize the electrochemical effect of anodizing treatment on titanium alloys (Ti CP2, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-4V, and Ti Beta-C) in NaOH and KOH electrolytes. The electrochemical techniques employed were electrochemical noise (EN) and electrochemical impedance spectroscopy (EIS), with the anodized alloys exposed to NaCl and H_2SO_4 solutions at 3.5 wt. %, simulating marine and industrial atmospheric conditions.

2. Materials and Methods

2.1. Materials

The materials employed were Ti CP2, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-4V, and Ti Beta-C, used in the received condition. Table 1 shows the chemical composition of these alloys obtained by X-ray fluorescence (Olympus DELTA XRF, Houston, TX, USA).

Table 1. Chemical composition of Ti and its alloys (wt. %).

Elements	Ti CP2	Alloys		
		Ti-6Al-2Sn-4Zr-2Mo	Ti-6Al-4V	Ti Beta-C
Fe	0.038 ± 0.005	–	0.21 ± 0.01	0.08 ± 0.01
Al	–	6.75 ± 0.20	7.14 ± 0.37	4.2 ± 0.13
V	–	–	4.03 ± 0.08	8.1 ± 0.07
Zr	–	4.18 ± 0.01	–	4.3 ± 0.01
Cr	–	–	–	3.3 ± 0.07
Mo	–	1.99 ± 0.008	–	3.9 ± 0.01
Sn	–	2.08 ± 0.01	–	–
Ti	99.94 ± 0.005	84.65 ± 0.19	87.71 ± 0.36	75.2 ± 0.14

2.2. Anodized Treatment

The alloys were pretreated for 10 min in an ultrasonic cleaner with ethanol and deionized water. The anodized treatment employed a platinum mesh as a cathode, and the

NaOH and KOH electrolytes were used at 1 M concentration. The anodized temperature was $25\text{ }^{\circ}\text{C} \pm 1$ [analytical grade reagents (JT Baker)]. The power source was the XLN300025-GL, applying a current density of $2.5 \times 10^{-3}\text{ A/cm}^2$. The anodizing time was 10 min, and the standards employed were AMS2487B and AMS2488E [20,21].

2.3. Microstructural Characterization

The Ti and Ti alloys were prepared employing the metallographic technique. The materials were brazed with SiC sandpaper grade 800. All the samples were cleaned for 10 min in ethanol and deionized water by ultrasonic cleaning [22].

The surface and cross-section of anodized alloys were studied using secondary electron (SE) and backscattered electron (BSE) detectors in a scanning electron microscope (SEM, Hitachi, Tokyo, Japan) operating at 20 kV, with an 8.5 and 12 mm work distance.

2.4. Corrosion Measurements

Electrochemical noise (EN) and electrochemical impedance spectroscopy (EIS) were performed at room temperature, using VersaSTAT4 Princeton Applied Research software (Ametek, Inc., Oak Ridge, TN, USA), in 3.5 wt. % NaCl and H_2SO_4 electrolytes at room temperature and all the corrosion tests were performed in duplicate. The cell configuration was of three electrodes: the working electrode (WE), the reference of the saturated calomel electrode (SCE), and the counter electrode (CE) of platinum. The area exposed was 1 cm^2 [23]. For the EN technique, we acquired 4096 data points, at 1 datum per second, and the signal was processed with MATLAB 2018a [24]. EIS measurements were recorded at the corrosion potential over a frequency range from 100 kHz to 10 mHz, obtaining 10 points per decade, and applying an AC potential signal at 10 mV (root mean square, rms) amplitude according to the ASTM G106-15 standard. The results were interpreted through the development of typical impedance models for the electrode surface, as well as curve fitting based on an equivalent circuit using the Zview Impedance program. The time to obtain the steady state was 50 min in an open circuit.

3. Results

3.1. Microscopic Characterization

Figure 1 shows the superficial morphology of anodized alloys in NaOH obtained by SEM-SE. In this anodizing electrolyte, the oxide distribution is heterogeneous. Figure 1b shows the preferential oxide deposition, where Ti-6Al-2Sn-4Zr-2Mo presented different altitudes. Also, the anodized alloy presented cracking in that zone. A similar morphology is observed in Figure 1c, presenting a preference for the accumulation of oxide in specific areas. The anodizing shown in Figure 1d, corresponding to Ti Beta-C, shows low coating generation.

Figure 2 shows the micrographics of anodized alloys in KOH. When alloys were anodized in KOH, they presented a higher heterogeneity than in NaOH; in Figure 2a, the anodized Ti CP2 presents different altitudes of oxide. A similar behavior is observed in Figure 2d for Ti Beta-C, but the polish lines are higher. Figure 2b,c presents similar behavior, with a higher anodized generation, but it continues to be non-homogenous.

Figure 3 shows the transversal section of anodized alloys in NaOH. Figure 3a shows the transversal section of Ti CP2, where the anodized alloy presented a thickness of 376 to 400 nm, and the mapping shows the presence of O and an increase in the oxide layer. Ti-6Al-2Sn-4Zr-2Mo presented a higher thickness, with values from 1.92 to 2.63 μm ; the presence of O and Ti in the oxide layer is higher (see Figure 3b). On the other hand, Figure 3c shows the anodized alloy of Ti-6Al-4V, which presented lower values, with thicknesses from 23 to 25 nm. Finally, Figure 3d shows the anodization of Ti Beta-C, where the thickness obtained was 660 and 756 nm; the mapping shows the presence of oxygen in the coating zone. Only the anodized version of Ti-6Al-2Sn-4Zr-2Mo meets the requirements of AMS2487B specifications.

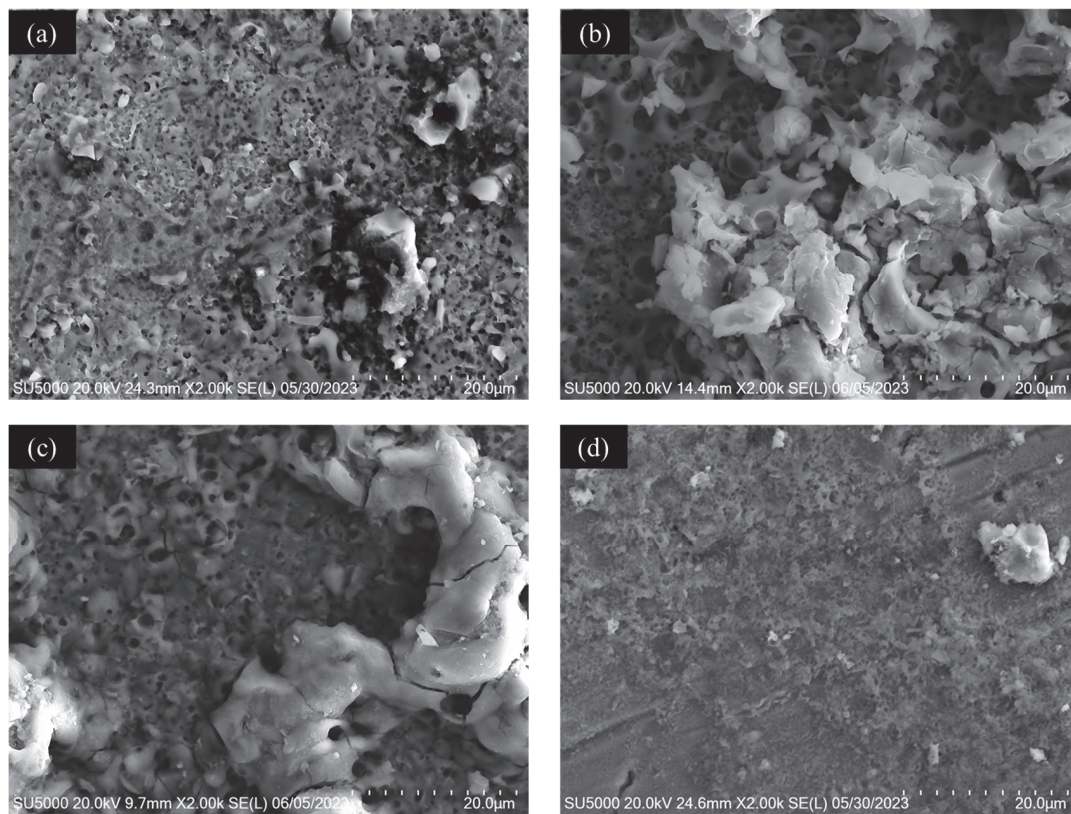


Figure 1. SEM-SE of superficial morphology of anodized in NaOH in 2000 $\times$; (a) Ti CP2, (b) Ti-6Al-2Sn-4Zr-2Mo, (c) Ti-6Al-4V y (d) Ti Beta C.

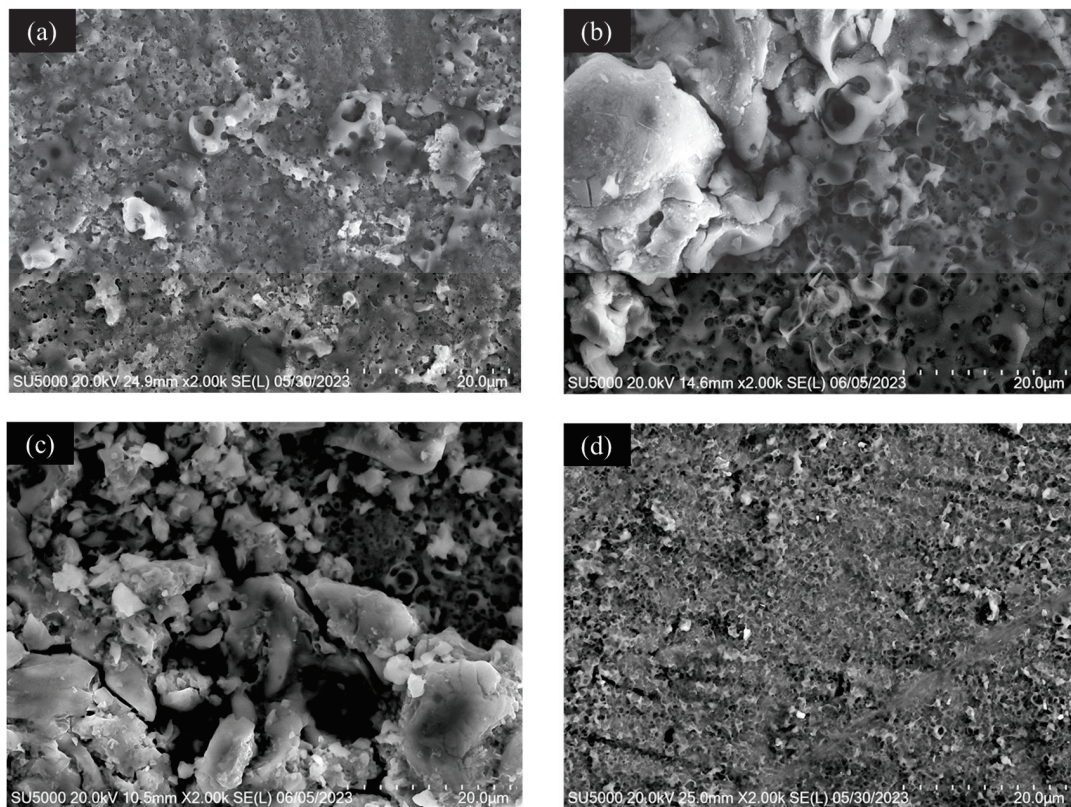


Figure 2. SEM-SE of superficial morphology of anodized in KOH in 2000 $\times$; (a) Ti CP2, (b) Ti-6Al-2Sn-4Zr-2Mo, (c) Ti-6Al-4V y (d) Ti Beta C.

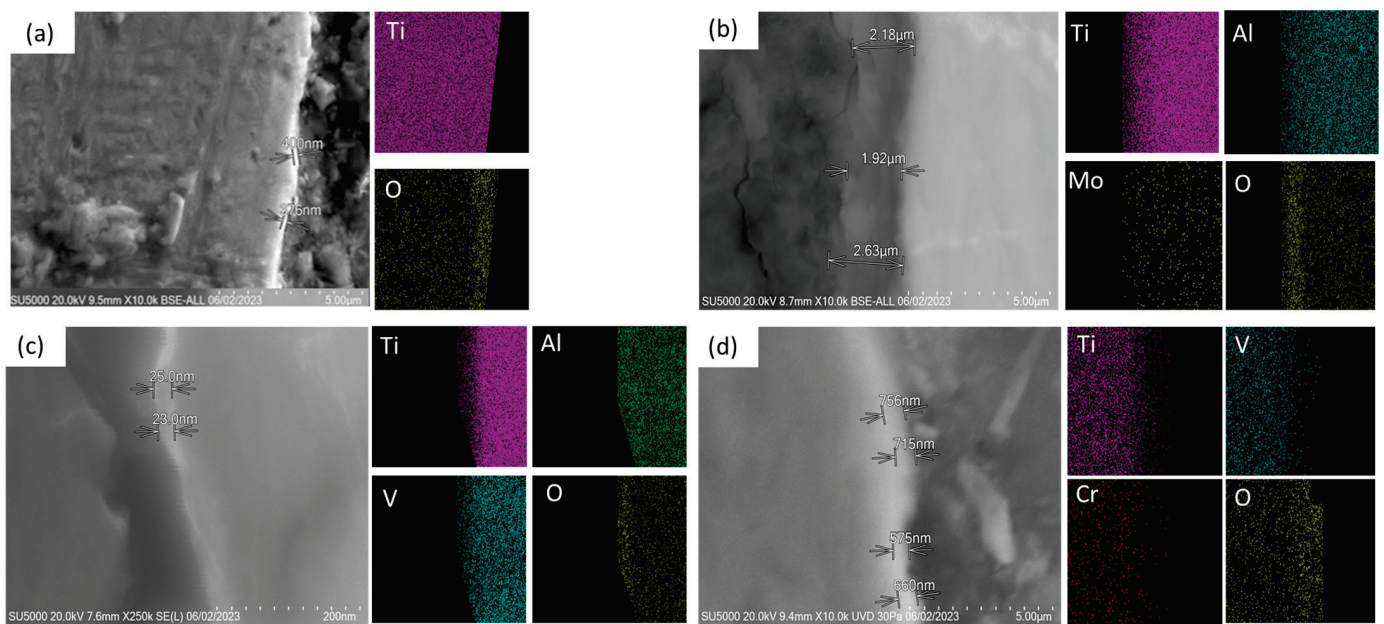


Figure 3. SEM-SE/BSE of transversal section of anodized titanium alloys in NaOH at 10,000×, and element mapping by EDS of (a) Ti CP2, (b) Ti-6Al-2Sn-4Zr-2Mo, (c) Ti-6Al-4V y (d) Ti Beta C.

Figure 4 shows the transversal section of anodized alloys in KOH, where Ti CP2 presents a thickness from 2.1 to 2.7 μm, being the highest in both anodizing electrolytes. Also, this layer presented acceptable adhesion characteristics to metal; however, the thickness is heterogeneous. Figure 4b shows the anodization of Ti-6Al-2Sn-4Zr-2Mo, where the thickness varies from 1.02 to 2.02 μm and is non-homogenous. The mapping presented a greater presence of oxygen in the anodized layer. Figure 4c presents a thickness from 208 to 248 nm, and the thickness of Figure 4d ranges from 525 to 1.03 μm (see Table 2). All the anodized alloys presented oxygen in the coating. In this case, only the anodized Ti CP2 and Ti-6Al-2Sn-4Zr-2Mo satisfied the AMS2487B specifications.

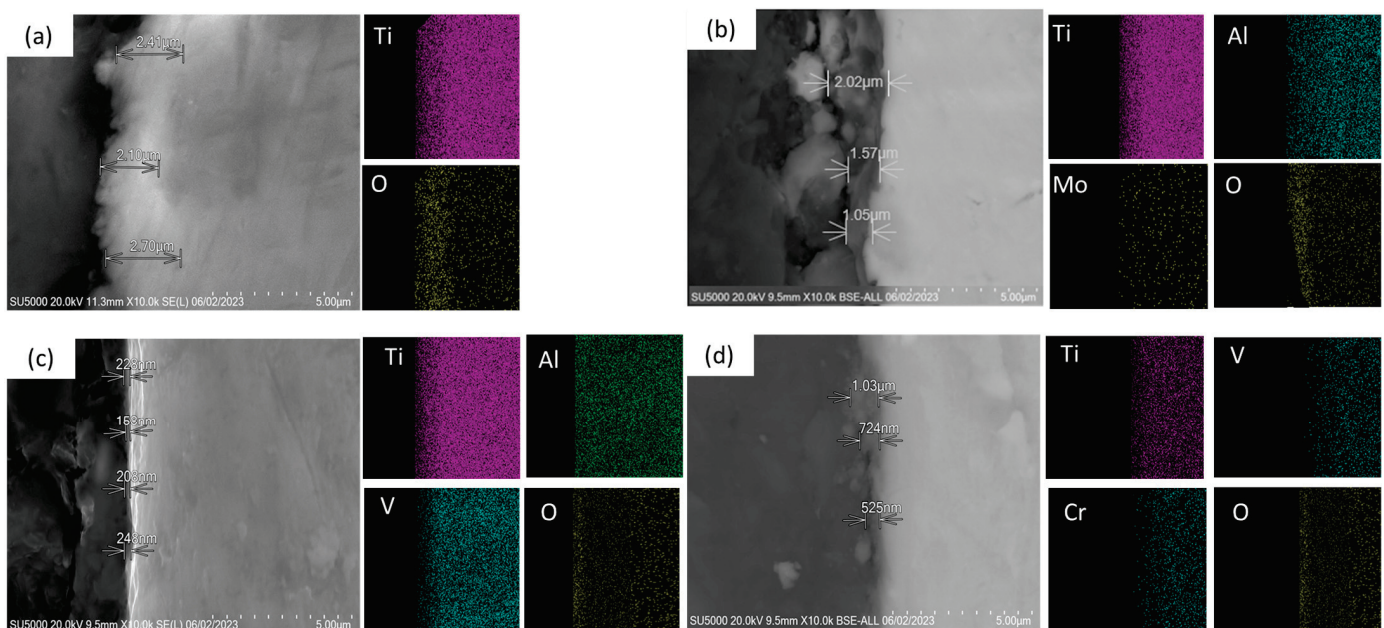


Figure 4. SEM-SE/BSE of transversal section of anodized titanium alloys in KOH at 10,000×, and element mapping by EDS of (a) Ti CP2, (b) Ti-6Al-2Sn-4Zr-2Mo, (c) Ti-6Al-4V y (d) Ti Beta C.

Table 2. Thicknesses of anodized titanium alloys.

Alloy	Electrolyte	Average Thickness (μm)
Ti CP2	NaOH	0.45
	KOH	2.4
Ti-6Al-2Sn-4Zr-2Mo	NaOH	2.45
	KOH	1.5
Ti-6Al-4V	NaOH	0.024
	KOH	0.2
Ti Beta-C	NaOH	0.67
	KOH	0.75

3.2. Electrochemical Noise

3.2.1. Hilbert–Huang Transform (HHT)

The electrochemical noise (EN) technique describes the electrochemical phenomenon that occurs during the corrosion process. One method to characterize the EN technique is Hilbert–Huang analysis. This method helps the frequency and time in which an energy interchange occurs; the energy is called instantaneous energy and is obtained by the decomposition of the signal obtained by the intrinsic function of the signal [25–30]. The empirical method of decomposition (EMD) can be explained by the Equation (1):

$$x(t) = \sum_{i=1}^N h^{(i)}(t) + d(t) \quad (1)$$

where $d(t)$ is the average of the trend at a low frequency of the time series $x(t)$ and cannot be decomposed and $h^{(i)}(t)$ is the i -th term of IMF that is generated. These numbers must satisfy the conditions that the extreme and cross numbers are equal or differ by a maximum of 1 and that each point using the local maximum and minimum must be 0. The HHT is represented by Equation (2):

$$y_j(t) = \frac{1}{\pi} p \int_{-\infty}^{\infty} \frac{h_j(\tau)}{t - \tau} d\tau \quad (2)$$

where $y_j(t)$ is the Hilbert transform and IMF is represented with h_j ; p is related to the Cauchy principle and is linked with an average of IMF.

Figure 5 shows the behavior of Ti alloys anodized in NaOH when analyzed using the HHT method. All the alloys anodized shown in that figure demonstrate the same pattern: the presence of energy in middle and low frequencies, with high energy at middle frequencies. This behavior is related to non-homogenous anodization on the surface, but a protective layer is present due to energy at a low frequency. The only anodized alloy that presented energy at high frequencies is Ti Beta-C, anodized in H_2SO_4 , in Figure 5h, meaning that the anodized alloy is weak in the presence of the acid media. The high energy at middle frequencies means that the ions first attack preference zones of the anodized surface. However, after time passes, the energy decreases and is accumulated at low frequencies due to the accumulation of those ions on the surface.

Figure 6 shows the Hilbert specters of Ti alloys anodized in KOH in both media. The anodized Ti CP2 of Figure 6a,b presents energy at high and middle frequencies, even in NaCl and H_2SO_4 ; irregular behavior is associated with a heterogeneous anodized alloy. The energy at low frequencies in Figure 6b indicates the ions' accumulation on the surface. Figure 6c–f for Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V showed a more homogenous anodized alloy than Ti CP2 and Ti Beta-C. The anodized Ti Beta-C presented high instability in both media when exposed to NaCl (Figure 6g). The anodized alloy showed high energy accumulation at high frequencies in all the time series, indicating that it is heterogeneous

and that ions attack in preferential zones. Figure 6h shows a similar behavior, but the presence of energy is not higher than in Figure 6g; this occurs due to the susceptibility of anodized alloys to Cl^- ions.

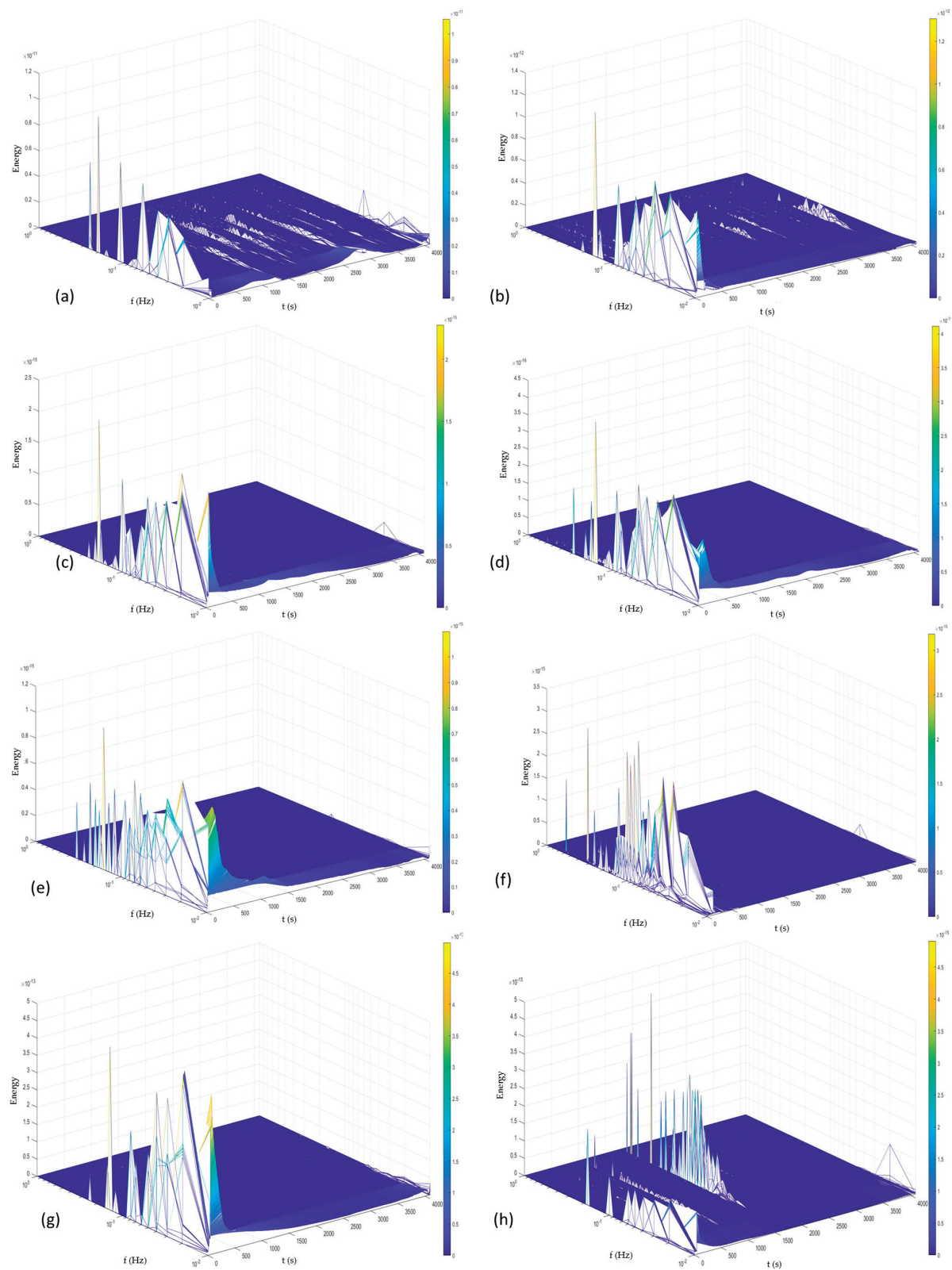


Figure 5. Hilbert specter for anodized titanium alloys in NaOH in NaCl (left) and H_2SO_4 (right) of Ti CP2 (a,b), Ti-6Al-2Sn-4Zr-2Mo (c,d), Ti-6Al-4V (e,f), and Ti Beta-C (g,h).

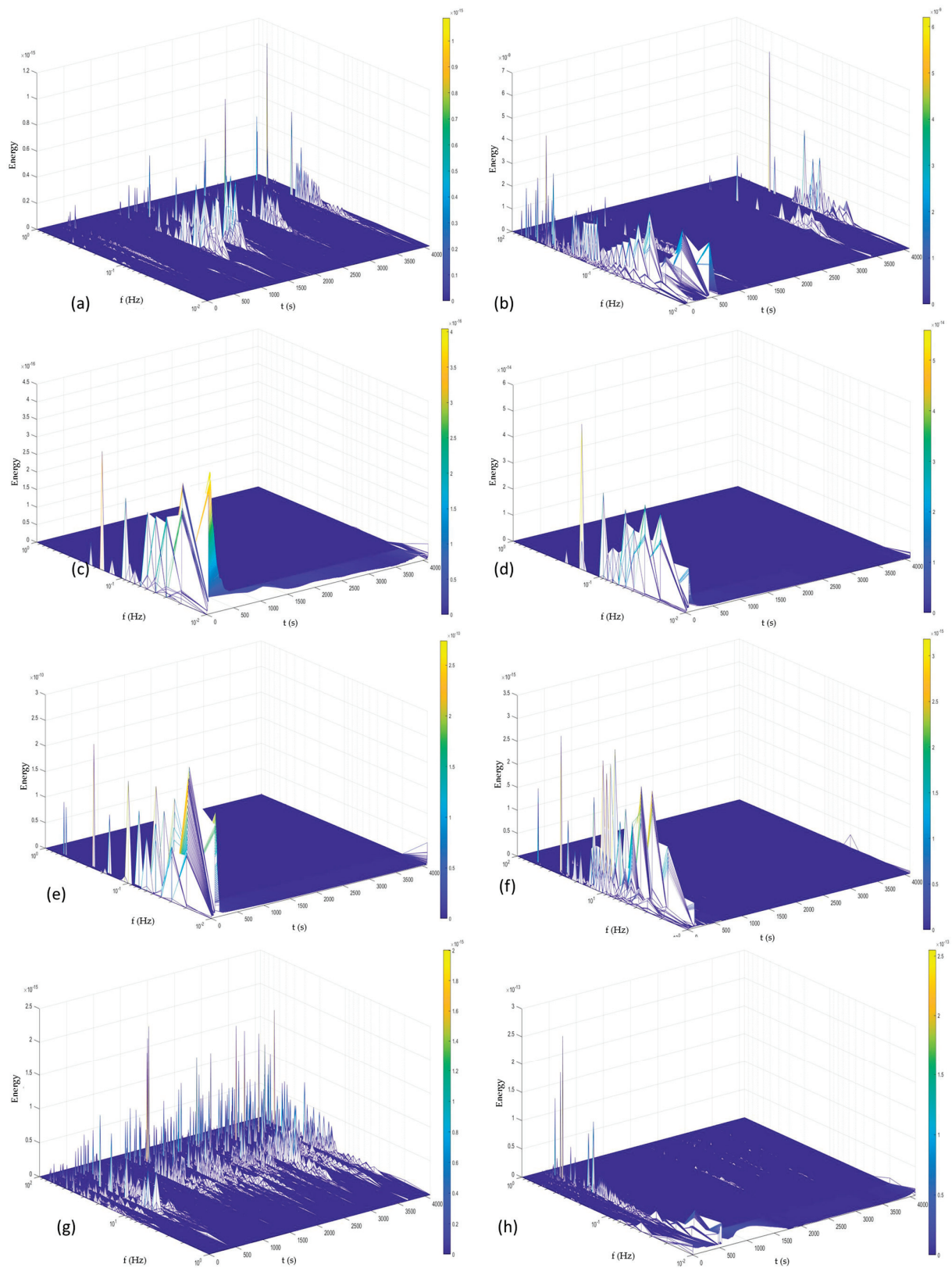


Figure 6. Hilber specter for anodized titanium alloys in KOH in NaCl (left) and H₂SO₄ (right) of Ti CP2 (a,b), Ti-6Al-2Sn-4Zr-2Mo (c,d), Ti-6Al-4V (e,f), and Ti Beta-C (g,h).

3.2.2. Recurrence Plots Analysis (RP)

Recurrence plots are helpful tools for analyzing non-linear systems. As corrosion is a chaotic and non-linear system, it is necessary to employ different techniques to evaluate the corrosion type and process on the surface. RP is an excellent technique with which to conduct that analysis.

Recurrence plots are two-dimensional diagrams that are realized in time function. The trajectory of $x_i \in R_m$, where a dimension (m) of space is prescribed at a time limit of ε to i and j . The RP visualizes a two-dimensional square matrix from two dimensions with the times t_i and t_j . Equation (3) shows the matrix [31–34]:

$$R_{ij}(\varepsilon) = \Theta \left(\varepsilon - \left\| \vec{x}_i - \vec{x}_j \right\| \right), \quad i, j = 1, \dots, N \quad (3)$$

where N is the number of data or points x_i , ε is the distance umbral, $\Theta(x)$ is the Heaviside function, and $\| \cdot \|$ is the norm (Euclidean, maximum, or Manhattan).

The recurrence density is determined by the recurrence rate that Equation (4) shows:

$$RR(\varepsilon) = \frac{1}{N^2} \sum_{i,j=1}^N R_{i,j} \quad (4)$$

The recurrence rate (RR) gives the probability of reconstruction of one trajectory in an umbral zone.

The diagonal lines of RP represent the evolution of the trajectory in the space of the phase on different occasions and indicate the system's determinism. The determinism (DET) is calculated by the next equation:

$$DET = \frac{\sum_{l=l_{min}}^N l p(l)}{\sum_{l=1}^N l p(l)} \quad (5)$$

The laminarity is defined as the relation between the recurrence points in the vertical structures and the total number shown in Equation (6):

$$LAM = \frac{\sum_{v=v_{min}}^N v p(v)}{\sum_{v=1}^N v p(v)} \quad (6)$$

Figure 7 shows the anodized alloys' recurrence plots in NaOH when exposed to NaCl and H_2SO_4 . When the anodized alloys are exposed to NaCl, as Figure 7a–d shows, they present different behaviors. The anodized Ti CP2 and Ti-6Al-4V presented less deterministic behavior (see Table 3), meaning that the exposed oxide layer is more susceptible to Cl ions. On the other hand, anodized Ti-6Al-2Sn-4Zr-2Mo and Ti Beta-C presented more deterministic behavior, with values between 0.8270 and 0.9697, indicating that the localized process is reduced. The alloys anodized in H_2SO_4 are shown in Figure 8a–d; in this case, the anodized Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V (Figure 8b,c) presents low deterministic values, from 0.4723 to 0.5373, indicating that a localized process occurs at the surface; this is because horizontal and vertical lines decrease the laminarity of the system. The OH^- ions attack the porous surface.

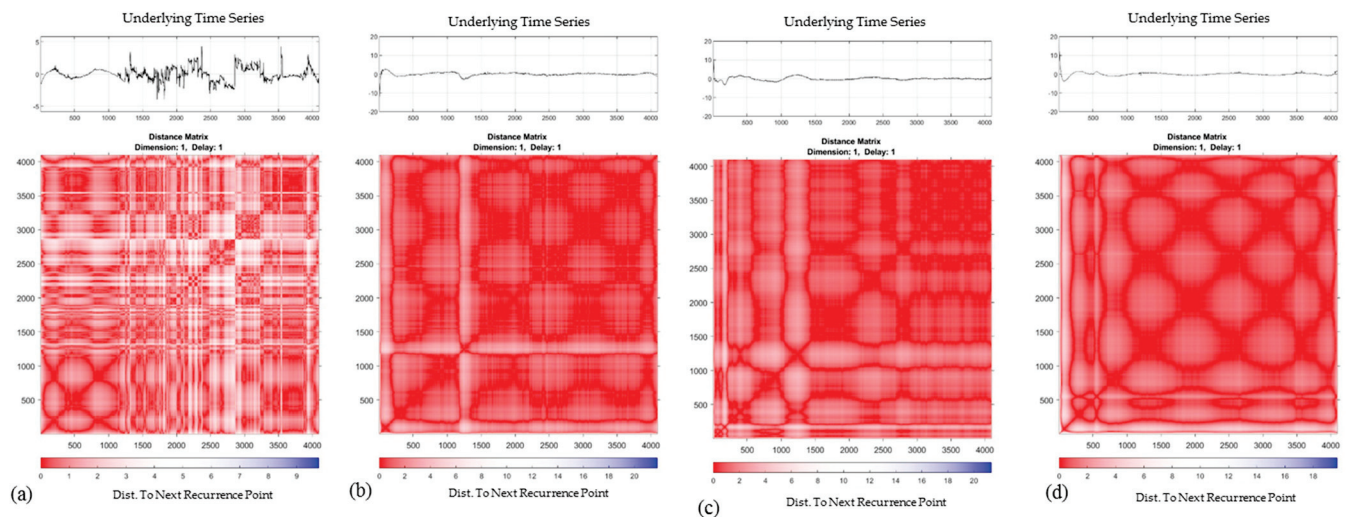


Figure 7. Recurrence plots of anodized titanium alloys in NaOH bath and exposed in NaCl for Ti CP2 (a), Ti-6Al-2Sn-4Zr-2Mo (b), Ti-6Al-4V (c) y Ti Beta-C (d).

Table 3. Parameters obtained of anodized titanium alloys in NaOH bath by Recurrence Plots analysis.

Anodized	Alloy	RR	DET
NaOH		NaCl	
	Ti CP2	0.0671	0.6951
	Ti-6Al-2Sn-4Zr-2Mo	0.0927	0.827
	Ti-6Al-4V	0.0816	0.7368
	Ti Beta-C	0.0988	0.9697
		H ₂ SO ₄	
	Ti CP2	0.0991	0.9155
	Ti-6Al-2Sn-4Zr-2Mo	0.0868	0.5373
	Ti-6Al-4V	0.1666	0.4723
	Ti Beta-C	0.1088	0.9001

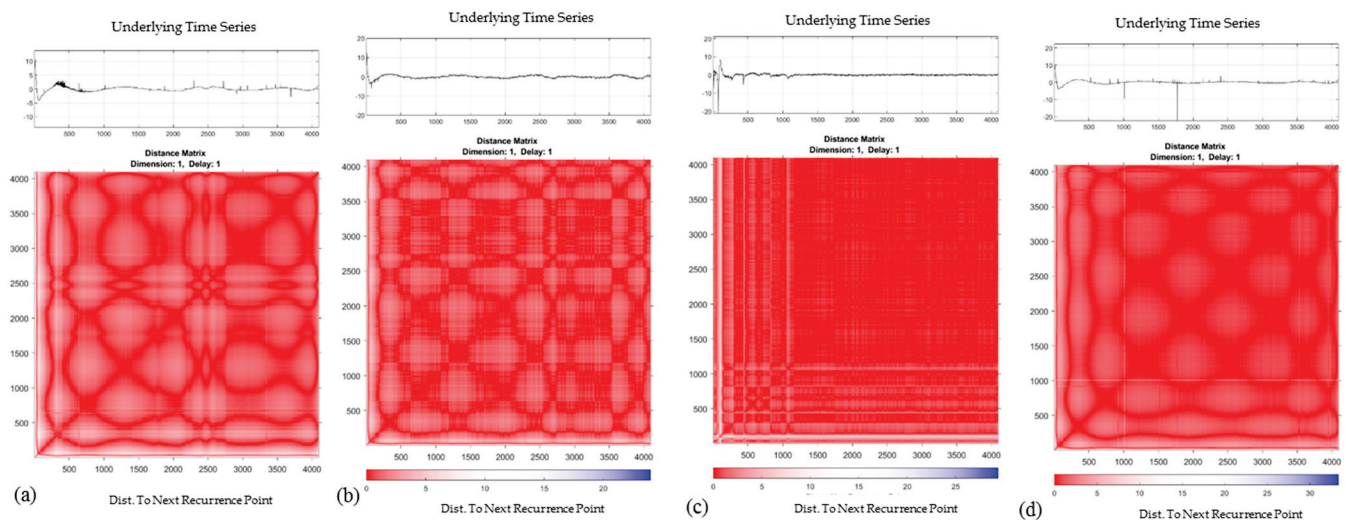


Figure 8. Recurrence plots of anodized titanium alloys in NaOH bath and exposed in H₂SO₄ for Ti CP2 (a), Ti-6Al-2Sn-4Zr-2Mo (b), Ti-6Al-4V (c) y Ti Beta-C (d).

Figure 9 shows the recurrence plots when alloys were anodized on KOH. The anodized exposure in NaCl (Figure 9a–d presents results of low determinism, especially for Ti CP2 and Ti Beta-C); this behavior is attributed to the great number of anodic and cathodic reactions occurring on the surface. Due to the low anodized quality in that medium and the susceptibility to Cl^- ions, the values of determinism are 0.5542 and 0.6901, respectively. The low determinism decreases the laminarity value to 0.7094 and 0.8070 for Ti CP2 and Ti Beta-C. The anodized Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V present a better performance in this media. When anodized surfaces are exposed to H_2SO_4 (Figure 10a–d), Ti-6Al-4V showed the lowest deterministic value (0.4718) due to transients that reflect instability on anodized surfaces by anodic reactions. The anodized Ti Beta-C presents low determinism in the first seconds and at the end, with values of 0.8696 and 0.9285 of determinism and laminarity, respectively. When transients increase, the lines create cross-sections and decrease the laminarity and determinism (see Table 4).

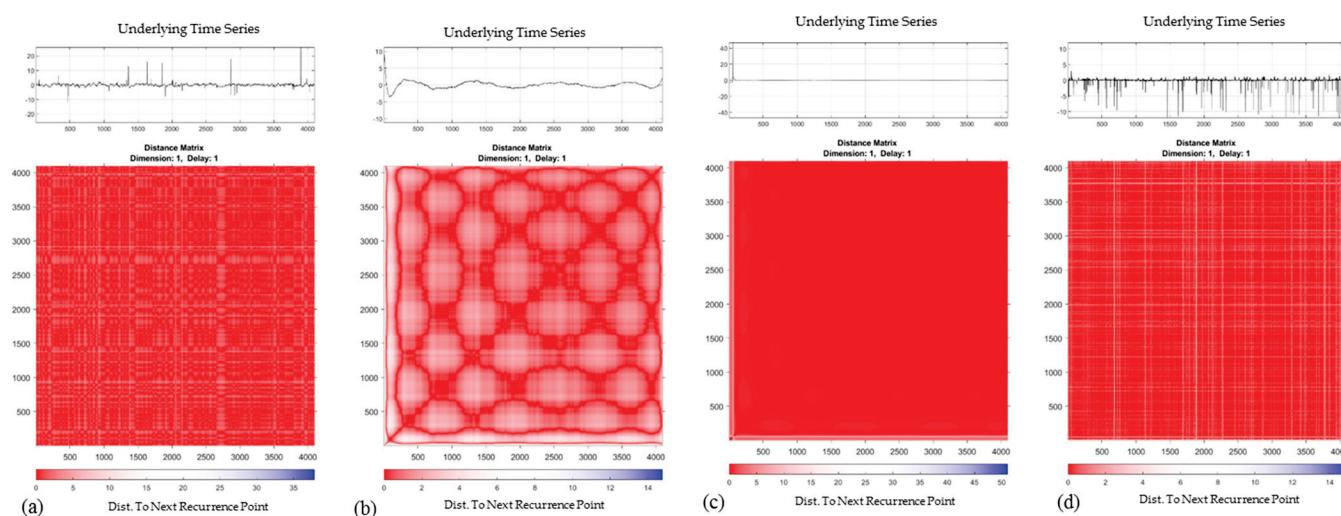


Figure 9. Recurrence plots of anodized in a KOH bath and exposed in NaCl for Ti CP2 (a), Ti-6Al-2Sn-4Zr-2Mo (b), Ti-6Al-4V (c) y Ti Beta-C (d).

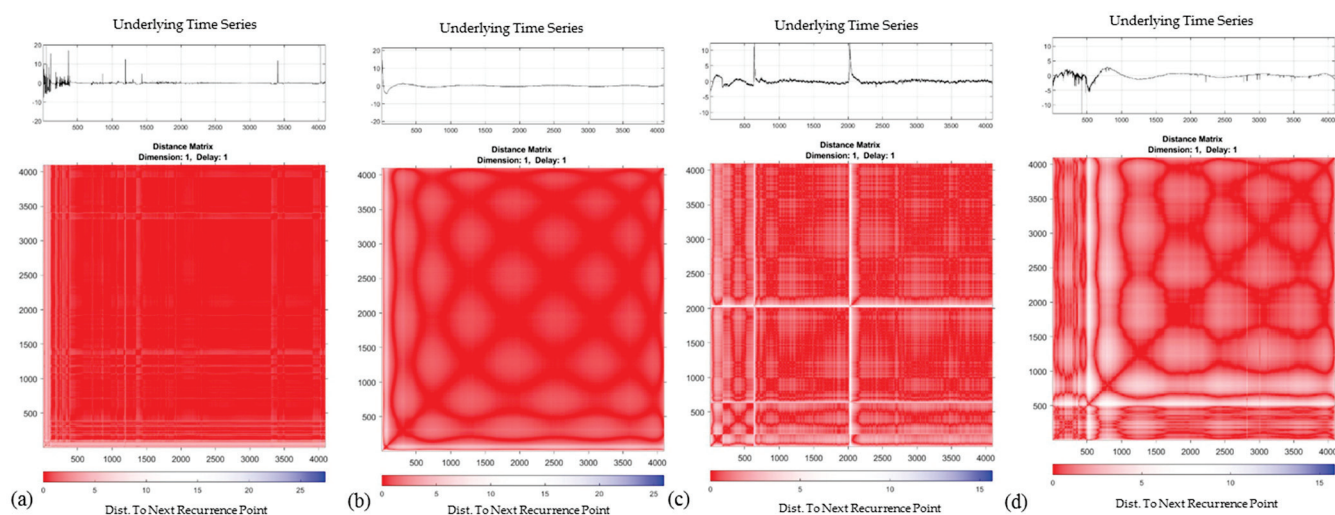


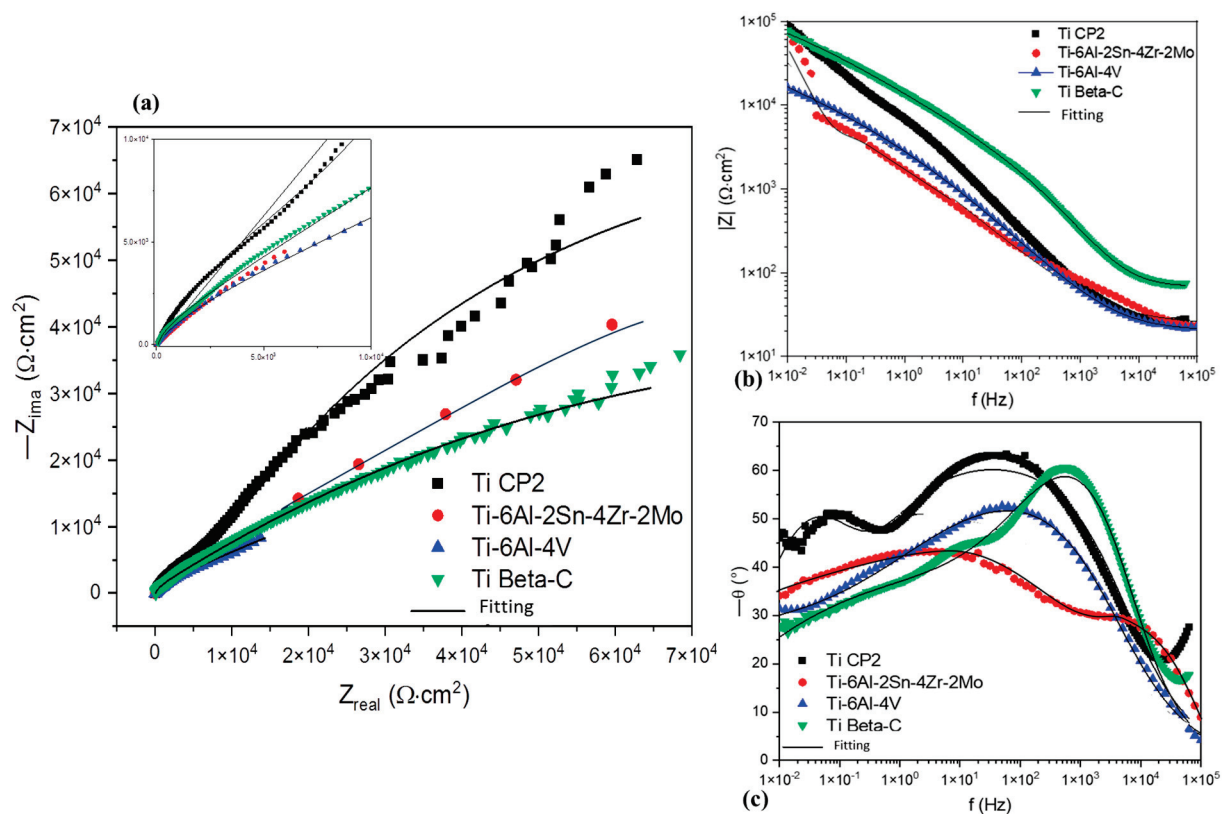
Figure 10. Recurrence plots of anodized in a KOH bath and exposed in H_2SO_4 for Ti CP2 (a), Ti-6Al-2Sn-4Zr-2Mo (b), Ti-6Al-4V (c) y Ti Beta-C (d).

Table 4. Parameters obtained of anodized titanium alloys in a KOH bath by recurrence plots analysis.

Anodized	Alloy	RR	DET
KOH		NaCl	
	Ti CP2	0.0824	0.5542
	Ti-6Al-2Sn-4Zr-2Mo	0.0788	0.8378
	Ti-6Al-4V	0.5779	0.9962
	Ti Beta-C	0.3508	0.6901
		H ₂ SO ₄	
	Ti CP2	0.3045	0.888
	Ti-6Al-2Sn-4Zr-2Mo	0.1421	0.9126
	Ti-6Al-4V	0.1105	0.4718
	Ti Beta-C	0.0829	0.8696

3.3. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) has been widely used to study the electrochemical mechanisms at electrodes. The characteristics of the EIS spectra of the samples investigated in the present study are presented in Figures 11–14; they show Nyquist and Bode plots for anodized titanium alloys immersed in 3.5 wt. % NaCl and H₂SO₄ solution.

**Figure 11.** EIS of anodized titanium alloys in NaOH exposed in NaCl. (a) Nyquist, (b) Bode of $|Z|$ vs. frequency, and (c) phase angle Bode.

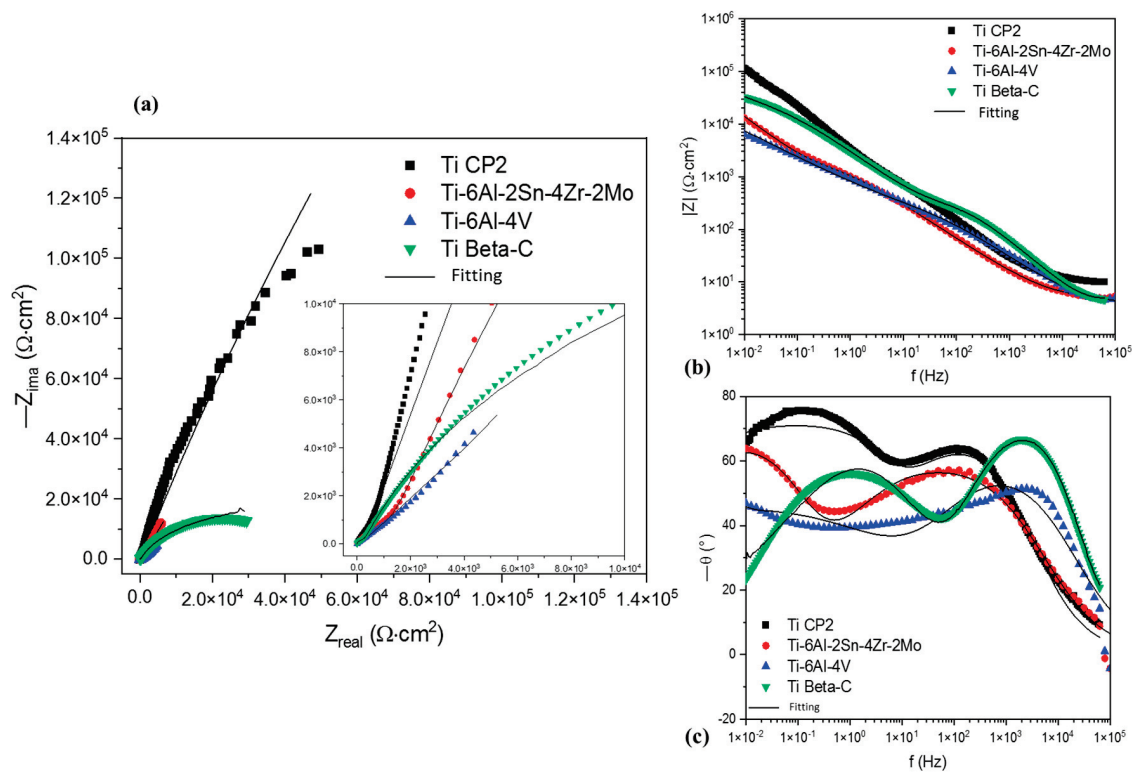


Figure 12. EIS of anodized titanium alloys in NaOH exposed in H_2SO_4 . (a) Nyquist, (b) Bode of $|Z|$ vs. frequency, and (c) phase angle Bode.

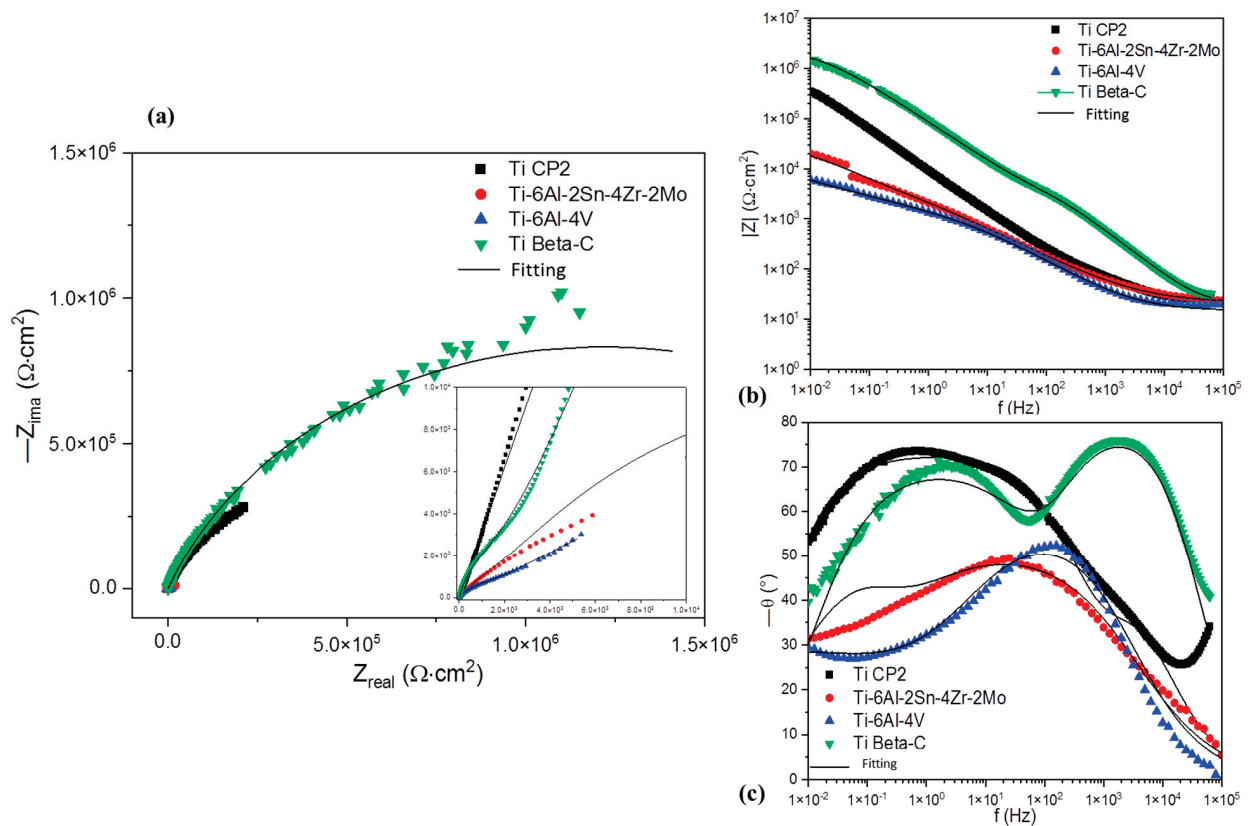


Figure 13. EIS of anodized titanium alloys in KOH exposed in NaCl. (a) Nyquist, (b) Bode of $|Z|$ vs. frequency, and (c) phase angle Bode.

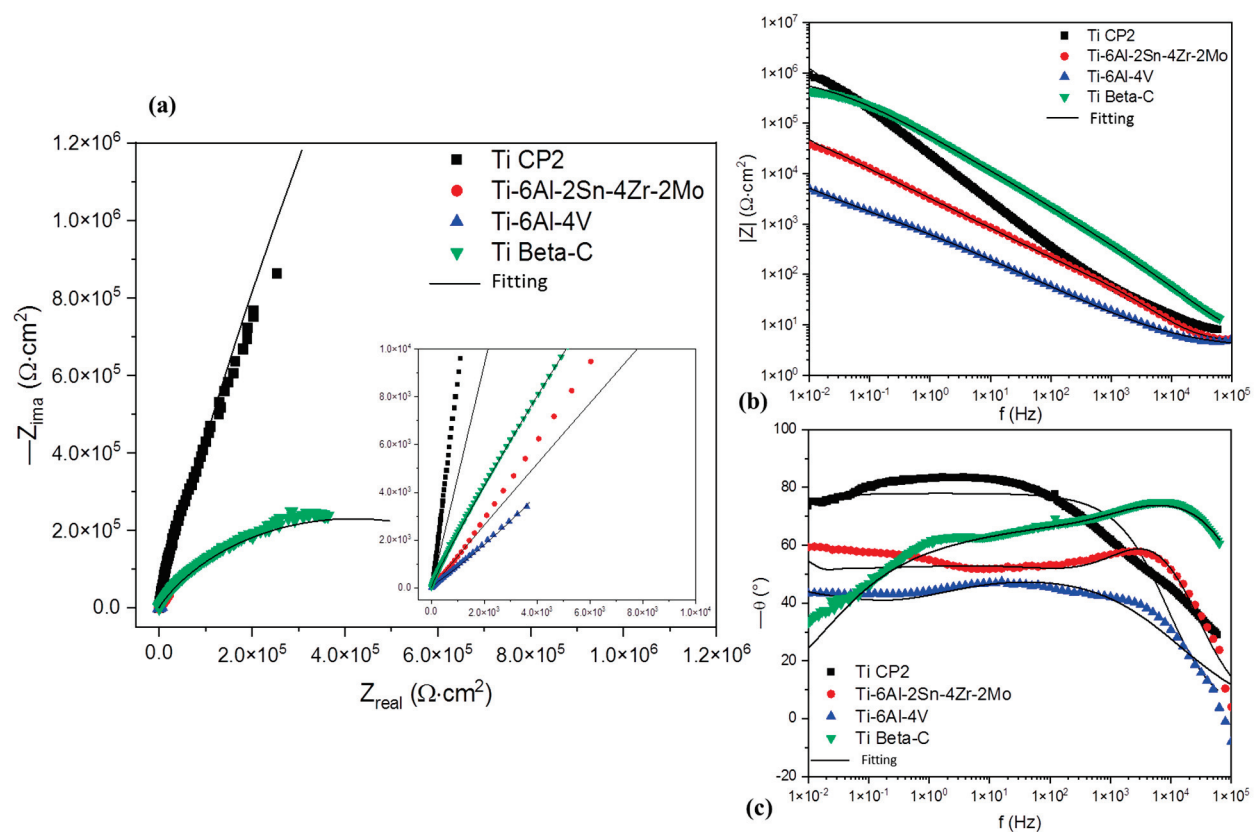


Figure 14. EIS of anodized titanium alloys in KOH exposed in H_2SO_4 . (a) Nyquist, (b) Bode of $|Z|$ vs. frequency, and (c) phase angle Bode.

Figure 11 shows Ti alloys anodized in NaOH exposed to NaCl. The anodized Ti CP2 showed a high resistance with $2.4 \times 10^4 \Omega \cdot \text{cm}^2$, and the lowest capacitance of 3.37×10^{-5} and $4.75 \times 10^{-5} \text{ F/cm}^2$ (see Table 5). This behavior indicates that the layer of this anodized alloy presented acceptable properties against corrosion. The “ n ” values for the anodized Ti CP2 are 0.7 and 0.8 in both high- and low-frequency interfaces, meaning there is a capacitive system predominance. On the other hand, the anodized Ti-6Al-4V and Ti Beta-C presented in the first have interface values of 0.8 and 0.7, respectively, indicating capacitive behavior in the first porous layer. However, in the second interface, the n values were 0.3 and 0.4, respectively, indicating more resistive behavior; the alloys acted as resistors rather than capacitors. This is associated with the high value of capacitance (1.27×10^{-4} and $3.16 \times 10^{-5} \text{ F/cm}^2$), which suggests a faster ionic dissolution process due to the heterogeneities on the surface.

Table 5. Parameters obtained by EIS for anodized titanium alloy samples.

Alloy	R_s ($\Omega \cdot \text{cm}^2$)	R_{por} ($\Omega \cdot \text{cm}^2$)	CPE-T (F/cm^2)	n	R ($\Omega \cdot \text{cm}^2$)	CPE-T2 (F/cm^2)	n	W ($\Omega \cdot \text{cm}^2$)	χ^2
Ti CP2									
3.5% NaCl									
NaOH	19.1	2.4×10^4	3.37×10^{-5}	0.7	1.72×10^5	4.75×10^{-5}	0.8	-	0.01
KOH	20.3	92.4	9.78×10^{-6}	0.8	1.01×10^6	1.36×10^{-5}	0.8	-	0.01

Table 5. Cont.

Alloy	Rs ($\Omega \cdot \text{cm}^2$)	R _{por} ($\Omega \cdot \text{cm}^2$)	CPE-T (F/cm ²)	n	R ($\Omega \cdot \text{cm}^2$)	CPE-T2 (F/cm ²)	n	W ($\Omega \cdot \text{cm}^2$)	X ²
3.5% H ₂ SO ₄									
NaOH	9.8	1530	4.29×10^{-5}	0.8	2.41×10^6	2.59×10^{-5}	0.8	-	5×10^{-3}
KOH	9.1	2.65×10^7	8.92×10^{-6}	0.9	-	-	-	-	5×10^{-2}
Ti-6Al-2Sn-4Zr-2Mo									
3.5% NaCl									
NaOH	21.3	20.8×10^3	1.47×10^{-4}	0.6	18×10^3	2.05×10^{-4}	0.8	-	7×10^{-4}
KOH	21.8	8409	1.34×10^{-4}	0.7	2.88×10^4	1.11×10^{-4}	0.7	-	9×10^{-3}
3.5% H ₂ SO ₄									
NaOH	4.5	2473	1.96×10^{-4}	0.8	3.15×10^5	4.06×10^{-4}	0.8	-	2×10^{-3}
KOH	4.6	83.5	5.64×10^{-6}	-	-	-	-	1.39×10^5	6×10^{-3}
Ti-6Al-4V									
3.5% NaCl									
NaOH	20.1	1761	6.55×10^{-5}	0.7	7.85×10^5	1.27×10^{-4}	0.3	-	3×10^{-4}
KOH	14.8	1238	9.34×10^{-5}	0.7	1.12×10^5	5.01×10^{-4}	0.4	-	1×10^{-2}
3.5% H ₂ SO ₄									
NaOH	3.7	296	7.61×10^{-5}	0.7	-	-	-	2.7×10^4	1×10^{-2}
KOH	3.57	2158	4.70×10^{-4}	0.6	-	-	-	3.15×10^4	7×10^{-3}
Ti Beta-C									
3.5% NaCl									
NaOH	66.9	1589	2.11×10^{-6}	0.8	2.1×10^5	3.16×10^{-5}	0.4	-	1×10^{-3}
KOH	20.7	5418	6.23×10^{-7}	0.9	2.43×10^6	2.17×10^{-6}	0.7	-	6×10^{-3}
3.5% H ₂ SO ₄									
NaOH	4.1	284	6.93×10^{-6}	0.9	4.4×10^4	8.94×10^{-5}	0.7	-	1×10^{-3}
KOH	3.7	1201	1.05×10^{-7}	0.9	8.54×10^5	4.31×10^{-6}	0.6	-	1×10^{-3}

Figure 12 shows the results of samples anodized in NaOH exposed to H₂SO₄. The samples showed a similar trend to the samples exposed on NaCl, where the Nyquist and frequency vs. $|Z|$ diagrams of Figure 12a,b show a high impedance module for anodized Ti CP2, as well as higher values of impedance in the Nyquist diagram. Ti Beta-C presented high values of resistance. On the other hand, Ti-6Al-4V presented a behavior associated with a diffusion system. The Warburg process can be observed in the windowing performed on the Nyquist diagram of Figure 12a and in the diagram of Figure 12c, where the phase angle finished at 45° at low frequencies, indicating that the diffusion process occurs at low frequencies. The Warburg resistance is $2.7 \times 10^4 \Omega \cdot \text{cm}^2$. At the same time, the first process presented a resistance of $289 \Omega \cdot \text{cm}^2$ and a capacitance of $7.61 \times 10^{-5} \text{ F/cm}^2$, with an n value of 0.7. The first process is related to a capacitive system with a heterogeneous surface. Ti CP presented n values of 0.8 and 0.9, meaning that the distribution of ionic charges is more homogenous [35].

Figure 13 shows the samples anodized on KOH exposed to NaCl. In this medium, all the anodized alloys showed a double-layer behavior, where Ti Beta-C presented better performance against corrosion. Ti CP2 also presented good behavior against corrosion. Ti-6Al-4V presented the lower impedance values, with $1238 \Omega \cdot \text{cm}^2$, with n values of 0.7 and 0.4. This means that the surface is homogenous, and the process in the second layer

is predominantly resistive. Also, this indicates a dissolution process that occurs on the anodized surface.

Figure 14 shows the results of samples anodized in KOH exposed to H_2SO_4 . Ti CP2 and Ti Beta-C alloys presented a higher impedance; however, Ti CP2 only presented a one-time variable. This behavior is related to a compact oxide layer due to the impedance value of $2.65 \times 10^7 \Omega \cdot \text{cm}^2$ with a capacitance of $8.92 \times 10^{-6} \text{ F/cm}^2$ and an n value of 0.9, indicating that the charges distribution is homogenous. On the other hand, Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo presented a diffusion process at low frequencies, indicating the dissolution of the oxide layer. The Warburg resistance of alloys is 1.39×10^9 and $3.15 \times 10^4 \Omega \cdot \text{cm}^2$.

The table below shows the results of EIS parameters. The results were discussed in the diagram topic. The values of X^2 are related to the error of fitting, meaning the values are lower and the fitting is better [36]. In this case, the value increases when, at high frequencies, the impedance is dispersed (the first four or five values).

The physical and mathematical model of the metal/anodized layer film/solution system is presented in Figure 15. The electrochemical impedance technique provides parameters such as solution resistance (R_s), transference charge resistance (R_{ct}), capacitance (C_{dl}), constant phase element (CPE), or diffusion (W), depending on the case [referencia nueva].

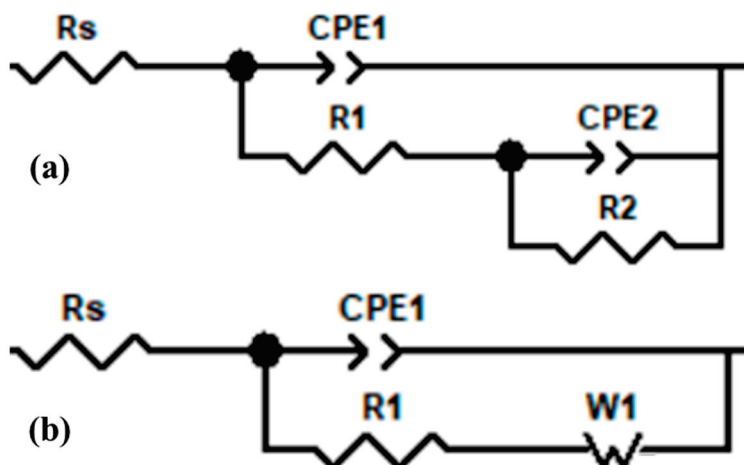


Figure 15. Equivalent circuits for (a) double-layer system and (b) Warburg's system.

The impedance of the system is obtained using the following equation [37]:

$$Z = \frac{E}{I} = Z_0 \exp(i\Phi) = Z_0(\cos\Phi + i\sin\Phi) \quad (7)$$

Z , E , I , ω , and Φ are the impedance, potential, current, frequency, and the phase angle between E and I .

Hence, the following equation can interpret the capacitance obtained by EIS measurements.

$$Z_c(\omega) = \frac{1}{i\omega C} \quad (8)$$

where C is the capacitance value; nevertheless, if the value of the capacitance is not close, it is possible that a CPE phenomenon is occurring in the system, and the equation that governs this is:

$$Z_{CPE}(\omega) = \frac{1}{(i\omega)^{\alpha_{dl}} Q^{dl}} \quad (9)$$

where α is a constant related to the uniform charge distribution and Q is the system's capacitance.

On the other hand, when a mass diffusion occurs in the system, a Warburg's element is possibly present on the equivalent circuits [38,39].

$$Z_w(\omega) = \sigma\omega^{-1/2} - i\left(\sigma\omega^{-\frac{1}{2}}\right) \quad (10)$$

4. Discussion

The anodized NaOH noted in another paper was reported to have oxide-layer porosities of 0.1 to 1 μm . This supports the idea that the percentage of porosity depends directly on the alloys' chemical composition [40]. Also, Afshar et al. [18] obtained anodized alloys with thicknesses from 0.4 to 1.5 μm . They related the anodized time to the thickness of the oxide layer. In this research, the anodized thickness ranged from 23 nm to 2.63 μm , where Ti-6Al-2Sn-4Zr-2Mo and Ti Beta-C presented higher thicknesses. Considering that the anodized parameters were the same for all experiments, the anodized thickness depends on the chemical composition of the alloy. Ti-6Al-4V generated an oxide layer of 23 nm related to the presence of V. However, Mo, Cr, and Zr alloys presented better oxide-layer generation.

When the KOH was employed as the anodized electrolyte, Burleigh et al. [41] obtained oxide layers of 300 nm; they concluded that NaOH and KOH are very similar in terms of generating oxide layers in Ti alloys. Hsu et al. [42] conducted research in which they anodized Ti-7.5 Mo in alkaline electrolytes and obtained a thin oxide layer with nanopores. The generation of the porosities was attributed to the penetration of Na^+ and OH^- ions in the anodized surface, provoking a porous layer of sodium and hydroxide titanate ($\text{Na}_x\text{H}_2\text{-xTi}_3\text{O}_7$) after exposition to the alkaline media. Due to the valence number of K, the surface reaction is very similar to the anodized NaOH.

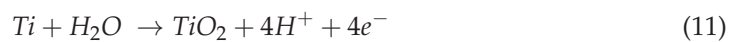
Laurindo et al. [43] related the size porosity increase to the thickness when the current density increases. However, this will create surface cracks. This occurs on anodized Ti Beta-C. Additionally, Zhang et al. [44] found that pore size depends on the ionic current anodized. Also, Mazzarolo et al. [45] conclude that an amorphous barrier is created on the Ti surface, making the alloy susceptible to generating oxide in preferential zones when small ions such as Na^+ and K^+ are deposited in specific zones and generate oxide in specific zones. This behavior was presented in this research.

It is important to mention that Cl^- acts as an interstitial element, so when the anodized has tiny pores or cracks, the ion penetrates the surface to attack [46]. Cl^- 's presence induces localized corrosion because the ions attack the more susceptible zones. The accumulation of oxychlorides is expected to occur on the metal–oxide interface; this is due to the breaking of the oxide layer, and it provokes a localization process [47,48]. This occurs when the “n” of CPE values differ by 0.5, which is associated with the accumulation of Cl^- on the surface until they break the interface; this is the double-layer mechanism. The capacitance values obtained are related to the resistance or the opposition of ionic transference on the surface [49].

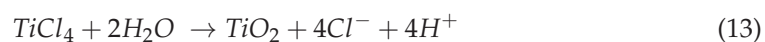
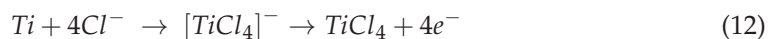
Song et al. [50] reported the effects of different Ti alloys exposed to saline media. They found that the alloys with V presented a lower corrosion resistance than the other alloys; this occurred due to the V oxide layer created in the corrosion process being dissolved faster than the other oxide layers. This behavior is presented in all Ti-6Al-4V alloys, with lower corrosion resistance. The corrosion resistance increased for alloys that showed Cr, Mo, or Zr. Also, the susceptibility to Cl^- can be observed on HHT specters when high energy is present at the middle and high frequencies.

A helpful technique is EIS for barrier systems. The values obtained on “n” are related to capacitive behavior (near to 1), the diffusive system (0.5), or the resistive system (less than 0.5) [51]. Gomes et al. [52] related the “n” value to the charge distribution on the oxide layer determined by the thickness. Also, authors such as Gateman [53] conclude that the CPE behavior is related to the interface system, and a correct analysis will depend on the knowledge of the system. Therefore, if “n” is a value of 1, the surface is homogenous. Still, a different value is associated with a heterogeneous surface.

For the cases that presented diffusion, the processes that govern the Warburg element are absorption, penetration, and diffusion. The absorption occurs in the porous zones, while the diffusion occurs in the more compact oxide zones. This can create a higher corrosion resistance when the diffuser elements generate another passive layer [54–57]. The basic chemical reactions that occur in diffusion are:



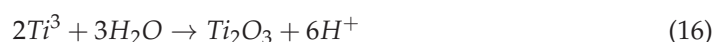
However, when the diffusion process begins in a saline environment, the Cl^- has an important role and changes the chemical reactions:



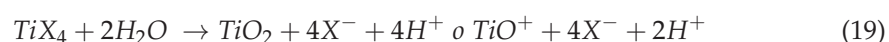
This behavior is very similar in all the aqueous solutions; independently of the composition, the hydrogen will react due to evolution, given by the next equation [58]:



This phenomenon occurs in cathodic reactions where hydrogen reacts. On the other hand, the growth of a passive layer in electrochemical conditions is represented by the next equations [59–61]:



The results show that the diffusion process on titanium and anodized alloys occurs in the solid state due to the ions' diffusion in the porous zone. The micropores from the first barrier act as diffusion zones [62–66]. That means the anodized alloys also have some corrosion resistance, so the Cl^- can break the protective barrier. Prando et al. [56] associated this behavior with the susceptibility of Ti to halides and proposed the next reaction:



X is a halide. When the solution does not have perturbation, water is the only transport for pitting the TiO_2 and H^+ out of the system. This permits the electrolyte to permeate the anodized breaking alloy and reduce the corrosion resistance. Additionally, elements such as Nb, Pd, and Cr increase the corrosion resistance, as occurs on Ti Beta-C.

On the other hand, when the electrolyte is H_2SO_4 , the ions generate cathodic reactions, hydroxide diffusion, and passive layers. Therefore, the system with HHT and recurrence plots must be studied. The common behavior of anodization in this medium is the generation of an oxide layer that is broken and re-generated. Also, OH^- and SO_4^{2-} generate unstable systems and generate cracks in anodized alloys [30,67].

Sadek et al. [59] mentioned that heterogeneities and susceptibility to localized attacks are due to the formation of hydroxides ($\text{Ti}(\text{OH})_x\text{O}_y$), as the hydroxides avoid the generation of an oxide layer. The porous barrier of the hydroxides generates the anodized diffusion process [68–73].

Also, when exposed to H_2SO_4 , the reactions generate an oxide layer (diffusion). However, if the oxide is not solid, it will degrade. The diffusion process is blocked when the “n” values are 0.4 or 0.6. Authors Gonzalez, Pardave, Rodriguez, et al. [74–77] mentioned that when the “n” value is 0.4 and 0.6, the diffusion process is not perfect; it may signal trapped diffusion or blocked diffusion due to differences in surface quality. For that reason,

in this research, when the “*n*” value was not 0.5, we did not consider it diffusion. The next equation shows the behavior of a diffusion government process.

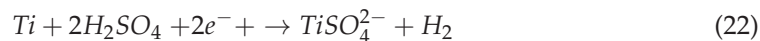
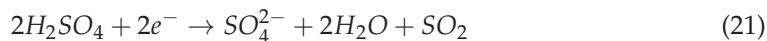


Figure 16 shows the equivalent circuit for the two different systems. Figure 16a shows the double-layer system, where the first resistance is related to the solution resistance, the second is with R_{ct} (R_{por}), and the third is more linked with the double layer of oxide. The anodized alloys with less presence of β elements presented a higher R_{por} when anodized on NaOH than those with a high presence of β alloying elements, which presented higher R_{por} values when anodized in the KOH electrolyte.

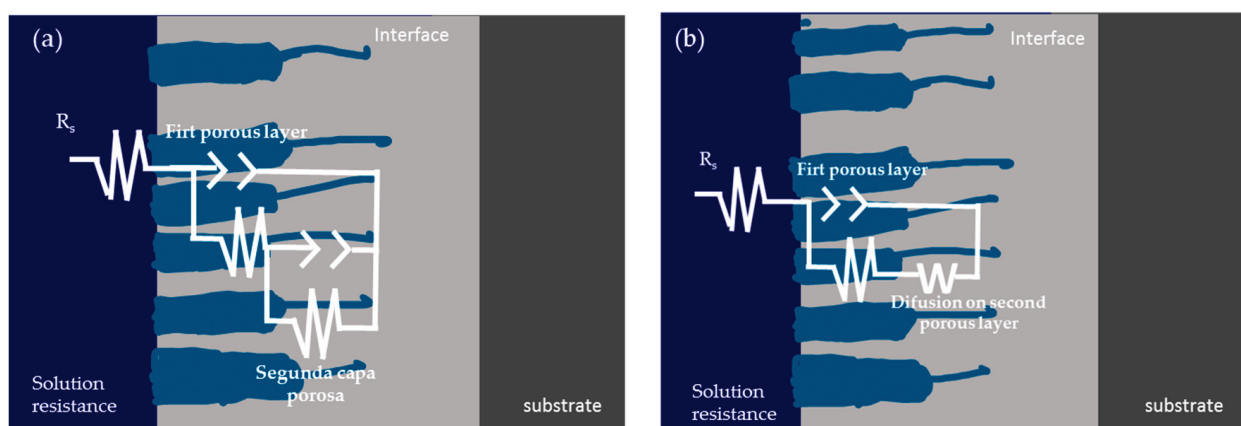


Figure 16. Schematic of ECC for the two different models. (a) double-barrier system, (b) diffusion system.

Furthermore, the electrolyte of H_2SO_4 trends to generate a diffusion process in the anodized Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-4V. In this last case, for anodized Ti-6Al-4V, the ECC showed *n* values of 0.4 and 0.3. This is controversial because some authors related it to a diffusion process and others to a resistive process. The physical value of “*n*” has been discussed by many authors. CPE is related to the conductive behavior of the dielectric. However, as the modeling is complex, it is difficult to determine the system. Moreover, the authors related the “*n*” value to factors such as roughness; if “*n*” has values from 1 to 0.9, it is governed by power law. However, if the value is from 0.5, it suggests a contorted surface, indicating Warburg diffusion. Also, the value of “*n*” is linked with the homogeneity of the surface and the variation in surface composition. For coatings, “*n*” values near 1 are related to uniform surfaces that present good anti-corrosion properties [78–84].

The second corrosion process is linked to another porous layer, so the scheme of Figure 16 is linked with two porous layers.

The use of recurrence plots in passive systems has been discussed because they present similar values to uniform corrosion. However, when the porosities increase, the determinism values decrease. This is due to the anodic–cathodic process that occurred on the surface; this is characteristic of passivation systems. The low determinism values occurred in anodized alloys with more corrosion resistance [85–89].

5. Conclusions

- The results indicated that the anodizing treatment on titanium alloys had a better effect when NaOH baths were used due to increased impedance, meaning greater corrosion resistance.

- The chemical composition of alloys is vital to generate a good, anodized alloy. The alloys with more β elements presented problems in generating a uniform oxide layer.
- Ti-6Al-4V presented more problems when generating a homogenous oxide layer due to the presence of V in the alloy. The generation of vanadium oxide made the anodized alloy susceptible to pitting attacks because the vanadium oxide has more interstitial spaces.
- The anodized alloys with fewer β elements (Ti CP2 and Ti-6Al-2Sn-4Zr-2Mo) presented higher R_{por} (R_{ct}) resistance when anodized on NaOH. On the other hand, alloys with a high presence of β elements presented more anodized R_{por} (R_{ct}) on KOH.
- Ti-6Al-4V presented a lower thickness, at 25 nm, when it was anodized in an NaOH bath.
- Ti Beta-C presented better activity against corrosion due to the presence of Cr in the alloy.
- The EN technique analyzed by HHT and RP helps determine the type of corrosion process that predominates in the electrochemical system. In this type of case, the use of EN is helpful for observing the behavior of the localization process due to the limitation of other techniques in evaluating systems that do not present uniform corrosion processes.
- Recurrence plots analysis showed that anodized alloys are more susceptible to pitting when exposed to NaCl media due to the vertical and horizontal reaction distribution. On the other hand, when exposed to H_2SO_4 , the anodized alloys presented behavior related to passive and uniform systems.
- The EIS results indicated that Ti Beta-C presented better resistance against corrosion for obtained values of $9.7 \times 10^7 \Omega \cdot cm^2$. Also, the anodized KOH presented more impedance.
- The values of CPE for the anodized alloy in KOH are in the order of 10^{-7} and 10^{-6} (F/cm^2), indicating low capacitance and a better performance against ionic transference.
- The H_2SO_4 made the anodized alloys susceptible to present diffusion. However, NaCl can present more damage due to the generation of hydroxides and salts on the metal-coating interface.

Author Contributions: Conceptualization, F.A.-C., J.M.J.-M. and C.G.-T.; methodology, J.M.J.-M., D.N.-M., M.L.-B., M.Á.B.-Z., E.M.-B., M.A.L.-M., L.L.-R. and H.R.-B.; data curation, F.A.-C., J.M.J.-M., E.M.-B., D.N.-M.; M.L.-B., L.L.-R., H.R.-B., L.D.L.-L. and C.G.-T.; formal analysis, C.G.-T., M.Á.B.-Z., F.A.-C., L.D.L.-L. and J.M.J.-M.; writing—review and editing, F.A.-C., J.M.J.-M. and C.G.-T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Universidad Autónoma de Nuevo León (UANL).

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding authors.

Acknowledgments: The authors acknowledge The Academic Body UANL—CA-316 “Deterioration and integrity of composite materials”.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Gialanella, S.; Malandrucolo, A. *Aerospace Alloys*; Topics in Mining, Metallurgy and Materials Engineering; Springer International Publishing: Cham, Switzerland, 2020; ISBN 9783030244392.
2. Mouritz, A.P. *Introduction to Aerospace Materials*; Elsevier Inc.: Amsterdam, The Netherlands, 2012; ISBN 9781855739468.
3. Giurgiutiu, V. Introduction. In *Structural Health Monitoring of Aerospace Composites*; Elsevier: Boston, MA, USA, 2016; pp. 1–23. [CrossRef]
4. Schweitzer, P.E. *PA Corrosion Engineering Handbook—3 Volume Set*; CRC Press: Boca Raton, FL, USA, 2018; ISBN 9780429188084.
5. Hebert, K.; Alkire, R. Dissolved Metal Species Mechanism for Initiation of Crevice Corrosion of Aluminum: II. Mathematical Model. *J. Electrochem. Soc.* **1983**, *130*, 1007–1014. [CrossRef]

6. Rashidi, N.; Alavi-Soltani, S.R.; Asmatulu, R. *Crevice Corrosion Theory, Mechanisms and Prevention Methods*; SOAR: Cambridge, UK, 2007.
7. Rodrigues, D.C.; Urban, R.M.; Jacobs, J.J.; Gilbert, J.L. In Vivo Severe Corrosion and Hydrogen Embrittlement of Retrieved Modular Body Titanium Alloy Hip-Implants. *J. Biomed. Mater. Res. B Appl. Biomater.* **2009**, *88*, 206–219. [CrossRef]
8. Zieliński, A.; Sobieszczyk, S. Corrosion of Titanium Biomaterials, Mechanisms, Effects and Modelisation. *Corros. Rev.* **2008**, *26*, 1–22. [CrossRef]
9. Pourbaix, M.; Burbank, J. Atlas D-Equilibres Electrochimiques. *J. Electrochem. Soc.* **1964**, *111*, 14C. [CrossRef]
10. Ono, S.; Ichinose, H.; Kawaguchi, T.; Masuko, N. The Observation of Anodic Oxide Films on Aluminum by High Resolution Electron Microscopy. *Corros. Sci.* **1990**, *31*, 249–254. [CrossRef]
11. Palibroda, E.; Marginean, P. Considerations on the Adsorbed Water Concentration of Sulfuric Porous Aluminium Oxide. *Thin Solid Film.* **1994**, *240*, 73–75. [CrossRef]
12. Voon, C.H.; Derman, M.N.; Hashim, U.; Ahmad, K.R.; Foo, K.L. Effect of Temperature of Oxalic Acid on the Fabrication of Porous Anodic Alumina from Al-Mn Alloys. *J. Nanomater.* **2013**, *2013*, 167047. [CrossRef]
13. Lee, W.; Park, S.J. Porous Anodic Aluminum Oxide: Anodization and Templated Synthesis of Functional Nanostructures. *Chem. Rev.* **2014**, *114*, 7487–7556. [CrossRef]
14. Salman, S.A.; Okido, M. Anodization of Magnesium (Mg) Alloys to Improve Corrosion Resistance. *Corros. Prev. Magnes. Alloys* **2013**, *8*, 197–231. [CrossRef]
15. Martínez-Viademonte, M.P.; Abrahami, S.T.; Hack, T.; Burchardt, M.; Terry, H. A Review on Anodizing of Aerospace Aluminum Alloys for Corrosion Protection. *Coatings* **2020**, *10*, 1106. [CrossRef]
16. Regonini, D.; Bowen, C.R.; Jaroenworarluck, A.; Stevens, R. A Review of Growth Mechanism, Structure and Crystallinity of Anodized TiO₂ Nanotubes. *Mater. Sci. Eng. R Rep.* **2013**, *74*, 377–406. [CrossRef]
17. Hugot-Le Goff, A. Structure of Very Thin TiO₂ Films Studied by Raman Spectroscopy with Interference Enhancement. *Thin Solid Film.* **1986**, *142*, 193–197. [CrossRef]
18. Afshar, A.; Vaezi, M.R. Anodizing of Titanium in NaOH Solution and Its Corrosion Resistance in PBS Physiologic Solution. *Sci. Iran.* **2003**, *10*, 361–366.
19. Jáquez-Muñoz, J.M.; Gaona-Tiburcio, C.; Chacón-Nava, J.; Cabral-Miramontes, J.; Nieves-Mendoza, D.; Maldonado-Bandala, E.M.; Delgado, A.D.; Flores-De Los Rios, J.P.; Bocchetta, P.; Almeraya-Calderón, F. Electrochemical Corrosion of Titanium and Titanium Alloys Anodized in H₂SO₄ and H₃PO₄ Solutions. *Coatings* **2022**, *12*, 325. [CrossRef]
20. AMS2487B; Anodic Treatment of Titanium and Titanium Alloys Solution PH 12.4 Maximum. SAE: Warrendale, PA, USA, 2018; pp. 1–7.
21. AMS2488E; Anodic Treatment-Titanium and Titanium Alloys, Solution PH 13 or Higher. SAE International: Warrendale, PA, USA, 2019. Available online: <https://www.sae.org/standards/content/ams2488e/?src=ams2487b> (accessed on 23 June 2023).
22. ASTM E407-07; Standard Practice for Microetching Metals and Alloys. ASTM International: West Conshohocken, PA, USA, 2007.
23. ASTM G106-03; Standard Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements. ASTM International: West Conshohocken, PA, USA, 1999.
24. ASTM G199-09; Standard Guide for Electrochemical Noise Measurement. ASTM International: West Conshohocken, PA, USA, 2020.
25. Bertocci, U.; Huet, F. Noise Analysis Applied to Electrochemical Systems. *Corrosion* **1995**, *51*, 131–144. [CrossRef]
26. Coakley, J.; Vorontsov, V.A.; Littrell, K.C.; Heenan, R.K.; Ohnuma, M.; Jones, N.G.; Dye, D. Nanoprecipitation in a Beta-Titanium Alloy. *J. Alloys Compd.* **2015**, *623*, 146–156. [CrossRef]
27. Cai, C.; Zhang, Z.; Cao, F.; Gao, Z.; Zhang, J.; Cao, C. Analysis of Pitting Corrosion Behavior of Pure Al in Sodium Chloride Solution with the Wavelet Technique. *J. Electroanal. Chem.* **2005**, *578*, 143–150. [CrossRef]
28. Hai, L.; Guo-qiang, X.; Pan, Z.; Hua-sen, Z.; Khan, M.Y. The Hilbert–Huang Transform-Based Denoising Method for the TEM Response of a PRBS Source Signal. *Pure Appl. Geophys.* **2016**, *173*, 2777–2789. [CrossRef]
29. Zhang, Z.; Zhao, Z.; Bai, P.; Li, X.; Liu, B.; Tan, J.; Wu, X. In-Situ Monitoring of Pitting Corrosion of AZ31 Magnesium Alloy by Combining Electrochemical Noise and Acoustic Emission Techniques. *J. Alloys Compd.* **2021**, *878*, 160334. [CrossRef]
30. Homborg, A.M.; Tinga, T.; Van Westing, E.P.M.; Zhang, X.; Ferrari, G.M.; De Wit, J.H.W.; Mol, J.M.C. A Critical Appraisal of the Interpretation of Electrochemical Noise for Corrosion Studies. *Corrosion* **2014**, *70*, 971–987. [CrossRef] [PubMed]
31. Marwan, N.; Carmen Romano, M.; Thiel, M.; Kurths, J. Recurrence Plots for the Analysis of Complex Systems. *Phys. Rep.* **2007**, *438*, 237–329. [CrossRef]
32. Acuña-González, N.; García-Ochoa, E.; González-Sánchez, J. Assessment of the Dynamics of Corrosion Fatigue Crack Initiation Applying Recurrence Plots to the Analysis of Electrochemical Noise Data. *Int. J. Fatigue* **2008**, *30*, 1211–1219. [CrossRef]
33. Mayorga-Cruz, D.; Sarmiento-Martinez, O.; Menchaca Campos, C.; Uruchurtu, J. Analysis of Michelson Optical Interferometry Using Recurrence Plots During Corrosion of Aluminium in NaCl Solution. *ECS Trans.* **2009**, *20*, 433–446. [CrossRef]
34. Jirón-Lazos, U.; Corvo, F.; De la Rosa, S.C.; García-Ochoa, E.M.; Bastidas, D.M.; Bastidas, J.M. Localized Corrosion of Aluminum Alloy 6061 in the Presence of *Aspergillus Niger*. *Int. Biodeterior. Biodegrad.* **2018**, *133*, 17–25. [CrossRef]
35. Luo, Z.; Zhang, Y.; Wang, H.; Wan, S.; Song, L.; Liao, B.; Guo, X. Modified nano-lignin as a novel biomass-derived corrosion inhibitor for enhanced corrosion resistance of carbon steel. *Corros. Sci.* **2024**, *227*, 111705. [CrossRef]

36. Zhou, F.; Ma, Y.; Chen, Y.; Zhang, L.; Sheng, X. Triple-function smart anticorrosion composite coating based on graphene and ZIF-8 with excellent pH-responsive self-healing and in vitro antimicrobial properties. *Prog. Org. Coat.* **2024**, *186*, 108007. [CrossRef]
37. Magar, H.S.; Hassan, R.Y.A.; Mulchandani, A. Electrochemical Impedance Spectroscopy (EIS): Principles, Construction, and Biosensing Applications. *Sensors* **2021**, *21*, 6578. [CrossRef]
38. Orazem, M.E.; Tribollet, B. Constant-Phase Elements. In *Electrochemical Impedance Spectroscopy*; Wiley: Hoboken, NJ, USA, 2017; pp. 395–419.
39. Harrington, D.A.; Van Den Driessche, P. Mechanism and Equivalent Circuits in Electrochemical Impedance Spectroscopy. *Electrochim. Acta* **2011**, *56*, 8005–8013. [CrossRef]
40. Peixoto Barbosa, D.; Knörnschild, G. Anodization of Mg-Alloy AZ91 in NaOH Solutions. *Surf. Coat. Technol.* **2009**, *203*, 1629–1636. [CrossRef]
41. Burleigh, T.D.; Dotson, T.C.; Dotson, K.T.; Gabay, S.J.; Sloan, T.B.; Ferrell, S.G. Anodizing Steel in KOH and NaOH Solutions. *J. Electrochem. Soc.* **2007**, *154*, C579. [CrossRef]
42. Hsu, H.C.; Hsu, S.K.; Wu, S.C.; Hung, Y.H.; Ho, W.F. Surface Modification of Nanotubular Anodized Ti–7.5Mo Alloy Using NaOH Treatment for Biomedical Application. *Thin Solid Film.* **2020**, *710*, 138273. [CrossRef]
43. Laurindo, C.A.H.; Torres, R.D.; Mali, S.A.; Gilbert, J.L.; Soares, P. Incorporation of Ca and P on Anodized Titanium Surface: Effect of High Current Density. *Mater. Sci. Eng. C* **2014**, *37*, 223–231. [CrossRef] [PubMed]
44. Zhang, Y.; Fan, H.; Ding, X.; Yan, Q.; Wang, L.; Ma, W. Simulation of Anodizing Current-Time Curves and Morphology Evolution of TiO₂ Nanotubes Anodized in Electrolytes with Different NH₄F Concentrations. *Electrochim. Acta* **2015**, *176*, 1083–1091. [CrossRef]
45. Mazzarolo, A.; Curioni, M.; Vincenzo, A.; Skeldon, P.; Thompson, G.E. Anodic Growth of Titanium Oxide: Electrochemical Behaviour and Morphological Evolution. *Electrochim. Acta* **2012**, *75*, 288–295. [CrossRef]
46. Lee, C.C.; Mansfeld, F. Analysis of Electrochemical Noise Data for a Passive System in the Frequency Domain. *Corros. Sci.* **1998**, *40*, 959–962. [CrossRef]
47. Xia, D.H.; Song, S.Z.; Behnamian, Y. Detection of Corrosion Degradation Using Electrochemical Noise (EN): Review of Signal Processing Methods for Identifying Corrosion Forms. *Corros. Eng. Sci. Technol.* **2016**, *51*, 527–544. [CrossRef]
48. Xia, D.H.; Qin, Z.; Song, S.; Macdonald, D.; Luo, J.L. Combating Marine Corrosion on Engineered Oxide Surface by Repelling, Blocking and Capturing Cl[−]: A Mini Review. *Corros. Commun.* **2021**, *2*, 1–7. [CrossRef]
49. Pan, C.; Wang, X.; Behnamian, Y.; Wu, Z.; Qin, Z.; Xia, D.H.; Hu, W. Monododecyl Phosphate Film on LY12 Aluminum Alloy: PH-Controlled Self-Assembly and Corrosion Resistance. *J. Electrochem. Soc.* **2020**, *167*, 161510. [CrossRef]
50. Song, H.J.; Kim, M.K.; Jung, G.C.; Vang, M.S.; Park, Y.J. The Effects of Spark Anodizing Treatment of Pure Titanium Metals and Titanium Alloys on Corrosion Characteristics. *Surf. Coat. Technol.* **2007**, *201*, 8738–8745. [CrossRef]
51. Fouda, M.E.; Allagui, A.; Elwakil, A.S.; Das, S.; Psychalinos, C.; Radwan, A.G. Non-linear Charge-Voltage Relationship in Constant Phase Element. *AEU Int. J. Electron. Commun.* **2020**, *117*, 153104. [CrossRef]
52. Gomes, M.P.; Costa, I.; Pébère, N.; Rossi, J.L.; Tribollet, B.; Vivier, V. On the Corrosion Mechanism of Mg Investigated by Electrochemical Impedance Spectroscopy. *Electrochim. Acta* **2019**, *306*, 61–70. [CrossRef]
53. Gateman, S.M.; Gharbi, O.; Gomes de Melo, H.; Ngo, K.; Turmine, M.; Vivier, V. *On the Use of a Constant Phase Element (CPE) in Electrochemistry*; Elsevier: Amsterdam, The Netherlands, 2022; Volume 36, p. 101133.
54. Martínez-Aparicio, B.; Martínez-Bastidas, D.; Gaona-Tiburcio, C.; Martín, U.; Cabral-Miramontes, J.; Almeraya-Calderón, F. Localized corrosion of 15–5 PH and 17–4 PH stainless steel in NaCl solution. *J. Solid State Electrochem.* **2023**, *27*, 2993–3001. [CrossRef]
55. Rajan, S.T.; VV, A.T.; Terada-Nakaishi, M.; Chen, P.; Hanawa, T.; Nandakumar, A.K.; Subramanian, B. Zirconium-Based Metallic Glass and Zirconia Coatings to Inhibit Bone Formation on Titanium. *Biomed. Mater.* **2020**, *15*, 065019. [CrossRef]
56. Radovanović, M.B.; Tasić, Ž.Z.; Simonović, A.T.; Petrović Mihajlović, M.B.; Antonijević, M.M. Corrosion Behavior of Titanium in Simulated Body Solutions with the Addition of Biomolecules. *ACS Omega* **2020**, *5*, 12768–12776. [CrossRef]
57. Almeraya-Calderón, F.; Jáquez-Muñoz, J.M.; Maldonado-Bandala, E.; Cabral-Miramontes, J.; Nieves-Mendoza, D.; Olgui-Coca, J.; Lopez-Leon, L.D.; Estupiñán-López, F.; Lira-Martínez, A.; Gaona Tiburcio, C. Corrosion Resistance of Titanium Alloys Anodized in Alkaline Solutions. *Metals* **2023**, *13*, 1510. [CrossRef]
58. Dubent, S.; Mazard, A. Characterization and corrosion behaviour of grade 2 titanium used in electrolyzers for hydrogen production. *Int. J. Hydrogen Energy* **2019**, *44*, 15622–15633. [CrossRef]
59. Escrivá-Cerdán, C.; Blasco-Tamarit, E.; García-García, D.M.; Akid, R.; Walton, J. Effect of temperature on passive film formation of UNS N08031 Cr-Ni alloy in phosphoric acid contaminated with different aggressive anions. *Electrochim. Acta* **2013**, *111*, 552–561. [CrossRef]
60. Liu, C.; Leyland, A.; Bi, Q.; Matthews, A. Corrosion resistance of multi-layered plasma-assisted physical vapour deposition TiN and CrN coatings. *Surf. Coat. Technol.* **2001**, *141*, 164–173. [CrossRef]
61. Balla, A.; Marcu, C.; Axante, D.; Borodi, G.; Lazar, D. Catalytic reduction of sulfuric acid to sulfur dioxide. *Cent. Eur. J. Chem.* **2012**, *10*, 1817–1823. [CrossRef]
62. Vasilescu, C.; Drob, S.I.; Osiceanu, P.; Moreno, J.M.C.; Prodana, M.; Ionita, D.; Demetrescu, I.; Marcu, M.; Popovici, I.A.; Vasilescu, E. Microstructure, Surface Characterization, and Electrochemical Behavior of New Ti-Zr-Ta-Ag Alloy in Simulated Human Electrolyte. *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* **2017**, *48*, 513–523. [CrossRef]

63. Munirathinam, B.; Neelakantan, L. Titania Nanotubes from Weak Organic Acid Electrolyte: Fabrication, Characterization and Oxide Film Properties. *Mater. Sci. Eng. C* **2015**, *49*, 567–578. [CrossRef] [PubMed]
64. Cui, W.F.; Jin, L.; Zhou, L. Surface Characteristics and Electrochemical Corrosion Behavior of a Pre-Anodized Microarc Oxidation Coating on Titanium Alloy. *Mater. Sci. Eng. C* **2013**, *33*, 3775–3779. [CrossRef] [PubMed]
65. Sun, J.; Liu, Y. Unique Constant Phase Element Behavior of the Electrolyte–Graphene Interface. *Nanomaterials* **2019**, *9*, 923. [CrossRef]
66. Prando, D.; Nicolis, D.; Peddeferri, M.P.; Ormellese, M. Pitting Corrosion on Anodized Titanium: Effect of Halides. *Mater. Corros.* **2018**, *69*, 1441–1446. [CrossRef]
67. Fattah-Alhosseini, A.; Attarzadeh, F.R.; Vakili-Azghandi, M. Effect of Multi-Pass Friction Stir Processing on the Electrochemical and Corrosion Behavior of Pure Titanium in Strongly Acidic Solutions. *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* **2017**, *48*, 403–411. [CrossRef]
68. Sadek, A.Z.; Zheng, H.; Latham, K.; Wlodarski, W.; Kalantar-Zadeh, K. Anodization of Ti Thin Film Deposited on ITO. *Langmuir* **2009**, *25*, 509–514. [CrossRef]
69. Mor, G.K.; Varghese, O.K.; Paulose, M.; Mukherjee, N.; Grimes, C.A. Fabrication of Tapered, Conical-Shaped Titania Nanotubes. *J. Mater. Res.* **2003**, *18*, 2588–2593. [CrossRef]
70. Galván-Martínez, R.; Cabrera-de la Cruz, D.; Contreras, A.; Orozco-Cruz, R. A Novel Experimental Arrangement for Corrosion Study of X60 Pipeline Steel Weldments at Turbulent Flow Conditions. *Corros. Eng. Sci. Technol.* **2016**, *51*, 400–407. [CrossRef]
71. Galvan-Martinez, R.; Orozco-Cruz, R.; Torres-Sanchez, R.; Martinez, E.A. Corrosion Study of the X52 Steel Immersed in Seawater with a Corrosion Inhibitor Using a Rotating Cylinder Electrode. *Mater. Corros.* **2010**, *61*, 872–876. [CrossRef]
72. Chávez-Díaz, M.P.; Luna-Sánchez, R.M.; Vazquez-Arenas, J.; Lartundo-Rojas, L.; Hallen, J.M.; Cabrera-Sierra, R. XPS and EIS Studies to Account for the Passive Behavior of the Alloy Ti-6Al-4V in Hank's Solution. *J. Solid State Electrochem.* **2019**, *23*, 3187–3196. [CrossRef]
73. Xia, D.-H.; Song, S.; Behnamian, Y.; Hu, W.; Cheng, Y.F.; Luo, J.-L.; Huet, F. Review—Electrochemical Noise Applied in Corrosion Science: Theoretical and Mathematical Models towards Quantitative Analysis. *J. Electrochem. Soc.* **2020**, *167*, 081507. [CrossRef]
74. Scharifker, B.K.; Monstany, J.; Palomar-Pardave, M.; González, I. On the Theory of the Potentiostatic Current Transient for Diffusion-Controlled Three-Dimensional Electrocrystallization Processes. *J. Electrochem. Soc.* **1999**, *146*, 1005. [CrossRef]
75. Gil, A.; Galicia, L.; González, I. Diffusion coefficients and electrode kinetic parameters of different Fe(III)-sulfate complexes. *J. Electroanal. Chem.* **1996**, *417*, 129–134. [CrossRef]
76. Cabrera-Sierra, R.; Hallen, J.M.; Vazquez-Arenas, J.; Vázquez, G.; González, I. EIS characterization of tantalum and niobium oxide films based on a modification of the point defect model. *J. Electroanal. Chem.* **2010**, *638*, 51–58. [CrossRef]
77. Rivero, E.P.; Rodríguez, F.A.; Cruz-Díaz, M.R.; González, I. Reactive diffusion migration layer and mass transfer wall function to model active chlorine generation in a filter press type electrochemical reactor for organic pollutant degradation. *Chem. Eng. Resear. Des.* **2018**, *138*, 533–545. [CrossRef]
78. Barsoukov, E.; Macdonald, J.R. *Impedance Spectroscopy: Theory, Experiment, and Applications*, 3rd ed.; John Wiley & Sons, Inc.: New York, NY, USA, 2018; pp. 175–478.
79. Macdonald, J.R. Frequency response of inifield dielectric and conductive systems involving an exponential distribution of activation energy. *J. Appl. Phys.* **1985**, *58*, 1955. [CrossRef]
80. Macdonald, J.R. Generalizations of “universal dielectric response” and a general distribution-of-activation-energies model for dielectric and conductive systems. *J. App. Phys.* **1985**, *58*, 1971. [CrossRef]
81. Mulder, W.H.; Sluyters, J.H.; Pajkossy, T.; Nyikos, L. Tafel current at fractal electrodes: Connection with admittance spectra. *J. Electroanal. Chem.* **1990**, *285*, 103. [CrossRef]
82. Kim, C.; Pyun, S.; Kim, J. An investigation of the capacitance dispersion on the fractal carbon electrode with edge and basal orientations. *Electrochim. Act.* **2003**, *48*, 3455. [CrossRef]
83. Schiller, C.A.; Strunz, W. The evaluation of experimental dielectric data of barrier coatings by means of different models. *Electrochim. Act.* **2001**, *46*, 3619. [CrossRef]
84. Córdoba-Torres, P. Relationship between constant-phase element (CPE) parameters and physical properties of films with a distributed resistivity. *Electrochim. Act.* **2017**, *225*, 592. [CrossRef]
85. Jáquez-Muñoz, J.M.; Gaona-Tiburcio, C.; Cabral-Miramontes, J.; Nieves-Mendoza, D.; Maldonado-Bandala, E.; Olguín-Coca, J.; López-Léon, L.D.; De Los Rios, J.P.F.; Almeraya-Calderón, F. Electrochemical Noise Analysis of the Corrosion of Titanium Alloys in NaCl and H₂SO₄ Solutions. *Metals* **2021**, *11*, 105. [CrossRef]
86. Du, X.Q.; Yang, Q.S.; Chen, Y.; Yang, Y.; Zhang, Z. Galvanic Corrosion Behavior of Copper/Titanium Galvanic Couple in Artificial Seawater. *Trans. Nonferrous Met. Soc. China* **2014**, *24*, 570–581. [CrossRef]
87. Martínez-Villafañe, A.; Almeraya-Calderón, M.F.; Gaona-Tiburcio, C.; Gonzalez-Rodriguez, J.G.; Porcayo-Calderón, J. High-Temperature Degradation and Protection of Ferritic and Austenitic Steels in Steam Generators. *J. Mater. Eng. Perform* **1998**, *7*, 108–113. [CrossRef]

88. Gaona-Tiburcio, C.; Ramirez, A.; Gonzalez-Rodriguez, J.; Campillo, B. An Electrochemical Study of the Corrosion Behavior of a Dual Phase Steel in 0.5 m H₂SO₄. *Int. J. Electrochem. Sci.* **2010**, *5*, 1786.
89. Martínez-Ramos, C.; Olguin-Coca, J.; Lopez-Leon, L.D.; Gaona-Tiburcio, C.; Lara-Banda, M.; Maldonado-Bandala, E.; Castañeda-Robles, I.; Jaquez-Muñoz, J.M.; Cabral-Miramontes, J.; Nieves-Mendoza, D.; et al. Electrochemical Noise Analysis Using Experimental Chaos Theory, Power Spectral Density and Hilbert–Huang Transform in Anodized Aluminum Alloys in Tartaric–Phosphoric–Sulfuric Acid Solutions. *Metals* **2023**, *13*, 1850. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

The Effect of Pore Sealing in a Multilayer Si–O–Zr/Al₂O₃ Coating Designed to Protect Aluminium from Corrosion

Peter Rodič, Barbara Kapun and Ingrid Milošev *

Department of Physical and Organic Chemistry, Jožef Stefan Institute, Jamova c. 39, SI-1000 Ljubljana, Slovenia; peter.rodic@ijs.si (P.R.); barbara.kapun@ijs.si (B.K.)

* Correspondence: ingrid.milosev@ijs.si

Abstract: This study deals with the combination of two corrosion protection strategies for aluminium: barrier protection (provided by a 3.8 µm thick hybrid sol–gel coating) and aluminium pore sealing via the use of a 100 nm thick layer of aluminium oxide. A Si–O–Zr hybrid sol–gel coating (TMZ) was synthesised by combining two separately prepared sols (i) tetraethyl orthosilicate and 3-methacryloxypropyl trimethoxysilane and (ii) zirconium(IV) n-propoxide chelated with methacrylic acid. The synthesis of the Si–O–Zr hybrid sol–gel was evaluated at various stages using real-time infrared spectroscopy. A 100 nm thick Al₂O₃ film was prepared via thermal atomic layer deposition at 160 °C using trimethyl aluminium and water as precursors. The coating and film properties were assessed via focused ion beam/scanning electron microscopy coupled with energy-dispersive X-ray spectrometry. Sealing with the Al₂O₃ film did not affect the microstructure and composition of the underlying sol–gel coating. The coating’s corrosion performance in 0.1 M NaCl solution was evaluated using electrochemical impedance spectroscopy. Compared to individual coatings, the multilayer TMZ/Al₂O₃ coating ensured prolonged (more than three weeks) durable corrosion protection for the aluminium. The impedance magnitude increased by two orders compared to the uncoated substrate ($|Z|_{10\text{ mHz}}$ from 16 kΩ cm² to almost 830 MΩ cm²). Thus, the pore sealing of the sol–gel coating using an ALD alumina film produced a protective multilayer coating system, with $|Z|_{10\text{ mHz}}$ remaining above 5 MΩ cm² after four weeks in NaCl solution.

Keywords: aluminium; hybrid sol–gel; atomic layer deposition; corrosion; pore sealing

1. Introduction

In recent decades, the protection of metals and alloys from corrosion in different corrosive environments has been provided mainly via the hexavalent chromium-based compounds (chromate) used in coating systems and chromate conversion coatings [1–4]. However, chromate compounds are hazardous for humans and the environment [5], and their use must be reduced [6]. Since September 2017, stricter regulations have been mandated, and chromates have been banned or restricted in several industrial sectors [6]. As a result, there is a significant need to develop and replace hazardous chromates with environmentally friendly, non-toxic surface treatments capable of providing sufficient corrosion protection [4,7,8].

One of the promising alternatives of surface barrier prevention is the deposition of hybrid sol–gel coatings on the metal surface, which provide a physical barrier against water and the penetration of aggressive ions (i.e., Cl[−]) to the metal surface [9,10]. In the literature, many organically modified silicates (ormosils) have demonstrated good corrosion protection on aluminium [11,12], even in acidic and alkaline conditions [11]. In addition, coatings containing zirconium in the sol–gel network further improve the silane matrix’s coating properties [13–15]. This was confirmed in Si–O–Zr (Si/Zr) hybrid coatings based on tetraethyl orthosilicate (TEOS), 3-methacryloxypropyl trimethoxysilane (MAPTMS), zirconium(IV) n-propoxide (ZTP), and methacrylic acid (MAA) [11,16–20].

Hydrolysis, condensation, and polymerisation reactions in such systems were studied in detail at various stages using several techniques, such as spectroscopic techniques, solution characterisation techniques, and coating characterisation techniques [11,16,18,20]. The coatings deposited on the aluminium [11,18] or aluminium alloys [17,21] were amorphous, homogeneous, and only a few micrometres thick, with very low porosity (between 0.85 and 0.49%) [20]. The degree of corrosion protection depends on several parameters, and the ZTP content in the coating and ZTP/MAA ratio are the main ones [16]. Under optimal conditions, ZTP can stimulate the condensation reaction and formation of large domains of polycondensed Si species [11]. In neutral chloride solutions, TMZ coatings containing more ZTP expressed greater corrosion resistance [20], but the dependence on coating properties is not straightforward due to other parameters such as ageing time, curing temperature, etc., which are still poorly understood [21]. In the present study, we first focused on conducting a real-time analysis of the kinetics of hydrolysis and condensation reactions for coatings with greater ZTP contents (ZTP/MAA = 1:2) during synthesis and then characterised the coatings' morphologies, structures, and thicknesses.

Aluminium, in the presence of oxygen or humidity/water, instantly forms a native (passive) oxide film that is a few nanometres thick [22,23]. Its thickness, composition, and porosity depend on several parameters, such as temperature, surface structure, topography, or other metal impurities present in the structure [22,24]. Such films are stable in a pH range between 4.5 and 8 [25], but in more aggressive acidic [26,27] and alkaline media [27,28], they can be dissolved [27,28]. In addition, pits can be formed in a chloride-containing corrosive environment due to the passive film breakdown [22,29,30].

The shortcomings of the aluminium native passivation process can be minimised by depositing an additional barrier film using atomic layer deposition (ALD). This technique allows for the deposition of highly uniform ultra-thin films with thicknesses in the range of atomic or molecular layers due to the self-limiting reactions of the deposited materials [23,31]. The use of ALD for protecting metallic substrates from corrosion was proposed in the late 1980s and early 1990s [23]. Nowadays, ALD is widely used in the industry for the deposition of metal and metal nitride films (Al, Ti, AlN, TiN) and the deposition of dielectric thin films (HfO₂, ZrO₂, and Al₂O₃) [32–36]. The coatings deposited by ALD provide new applications in diverse areas of corrosion [37] because a thin ALD film serves as an efficient barrier protection against gases [38,39] and liquids [36,40]. Up to now, the most frequently used ALD corrosion protection coating has been Al₂O₃, which is usually deposited from trimethyl aluminium (Al(CH₃)₃) and water [39,41–44] at temperatures ranging from 33 to 500 °C [37,45–47]. The deposition of ALD films at higher temperatures improves the reaction between TMA and Al–OH at the surface. However, deposition at higher temperatures is challenging for metals, as overheating may cause surface oxidation, potentially weakening the protective layer as a result [45]. This can be problematic, especially for corrosion-resistance applications that require dense films without defects [33,45,48]. A low deposition temperature is also relevant to the energetic efficiency for obtaining amorphous coatings, preventing the growth of crystallite-/grain-defective boundaries as possible diffusion channels for corrosive species [35,45,48].

Ultra-thin Al₂O₃ films have been reported to efficiently protect various metals, such as steel [47–50], copper [51,52], and aluminium and its alloys [40,47]. In addition to depositing individual films, ALD is also used as a sealing method to block the pinholes in hard coatings prepared via physical and chemical vapour deposition (PVD and CVD) [37,53] and anodised aluminium [54]. ALD precursors penetrate deep into the coating, forming a film and blocking the pinholes. The sealing performance is reflected by decreasing the corrosion current density and increasing the corrosion potential to less negative potential [37,41]. Various ALD films have been tested to protect different polymeric surfaces or flexible polymer films [55,56], but we failed to find any studies on pore sealing Si–O–Zr coatings using ALD films in the literature.

Based on the literature summary presented above, the main aim of this work was to investigate the possibility of using a thin ALD alumina film to seal the pores of a

Si–O–Zr hybrid sol–gel coating. First, individual coatings (TMZ and ALD Al_2O_3) were characterised using microstructure and compositional analysis at the top and cross-section. In addition, the Si–O–Zr synthesis kinetics were followed using real-time Fourier-transform infrared spectroscopy. The level of corrosion protection was analysed using electrochemical impedance spectroscopy in 0.1 M NaCl solution. Second, a multilayer TMZ/ Al_2O_3 coating was prepared and comparatively analysed to confirm the benefits of multilayer coatings in terms of prolonged corrosion protection.

2. Materials and Methods

2.1. Aluminium Substrate

One-millimetre-thick aluminium (Al > 99.0%) flat sheets were supplied by Goodfellow, Cambridge Ltd. (Huntingdon, UK) The sheets were cut into 14 mm diameter disks, and then the surface was ground using a Struers LaboSystem LaboPol-20 machine employing 2400- and 4000-grit SiC emery papers (distributed by Struers ApS, Ballerup, Denmark) to remove the natural oxide layer from the aluminium surface. After the grinding process, the sample was rinsed with distilled water and further cleaned in anhydrous ethanol utilising an ultrasonic cleaner for 10 min to eliminate any organic substances. Finally, the samples were dried using compressed nitrogen.

2.2. Coating/Film Deposition

Table 1 summarises the coatings' precursors, deposition methods, and thicknesses.

Table 1. Summary of the coatings' characteristics.

Coating	Precursors	Preparation	Coating Deposition	Thickness
TMZ sol-gel	MAPTMS, TEOS, ZTP and MAA	Synthesis at room temperature.	Spin-coating.	3.8 μm
Al_2O_3 -ALD	TMA, H_2O	Deposition in vacuum at 150 $^\circ\text{C}$.	Layer-by-layer deposition.	100 nm

2.2.1. Hybrid Sol–Gel Coating

The hybrid sol–gel coating was synthesised by mixing two separately prepared solutions from silicon (Sol 1) and zirconium sol–gel reagents (precursors) (Sol 2): tetraethyl orthosilicate (TEOS: $\text{Si}(\text{OC}_2\text{H}_5)_4$, 99.9%, Sigma-Aldrich (St. Louis, MO, USA), CAS Number 78-10-4), 3-methacryloxypropyl trimethoxysilane (MAPTMS: $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\geq 98\%$, Sigma-Aldrich, CAS Number 2530-85-0), zirconium(IV) n-propoxide solution, (ZTP: $\text{Zr}(\text{OPr})_4$, 70 wt.%, in 1-propanol, Sigma-Aldrich, CAS Number 23519-77-9), and methacrylic acid (MAA: $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COOH}$, 99.0% Sigma-Aldrich, CAS Number 79-41-4). The hydrolysis was initiated by adding deionised Milli-Q water containing hydrochloric acid (HCl: >37%, AppliChem, Darmstadt, Germany).

The detailed synthesis procedure has been described in the literature [11,16–18]. The molar ratio of the reagents was as follows: TEOS/MAPTMS/ZTP/MAA = 0.18:1:0.48:0.96 (ZTP/(TEOS + MAPTMS) = 0.48/1.18; Zr/Si = 0.41). The final sol and coating are denoted with the abbreviation TMZ. All syntheses were performed in a 25 mL reactor at atmospheric pressure open to the air using the EasyMax 102 advanced synthesis workstation. The reactor jacket temperature was kept constant at 23 ± 0.1 $^\circ\text{C}$.

The sol–gel synthesis reactions were characterised by recording real-time ATR-FTIR spectra at intervals of 1 min in the range of 600–2800 cm^{-1} . The spectra were measured using a ReactIRTM 45 spectrometer (Mettler Toledo, Columbus, OH, USA) with a resolution of 4 cm^{-1} , averaging 256 scans. An EasyMax 102 controller (Mettler Toledo, Columbus, OH, USA) was used to control the conditions during the reaction. The instruments were controlled using iControl EasyMax 6.1 and iC IR 7.1 software. The spectra were recorded from 1800 to 500 cm^{-1} , where the most intensive and characteristic bands were present. The intensities of the spectra are shown in absorbance units (A.U.). The intensity of the selected band was compared to zero in the spectra baseline.

The prepared sol–gel solutions were applied to the ground aluminium substrate after one hour of synthesis using a spin-coater (Laurell—WS-650-23NPP/LITE/IND, Laurell Technology Corporation, Lansdale, PA, USA). Excess sol was applied by injecting the fluid through a polytetrafluoroethylene (PTFE) syringe filter with a 0.2 µm membrane onto the centre of the substrate. Then, the sample was spun with a rotation speed of 4000 rpm for 30 s. During rotation, excess sol was removed, leaving the substrate covered with an evenly thick coating. The coated samples were kept in ambient conditions for 10 min and then cured on a preheated hot plate at 160 °C for 1 h in an air atmosphere.

2.2.2. Atomic Layer Deposition of the ALD Al₂O₃ Film

The thermal ALD Al₂O₃ (alumina) films were grown in a flow-type ALD reactor Beneq (Beneq Oy, Espoo, Finland). The films were grown using trimethyl aluminium (TMA, Al(CH₃)₃, Elec. Gr., 99.99%-Al, Puratrem, manufactured by STREM Chemicals, Inc, Bischheim, France, Europe) as a precursor and H₂O (deionised Milli-Q water) as a co-reagent. Both chemicals were vapourised at room temperature. Dry compressed nitrogen (>99.999%, HiQ Nitrogen 5.0, Instrabenz Plini, Bertoki, Slovenia) was used as a carrier and purging gas. The chamber of the ALD system was constantly pumped using a turbomolecular vacuum pump, and the chamber pressure during the process was approximately 10 mbar. The time sequence of deposition precursor/purge/water/purge was 0.3/1/0.35/1 s. The deposition temperature was set to 160 °C. The stabilisation time (heating the chamber to set temperature) was about 30 min. The final Al₂O₃ film thickness was ~100 nm (obtained after 1000 cycles). The samples were taken from the ALD chamber when the chamber temperature was below 100 °C.

2.2.3. Multilayer TMZ/Al₂O₃ System

A multilayer Si–O–Zr hybrid sol–gel/Al₂O₃ system (abbreviation TMZ/Al₂O₃) was prepared by applying one layer of TMZ coating followed by the deposition of 100 nm ALD film (as described in the above text).

2.3. Coating Characterisation

2.3.1. Composition Characterisation

FTIR spectra of the uncoated (ground) aluminium and aluminium coated with the TMZ, Al₂O₃, and TMZ/Al₂O₃ coatings were recorded using a PerkinElmer Spectrum 100 (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) instrument with the attenuated total reflection (ATR) sampling accessory. The spectra were recorded from 4000 to 500 cm^{−1} with a resolution of 4 cm^{−1}, averaging 4 scans. The spectra were normalised and are presented as transmittance in % from 3800 to 2800 cm^{−1} and 1800 to 500 cm^{−1}, where the most intensive and characteristic bands were present.

2.3.2. Surface and Cross-Section Analysis

Field emission scanning electron microscopy (FE-SEM) was used to analyse the morphologies and microstructures of the TMZ, Al₂O₃, and TMZ/Al₂O₃ deposited on the aluminium. Coating thickness and composition were evaluated via focused ion beam/scanning electron microscopy (FEI Helios NanoLab 600 Dual beam, Waltham, MA, USA). The cross-section of selected regions on the samples was obtained after the deposition of a thin layer of platinum on the surface (first, 0.2 µm thick layer at 2 kV, 0.4 nA; second, 1 µm thick layer deposited at 30 kV, 0.24 nA), followed by cutting the coating using a Ga FIB beam at 30 kV, 9.4 nA. Ultimately, the surface was polished using a Ga beam at 30 kV, 0.4 nA. Imaging along the cross-section was performed via SEM using the secondary electron and (SE) and back-scattered electron (BSE) modes at 5 kV energy. EDS mapping analysis of the coatings' compositions was conducted using EDS Aztec software at 10 kV voltage. The mapping of EDS lasted for 1000 s.

2.3.3. Electrochemical Corrosion Testing

Corrosion performance was tested using EIS. Measurements were performed in a three-electrode corrosion cell, where 1 cm² of the sample was exposed to the corrosive medium (0.1 M NaCl). Silver/silver chloride (Ag/AgCl 0.25 V vs. saturated hydrogen electrode) were used as reference electrodes, and a carbon rod served as a counter electrode. Measurements were performed at ambient temperature using a Multi Autolab PGSTAT M204 (Metrohm Autolab, Utrecht, The Netherlands) potentiostat/galvanostat controlled via Nova 2.1 software. Electrochemical impedance spectra were recorded between 10 mHz and 100 kHz using a frequency response analyser (FRA) module. The amplitude of the sinusoidal voltage signal was 10 mV (RMS). Impedance responses were recorded after selected periods of immersion (from 1 h up to 4 weeks). Measurements were performed at least in triplicate for each sample type (uncoated and coated). The representative ones are plotted in the Bode plots as impedance magnitude and phase angle versus frequency.

3. Results and Discussion

3.1. Preparation and Analysis of the TMZ Sol–Gel

3.1.1. Real-Time FTIR Analysis of the Sol–Gel TMZ Solution

The hydrolysis and condensation reactions during the synthesis of hybrid sol–gel coatings are essential for obtaining desirable properties, such as a desirable composition, homogeneity, and density. Therefore, the synthesis process at selected steps was optimised using real-time FTIR spectroscopy. In the first step, the synthesis of Sol 1 was followed at different synthesis stages (Figure 1).

FTIR spectra from 1250 to 750 cm^{−1} were recorded to determine the hydrolysis of the mixture of MAPTMS and TEOS after adding acidic water (H₂O/H⁺) (Table 2).

The mixture spectrum shows that the most intensive initial bands of both reagents were at 1164, 1081, 815, and 785 cm^{−1}. Molecular structures are presented in Figure 1b. Reactions between the initial reagents did not occur, and the changes in the band intensities were solely due to the fact that they were combined in the reactor (Figure 1c, relative time less than 10 min). This process has been described in detail for similar systems [11,18]. The focus herein is on the kinetics of the reactions (Figure 1c). The reactions started immediately after the addition of H₂O/H⁺, as evident due to the intensive decrease in all the characteristic bands of initial precursors (1164, 1081, and 815 cm^{−1}) and the appearance of an intensive broad Si–O–Si band at 1027 cm^{−1}. The latter is related to asymmetric stretching; another Si–O–Si band was also noticed at 1084 cm^{−1} (Figure 1a,b). The hydrolysis and condensation reactions were accompanied by by-products such as ethanol (a band at 882 cm^{−1}) and the formation of a Si–O[−] band at 914 cm^{−1} and Si–OH at 942 cm^{−1}.

The reactions were most predominant after the first 10 min after the addition of H₂O/H. At longer times, the changes were smaller (Figure 1c). In the next 30 min, the intensities of the Si–OR and Si–O–Si bands changed slowly, but the Si–OH band gradually increased even after 45 min of mixing. This is due to the instability of Sol 1, with many Si–OH groups available for further condensation. However, a band at 1164 cm^{−1} representing the methoxy silane (Si–O–Me) in the MAPTMS molecule remained in the spectra, confirming that all groups did not react. This is probably related to the low ratio between the three methoxy groups in MAPTMS and H₂O/H⁺. The unreacted groups can be further hydrolysed/condensed after combining with Sol 2.

The MAPTMS precursor also contains an acrylate group (Figure 1b). Due to the absence of a polymerisation initiator, the reaction of acrylate groups did not occur at this preparation stage at ambient temperature [11,16].

In the second step, the characterisation of Sol 2 was related to reducing the high reactivity of ZTP with water and its chelation with MAA (Figure 2).

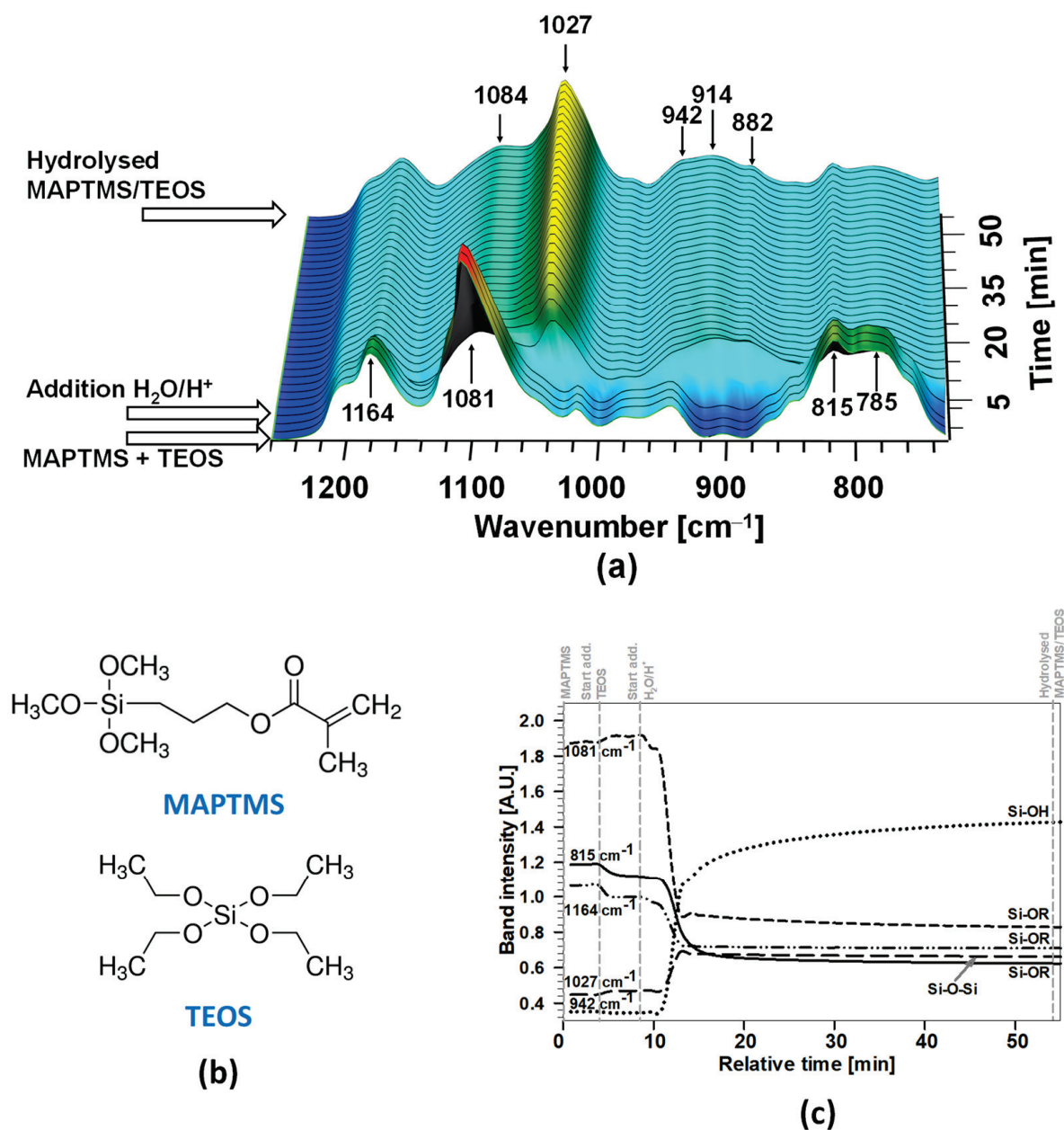


Figure 1. (a) Three-dimensional real-time FTIR spectra of hydrolysed MAPTMS and TEOS to obtain Sol 1; (b) molecular structures of 3-methacryloxypropyl trimethoxysilane (MAPTMS) and tetraethyl orthosilicate TEOS; (c) intensities of selected bands in the FTIR spectra vs. the time denoted in (a).

Table 2. Most characteristic bands in the FTIR spectra for bonds in initial precursors and TMZ sols. Data from [11,16].

Chemical Bonds	Wavenumber [cm^{-1}]
Si-O-R (MAPTMS or TEOS)	1164, 1081, 815, 785
Si-OH	942
Si-O-Si	1084, 1027
Zr-O-R (ZTP)	1555, 1376, 1459, 1130, 1044, 1003, 890, 834
MAA	1691, 1634, 1455, 1428, 1298, 1203, 810
ZTP/MAA	1646, 1055, 1248, 834
Si-O-Zr (TMZ)	1014, 1031, 943, 969

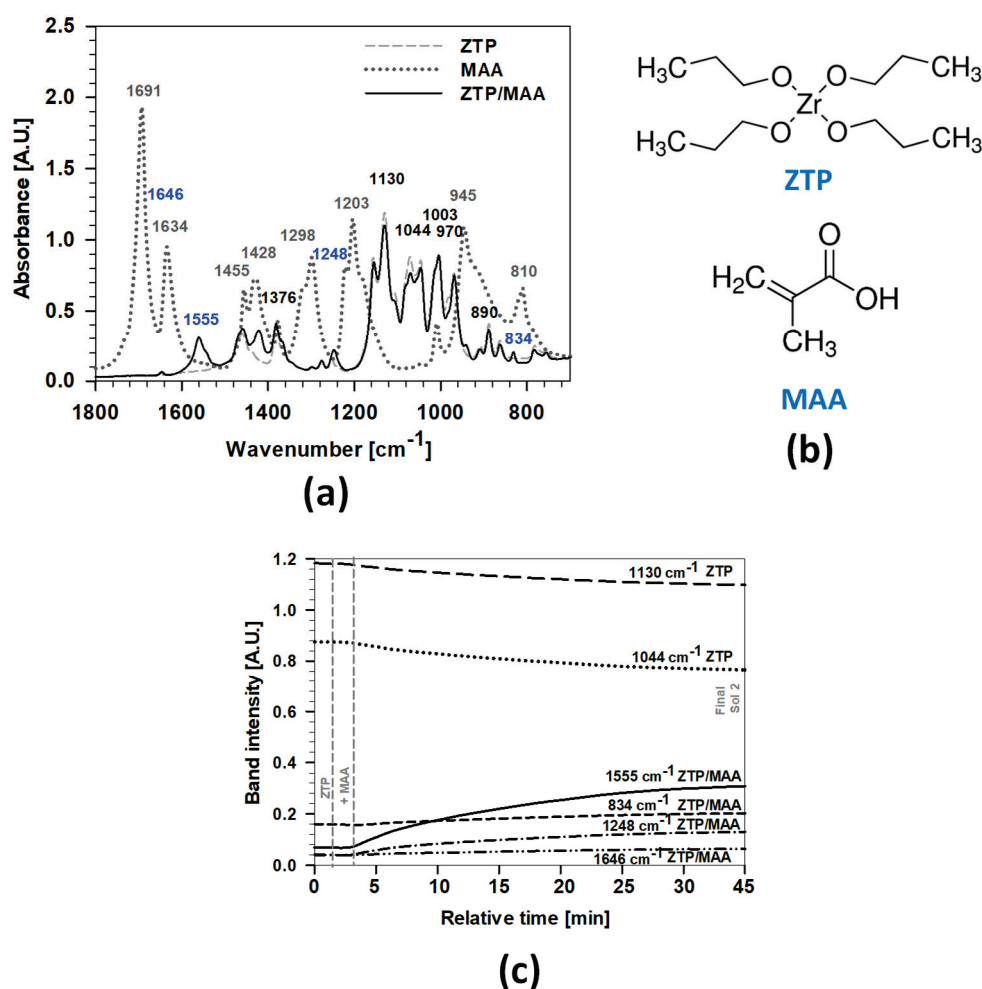
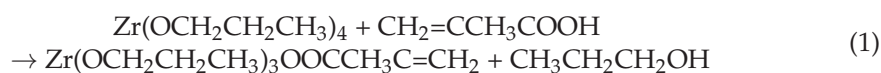


Figure 2. (a) Individual FTIR spectra of ZTP, MAA, and ZTP+MAA of Sol 2; (b) molecular structures of zirconium(IV) n-propoxide and methacrylic acid; (c) intensities of selected bands denoted in (a) during the chelation process of ZTP during the addition of MAA to obtain the Sol 2 (ZTP/MAA = 1:2).

The molecular structures of the reagents are presented in Figure 2b. ZTP shows six characteristic absorbance bands at 1130, 1044, 1003, 890, and 834 cm⁻¹, and the two other characteristic bands located between 1376 and 1459 cm⁻¹ are related to the stretching vibrations of the aliphatic C–H groups in the ZTP molecule (Figure 2a) (Table 2). Bands related to the chelating product (1-propanol) also appeared between 970 and 1100 cm⁻¹ and can partially contribute to the ZTP bands in this range. The MAA can be characterised by the bands at 1691 cm⁻¹ (C=O), 1634 cm⁻¹ (C=C), 1455 and 1428 cm⁻¹ (CH₃ and CH₂), 1298 and 1203 cm⁻¹ (C–O stretching in acid), 945 cm⁻¹ (COO⁻), and 810 cm⁻¹ (C=C).

After the dropwise addition of MAA to ZTP, the FTIR spectra provided clear evidence of the formation of a zirconium complex with an organic ligand (MAA) (Figure 2c). This process can be described by reaction (1):



The spectrum of chelated ZTP/MAA (Sol 2) spectra combine the spectral characteristics of both substances, ZTP and MAA, and show two additional bands characteristic of chelating at 1555 and 834 cm⁻¹. The bands characteristic for ZTP remained visible. Except for the bands in the CH₃ range, all bands characteristic of MAA were almost absent in the spectrum for Sol 2, showing a small amount of free MAA during chelation.

In the next 40 min of mixing, the most characteristic bands did not change significantly (Figure 2c). The only exception was the band at 1555 cm^{-1} (related to the chelating process of ZTP/MAA), which confirmed that Sol 2 was incompletely stabilised. Therefore, the ZTP remained active for further reactions.

In the last step, Sol 2 was added to Sol 1 to form the final sol TMZ (Figure 3).

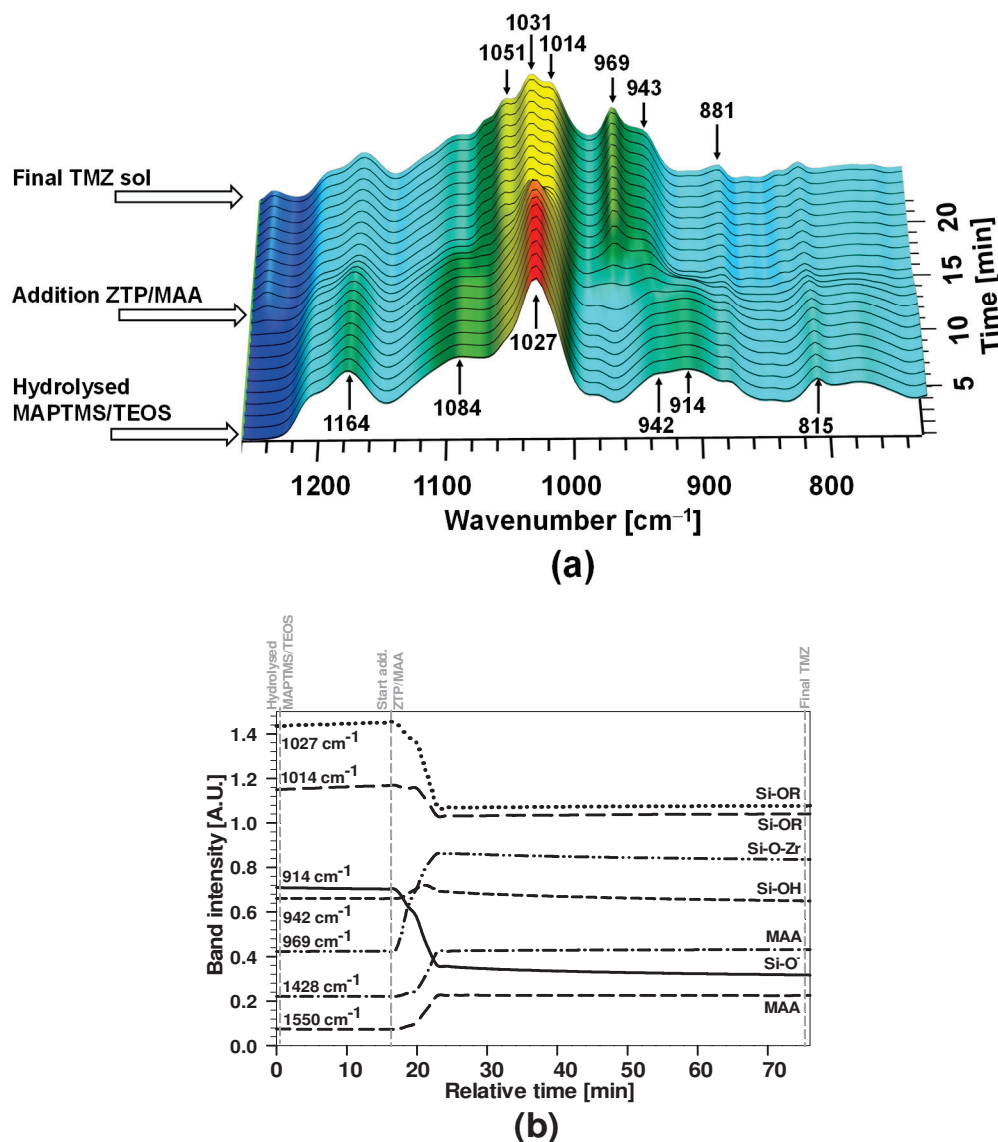


Figure 3. (a) Three-dimensional real-time FTIR spectra of hydrolysed MAPTMS and TEOS (Sol 1), followed by the addition of ZTP/MAA (Sol 2) to obtain the final TMZ sol; (b) intensities of selected bands in the FTIR spectra vs. time from (a) (part of the FTIR spectra for bands 1428 and 1550 cm^{-1} is not shown).

The marked decrease in the characteristic bands between 650 and 940 cm^{-1} for Sol 1 occurred due to dilution after adding Sol 2. The reactions between the sols took place in the first 5 min (Figure 3b). The decrease in the Si-OH groups at 942 cm^{-1} and non-reacted Si-O⁻ (ion) at 914 cm^{-1} indicate the induction of condensation and the formation of more complex networks (Si-O-Zr) after the addition of ZTP/MAA to the hydrolysed sol. The decrease in the band at 942 cm^{-1} is less significant due to the overlapping with the formed product of Si-O-Zr at 943 and 969 cm^{-1} ; the condensation can be better seen via the Si-O-Zr bands at 1014 and 1031 cm^{-1} . The presence of these bands confirms a co-hybrid system between the two precursors. The intensive band at 1027 cm^{-1} corresponds to the

linear Si–O–Si groups, whilst that at 1031 cm^{-1} is related to cyclic, more condensed groups (Figure 3b). The intensive bands for non-hydrolysed Si–O–R at 1084 and 1164 cm^{-1} were also reduced.

The characteristic C–H band related to 1-propanol (formed as a by-product) is at 881 cm^{-1} . The slow release of MAA during condensation was identified via the increase in the characteristic bands at 1428 and 1550 cm^{-1} , corresponding to vibrations of the carboxylic group (COO^-) (Figure 3b). During the coating thermal curing process, the released MAA can later participate in co-polymerisation with MAPTMS.

Hydrolysis–condensation reactions proceeded continuously for 1 h of mixing (Figure 3b). The main effect was on the siloxane bands due to the formation of more complex networks with linear or cyclic chains. The characteristic bands of the remaining non-reacted species are located between 914 and 942 cm^{-1} ; their intensity decreased during mixing due to the formation of a more condensed solution.

To sum up, the hydrolyses and condensation reactions formed Si–O–Si and Si–O–Zr networks. The reactions proceeded faster at the beginning, but after optimised times, the sols were partially stabilised to obtain a good incorporation of Zr and the formation of the solution network.

3.1.2. FTIR Analysis of the Sol–Gel TMZ Coating

Sol TMZ was deposited on the ground Al surface as a coating. Several main differences between the real-time FTIR spectrum of the TMZ sol (Figure 3) and the ATR FTIR spectrum of TMZ coating (Figure 4) were observed in the region between 1250 and 700 cm^{-1} . These differences resulted from the network formed between silicon, zirconium, and oxygen (Si–O–Si and Si–O–Zr). The decrease in the bands characteristic of the initial precursors between 750 and 850 cm^{-1} indicates that hydrolysis and condensation reactions finally occurred during the curing process. As a result, several characteristic siloxane (Si–O–Si) and siloxane-Zr (Si–O–Zr) bands appeared between 1200 and 900 cm^{-1} , with the maximum appearing at 1010 cm^{-1} .

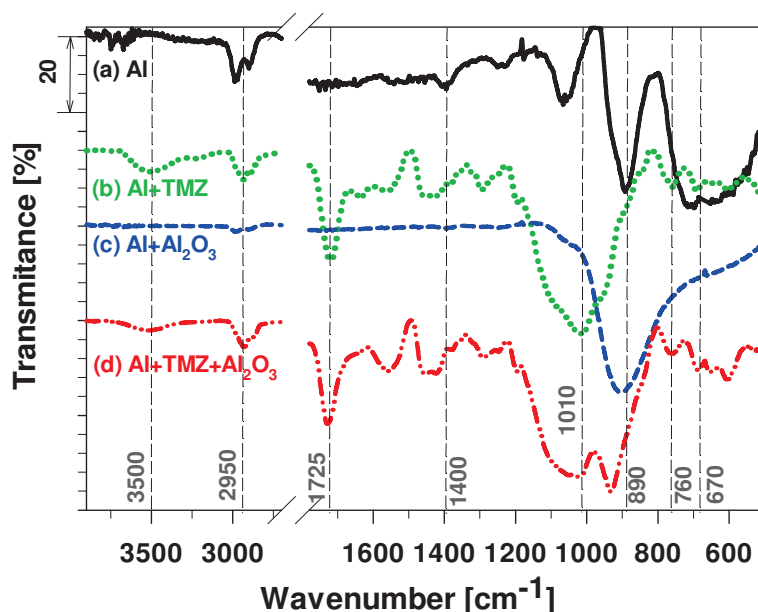


Figure 4. Normalised FTIR spectra of (a) the ground aluminium surface and ground aluminium surfaces coated with (b) the TMZ coating, (c) the Al_2O_3 film, and (d) the multilayer TMZ/ Al_2O_3 system (vertical dashed lines denote some of the characteristic bands in the FTIR spectra).

Additionally, the co-polymerisation process of acrylate groups in the MAPTMS and MAA was thermally induced during curing at 160°C (Figure 4).

The low intensity of the C=C bands at 1640 cm^{-1} and slightly shifted carbonyl group C=O (from 1720 cm^{-1} to 1725 cm^{-1}) indicate that co-polymerisation occurred, as evidenced by the band at 1640 cm^{-1} , which is related to the C=C bond. The co-polymerisation remained incomplete due to the absence of a co-polymerisation initiator. The polymerisation degree is difficult to evaluate due to the overlapping of the C=C band with a band characteristic of water (1638 cm^{-1}). In addition, the broad absorption band, extending from 3000 cm^{-1} to 3800 cm^{-1} , is the sum of the band at wavenumber generated by the stretching vibration of the O–H groups belonging to the external silanols (Si–OH) at 3610 cm^{-1} and water molecules adsorbed in solution (free water is at ca. 3600 cm^{-1}) (Figure 4).

3.2. Preparation and Analysis of the ALD Al_2O_3 Film

The growth mechanism of ALD Al_2O_3 films fabricated using trimethylaluminium (TMA; $\text{Al}(\text{CH}_3)_3$) and H_2O vapour has been studied extensively [39,48,57]. The ALD process is well controlled and self-limiting, and it occurs on the exposed surface. During deposition, precursors are separately present in the chamber (Figure 5a).

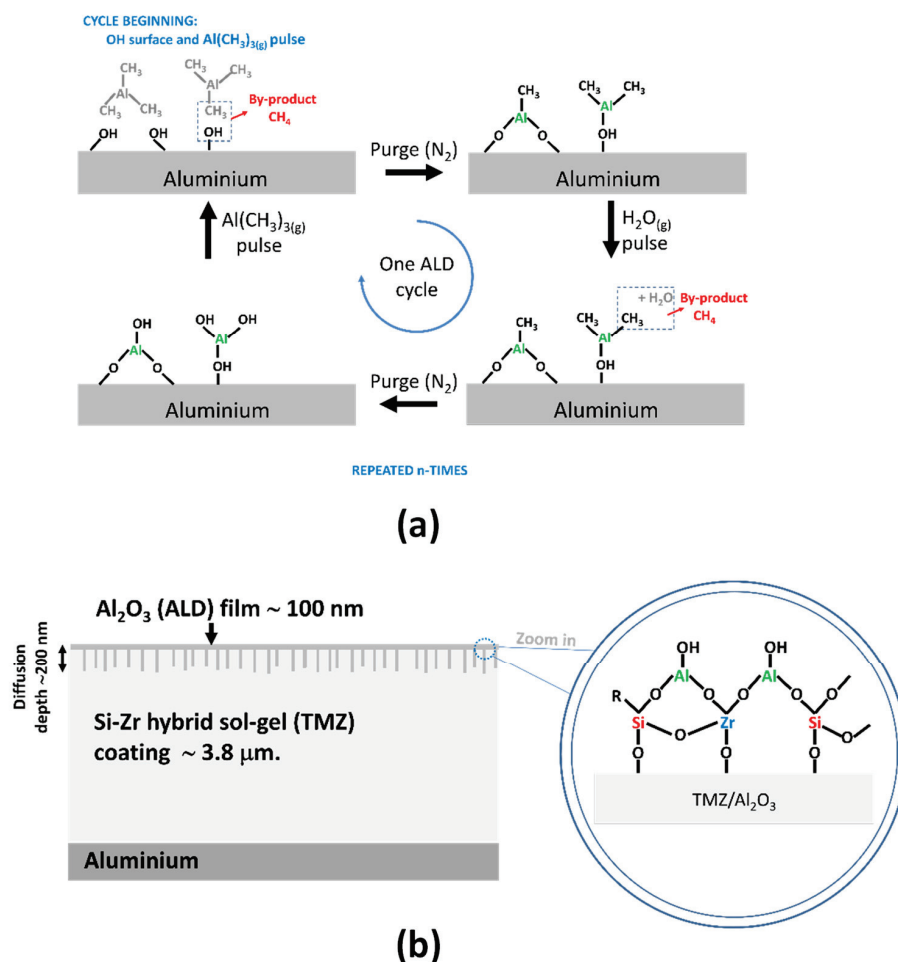


Figure 5. Schematic presentation of (a) the ALD cycle using trimethyl aluminium (TMA) and water as co-reagent and (b) the multilayer TMZ/ Al_2O_3 coatings system deposited on the aluminium surface. The inset figure schematically presents the principle of the ALD pore-sealing effect of a TMZ coating (Si–O–Zr hybrid sol–gel coating).

The first ALD reaction cycle reaction occurs on the aluminium surface. After one cycle, it is adsorbent only on ALD-grown film [23]. The reagent completely covers the metal surface regardless of the shape, and during one cycle, deposition occurs half a monolayer at a time.

The water vapour is introduced into the chamber, leading to hydroxyl groups forming bonds with the metal surface. Excess water is then purged from the chamber. The purge is followed by introducing TMA, which reacts with the adsorbed hydroxyl groups. The metal atom bonds react with oxygen. Meanwhile, the hydrogen atom leaves the surface as a reaction by-product in methane, which is evacuated from the chamber. TMA continuously reacts with the remaining hydroxyl group but does not react with itself. Thus, the growth is terminated after one layer. The remaining precursor TMA is then evacuated from the chamber and purged with nitrogen. The cycle is repeated until the desired thickness is achieved. Another critical parameter is the water dose, which should be optimised because increasing the water dose could enhance the growth rate [58]. However, the amount of water has a low influence on the composition and electrical or optical properties [58].

Formed aluminium oxide is a chemically stable amphoteric compound, but its stability is reduced in acid or base solutions. The solubility is higher if the film is formed at lower temperatures [42].

The mechanism of film formation can be described by reactions (2) and (3):



In the reaction processes, the surface $-\text{OH}$ is a crucial reactive group that determines the successive self-limiting reactions. Higher temperatures can reduce the number of reactive surface sites and the type of chemisorbed species [23].

FTIR Analysis of the Ground Al and Al Coated with the Al_2O_3 ALD Film

FTIR spectra of ground Al covered by a naturally formed oxide (passive) film and Al_2O_3 -coated Al are presented in Figure 4. The naturally formed passive film on the Al is a mixture of aluminium oxide (Al_2O_3) and hydroxide ($\text{Al}(\text{OH})_3$, $\text{AlO}(\text{OH})$) [59]. The band at $\sim 1060 \text{ cm}^{-1}$ is characteristic of the Al–O vibration mode in alumina. The band at 890 cm^{-1} is assigned to the bending vibrations of the Al–O bond. The Al–O–Al bond in the γ -alumina generates the broad band centred at 710 cm^{-1} [60]. The bands between 2900 and 3000 cm^{-1} and at 1400 cm^{-1} are characteristic of CH groups. They are present due to organic contamination during surface preparation (grinding the surface). The critical information that can be derived from these FTIR spectra is the presence of hydroxide groups on the aluminium surface, evidenced by an intensive band at 910 cm^{-1} . As explained in the text above, $-\text{OH}$ groups help form strong covalent bonds with the substrate.

The differences in the FTIR spectra of natural passivated and thermally deposited ALD Al_2O_3 films are compared in Figure 4. For the former, the broad absorption band in the range of 750 – 1100 cm^{-1} was attributed to the mixed contributions of the Al–O bending and stretching modes. The absorption peak at 905 cm^{-1} represents O–Al–O bending. Compared to the naturally passivated surface, the FTIR spectrum of the ALD film exhibits a relatively small band intensity of the C–H bending modes. The absorption band at 1385 cm^{-1} usually reflected the remaining formate species' OCOH bending [57,61], but due to the efficient reaction, this band was not present in the FTIR spectra. Some other relatively very small bands for the C–H bending mode of the H_2O -based Al_2O_3 film were observed, such as the absorption band attributable to carbon species, including C–H stretching vibrations, at 2850 – 3050 cm^{-1} , but its intensity was much lower compared to the ground surface (Figure 4). During the ALD process at 160°C , the carbon species of the TMA are not entirely removed from the surface, and their presence in the H_2O -based Al_2O_3 film hinders the self-limiting reaction of the ALD process. In addition, the absence of a broad band between 3200 and 3700 cm^{-1} , the band at 1638 cm^{-1} , and the band at 1470 cm^{-1} in the ALD/ Al_2O_3 FTIR spectrum confirmed that applying the controlled pulse and purge process during thermal ALD deposition allowed for the formation of the film without any physisorbed water.

3.3. Preparation and Analysis of the Multilayer TMZ/ Al_2O_3

The multilayer Si–O–Zr hybrid sol–gel/ Al_2O_3 (abbreviation TMZ/ Al_2O_3) was prepared by applying one layer of TMZ coating, followed by the deposition of 100 nm ALD. This multilayer thus consists of a thick sol–gel TMZ coating sealed by a thin ALD film.

The corresponding FTIR spectrum confirmed the presence of the ALD Al_2O_3 film on the TMZ coating (Figure 4) since it shows a characteristic band of Al–O–Al at 920 cm^{-1} . The spectrum also contained several bands related to TMZ coating (Si–O–Si and Si–O–Zr bands), which can be detected below that of the thin ALD Al_2O_3 film. The main difference is the reduced intensity of the band related to hydroxy groups at $\sim 3500\text{ cm}^{-1}$, confirming the reaction between non-hydrolysed –OH groups on the TMZ surface with the ALD film according to reaction (4).



The asterisks mark the surface species during film deposition. Therefore, the FTIR spectrum confirmed that the deposited ALD Al_2O_3 film reacted with the hydroxyl groups on the TMZ coating surface, forming a more condensed coating. Further, the spectrum of the multilayer system is comparable to that of the TMZ coating, indicating similar polymerisation degrees and Si–O–Zr network formation (band at 1640 cm^{-1}).

3.3.1. Surface and Cross-Section Analysis

SEM/EDS analysis results are shown for uncoated (ground) aluminium and aluminium coated with TMZ, Al_2O_3 , and TMZ/ Al_2O_3 in Figures 6–10. Since Al is a relatively soft metal (the Rockwell hardness of pure aluminium is typically in the range of B20 to B30), grinding affects its surface texture. The top-view SEM image of the ground Al (Figure 6a,b) shows an uneven surface with many irregularities and grinding residuals in the direction of the grinding (marked with black arrows), resulting in a complex and rough surface texture.

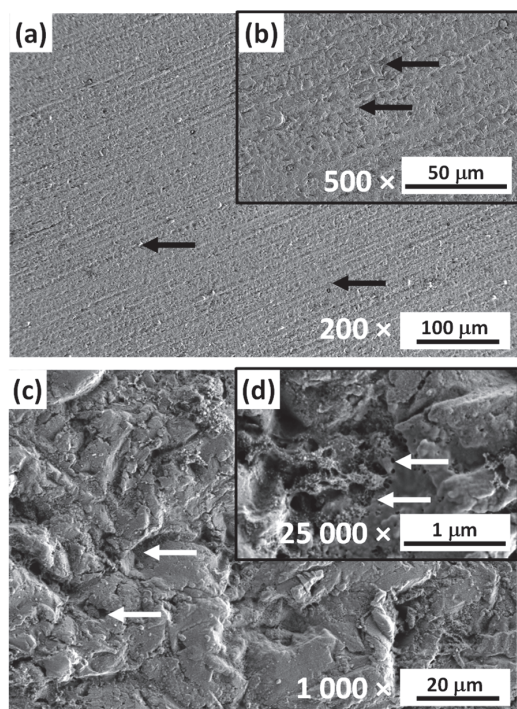


Figure 6. SEM morphology images of the ground aluminium surface at (a,b) low and (c,d) high magnification. The black arrows in (a,b) mark the irregularities and grinding residuals in the direction of the grinding. The white arrows in (c,d) mark the voids and pores in the naturally passivated aluminium surface.

At higher SEM magnification (Figure 6c,d), many small, nanometre-sized voids (marked with white arrows) can be noticed. These represent weak points for surface passivation and, consequently, for initiating corrosion.

The aluminium surface coated with the TMZ coating is characterised by the top-view SEM image in Figure 7a.

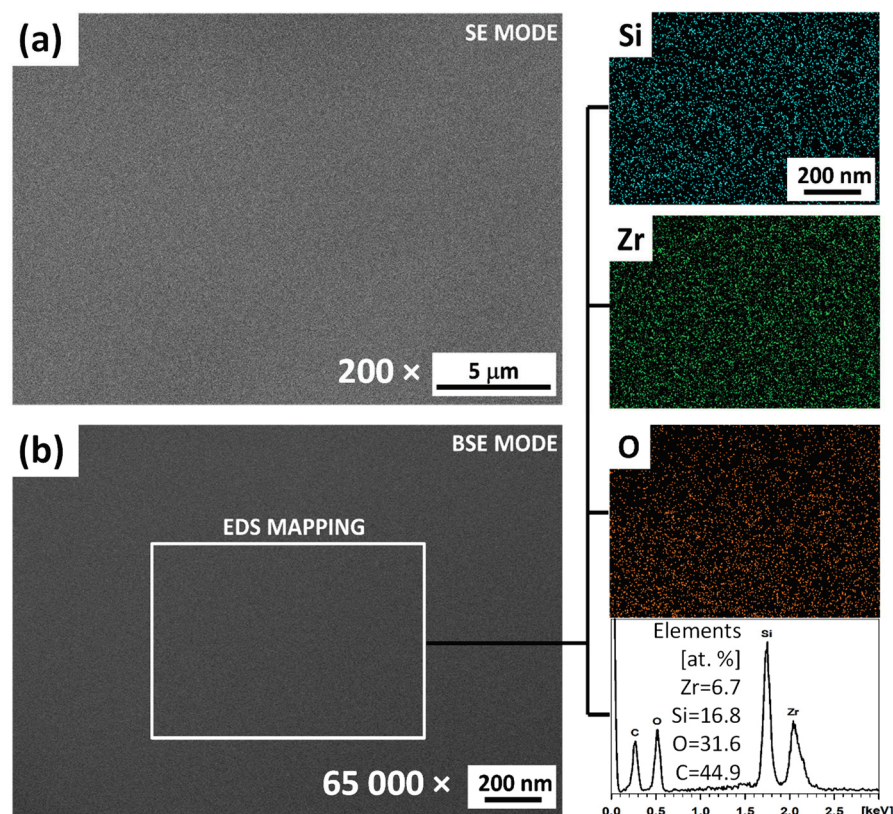


Figure 7. SEM morphology images of aluminium coated with TMZ coating using (a) the secondary electron (SE) and (b) back-scattering electron (BSE) imaging modes. The square marks the positions where the EDS mapping was performed. The elemental mapping analyses of silicon, zirconium, and oxygen are shown on the right. Additionally, the EDS spectrum and composition are given in the atomic percentage.

The coating was uniform and smooth without any micro-cracks or visible defects. Its composition was homogenous, even at high magnifications (see BSE SEM image Figure 7b). EDS mapping was performed at the area marked in Figure 7b. Si and Zr are evenly distributed in the formed coating. The atomic ratio between Zr and Si is 1:2.5, which agrees with the starting composition of the sol ($Zr/Si = 0.41$). Such an evenly formed structure is related to well-optimised synthesis conditions to achieve efficient degrees of condensation between the initial Si and Zr precursors and co-polymerisation between the acrylate group in MAPTMS and MAA forming dense coating [18,20].

The coating composition along the cross-section was characterised via FIB/SEM/EDS (Figure 8). The compact coating structure without any visible defects along the performed cross-section was confirmed. Based on previous research, these types of coatings are slightly porous, but this porosity cannot be observed using SEM. In previous publications, the determined porosity for similar coatings using photothermal beam deflection spectroscopy or electrochemical measurements was between 0.85 and 0.49% [20]. The coating covered the aluminium surface entirely despite its rough surface. The coating thickness estimated based on FIB-SEM imaging was $\sim 3.8 \mu m$ (Figure 8).

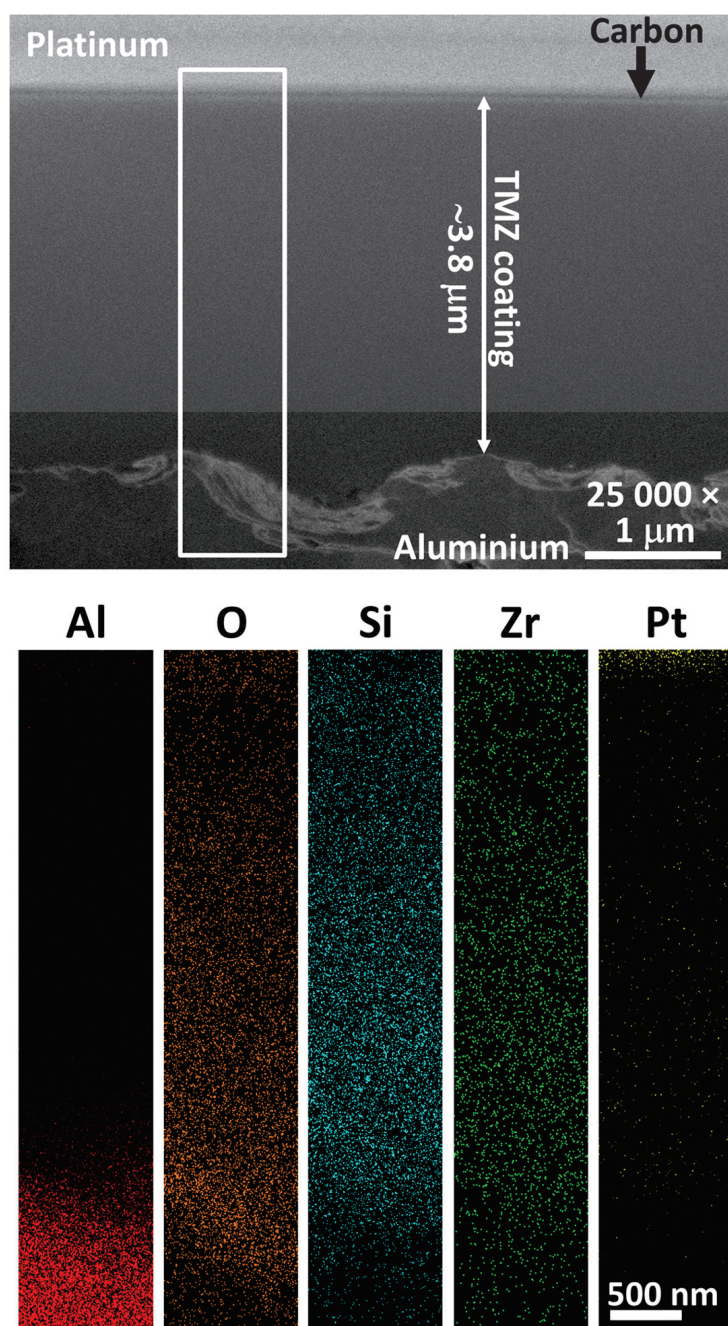


Figure 8. FIB-SEM cross-section morphology of aluminium coated with TMZ coating and elemental mapping analysis of aluminium, oxygen, silicon, zirconium, and platinum of the marked white rectangle.

The coating appearance resembles other TMZ coatings with different TEOS/MAPTMS and ZTP ratios [18]. Still, the slightly greater thickness of the TMZ coating is probably related to the higher condensation degree between ZTP and TEOS/MAPTMS. In addition, the MAA remained unreacted during the incomplete chelation of ZTP in Sol 2 (Figure 2) and can further co-polymerise with MAPTMS. The homogeneity of the coating was also confirmed with EDS mapping analysis on the marked rectangle in Figure 8, where the efficient incorporation of Zr in the Si–O–Si sol–gel structure is evidenced.

Top-view and cross-section SEM images of the ALD Al_2O_3 -coated Al are presented in Figure 9.

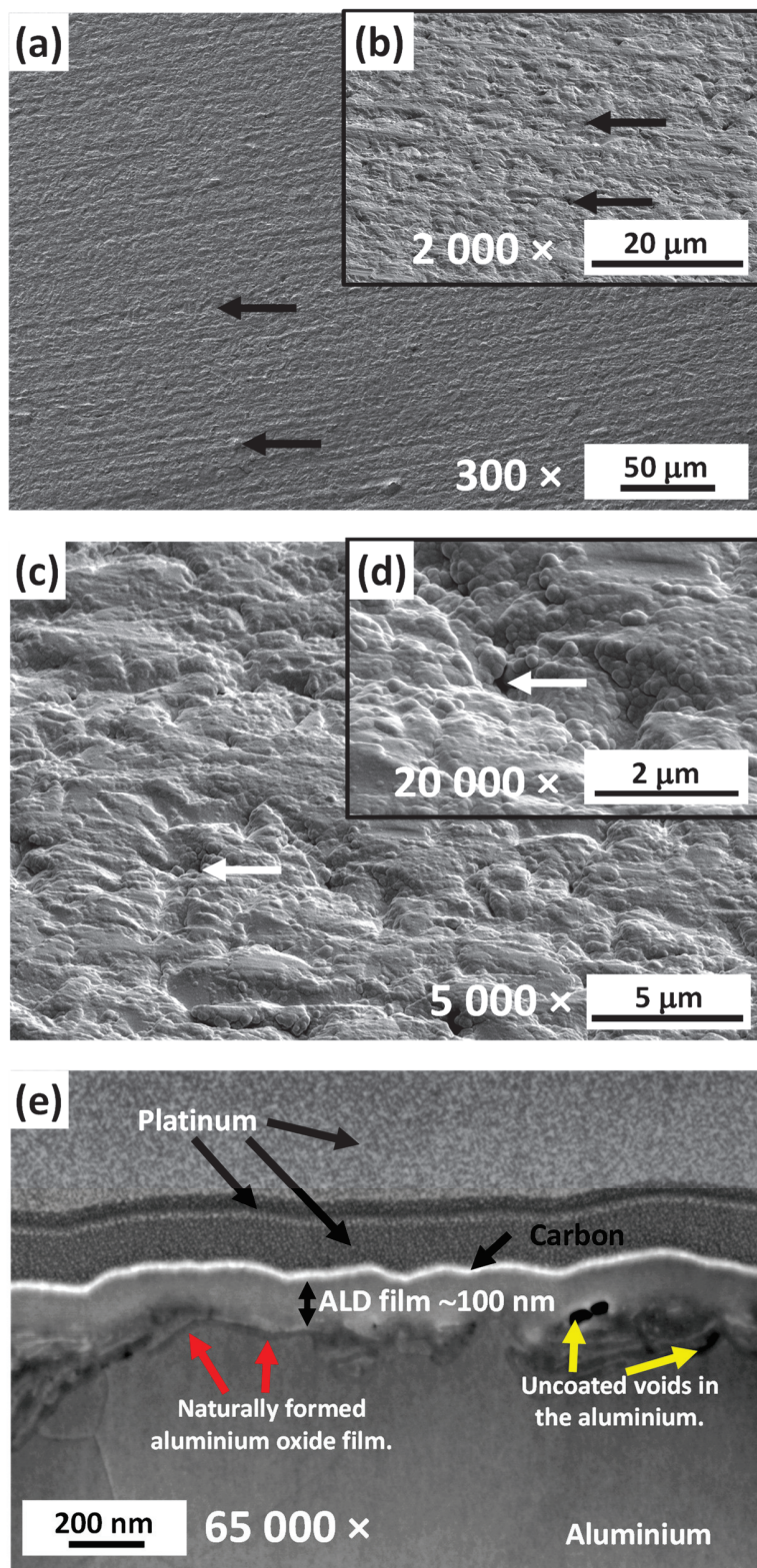


Figure 9. SEM morphology images of the surface of ground aluminium after the thermal deposition of 100 nm ALD Al_2O_3 at 160 °C presented at (a,b) at low and (c,d) high magnification. The black arrows in (a,b) mark the grinding residuals, and the white arrows in (b) mark the voids and pores. Figure (e) shows a cross-section of ALD film on the ground Al. The red arrows in (e) mark the naturally formed aluminium oxide film, and the yellow arrows mark the uncoated voids in the aluminium structure.

Despite the ALD film having a small thickness of only 100 nm, there was a difference in the macroscopic observations of the alumina (Figure 9a) compared to the ground aluminium (Figure 6a). The number of irregularities and voids observed on the ground Al was significantly reduced after the deposition of the ALD film (Figure 6c,d). The surface was more uniform, containing less visible lines from the grinding process (Figures 6a,b and 9a,b). The deposited Al_2O_3 film perfectly covers the surface and decreases the surface roughness. From the top-view imaging, it is impossible to distinguish the naturally formed Al_2O_3 and the ALD Al_2O_3 film (Figures 6d and 9d). This was obtained using a FIB-SEM cross-section (Figure 9e). The ALD Al_2O_3 film is much thicker (~ 100 nm), more compact, and more homogeneous compared to a naturally formed layer. The ALD film also covers the irregularities in the Al structure and the other defects marked with white arrows.

Top-view SEM images of the aluminium coated with a multilayer (TMZ/ Al_2O_3) system is presented in Figure 10.

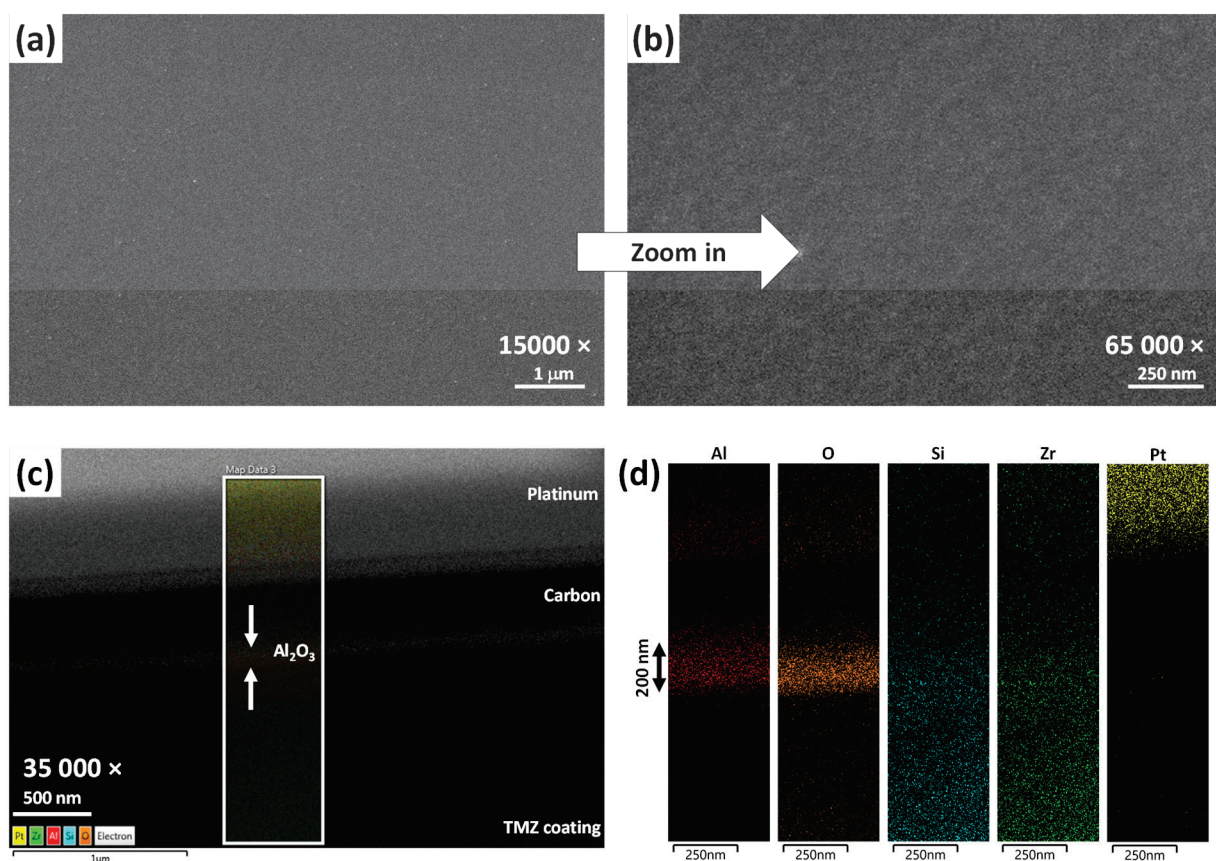


Figure 10. (a,b) SEM morphology images of the TMZ/ Al_2O_3 multilayer system on Al. (c) FIB-SEM cross-section image of the multilayer system and (d) elemental mapping analysis of aluminium, oxygen, silicon, zirconium, and platinum of the marked white rectangle in (c).

Due to the low thickness of the ALD film (100 nm thin Al_2O_3), there were no significant differences observed between the TMZ and TMZ/ Al_2O_3 coatings' surface appearances (Figures 7 and 10a,b). The ALD film was better distinguished in the cross-section FIB-SEM imaging and analyses where the in-depth chemical composition was obtained (Figure 10c,d). EDS maps of aluminium, oxygen, silicon, zirconium, and platinum are presented in Figure 10d. Please note that the upper part of the cross-section is related to the carbon and platinum layers deposited during the FIB procedure. The multilayer composition is divided into two layers: Al_2O_3 at the top and TMZ at the bottom. The reaction between the TMZ coating and ALD film is presented in Figure 5b. It is thought that the TMA reacts with the Si-OH and Zr-OH bonds and forms a covalent bond Si/Zr-O-Al,

as described in reaction (4). The TMZ was homogeneous throughout the whole depth. The signal ratio of Si and Zr follows the molar composition of the synthesised TMZ sols, confirming the homogeneous contribution of both of the major elements in the coating. The increased content of Al and O at the top is related to the formed Al_2O_3 . The thickness of the Al_2O_3 film on the TMZ coating was determined from the cross-section mapping. The estimated thickness of the Al_2O_3 film was ~ 200 nm. There is a discrepancy between the thickness of the individual ALD Al_2O_3 film (100 nm, Figure 9e) and the multilayer system (200 nm, Figure 10c,d). The reason for this is probably the sealing of the open pores within the sol–gel coating, where alumina diffuses during the ALD process through the coating pores in the outer part (ca. 100 nm), reacts with Si/Zr–OH groups, and forms a denser structure, as shown schematically in Figure 5b.

3.3.2. Electrochemical Corrosion Testing

The electrochemical properties of the uncoated and TMZ-, Al_2O_3 - and TMZ/ Al_2O_3 -coated Al samples were studied via EIS while being immersed in 0.1 M NaCl. The EIS spectra recorded after 1 h immersion are given in the Bode plots (magnitudes of the impedance, $|Z|$, and the phase angle, ϕ , as a function of the frequency) presented in Figure 11. The Nyquist spectra are presented in Figures S1–S3.

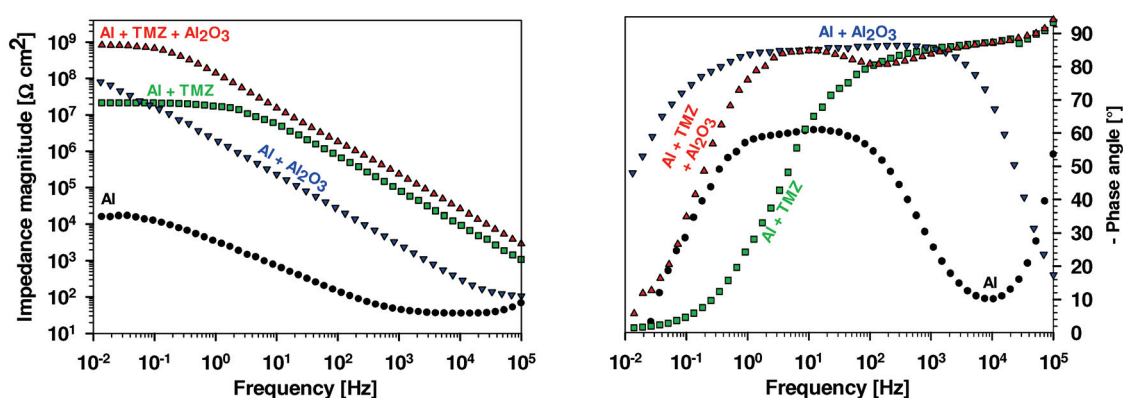


Figure 11. Bode plots (impedance magnitude and phase angle) of the aluminium coated with TMZ, ALD Al_2O_3 , and TMZ/ Al_2O_3 after 1 h of immersion. A curve for the ground aluminium immersed for 1 h has been plotted for comparison.

The impedance magnitudes at the lowest frequency of 10 mHz ($|Z|_{10 \text{ mHz}}$) were taken as critical values to be considered when evaluating the protective properties of different protective systems. Table 3 summarises the $|Z|_{10 \text{ mHz}}$ values for the TMZ-, Al_2O_3 - and TMZ/ Al_2O_3 -coated Al samples after different immersion times.

The Bode plots reflect that the aluminium surface was passivated with spontaneously formed oxide. The impedance magnitude at low frequency ($|Z|_{10 \text{ mHz}}$) was $16 \text{ k}\Omega \text{ cm}^2$, and the maximum ϕ of around -61° was in the middle range frequency. These data indicate that the oxide layer offers a limited barrier to the diffusion of corrosive species. In contrast, the TMZ-, Al_2O_3 -, and especially the multilayer TMZ/ Al_2O_3 -coated samples showed different Bode plots compared to the uncoated Al (Figure 11). The EIS response of the TMZ-coated Al showed improved corrosion protection, as expressed by a more extended constant impedance modulus plateau in the low- and middle-frequency part. After 1 h of immersion, the $|Z|_{10 \text{ mHz}}$ of the TMZ coating was significantly greater than that of the uncoated coating ($25.5 \text{ M}\Omega \text{ cm}^2$ compared to $16 \text{ k}\Omega \text{ cm}^2$, respectively). For the Bode ϕ vs. f plot, values close to -90° were obtained, stretching over a high-frequency range and indicating the coating's highly capacitive character. The plateau of the constant phase angle was extended up to 10^2 Hz frequencies, showing the capacitive behaviour of the coating. The measured values of the studied TMZ coating were greater than similar

TMZ coatings with a lower amount of Zr, confirming the beneficial effect of increasing the Zr content in the coating [11,18,20].

Table 3. Impedance magnitude at 10 mHz ($|Z|_{10 \text{ mHz}}$) determined from EIS spectra in Figure 12 for the TMZ-, Al_2O_3 - and TMZ/ Al_2O_3 -coated Al samples after different immersion times in 0.1 M NaCl.

Sample	Immersion Time	$ Z _{10 \text{ mHz}}$ [$\text{M}\Omega \text{ cm}^2$]
Ground Al	1 h	0.016
Al coated with TMZ	1 h	25.5
	1 day	15.4
	1 week	6.1
	2 weeks	4.1
	3 weeks	2.5
	4 weeks	0.54
Al coated with ALD	1 h	80.4
	1 day	78.5
	1 week	11.1
	2 weeks	0.23
Al coated TMZ+ALD	1 h	827.2
	1 day	580.9
	1 week	280.2
	2 weeks	124.8
	3 weeks	31.9
	4 weeks	5.0

The results regarding the EIS measurements on the ALD Al_2O_3 -coated aluminium (Figure 11, Table 3) indicated impedance values even higher ($80.4 \text{ M}\Omega \text{ cm}^2$) than those of the TMZ-coated aluminium. The deposited ALD coating showed increased impedance values and a widened high phase angle region, reflecting the extended passivation range in the case of the samples coated with 100 nm thin coating compared to the naturally passivated aluminium surface. Thus, the ALD Al_2O_3 film presents better (more efficient) resistance against corrosion. The Bode ϕ vs. f plot showed that values close to -90° were obtained, stretching over a high-frequency range and indicating that the ALD Al_2O_3 exhibits a highly capacitive character.

The greatest $|Z|_{10 \text{ mHz}}$ values of $827.2 \text{ M}\Omega \text{ cm}^2$ were obtained for the multilayer TMZ/ Al_2O_3 system coating (Figure 11). The Bode ϕ vs. f plot showed values close to -90° stretching from 5 Hz to a high-frequency range. The enhanced barrier properties of the multilayer system are related to the pore-sealing effect of the outer part of the TMZ coating with the ALD film, thus blocking the ingress of corrosive species from the solution.

The EIS measurements pertaining to an extended immersion time are presented in Figure 12. Deduced $|Z|_{10 \text{ mHz}}$ values are presented in Table 3, and the Nyquist spectra are presented in Figures S1–S3. The layer formed spontaneously on the Al surface offers only a limited degree of protection [18]. Thus, only the curve recorded after immersion for one hour is presented. The $|Z|_{10 \text{ mHz}}$ of the TMZ coating slightly decreased during immersion (to $15.4 \text{ M}\Omega \text{ cm}^2$ after 1 day and $2.5 \text{ M}\Omega \text{ cm}^2$ after 3 weeks), and the phase angle values shifted to higher frequencies (Figure 12a).

The extent of the impedance plateau remained unchanged, indicating that the degradation processes did not significantly affect the coating's structure and, in turn, the corrosion rate of the underlying Al substrate. However, the obtained spectra indicate that despite a minimal coating porosity [20,21], it can generate diffusion pathways for the aggressive electrolyte to access the substrate after a longer immersion time. This process was reflected in the shape of the middle-frequency part after 2 weeks of immersion. In the ϕ vs. f plot, signs of corrosion at the inner substrate/coating interface (low frequency) are visible (Figure 12a). On the high-frequency side, which reflects the coating capacitance, the value of ϕ also decreased, indicating the deterioration of the TMZ coating with increasing immersion time. Therefore, although the TMZ coating imparts good corrosion protection for the underlying

Al substrate, some pores and pathways were formed in the coating, starting after 2 weeks of the immersion, enabling the electrolyte to ingress to the substrate.

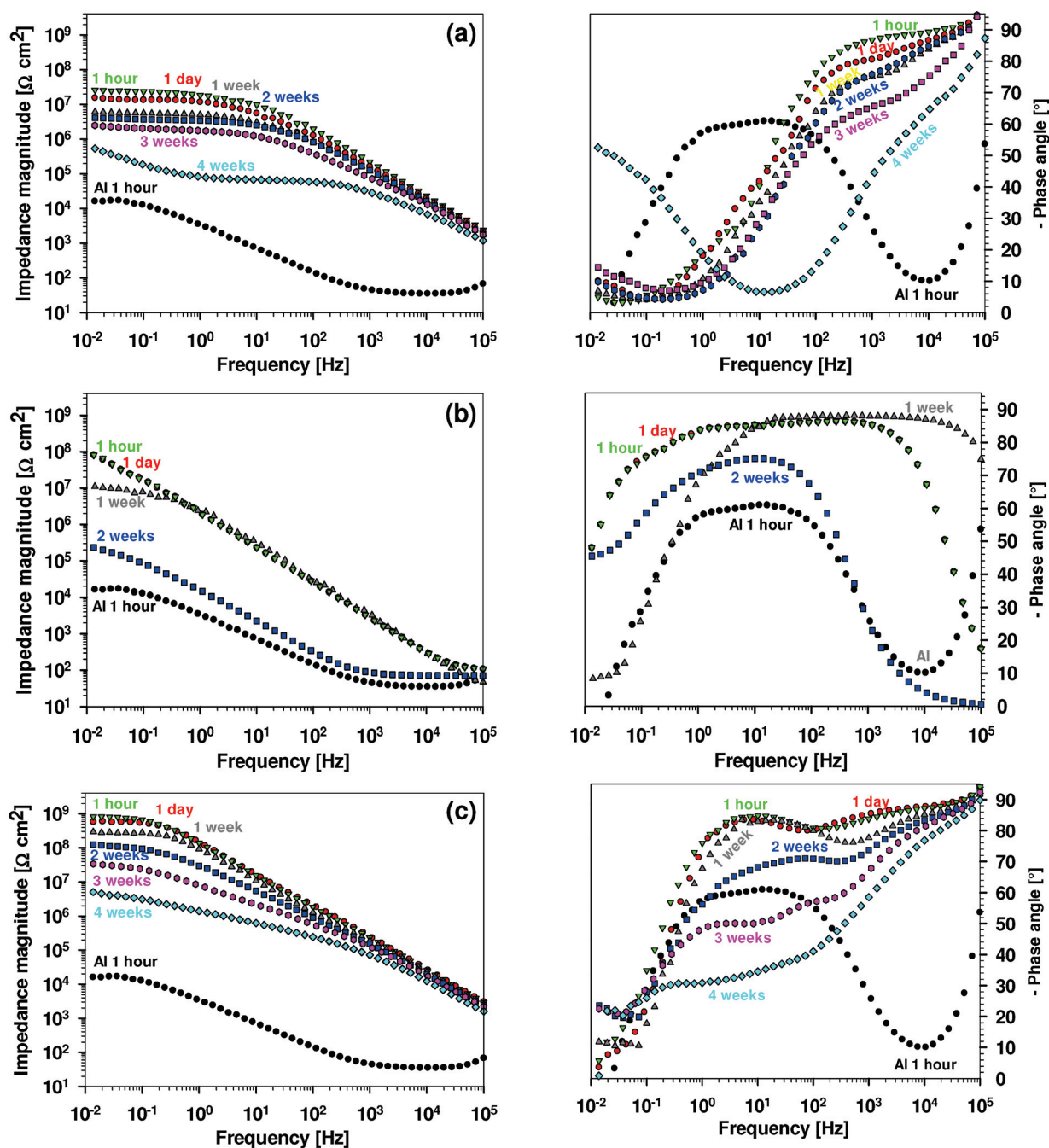


Figure 12. Bode plots (impedance magnitude and phase angle) of the aluminium coated with (a) TMZ, (b) ALD Al_2O_3 , and (c) TMZ/ Al_2O_3 at different immersion times. A curve for the ground aluminium immersed for 1 h has been plotted for comparison.

The ALD Al_2O_3 -coated Al samples showed less durable protection than the TMZ-coated samples (Figure 12b). Despite higher impedance at the beginning of immersion, the $|Z|_{10\text{ mHz}}$ values decreased after one week for almost one order of magnitude and then gradually further decreased after 2 weeks of immersion (Table 3). The low durability of the ALD Al_2O_3 film is probably related to the nanometric thickness of the film and, possibly, voids in the film (Figure 9c). Further, due to deposition at low temperatures, the chemisorption of $\text{Al}(\text{CH}_3)_3$ to the surface may not be completed [45,48] (Figure 4).

Therefore, the film formed under such conditions contains carbon at the surface, reducing the corrosion efficiency after extended immersion time.

In the Bode plots for the multilayer TMZ/ Al_2O_3 coating system, two distinct regions can be observed (Figure 12c). The high-frequency range is related to the outer part of the TMZ/ Al_2O_3 coating at the coating/electrolyte interface, and the intermediate frequency range is related to the inner part of the TMZ coating. For up to 4 weeks of immersion, the multilayer coating acted as a barrier, as evidenced by the increased $|Z|_{10\text{ mHz}}$ for over one order of magnitude compared to the TMZ-coated Al (Table 3). After 4 weeks of immersion, the impedance magnitude decreased in the whole frequency range, but this decrease was much slower than that of the TMZ-coated Al ($|Z|_{10\text{ mHz}}$ $5\text{ M}\Omega\text{ cm}^2$). Despite a stable and dense interface, the coating formed some pores, but in the ϕ vs. f plot, no signs of corrosion at the inner substrate/coating interface (low frequency) were visible (Figure 12c). On the high-frequency side, reflecting the coating capacitance, the value of ϕ also remained similar, indicating that the multilayer coating system remained more protective at longer immersion times.

4. Conclusions

This study focused on the possibility of combining two strategies of corrosion protection—a micrometre-thick sol–gel hybrid coating sealed with a nanometre-thick alumina layer—and evaluating their properties and corrosion resistance in 0.1 M NaCl when deposited on aluminium.

The preparation of hybrid sol–gel coatings from silica and zirconia precursors Si/Zr was characterised using real-time FTIR spectroscopy. After hydrolysis and condensation, chelating reactions stopped at a certain level, at which the efficient incorporation of zirconia into the siloxane network occurred. The reactions were completed after thermal curing.

FTIR spectra of the aluminium surface showed the difference in composition between the naturally formed aluminium oxide film (consisting of a mixture of aluminium oxides) and the well-defined ALD Al_2O_3 deposited film.

The FTIR spectrum of the multilayer system showed the presence of the ALD film on the TMZ coating. During deposition, the ALD film reacted with a Si–O–Zr network, mainly with unreacted –OH groups forming a Si/Zr–O–Al film. The multilayer was homogeneous and exhibited a low number of defects, as shown by the top and cross-section SEM/EDS images. The ALD alumina film diffused in the TMZ coating structure, thus sealing the pores in the outer part of the TMZ coating.

The aluminium coated with the multilayer TMZ/ Al_2O_3 coating imparted excellent corrosion resistance to the underlying aluminium substrate during three weeks of immersion in 0.1 M NaCl. The impedance magnitude increased by two orders compared to the uncoated aluminium substrate ($|Z|_{10\text{ mHz}}$ from $16\text{ k}\Omega\text{ cm}^2$ to almost $830\text{ M}\Omega\text{ cm}^2$). Thus, the pore sealing of the sol–gel coating using the ALD alumina film produced a protective multilayer coating system because $|Z|_{10\text{ mHz}}$ remained above $5\text{ M}\Omega\text{ cm}^2$ after four weeks in sodium chloride solution.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met13121960/s1>, Figure S1: Nyquist plots of the aluminium coated with the TMZ coating at different immersion times; Figure S2: Nyquist plots of the aluminium coated with the ALD Al_2O_3 coating at different immersion times; Figure S3: Nyquist plots of the aluminium coated with the TMZ/ Al_2O_3 coating at different immersion times.

Author Contributions: Conceptualisation, P.R. and I.M.; methodology, P.R.; validation, P.R.; formal analysis, P.R. and B.K.; writing—original draft preparation, P.R. and I.M.; writing—review and editing, I.M.; project administration, I.M.; funding acquisition, P.R. and I.M. All authors have read and agreed to the published version of the manuscript.

Funding: Financial support was provided by the Slovenian Research Agency (research core funding No. P2-0393 and No. P1-0134).

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to technical reasons.

Acknowledgments: The Centre of Excellence for Integrated Approaches in Chemistry and Biology of Proteins (CIPKeBiP) is acknowledged for allowing us to use the ReactIR™ 45 FTIR instrument and accompanying equipment. The Center of Excellence in Nanoscience and Nanotechnology (CENN) is acknowledged for allowing us to use their FIB/SEM/EDS.

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

References

- Hagans, P.L.; Haas, C.M. Chromate Conversion Coatings. In *Surface Engineerings*; ASM Handbook; ASM International: Cleveland, OH, USA, 1994; Volume 5, pp. 405–411.
- Pokorny, P.; Tej, P.; Szlag, P. Chromate Conversion Coatings and Their Current Application. *Metalurgija* **2016**, *55*, 253–256.
- Zhao, J.; Xia, L.; Sehgal, A.; Lu, D.; McCreery, R.L.; Frankel, G.S. Effects of Chromate and Chromate Conversion Coatings on Corrosion of Aluminum Alloy 2024-T3. *Surf. Coat. Technol.* **2001**, *140*, 51–57. [CrossRef]
- Peltier, F.; Thierry, D. Review of Cr-Free Coatings for the Corrosion Protection of Aluminum Aerospace Alloys. *Coatings* **2022**, *12*, 518. [CrossRef]
- Gharbi, O.; Thomas, S.; Smith, C.; Biribilis, N. Chromate Replacement: What Does the Future Hold? *npj Mater. Degrad.* **2018**, *2*, 12. [CrossRef]
- ECHA. *European Chemicals Agency Chromium VI Compounds—ANNEX XVII TO REACH—Conditions of Restrictions*; ECHA: Helsinki, Finland, 2016.
- Twite, R.; Bierwagen, G. Review of Alternatives to Chromate for Corrosion Protection of Aluminum Aerospace Alloys. *Prog. Org. Coat.* **1998**, *33*, 91–100. [CrossRef]
- Carreira, A.F.; Pereira, A.M.; Vaz, E.P.; Cabral, A.M.; Ghidini, T.; Pigliaru, L.; Rohr, T. Alternative Corrosion Protection Pretreatments for Aluminum Alloys. *J. Coat. Technol. Res.* **2017**, *14*, 879–892. [CrossRef]
- Metroke, T.L.; Parkhill, R.L.; Knobbe, E.T. Passivation of Metal Alloys Using Sol–Gel-Derived Materials—A Review. *Prog. Org. Coat.* **2001**, *41*, 233–238. [CrossRef]
- Chou, T.P.; Chandrasekaran, C.; Cao, G.Z. Sol–Gel-Derived Hybrid Coatings for Corrosion Protection. *J. Sol–Gel Sci. Technol.* **2003**, *26*, 321–327. [CrossRef]
- Rodič, P.; Milošev, I.; Lekka, M.; Andreatta, F.; Fedrizzi, L. Corrosion Behaviour and Chemical Stability of Transparent Hybrid Sol–Gel Coatings Deposited on Aluminium in Acidic and Alkaline Solutions. *Prog. Org. Coat.* **2018**, *124*, 286–295. [CrossRef]
- Figueira, R.B. Hybrid Sol–Gel Coatings for Corrosion Mitigation: A Critical Review. *Polymers* **2020**, *12*, 689. [CrossRef]
- Castro, Y.; Aparicio, M.; Moreno, R.; Duran, A. Silica-Zirconia Alkali-Resistant Coatings by Sol–Gel Route. *J. Sol–Gel Sci. Technol.* **2005**, *35*, 41–50. [CrossRef]
- Bae, J.-Y.; Yang, S.; Jin, J.H.; Jung, K.; Kim, J.-S.; Bae, B.-S. Fabrication of Transparent Methacrylate Zirconium Siloxane Hybrid Materials Using Sol–Gel Synthesised Oligosiloxane Resin. *J. Sol–Gel Sci. Technol.* **2011**, *58*, 114–120. [CrossRef]
- Chuah, G.K.; Liu, S.H.; Jaenicke, S.; Li, J. High Surface Area Zirconia by Digestion of Zirconium Propoxide at Different pH. *Microporous Mesoporous Mater.* **2000**, *39*, 381–392. [CrossRef]
- Rodič, P.; Iskra, J.; Milošev, I. Study of a Sol–Gel Process in the Preparation of Hybrid Coatings for Corrosion Protection Using FTIR and ¹H NMR Methods. *J. Non-Cryst. Solids* **2014**, *396–397*, 25–35. [CrossRef]
- Rodič, P.; Mertelj, A.; Borovšak, M.; Benčan, A.; Mihailović, D.; Malič, B.; Milošev, I. Composition, Structure and Morphology of Hybrid Acrylate-Based Sol–Gel Coatings Containing Si and Zr Composed for Protective Applications. *Surf. Coat. Technol.* **2016**, *286*, 388–396. [CrossRef]
- Rodič, P.; Zanna, S.; Milošev, I.; Marcus, P. Degradation of Sol–Gel Acrylic Coatings Based on Si and Zr Investigated Using Electrochemical Impedance, Infrared and X-Ray Photoelectron Spectroscopies. *Front. Mater.* **2021**, *8*, 756447. [CrossRef]
- Varma, P.C.R.; Colreavy, J.; Cassidy, J.; Oubaha, M.; Duffy, B.; McDonagh, C. Effect of Organic Chelates on the Performance of Hybrid Sol–Gel Coated AA 2024-T3 Aluminium Alloys. *Prog. Org. Coat.* **2009**, *66*, 406–411. [CrossRef]
- Rodič, P.; Katić, J.; Korte, D.; Desimone, P.M.; Franko, M.; Ceré, S.M.; Metikoš-Huković, M.; Milošev, I. The Effect of Cerium Ions on the Structure, Porosity and Electrochemical Properties of Si/Zr-Based Hybrid Sol–Gel Coatings Deposited on Aluminum. *Metals* **2018**, *8*, 248. [CrossRef]
- Rodič, P.; Milošev, I. Electrochemical and Salt Spray Testing of Hybrid Coatings Based on Si and Zr Deposited on Aluminum and Its Alloys. *J. Electrochem. Soc.* **2015**, *162*, C592–C600. [CrossRef]
- Bard, A.J.; Stratmann, M.; Frankel, G.S. *Encyclopedia of Electrochemistry: Volume 4: Corrosion and Oxide Films*, 1st ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2003.
- Puurunen, R.L. Surface Chemistry of Atomic Layer Deposition: A Case Study for the Trimethylaluminum/Water Process. *J. Appl. Phys.* **2005**, *97*, 121301. [CrossRef]
- George, S.M. Atomic Layer Deposition: An Overview. *Chem. Rev.* **2010**, *110*, 111–131. [CrossRef]
- Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*; National Association of Corrosion Engineers: Houston, TX, USA; Brussels, Belgium, 1974.

26. Ishwara Bhat, J.; Alva, V.D.P. A Study of Aluminium Corrosion Inhibition in Acid Medium by an Antimicrobial Drug. *Trans. Indian Inst. Met.* **2011**, *64*, 377–384. [CrossRef]
27. Boukerche, I.; Djerad, S.; Benmansour, L.; Tifouti, L.; Saleh, K. Degradability of Aluminum in Acidic and Alkaline Solutions. *Corros. Sci.* **2014**, *78*, 343–352. [CrossRef]
28. Emregül, K.C.; Aksüt, A.A. The Behavior of Aluminum in Alkaline Media. *Corros. Sci.* **2000**, *42*, 2051–2067. [CrossRef]
29. Strehblow, H.-H.; Marcus, P. Mechanisms of Pitting Corrosion. In *Corrosion Mechanisms in Theory and Practice*, 2nd ed.; Marcus, P., Ed.; Marcel Dekker, Inc.: Basel, Switzerland, 2011; pp. 349–393.
30. Natishan, P.M.; O'Grady, W.E. Chloride Ion Interactions with Oxide-Covered Aluminum Leading to Pitting Corrosion: A Review. *J. Electrochem. Soc.* **2014**, *161*, C421. [CrossRef]
31. Paranjpe, A.; Gopinath, S.; Omstead, T.; Bubber, R. Atomic Layer Deposition of AlO_x for Thin Film Head Gap Applications. *J. Electrochem. Soc.* **2001**, *148*, G465–G471. [CrossRef]
32. Seshan, K. *Handbook of Thin Film Deposition*; William Andrew (Elsevier): Amsterdam, The Netherlands, 2012.
33. Van Hemmen, J.L.; Heil, S.B.S.; Klootwijk, J.H.; Roozeboom, F.; Hodson, C.J.; van de Sanden, M.C.M.; Kessels, W.M.M. Plasma and Thermal ALD of Al₂O₃ in a Commercial 200 Mm ALD Reactor. *J. Electrochem. Soc.* **2007**, *154*, G165–G169. [CrossRef]
34. Marin, E.; Lanzutti, A.; Guzman, L.; Fedrizzi, L. Corrosion Protection of AISI 316 Stainless Steel by ALD Alumina/Titania Nanometric Coatings. *J. Coat. Technol. Res.* **2011**, *8*, 655–659. [CrossRef]
35. Ahvenniemi, E.; Akbashev, A.R.; Ali, S.; Bechelany, M.; Berdova, M.; Boyadjiev, S.; Cameron, D.C.; Chen, R.; Chubarov, M.; Cremers, V.; et al. Review Article: Recommended Reading List of Early Publications on Atomic Layer Deposition—Outcome of the “Virtual Project on the History of ALD”. *J. Vac. Sci. Technol. A* **2016**, *35*, 010801. [CrossRef]
36. Spajić, I.; Rodić, P.; Šekularac, G.; Lekka, M.; Fedrizzi, L.; Milošev, I. The Effect of Surface Preparation on the Protective Properties of Al₂O₃ and HfO₂ Thin Films Deposited on Cp-Titanium by Atomic Layer Deposition. *Electrochim. Acta* **2021**, *366*, 137431. [CrossRef]
37. Pehkonen, S.O.; Yuan, S. Chapter 7—The Inorganic Film Coatings for Corrosion Protection. In *Interface Science and Technology*; Pehkonen, S.O., Yuan, S., Eds.; Tailored Thin Coatings for Corrosion Inhibition using a Molecular Approach; Elsevier: Amsterdam, The Netherlands, 2018; Volume 23, pp. 185–255.
38. Dameron, A.A.; Davidson, S.D.; Burton, B.B.; Carcia, P.F.; McLean, R.S.; George, S.M. Gas Diffusion Barriers on Polymers Using Multilayers Fabricated by Al₂O₃ and Rapid SiO₂ Atomic Layer Deposition. *J. Phys. Chem. C* **2008**, *112*, 4573–4580. [CrossRef]
39. Carcia, P.F.; McLean, R.S.; Reilly, M.H.; Groner, M.D.; George, S.M. Ca Test of Al₂O₃ Gas Diffusion Barriers Grown by Atomic Layer Deposition on Polymers. *Appl. Phys. Lett.* **2006**, *89*, 031915. [CrossRef]
40. Oliveira, M.P.; Silva, R.M.; Yasakau, K.A.; Bastos, A.; Kallip, S.; Zheludkevich, M.L.; Silva, R.F.; Ferreira, M.G.S. Atomic Layer Deposition of Nanometric Alumina for Corrosion Protection of Heterogeneous Metallic Surfaces—The Case of Aeronautical Grade Aluminium Alloy 2024-T3. *Corros. Sci.* **2022**, *209*, 110773. [CrossRef]
41. Marin, E.; Lanzutti, A.; Andreatta, F.; Lekka, M.; Guzman, L. Atomic Layer Deposition: State-of-the-Art and Research/Industrial Perspectives. *Corros. Rev.* **2011**, *29*, 191–208. [CrossRef]
42. Matero, R.; Ritala, M.; Leskelä, M.; Salo, T.; Aromaa, J.; Forsén, O. Atomic Layer Deposited Thin Films for Corrosion Protection. *J. Phys. IV* **1999**, *09*, Pr8-493–Pr8-499. [CrossRef]
43. Im, H.; Wittenberg, N.J.; Lindquist, N.C.; Oh, S.-H. Atomic Layer Deposition: A Versatile Technique for Plasmonics and Nanobiotechnology. *J. Mater. Res.* **2012**, *27*, 663–671. [CrossRef]
44. King, D.M.; Spencer, J.A.; Liang, X.; Hakim, L.F.; Weimer, A.W. Atomic Layer Deposition on Particles Using a Fluidized Bed Reactor with in Situ Mass Spectrometry. *Surf. Coat. Technol.* **2007**, *201*, 9163–9171. [CrossRef]
45. Groner, M.D.; Fabreguette, F.H.; Elam, J.W.; George, S.M. Low-Temperature Al₂O₃ Atomic Layer Deposition. *Chem. Mater.* **2004**, *16*, 639–645. [CrossRef]
46. Choi, H.; Shin, S.; Jeon, H.; Choi, Y.; Kim, J.; Kim, S.; Chung, S.C.; Oh, K. Fast Spatial Atomic Layer Deposition of Al₂O₃ at Low Temperature (<100 °C) as a Gas Permeation Barrier for Flexible Organic Light-Emitting Diode Displays. *J. Vac. Sci. Technol. A* **2016**, *34*, 01A121. [CrossRef]
47. Potts, S.E.; Schmalz, L.; Fenker, M.; Díaz, B.; Światowska, J.; Maurice, V.; Seyeux, A.; Marcus, P.; Radnóczy, G.; Tóth, L. Ultra-Thin Aluminium Oxide Films Deposited by Plasma-Enhanced Atomic Layer Deposition for Corrosion Protection. *J. Electrochem. Soc.* **2011**, *158*, C132–C138. [CrossRef]
48. Díaz, B.; Härkönen, E.; Światowska, J.; Maurice, V.; Seyeux, A.; Marcus, P.; Ritala, M. Low-Temperature Atomic Layer Deposition of Al₂O₃ Thin Coatings for Corrosion Protection of Steel: Surface and Electrochemical Analysis. *Corros. Sci.* **2011**, *53*, 2168–2175. [CrossRef]
49. Díaz, B.; Härkönen, E.; Maurice, V.; Światowska, J.; Seyeux, A.; Ritala, M.; Marcus, P. Failure Mechanism of Thin Al₂O₃ Coatings Grown by Atomic Layer Deposition for Corrosion Protection of Carbon Steel. *Electrochim. Acta* **2011**, *56*, 9609–9618. [CrossRef]
50. Marin, E.; Lanzutti, A.; Paussa, L.; Guzman, L.; Fedrizzi, L. Long Term Performance of Atomic Layer Deposition Coatings for Corrosion Protection of Stainless Steel. *Mater. Corros.* **2015**, *66*, 907–914. [CrossRef]
51. Abdulagatov, A.I.; Yan, Y.; Cooper, J.R.; Zhang, Y.; Gibbs, Z.M.; Cavanagh, A.S.; Yang, R.G.; Lee, Y.C.; George, S.M. Al₂O₃ and TiO₂ Atomic Layer Deposition on Copper for Water Corrosion Resistance. *ACS Appl. Mater. Interfaces* **2011**, *3*, 4593–4601. [CrossRef] [PubMed]

52. Chang, M.L.; Wang, L.C.; Lin, H.C.; Chen, M.J.; Lin, K.M. Investigation of Defects in Ultra-Thin Al₂O₃ Films Deposited on Pure Copper by the Atomic Layer Deposition Technique. *Appl. Surf. Sci.* **2015**, *359*, 533–542. [CrossRef]
53. Härkönen, E.; Kolev, I.; Díaz, B.; Światowska, J.; Maurice, V.; Seyeux, A.; Marcus, P.; Fenker, M.; Toth, L.; Radnoczi, G.; et al. Sealing of Hard CrN and DLC Coatings with Atomic Layer Deposition. *ACS Appl. Mater. Interfaces* **2014**, *6*, 1893–1901. [CrossRef] [PubMed]
54. Merisalu, M.; Aarik, L.; Kozlova, J.; Mändar, H.; Tarre, A.; Sammelselg, V. Effective Corrosion Protection of Aluminum Alloy AA2024-T3 with Novel Thin Nanostructured Oxide Coating. *Surf. Coat. Technol.* **2021**, *411*, 126993. [CrossRef]
55. Parsons, G.N.; Atanasov, S.E.; Dandley, E.C.; Devine, C.K.; Gong, B.; Jur, J.S.; Lee, K.; Oldham, C.J.; Peng, Q.; Spagnola, J.C.; et al. Mechanisms and Reactions during Atomic Layer Deposition on Polymers. *Coord. Chem. Rev.* **2013**, *257*, 3323–3331. [CrossRef]
56. Guo, H.C.; Ye, E.; Li, Z.; Han, M.-Y.; Loh, X.J. Recent Progress of Atomic Layer Deposition on Polymeric Materials. *Mat. Sci. Eng. C* **2017**, *70*, 1182–1191. [CrossRef]
57. Wang, H.; Liu, Y.; Liu, H.; Chen, Z.; Xiong, P.; Xu, X.; Chen, F.; Li, K.; Duan, Y. Effect of Various Oxidants on Reaction Mechanisms, Self-Limiting Natures and Structural Characteristics of Al₂O₃ Films Grown by Atomic Layer Deposition. *Adv. Mater. Interfaces* **2018**, *5*, 1701248. [CrossRef]
58. Matero, R.; Rahtu, A.; Ritala, M.; Leskelä, M.; Sajavaara, T. Effect of Water Dose on the Atomic Layer Deposition Rate of Oxide Thin Films. *Thin Solid Film.* **2000**, *368*, 1–7. [CrossRef]
59. Lee, D.H.; Condrate, R.A. An FTIR Spectral Investigation of the Structural Species Found on Alumina Surfaces. *Mater. Lett.* **1995**, *23*, 241–246. [CrossRef]
60. Liu, C.; Shih, K.; Gao, Y.; Li, F.; Wei, L. Dechlorinating Transformation of Propachlor through Nucleophilic Substitution by Dithionite on the Surface of Alumina. *J. Soils Sediments* **2012**, *12*, 724–733. [CrossRef]
61. Goldstein, D.N.; McCormick, J.A.; George, S.M. Al₂O₃ Atomic Layer Deposition with Trimethylaluminum and Ozone Studied by in Situ Transmission FTIR Spectroscopy and Quadrupole Mass Spectrometry. *J. Phys. Chem. C* **2008**, *112*, 19530–19539. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Influence of pH on the Inhibiting Characteristics of Cresol Red Incorporated in Chitosan Coatings on Zinc

Regina Buier¹, Gabriella Stefania Szabó², Gabriel Katona², Norbert Muntean² and Liana Maria Muresan^{1,*}

¹ Department of Chemical Engineering, “Babes-Bolyai” University Cluj-Napoca, 400028 Cluj-Napoca, Romania; regina.buier@ubbcluj.ro

² Department of Chemistry and Chemical Engineering Hungarian Line, “Babes-Bolyai” University Cluj-Napoca, 400028 Cluj-Napoca, Romania; gabriella.szabo@ubbcluj.ro (G.S.S.); gabriel.katona@ubbcluj.ro (G.K.); norbert.muntean@ubbcluj.ro (N.M.)

* Correspondence: liana.muresan@ubbcluj.ro

Abstract: The present work focuses on the investigation of protective coatings produced on zinc from chitosan (Chit) and an anionic dye, namely cresol red. Cresol red (CR) fulfills the basic requirements to be used as a corrosion inhibitor because it possesses a relatively high molecular weight and includes in its structure oxygen and sulfur atoms as well as aromatic rings. Moreover, it is an anionic compound that can interact with positively charged chitosan to produce reinforced coatings for zinc anti-corrosion protection. The influence of cresol red as a possible corrosion inhibitor for zinc substrates was investigated either in solution or incorporated in Chit coatings. Two preparation methods for the coatings were used: (i) Chit coating impregnation by immersion in the CR solution after Chit deposition on Zn, and (ii) chitosan mixing with the CR solution before applying the dip-coating technique. Potentiodynamic polarization curves were used to determine the kinetic parameters of the corrosion process. Long-term measurements were carried out in wet/dry cyclic conditions by using electrochemical impedance spectroscopy. EIS measurements recorded in 0.2 g/L Na₂SO₄ at pH = 7 show an important increase in the impedance of the coatings occurring from the first until the fifty-fifth day in a row, in dry–wet cycles. This increase is due to the beneficial effect of CR incorporated in Chitosan and could be, at least partially, related to a consolidation of the Chit coating structure in the presence of CR by crosslinking between Chit and CR molecules. The structure of the coatings was studied, and the interactions between chitosan and cresol red were put into evidence by using FT-IR spectroscopy. Adhesion and wettability measurements were also carried out. The adhesion of Chit incorporating CR on Zn was better than that on glass substrates and reached ~99.99%, suggesting a better affinity of the chitosan coating towards the Zn substrate due to the existence of ZnO on the substrate surface. All the results show that CR could be used on zinc as a corrosion inhibitor incorporated in chitosan at basic pHs, but without taking advantage of its pH-indicating properties, which are lost due to the interactions occurring between the positively charged biopolymer and the negatively charged dye molecule. The preparation method of Chit coating impregnation with CR by immersion in the solution after deposition on Zn led to poorer results than the method in which chitosan was previously mixed with CR before applying the dip-coating technique.

Keywords: chitosan; cresol red; electrochemical methods; pH effect; zinc corrosion

1. Introduction

Zinc is a very important metal used in a wide range of applications by various industries, including civil engineering, constructions, etc., where it is often chosen as a sacrificial coating to protect iron and steel against corrosion. As zinc is an active metal that corrodes very quickly, its anti-corrosion protection is of real interest. In this regard, one commonly used method involves corrosion inhibitors, which minimize the corrosive attack of the environment and prolong the lifetime of zinc coatings.

A large number of chemical substances, especially organic, can be used as corrosion inhibitors for zinc, especially compounds containing heteroatoms such as nitrogen, oxygen, or sulfur [1,2], aromatic rings [3], or triple bonds [4]. Natural compounds were also reported [5,6], even if their efficiency is not as good as that of synthetic compounds.

In an attempt to improve the corrosion resistance of zinc, coating its surface with protective films of different natures is also a promising solution. Inorganic compounds [7–10], but also synthetic [11,12] and natural polymers [13–16] are used to modify the zinc surface by using different techniques such as sol–gel [7–9], electrodeposition [17], layer-by-layer deposition [18], electropolymerization [19], etc.

Among environmentally friendly polymers, chitosan (Chit) is a promising choice due to its low cost, lack of toxicity, and versatility. Chitosan (Chit) is a water-soluble, partially deacetylated derivate of chitin that can be easily applied to metal substrates as a protective coating [20] or used as a matrix for various composite materials [21–23]. Although there are countless arguments in favor of the production of chitosan coatings, such as thermal stability, chemical resistance, bioavailability, biocompatibility, and biodegradability, due to their loose structure, they can easily lose their barrier properties. This disadvantage can be eliminated through functionalization and the incorporation of various additives. Through its positive charge, chitosan can interact with anionic species, resulting in an efficient ionic crosslinking effect [16], leading to consolidated coatings with enhanced mechanical and insulating properties.

In our previous work [16], chitosan coatings crosslinked with indigo carmine (IC) were prepared on zinc by the dip-coating technique. The addition of IC to Chit coatings was proven to be useful in terms of active corrosion protection, with the Chit coatings acting as a reservoir for the corrosion inhibitor. The corrosion current density decreased by one order of magnitude, suggesting an ionic crosslinking of Chit.

Unfortunately, as a result of external factors (e.g., heat, light, moisture, and aggressive skin), the protective effect of the coating deteriorates. For this reason, it has become important to develop functions that can be used to monitor the deterioration of coatings. This can be imagined if the coating responds to the external factors that cause the deterioration and its result becomes noticeable. There have already been some solutions for this. Fluorescence detection of Fe^{3+} [24] and Cu^{2+} ions formed during corrosion through complex formation [25]. The detection of OH^- ions produced during corrosion with pH indicators can also be a solution [26].

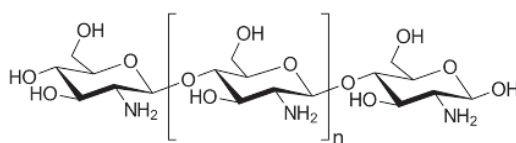
In this context, the present work focuses on the investigation of coatings produced on zinc from chitosan and another anionic dye, namely cresol red. Cresol red (CR) has a high molecular weight and includes in its structure oxygen and sulfur atoms as well as aromatic rings; these properties recommend it as a possible corrosion inhibitor. Moreover, it is an anionic compound that could interact with positively charged chitosan to produce reinforced coatings for zinc anti-corrosion protection. The influence of cresol red embedded in chitosan thin layers as a possible corrosion inhibitor for zinc substrates was investigated in wet/dry cyclic conditions. Moreover, as CR is a pH indicator in solution, early detection of corrosion processes in its presence would be a solution to tackle corrosion in a cost-effective way. Chitosan microspheres loaded with organic compounds having pH-indicating ability have been reported in the literature [27], but it is for the first time that Cresol red incorporated in a Chitosan coating deposited on zinc was investigated from both its inhibitive and pH sensing points of view.

For this purpose, the corrosion behavior of cresol red-loaded chitosan coatings on zinc prepared by dip-coating was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The interactions between chitosan and cresol red were put into evidence by using FT-IR spectroscopy. Adhesion and wettability measurements were also carried out.

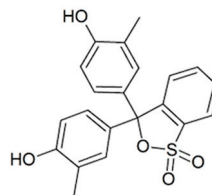
2. Experimental

2.1. Materials and Methods

Both zinc and glass plates were used as substrates. The zinc plates were obtained from AltDepozit (99% Zn) and the glass microscope slides from Biozyme. Medium-molecular-weight chitosan was purchased from Aldrich, Romania, cresol red from Chinoin Budapest, Hungary, 99.8% ethanol isopropanol from Nordic Chemicals, Romania and 99% Na₂SO₄ from Merck, Rahway, NJ, USA. In addition, 96% sulfuric acid was provided by Reactivul, and 99% NaOH was from Merck, Rahway, NJ, USA. All chemicals were of analytical grade and used without any purification steps.



Chitosan



Cresol Red

2.2. Coating Preparation

Before the coating preparation, the glass microscope substrates were 2 × 5 min ultrasonicated using an aqueous detergent solution, cleaned with a 10% V/V H₂SO₄ solution, isopropanol, and distilled water.

The zinc plates were polished with emery paper (different roughness: 1500, 2000, 2500, and 5000) and 2 × 5 min ultrasonicated in distilled water. Finally, 0.1 M HCl and isopropanol solutions were used to clean the surface of any remaining zinc oxide.

Two preparation methods for the coatings were used: (i) Chit coating impregnation by immersion in the CR solution after Chit deposition on Zn, and (ii) chitosan mixing with the CR solution before applying the dip-coating technique. Here, 1 w/w% chitosan solution prepared in 1 w/w% acetic acid solution was used, and the solution was prepared from chitosan powder by mixing until all the chitosan was totally dissolved and left overnight.

Method (i): chitosan coatings deposited on glass by dip-coating from chitosan solution prepared as described above were impregnated with cresol red by immersion in aqueous cresol red solution with different concentrations (10^{−5}, 5 × 10^{−4}, 10^{−4}, 10^{−3}, 10^{−2} M). The immersion time was 10 min.

Method (ii): the cresol red powder was added to the chitosan solution in different concentrations (10^{−5}, 5 × 10^{−4}, 10^{−4}, 10^{−3}, 10^{−2} M) and ultrasonicated for 24 h, until it totally dissolved. The coatings were prepared by the dip-coating method from the previously prepared cresol red containing chitosan solution with a withdrawal speed of 5 cm/min. The apparatus we used was a home-made dip coater machine. The coated samples were left to dry for 24 h at room temperature.

After that, the samples were left to dry, examined by sight, and then examined by optical spectroscopy.

2.3. Optical Characterization

The optical properties of different chitosan coatings deposited on glass substrates were determined by UV-VIS spectroscopy. For the measurements, a homemade spectrophotometer was used. The device contains a light source from a Spekol 20 spectrophotometer. The instrument's light beam was coupled to a homemade sample holder through an optical cable. The transmitted light was also sent to the spectrometer using another optical cable. An Ocean Optics HR 4000CG UV-VIS-NIR microspectrometer (Dunedin, FL, USA) was used to acquire the spectra. The spectrometer has the following characteristic parameters: a measurement range of 200–1100 nm, an entrance slit of 50 μm, a Toshiba CCD detector, a pixel count of 3648, and a spectral resolution of approximately 1.5 nm. The Spectra

Suite (Ocean Optics) program was used for processing the acquired data, enabling baseline correction, signal averaging, and various integration times. As a reference, we used an uncoated glass sample. The integration time was constant at 70 s.

2.4. Wettability Measurements

Wettability can be determined by measurements of the contact angle and the interfacial tension [28,29]. The wettability of cresol red-containing coatings was measured in comparison with native chitosan coatings by a sessile drop method. A sessile drop method based on the European Pharmacopoeia [30] was used to determine the contact angle using a drop of 0.2 g/L aqueous Na_2SO_4 solution, used in electrochemical measurements too, with a volume of 20 μL . Measurements were carried out in a closed space saturated with the vapor of the studied electrolyte. In each case, the contact angle evaluation was followed by taking pictures every minute for 20 min. To determine the contact angle evaluation, we used a specific measuring program.

2.5. Adhesion and Coating Thickness Measurements

For determining the adhesion between the substrate and the coating, the tape peel method was used with the Elcometer Cross Hatch Adhesion Tester. This is a qualitative mechanical method of determination. For the measurements, a special cutter with multiple preset blades is needed to make sure the incisions are properly spaced and parallel. The coatings were scratched by dividing them into 49 equal cubes. After the tape has been applied and pulled off, the cut area is then inspected and rated. The adhesion of thin films is influenced by a large number of parameters; some of these parameters are the substrate/coating materials, the substrate preparation, or the coating method.

The thickness of the coatings was measured by the TROTEC BB25 instrument, (GmbH and Co. KG Deutschland), a layer measuring instrument that works according to magnetic induction or turbulent flow principles for determining the coating thickness on magnetic and non-ferromagnetic metals.

2.6. FT-IR Analysis

For FT-IR analysis, chitosan and cresol red powder were used. The cresol red containing chitosan sol was prepared, evenly distributed on a clean Petri dish, and left to dry for 2 weeks, then scraped off the glass and powdered in an agate mortar. Infrared spectra for chitosan, cresol red, and chitosan containing cresol red were recorded on a Jasco FT/IR-6800 type A Spectrometer.

2.7. Electrochemical Measurements

Electrochemical measurements were carried out using a PARSTAT-2273 single channel potentiostat (Princeton Applied Research, UK) in a three-electrode cell containing the zinc substrates (2 cm^2 surface area) as a working electrode, a platinum electrode as a counter, and an Ag/AgCl , KCl sat reference electrode connected to the potentiostat. All experiments were made at room temperature (25 $^\circ\text{C}$) with an adjusted pH.

2.7.1. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy measurements were made for samples in two different ways: firstly, the samples were kept continuously in an electrolyte solution between the measurements (wet method), and secondly, the samples were taken out of the corrosive solution after every measurement and the solution was wiped off the sample (wet-dry method), left overnight in laboratory circumstances.

EIS measurements were conducted in a 0.2 g/L aqueous Na_2SO_4 solution at four different pH values (pH = 5, 7, 8, and 9). The frequency interval of the measurements was 10^{-2} Hz– 10^4 Hz at open circuit potential (OCP) measured for 60 min before EIS measurements. For pH studies, the pH of the electrolyte was adjusted with NaOH and H_2SO_4 to the corresponding levels.

2.7.2. Polarization Curves

Potentiodynamic polarization curves were recorded with a scan rate of 0.166 mV/s in a potential range of $OCP \pm 20$ mV vs. Ag/AgCl, KCl_{sat} (to determine the polarization resistance) and $OCP \pm 200$ mV vs. Ag/AgCl, KCl_{sat} (to determine the kinetic parameters with the Tafel method).

Corrosion current densities (i_{corr}) were determined using the Stern–Geary equation [31]:

$$i_{corr} = \frac{b_a \times b_c}{2.3R_p \times (b_a + b_c)} \quad (1)$$

where b_a and b_c are the Tafel coefficients determined from the polarization curves, and R_p is the polarization resistance determined from the Nyquist impedance diagrams.

The inhibition efficiency of the coatings was determined using the following equation:

$$IE = 100 \times \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \quad (2)$$

where i_{corr}^0 is the value of the corrosion current density of the uncoated Zn sample, while i_{corr} is the corrosion current density of coated systems.

3. Results and Discussion

3.1. Chitosan Coatings Impregnated with Cresol Red

Both glass and zinc substrates were used to investigate CR incorporation in the chitosan layer. As expected, the visual examination of the glass samples coated with chitosan and impregnated with CR by immersion put in evidence different color intensities, depending on the CR solution concentration (Figure 1a), proving the presence of the compound in the chitosan layer in an increasing amount, proportional to solution concentration. The impregnation with 10^{-5} M was invisible to the naked eye and is not shown in Figure 1. The incorporation of CR in the Chit coatings deposited on zinc is less visible than on glass (Figure 1b). Nevertheless, a concentration dependence was also noticed, reflecting the impregnation of the chitosan coatings with CR.

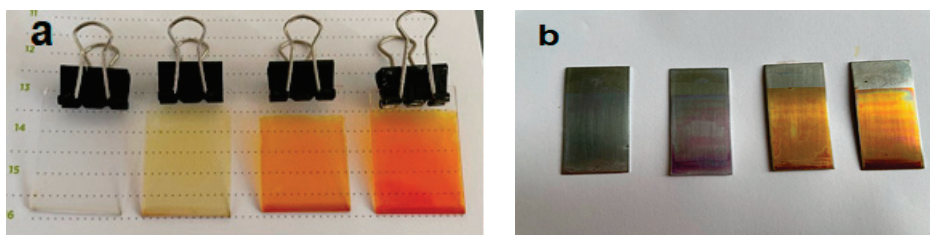


Figure 1. Chitosan coatings on glass (a) and on zinc substrates (b) impregnated with 0, 10^{-4} M, 10^{-3} M, and 10^{-2} M cresol red solutions (from left to right, respectively) for 10 min.

3.2. Optical Characterization

In order to establish the proportionality between the CR concentration and the color intensity of the coatings, three glass samples on which the color of CR was visible to the naked eye were analyzed with UV-Vis spectroscopy.

It can be observed from Figure 2 that, for cresol red, the spectrum exhibits two peaks, one larger at 442.01 nm and one smaller at 590.16 nm. The literature data [32] mention a peak appearance in the visible region of the cresol red spectrum in solution: at 430 nm at pH 4.5 and at 573 nm at pH 12. It can therefore be said that the maximum absorption of cresol red is influenced by the pH of the medium. The differences between the literature data reported for cresol red and those from our experiments could be attributed to the different pHs used and to the fact that in the first case, the values correspond to CR in solution, while in the later case, the values were recorded on chitosan coatings deposited

on glass sheets. The contribution of the glass sheets used in our experiments should also be taken into consideration.

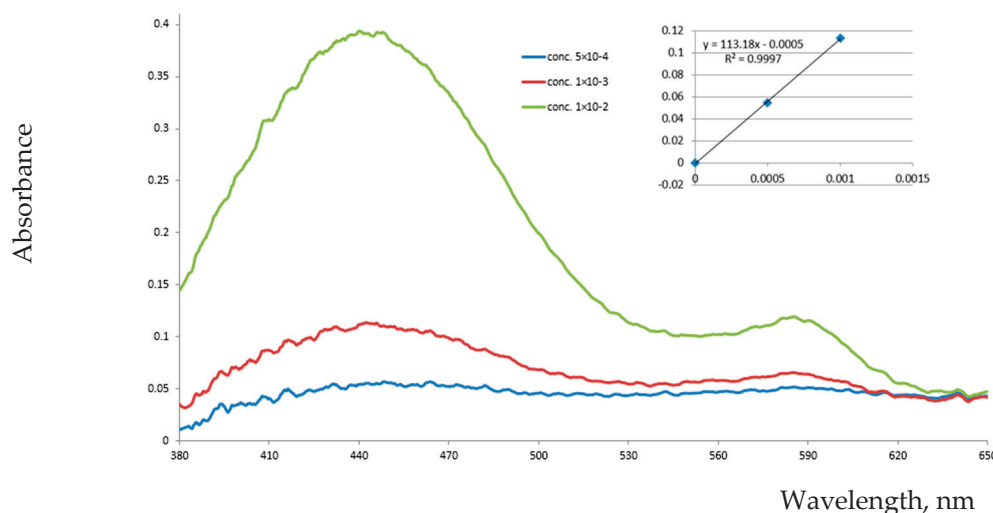


Figure 2. Absorbance spectra for samples of chitosan on glass substrates impregnated with three concentrations of cresol red. Inset: calibration curve for absorbances measured at 442 nm.

Moreover, the small second peak that appears is due either to the fact that the pH distribution within the chitosan-containing CR layer is not uniform or to the coexistence of the protonated form and the unprotonated one. Nevertheless, a linear dependence of the absorbance on the CR concentration in the layer is observed, ($y = 113.18x - 0.0005$, $R^2 = 0.9997$) proving its incorporation in chitosan (see inset in Figure 2).

3.3. FT-IR Measurements

Taking into account that CR is an anionic compound that could interact with positively charged chitosan, FT-IR spectroscopy was used to provide evidence of possible interactions between the two components of the coatings.

As it can be observed from Figure 3, the chitosan spectrum showed the characteristic $3500\text{--}3300\text{ cm}^{-1}$ band caused by the hydroxyl and amino groups' O--H and N--H stretchings. Bands at 2920 and 2870 cm^{-1} resulted from C--H stretching. Bands for C = O stretching at 1646 cm^{-1} (amide I), N--H bending at 1601 cm^{-1} (amide II), and C--N stretching (amide III) at 1323 cm^{-1} were visible. The peaks at 1423 , 1385 , and 1073 cm^{-1} are CH_2 , CH_3 bending, and C--O stretching signals. For the chitosan spectra, the peaks seem to be weak, but when it is alone, the spectra are similar to those found in the literature [32,33].

The Chit/CR_ 10^{-3} M spectrum showed strong OH stretches at about 3250 cm^{-1} in chitosan, which decreased highly because an etheric bond was formed between cresol and chitosan.

The C-O-C stretching from ether shows up in the region 1050 cm^{-1} . The chitosan-cresol complex showed a band at 1450 cm^{-1} for C-H bendings and C-C bands at 1500 cm^{-1} from chitosan. Also, C-H bendings from the aromatic ring are present at 1050 cm^{-1} .

As it will be demonstrated by the electrochemical measurements, the interactions between Chit and CR could explain the behavior of Chit-CR coatings in zinc anti-corrosion protection.

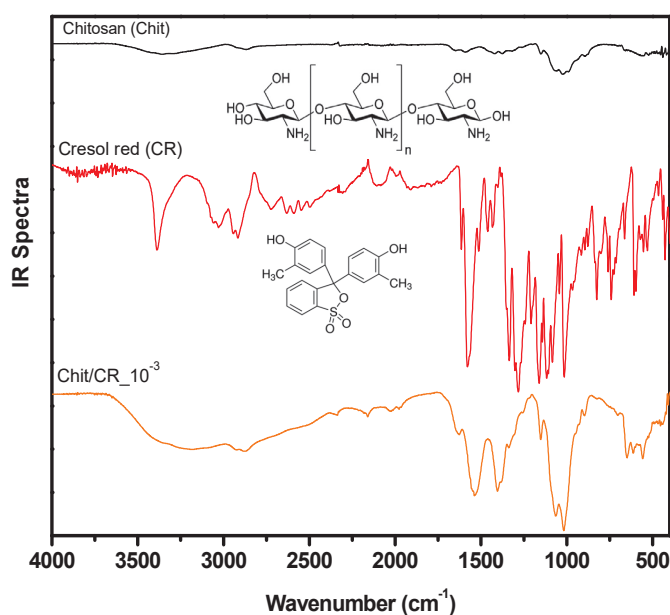


Figure 3. FT-IR spectra recorded for chitosan, cresol red, and Chit/CR_10^{−3} samples.

3.4. Influence of pH

It is well known that in aqueous solutions, CR changes color from yellow (in acidic media) to magenta (in basic solutions). In order to verify if CR still behaves as a pH indicator when it is incorporated in chitosan layers, glass samples covered with chitosan loaded with Cresol red 10^{−3} M were contacted with Na₂SO₄ solutions having different pH values: 5 (left) and 8.2 (right). Chit/CR_10^{−3} M in contact with a Na₂SO₄ solution of pH 5 changed to yellow, and the sample at pH = 8.2 showed a specific dark pink color (Figure 4).

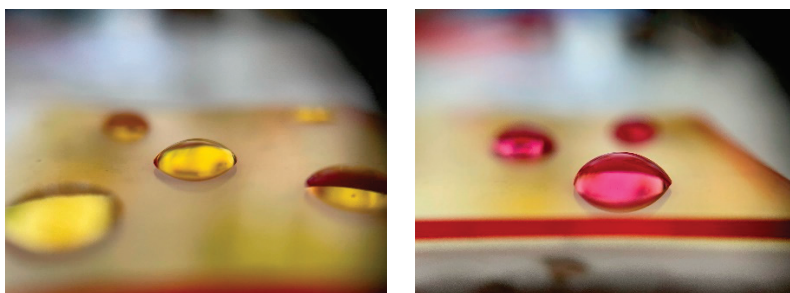


Figure 4. Color change of the chitosan/CR_10^{−3} g/L coatings at two different pH values, pH = 5 (left), pH = 8.2 (right), on glass substrates.

The color change in solutions as a function of pH is due to reactions (Figure 5).

Unfortunately, the color change of chitosan coatings incorporating CR deposited on zinc is less visible. Besides the dark color of the zinc substrate, it is possible that the incorporated CR does react with a zinc surface covered with a thin layer of ZnO, so that the functionalities acting in pH indication are blocked and the color change is no longer visible. ZnO interaction with CR was reported in the literature [33], as a function of pH. At acid pHs (<7), ZnO and CR molecules are both positively charged, so repulsion occurs. At neutral pHs, (7–8.2) ZnO is still positive, while the CR molecule is neutral or negatively charged, which results in a weak interaction between the two compounds. Finally, at strong basic pHs (>8.2), ZnO becomes negatively charged, which results in a strong repulsion between ZnO and CR.

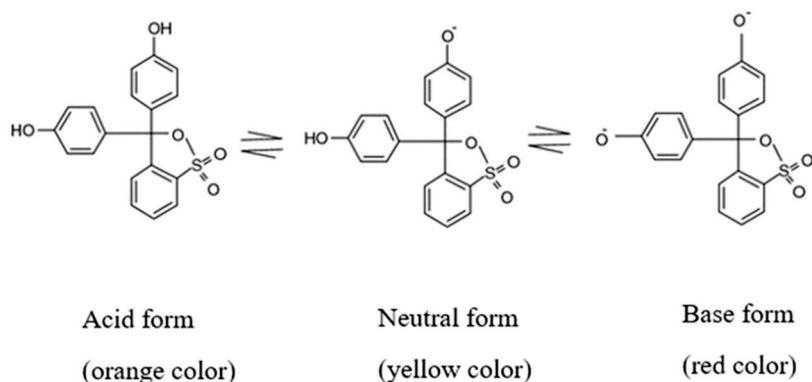


Figure 5. Structure of cresol red as a function of pH.

3.5. Electrochemical Measurements

3.5.1. Polarization Curves

To put in evidence if there is any effect of CR on zinc corrosion, potentiodynamic polarization curves in the absence and in the presence of different concentrations of CR-containing solutions were recorded on bare Zn. The semi-logarithmic polarization curves of Chit and Chit/CR-coated Zn samples are presented in Figure 6 and their characteristics in Table 1.

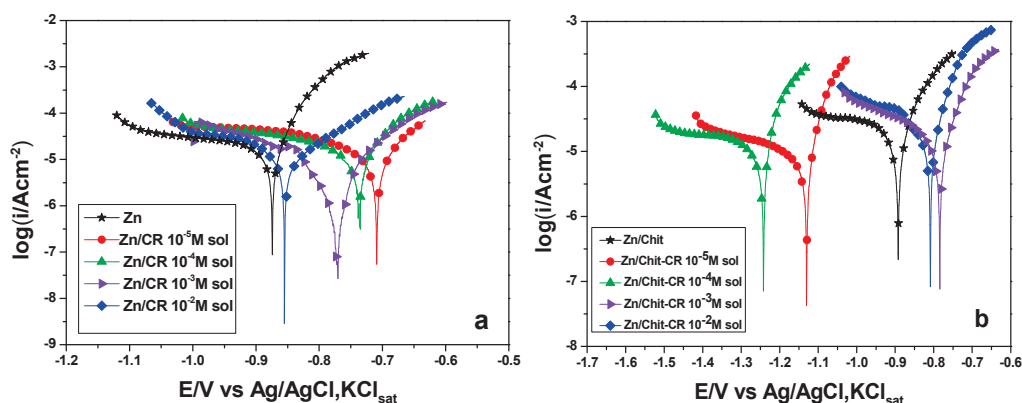


Figure 6. Semi-logarithmic polarization curves measured on Zn (a) and on Zn/Chit (b) in Na₂SO₄ solution containing different concentrations of cresol red. Experimental conditions: support electrolyte, 0.2 g/L aqueous Na₂SO₄ (pH = 7); scan rate, 0.166 mV/s; OCP, 60 min.

As it can be observed from Figure 6a, in solution, CR has a beneficial effect on Zn corrosion resistance, as even at small concentrations of the organic compound, a serious decrease in the corrosion current density is noticed, from 20.67 $\mu\text{A}/\text{Acm}^{-2}$ for bare Zn to 4.78 $\mu\text{A}/\text{Acm}^{-2}$ in the presence of 10⁻³ M CR (Table 1).

Encouraged by this result, potentiodynamic polarization curves were recorded for Zn coated with chitosan in CR solutions of different concentrations (Zn/Chit_{CR} 10^{-x} sol). The results are depicted in Figure 6b, and the kinetic parameters, including the current density (i_{corr}) and the corrosion potential (E_{corr}), are presented in Table 1.

When Cresol Red was added to the solution, the E_{corr} of Zn was shifted toward positive values, suggesting that an ennoblement of the surface took place. Surprisingly, even if all values of i_{corr} are smaller in the presence of CR in solution for both Zn and Zn/Chit than in its absence, it seems that the Chit layer does not offer convenient protection to Zn when CR is present in solution. Thus, the CR inhibiting effect is less effective when a Chit film is interposed between the solution and the zinc substrate, suggesting that the CR inhibiting effect is somewhat blocked after its immobilization in Chit. It should also be mentioned that high concentrations of CR are not beneficial, which is not surprising, as

for any specific inhibitor in any given medium there is an optimal concentration (in this case, 10^{-3} M).

Table 1. Kinetic parameters of the corrosion process of Zn and of Zn/Chit in solutions of different concentrations (10^{-5} M to 10^{-1} M) at pH 7.

Sample	E_{corr} (mV vs. RE)	i_{corr} (μAcm^{-2})	b_a mV/dec	$/b_c/$ (mV/dec)	IE (%)
Zn					
Zn	−942.5	20.67	112	389	-
Zn/CR 10^{-5} M sol	−708.9	18.49	99	622	10.54
Zn/CR 10^{-4} M sol	−736.9	15.99	73	301	22.64
Zn/CR 10^{-3} M sol	−773	4.78	82	191	76.87
Zn/CR 10^{-2} M sol	−855.4	9.44	141	194	54.32
Zn/Chit					
Zn/Chit	−892.7	22.93	110	745	-
Zn/Chit_CR 10^{-5} M sol	−1131.8	18.41	139	439	19.71
Zn/Chit_CR 10^{-4} M sol	−1242.5	12.94	134	403	43.56
Zn/Chit_CR 10^{-3} M sol	−784.4	11.25	70	208	50.93
Zn/Chit_CR 10^{-2} M sol	−808.8	18.17	67	213	20.75

In an attempt to improve the protective effect of the biopolymer layer in the presence of CR, another preparation method for the coatings was used. The chitosan solution was prepared, and cresol red was added in the same concentration previously mentioned. This mixture was ultrasonicated until a uniform solution was received, then deposited on Zn by the dip-coating technique. The zinc samples coated with this type of layer were named Zn/Chit_CR_ 10^{-x} M coat (10^{-x} = CR solution concentration). Next, corrosion tests of the coated zinc samples were carried out in Na_2SO_4 solutions of various pHs, with the results being presented in Figure 7 and Table 2.

Table 2. Kinetic parameters of the corrosion process on Zn, Zn/Chit, and Zn/Chit/CR_ 10^{-3} M coat samples at different pH values. Electrolyte: Na_2SO_4 with pH 5, 7, 8, and 9, respectively.

pH	Sample	E_{corr} mV vs. RE	i_{corr} μAcm^{-2}	$/b_c/$ mV/dec	b_a mV/dec	IE (%)
5	Zn	−1025	38.89	105	140	-
	Zn/Chit	−921	25.53	-	79	34.35
	Zn/Chit_CR_ 10^{-3} M coat	−917	17.10	926	73	56.02
7	Zn	−942	20.67	112	106	-
	Zn/Chit	−856	19.00	110	745	8.07
	Zn/Chit_CR_ 10^{-3} M coat	−922	11.17	59	476	45.96
8	Zn	−887	32.35	642	88	-
	Zn/Chit	−928	14.03	-	59	56.63
	Zn/Chit_CR_ 10^{-3} M coat	−784	8.95	804	63	72.98
9	Zn	−1219	47.75	31	111	-
	Zn/Chit	−880	9.13	-	63	80.87
	Zn/Chit_CR_ 10^{-3} M coat	−730	7.21	424	26	84.90

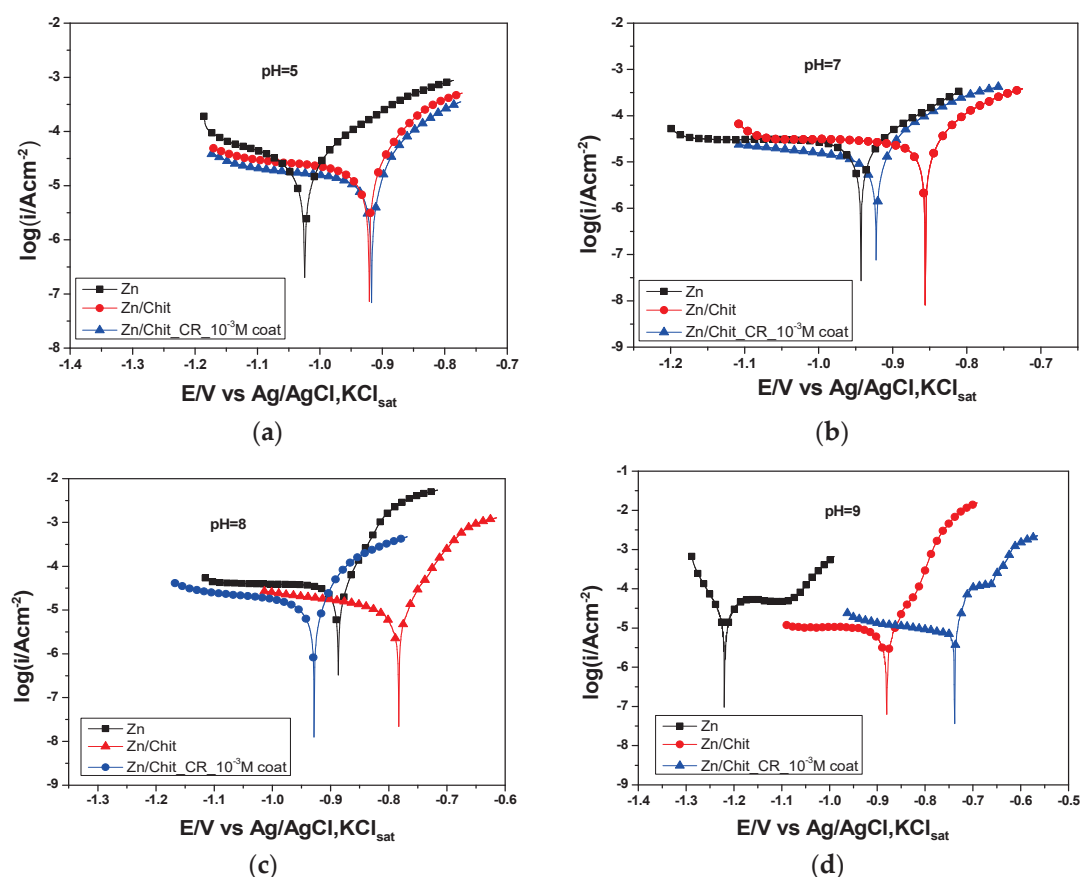
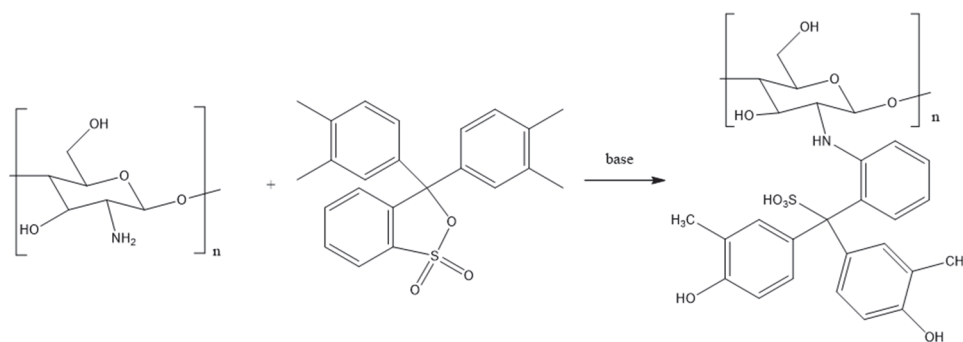


Figure 7. Semi-logarithmic polarization curves of Zn, Zn/Chit, and Zn/Chit_CR_10^{−3} M coat. Experimental conditions: 0.2 g/L aqueous Na₂SO₄ solution at pH = 5 (a), pH = 7 (b), pH = 8 (c), and pH = 9 (d); scan rate, 0.166 mV/s; OCP, 60 min.

Similar to the case when CR was present in the solution, the E_{corr} values of Zn samples coated with CR incorporated in Chit are shifted toward positive values, suggesting that an ennoblement of the surface takes place. The inhibiting effect of CR is more pronounced in the anodic branches of the polarization curves of the samples (Figure 7), suggesting that CR acts more as an anodic inhibitor. Looking at the results from Figure 7 and Table 2, it can be concluded that CR diminishes the corrosion current density at all pHs, but basic pHs seem to be more favorable than neutral or acidic ones, where chitosan is vulnerable and can be destroyed. At pH 9, CR decreases the corrosion current density of Zn and of Zn/Chit by one order of magnitude, and at a concentration of 10^{−3} M, it acts as an efficient corrosion inhibitor. A significant positive shift in the corrosion potential is also observed, especially at pH 9, suggesting an ennoblement of the coating in the presence of Chit and CR.

The explanation of the coating behavior at this pH could be the interactions taking place between the Zn surface (naturally covered with ZnO) and CR, whose electrical charge changes as a function of pH. Thus, at basic pHs (>8.2), ZnO is negatively charged, which results in a strong repulsion between ZnO and CR, which is also negative. The intercalation of the Chit layer between ZnO and the dianionic CR molecules reduces the repulsion between them, and at the same time, the Chitosan protective layer is consolidated through a crosslinking between Chitosan and CR, as confirmed by FT-IR measurements. The possibility of interactions between Chit and propane-sulfone rings was mentioned in the literature [34]. The formation of sulfopropyl chitosan derivatives at a pH exceeding 8 involves the engagement of the amino group of chitosan in a nucleophilic substitution on the benzene ring, leading to the opening of the sulfopropyl ring and the formation of sulfonic groups (see Scheme 1).



Scheme 1. Synthesis of chitosan derivatives by sulfopropyl ring opening.

Tafel slope can provide an important reference for exploring the reaction mechanism, especially in clarifying the reaction rate-determining steps and reaction paths. The results suggest that the corrosion mechanism differs from uncoated to coated zinc and, moreover, from one pH to another. It should also be mentioned that cathodic values should be regarded as less precise than the anodic ones, taking into account the horizontal shape of the cathodic branch in some cases due to the oxygen diffusion step that takes over the charge transfer.

It should be mentioned that the pH indicator property of CR is also affected by its incorporation in the Chit coating. CR becomes less active due to its immobilization in the biopolymer. Thus, the color change is not observed, and CR does not act as a pH indicator, its activity being partially ruined due to its incorporation in the coating. Nevertheless, at pHs > 8.2, it has a beneficial effect on the corrosion resistance of coated Zn, acting as a corrosion inhibitor when used in proper concentration.

3.5.2. Electrochemical Impedance Spectroscopy

Influence of pH

To gain a deeper insight into the corrosion process, electrochemical impedance spectroscopy (EIS) measurements were carried out on zinc, Zn/Chit, and Zn/Chit_CR_10^{−3} M coat samples at the same pH values as in the case of polarization measurements. The corresponding Bode plots of the impedance are presented in Figure 8.

As expected, all $|Z|_{0.01\text{Hz}}$ values are higher when Chit and CR are present and are clearly the largest at pH 9, meaning the coatings have the best corrosion resistance (Table 3). Moreover, the Zn/Chit_CR_10^{−3} M coat exhibited the largest $|Z|_{0.01\text{Hz}}$ value, possibly due to the smaller permeability of the Chit-CR layer, which could lengthen the pathway of the electrolyte. At the same time, it could be seen that the shape of the impedance curves at pH 9 is different from that of the diagrams recorded at lower pHs, suggesting a change in corrosion mechanism, which is in accordance with the results extracted from the polarization curves.

Table 3. $|Z|_{0.01\text{Hz}}$ values extracted from Bode curves presented in Figure 8 at different pHs.

Sample	$ Z _{0.01\text{Hz}}$ (Ω)			
	pH 5	pH 7	pH 8	pH 9
Zn	260	1384	915	65
Zn/Chit	1747	1393	2064	459
Zn/Chit_CR_10 ^{−3} M coat	2333	1568	2388	7140

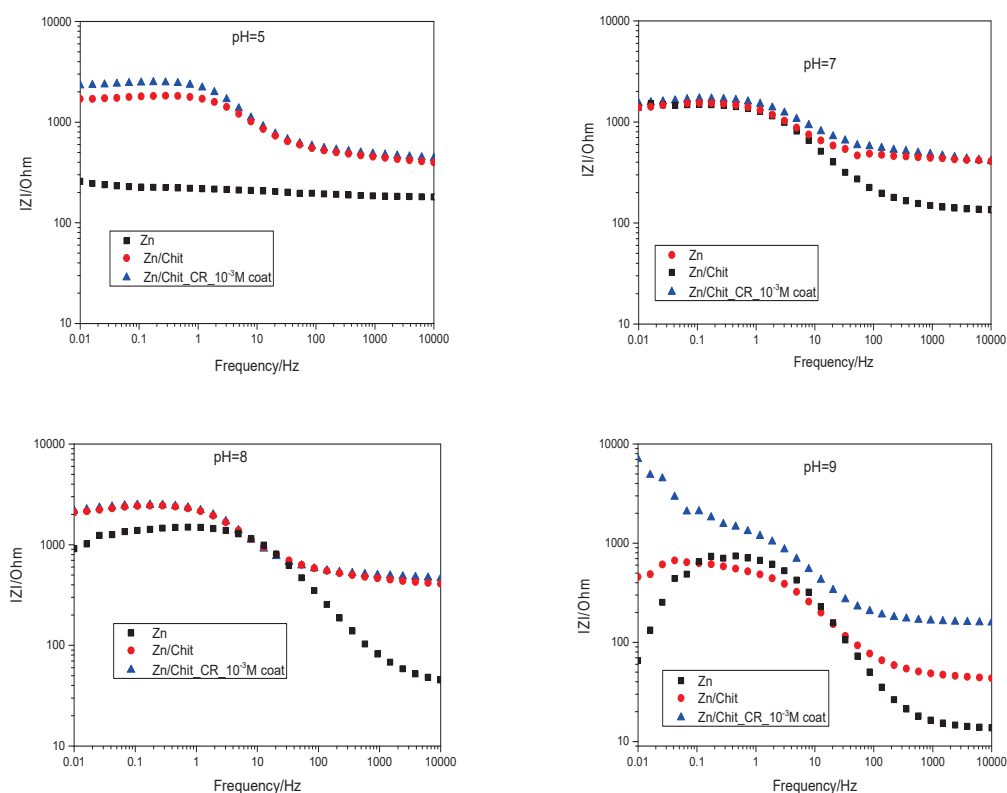


Figure 8. Initial Bode impedance curves obtained for Zn, Zn/Chit, and Zn/Chit_CR_10^{−3} M coat recorded in a 0.2 g/L aqueous Na₂SO₄ solution at various pHs. Experimental conditions: 0.2 g/L aqueous Na₂SO₄ solution; scan rate, 0.166 mV/s; OCP recorded during 60 min.

Long-Term Measurements

Further investigation performed over time reveals interesting behavior (Figure 9). It can be seen that Nyquist impedance diagrams exhibit capacitive behavior with a small inductive loop. According to the literature, the inductive loop originates from the coverage relaxation of the adsorbed species ZnI, ZnII, and ZnOH formed during the corrosion process [35].

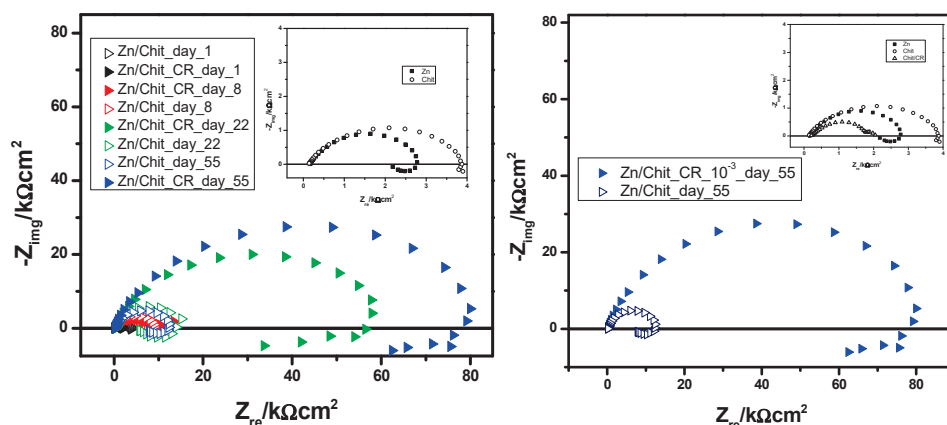


Figure 9. Nyquist impedance curves obtained for Zn/Chit and Zn/Chit_CR_10^{−3} M coat from the first until fifty-five days in a row recorded in 0.2 g/L Na₂SO₄ at pH = 7 in dry–wet cycles (left) and a direct comparison between Zn/Chit and Zn/Chit_CR_10^{−3} M coat after fifty-five days of dry–wet cycles (right).

A study carried out at pH 7 demonstrates that on the first day of immersion, the Zn/Chit_CR_10^{-x} M coat samples exhibit a smaller capacitive loop than the Zn/Chit sample, but the situation improves significantly after several dry-wet cycles.

As it can be observed from Figure 9, an important increase in the coating impedance recorded in 0.2 g/L Na₂SO₄ at pH = 7 in dry-wet cycles takes place from the first until the fifty-fifth day in a row. This increase is related to the beneficial effect of CR incorporated in Chitosan and could be, at least partially, related to a change in the Chit coating structure in the presence of CR due to the interaction between Chit and CR molecules, as revealed by the FT-IR spectra (Figure 3). It suggests a crosslinking of Chit by CR anion, which is a process leading to a consolidated coating. The increase in impedance in time could also be due to the formation of corrosion products at the interface, which exert a protective effect [36], and/or to a reaction of CR with the main reactive corrosion products during wet/dry cyclic conditions.

Moreover, it is also possible that SO₄²⁻ ions penetrate the Chit structure over time and consolidate the coating even more. This possibility is mentioned in the literature: SO₄²⁻ anions slowly interact with chitosan NH₃⁺ groups to form ionic bridges between the polymer chains [37]. This also points to a consolidation of the coating over time.

In order to better understand the underlying mechanism at the interface, the electrical equivalent circuits (EC) were fitted to EIS data for Zn/Chit_CR_10⁻³ M coat samples recorded in time. The obtained values are presented in Table 4 and the fitted EC in Figure 10. For the first 8 days, the appropriate EC was found to be R(Q1(R1(CR2))), where R stands for the electrolyte solution resistance, Q1 and R1 are attributed to the coating, and C and R2 represent the charge transfer at the metal/coating interface (Figure 10A). From the polarization resistance value R_p obtained as a sum of R1 and R2, one can observe that over time, this parameter shows an increasing tendency, suggesting an increasing anti-corrosion resistance. However, the corrosion process cannot be neglected, and the accumulation of the formed species as a result of metal oxidation changes the mechanism. Thus, as a result of fitting to the EIS data for the days that follow after the 8h, the obtained EC is R(Q1(R1(LR3))), where L represents the system's inductive behavior (Figure 10B). As already mentioned, the inductive loop originates from the coverage relaxation of adsorbed species ZnI, ZnII, and ZnOH formed during the corrosion process [35] and reflects the instability of the system.

Table 4. Electrochemical parameter values for Zn/Chit_CR_10⁻³ M coat samples obtained by fitting equivalent circuits to EIS diagrams from Figure 9.

Days	R (kΩcm ²)	R ₁ (kΩcm ²)	Q ₁ (μSs ⁿ)	n	R ₂ (kΩcm ²)	C (μSs ⁿ)	R _p (kΩcm ²)	L (kH)	R ₃ (kΩcm ²)
1	0.400	1.49	40.690	0.602	2.02	6.37	3.51		
2	0.476	2.52	8.696	0.748	2.57	5.14	7.66		
5	0.705	10.22	5.591	0.650	3.34	1191	13.56		
8	0.662	17.01	3.229	0.691	6.89	576.4	23.90		
18	0.327	108.80	0.887	0.781	-	-		913	263.1
22	0.703	116.00	0.763	0.793	-	-		1243	213.8
23	0.771	114.50	0.776	0.788	-	-		957	211.0
24	0.348	112.50	0.762	0.789	-	-		781	229.7
31	0.837	136.90	0.687	0.794				947	236.9
32	0.893	146.4	0.711	0.778				2938	437.7
55	0.340	159.5	0.597	0.826				4487	573.4

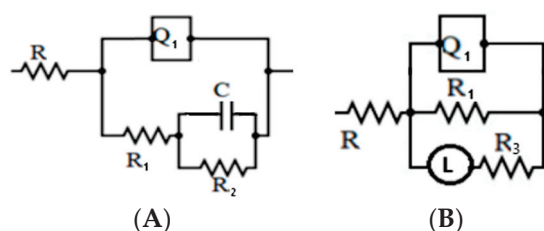


Figure 10. The fitted equivalent circuits to EIS plots for Zn/Chit_CR_10^{−3} M coat:for the first 8 days (A) and for the next days (B).

The analysis of Bode plots (Figure 11) also reveals that the impedance modulus $|Z|_{0.01\text{Hz}}$ for both Zn/Chit and Zn/Chit_CR_10^{−3} M coat samples is larger after 55 days of dry–wet cycles than in the first immersion day, and the $|Z|_{0.01\text{Hz}}$ value is the highest in the case of Zn/Chit/loaded with CR. This also points to a consolidation of the coating over time.

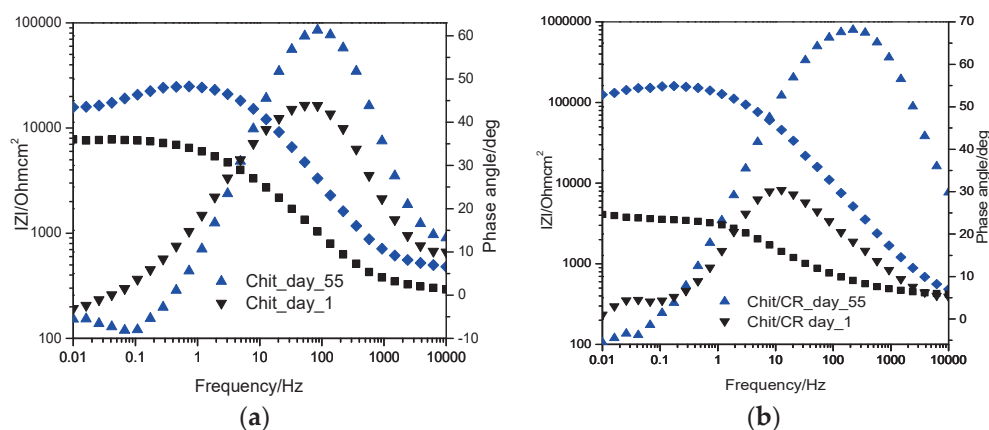


Figure 11. Bode plot obtained for Zn/Chit (a) and for Zn/Chit_CR_10^{−3} M coat (b) at the first day and after fifty-five days measured in dry–wet cycles. Electrolyte: 0.2 g/L Na₂SO₄ at a pH of 7.

3.6. Adhesion Measurements

Adhesion plays an important role in governing the performance of the coatings. The dependence of film integrity on adhesion forces is important from the viewpoint of the performance of the coatings. Thus, their durability is also determined by their adhesion to the substrate, since this determines the ease of removal. The adhesion was calculated with the formula:

$$\text{Adhesion (\%)} = 100 \times \frac{\text{Total number of cubes}}{\text{Total number of ripped cubes by tape peel method}}$$

The results of the peel-off method applied in the case of Zn and glass samples coated with Chit without or with CR led to the results presented in Figure 12 and Table 5.

Table 5. Results of the adhesion measurements. Total cubes: 49.

Substrate	Coating	Number of Ripped Cubes by the Tape Peel Method	Adhesion Ratio
Zn	Chit	0	~99.99%
Zn	Chit_CR_10 ^{−3} M coat	0	~99.99%
Glass	Chit_CR_10 ^{−3} M coat	4	~91.84%

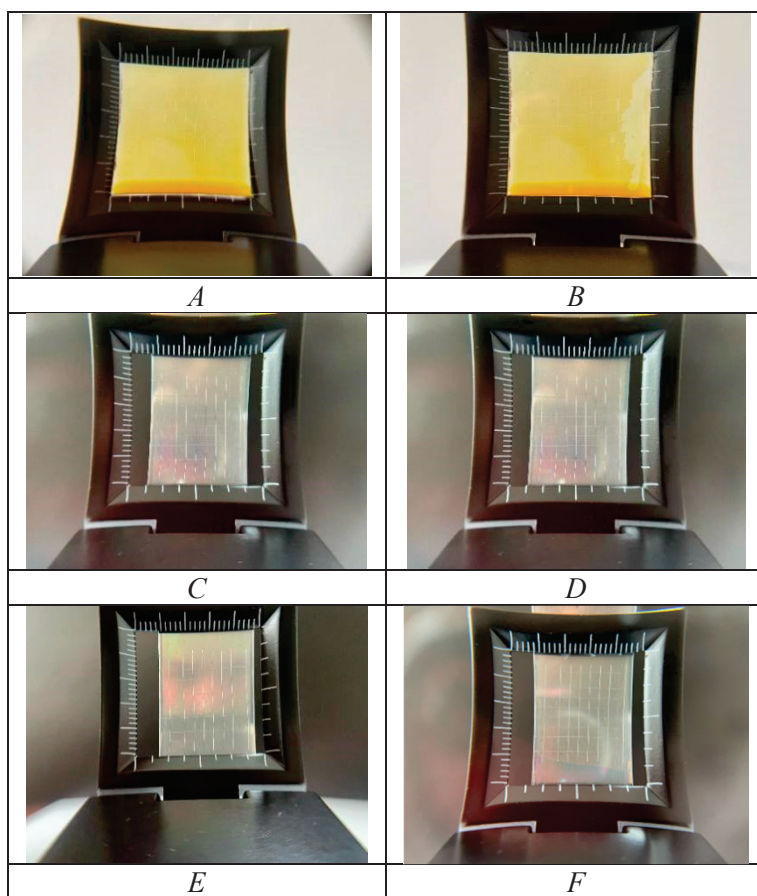


Figure 12. Chit/CR_{10^{−3}} Mcoat before (A) and after (B) adhesion test on glass substrate; Chit/CR_{10^{−3}} M coat on zinc substrates before (C) and after (D) test; Chit coating test on zinc substrate before (E) and after (F).

The adhesion of Chit incorporating CR was better on Zn than on glass substrate. It is confirmed once more that adhesion depends strongly on the physical and chemical properties of the substrate as well as its morphology. The nature and strength of the binding forces between the two materials in contact clearly determine the adhesion of the coatings to the substrate. The ZnO existence on Zn substrates plays a certain positive role in the Chit_CR layer adhesion.

3.7. Wettability Measurements

A more hydrophobic surface is beneficial for the anti-corrosion protection of metals. The hydrophobicity of the coatings increased slightly after CR incorporation in Chitosan, as proven by the increase in contact angle (Figure 13). This result differs from other situations reported in the literature, when a slight decrease in hydrophobicity was noticed after the introduction of indigo carmine molecules in chitosan coatings [16]. However, the differences between these values and those noticed for Chit containing CR are not very large and are probably due to the different water-absorption properties of the involved compounds and to the swelling and/or reorientation of the surface groups of the coatings. Moreover, the different film-forming conditions also had an influence on the surface porosity and, hence, on the wettability of the coatings.

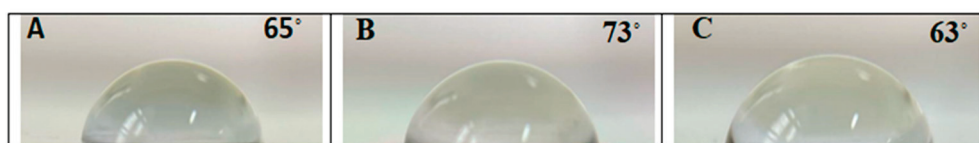


Figure 13. Results of contact angle measurements for Zn/Chit (A), Zn/Chit_CR- 10^{-3} M coat (B), and uncoated Zn (C) samples using droplets of 20 μ L Na_2SO_4 solution.

4. Conclusions

After analyzing the results, several conclusions can be drawn:

- Cresol red acts as a corrosion inhibitor of zinc corrosion when used in solution in different concentrations; this effect is smaller when CR is embedded in chitosan due to the blocking of its functional groups during incorporation.
- The preparation method of Chit coating impregnation with CR by immersion in the solution after deposition on Zn led to poorer results than the method in which chitosan was previously mixed with CR before applying the dip-coating technique.
- FT-IR measurements carried out on chitosan powder embedding CR provided evidence that anionic CR interacts with positively charged chitosan. The pH indicator property of CR is affected by its incorporation in the Chit coating. CR becomes less active due to its immobilization in the biopolymer. Consequently, no color change is observed, and CR does not act as a pH indicator.
- The examination of the potentiodynamic polarization curves indicates that corrosion at higher pHs of zinc coated with Chit and CR is slower than in neutral or acidic media, where Chitosan is more vulnerable and can be destroyed. At pH 9, CR decreases the corrosion current density of Zn and of Zn/Chit, and in proper concentrations (10^{-4} M– 10^{-3} M), it acts as a corrosion inhibitor.
- The chitosan coatings containing cresol red prepared by method (ii) were monitored in dry–wet cycles for 55 days. EIS measurements recorded in 0.2 g/L Na_2SO_4 at pH = 7 show an important increase in the impedance of the coatings occurring from the first until the fifty-fifth day in a row, in dry–wet cycles. This increase is related to the beneficial effect of CR incorporated in Chitosan and could be, at least partially, related to a consolidation of the Chit coating structure in the presence of CR by crosslinking between Chit and CR molecules.
- A change in the corrosion mechanism at pH 9 is observed from the shape of the impedance diagrams.
- The adhesion of Chit incorporating CR on Zn was better than that on glass substrates and reached ~99.99%, suggesting a better affinity of the chitosan coating towards the Zn substrate, probably due to the existence of ZnO on the substrate surface.

Concluding, CR could be used on zinc as a corrosion inhibitor incorporated in chitosan at basic pHs, but without taking advantage of its pH-indicating properties, which are lost due to the interactions occurring between the biopolymer and the dye molecule.

Author Contributions: Conceptualization, G.S.S. and L.M.M.; Methodology, G.S.S.; Investigation, R.B., G.K. and N.M.; Writing—review and editing, L.M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study, in the collection, analysis, or interpretation of data, in the writing of the manuscript, or in the decision to publish the results.

References

- Guan, X.; Shi, J. Protection of galvanized steel using benzotriazole as a corrosion inhibitor in simulated concrete pore solution and alkali-activated fly ash solution. *Cem. Concr. Compos.* **2023**, *136*, 104880. [CrossRef]
- Masuku, G.M.; Nxumalo, W.; Kabanda, M.M.; Murulana, L.C.; Bahadur, I. Quinoxaline derivatives as corrosion inhibitors of zinc in 1.0 M hydrochloric and sulphuric acid solutions: Adsorption, electrochemical, spectroscopic, and computational studies. *J. Mol. Liq.* **2023**, *386*, 122458. [CrossRef]
- Qiang, Y.; Zhang, S.; Guo, L.; Xu, S.; Feng, L.; Obot, I.B.; Chen, S. Sodium dodecyl benzene sulfonate as a sustainable inhibitor for zinc corrosion in 26% NHACl solution. *J. Clean. Prod.* **2017**, *152*, 17–25. [CrossRef]
- Fouda, A.S.; Rashwan, S.; Emam, A.; El-Morsy, F.E. Corrosion Inhibition of Zinc in Acid Medium using some Novel Organic Compounds. *Int. J. Electrochem. Sci.* **2018**, *13*, 3719–3744. [CrossRef]
- Lebrini, M.; Suedile, F.; Salvin, P.; Roos, C.; Zarrouk, A.; Jama, C.; Bentiss, F. Bagassa guianensis ethanol extract used as sustainable eco-friendly inhibitor for zinc corrosion in 3% NaCl: Electrochemical and XPS studies. *Surf. Interfaces* **2020**, *20*, 100588. [CrossRef]
- Femandes, F.D.; Ferreira, L.M.; da Silva, M.L.C.P. Evaluation of the corrosion inhibitory effect of the ecofriendly additive of *Terminalia Catappa* leaf extract added to soybean oil biodiesel in contact with zinc and carbon steel 1020. *J. Clean. Prod.* **2021**, *321*, 128863. [CrossRef]
- Szabo, G.; Albert, E.; Both, J.; Kócs, L.; Safrán, G.; Szöke, A.; Hórvölgyi, Z.; Muresan, L.M. Influence of embedded inhibitors on the corrosion resistance of zinc coated with mesoporous silica layers. *Surf. Interfaces* **2019**, *15*, 216–223. [CrossRef]
- Albert, E.; Cotelan, N.; Nagy, N.; Safrán, G.; Szabó, G.; Muresan, L.M.; Hórvölgyi, Z. Mesoporous silica coatings with improved corrosion protection properties. *Microporous Mesoporous Mater.* **2015**, *206*, 102–113. [CrossRef]
- Huang, Y.; Zhao, C.; Li, Y.; Wang, C.; Shen, T.; Cheng, D.; Yang, H. Development of self-healing sol-gel anticorrosion coating with pH-responsive 1H-benzotriazole-inbuilt zeolitic imidazolate framework decorated with silica shell. *Surf. Coat. Technol.* **2023**, *466*, 129622. [CrossRef]
- Cotelan, N.; Varvara, S.; Albert, E.; Szabó, G.; Hórvölgyi, Z.; Mures, L.M. Evaluation of corrosion inhibition performance of silica sol-gel layers deposited on galvanised steel. *Corros. Eng. Sci. Technol.* **2016**, *51*, 373–382. [CrossRef]
- Kahvazi Zadeh, M.; Yeganeh, M.; Shoushtari, M.T.; Esmaeilkhani, A. Corrosion performance of polypyrrole-coated metals: A review of perspectives and recent advances. *Synth. Met.* **2021**, *274*, 116723. [CrossRef]
- Qi, C.; Johansen, K.D.; Weinell, C.E.; Bi, H.; Wu, H. Enhanced anticorrosion performance of zinc rich epoxy coatings modified with stainless steel flakes. *Prog. Org. Coat.* **2020**, *163*, 106616. [CrossRef]
- Silva, A.O.; Cunha, R.S.; Hotza, D.; Machado, R.A.F. Chitosan as a matrix of nanocomposites: A review on nanostructures, processes, properties, and applications. *Carbohydr. Polym.* **2021**, *272*, 118472. [CrossRef]
- Cheng, J.; Tian, B.; Wang, J.; Wang, Z.; Liu, Y. Development of multifunctional films based on chitosan, nano silica and hops extracts. *Eur. Polym. J.* **2021**, *161*, 110816. [CrossRef]
- Szöke, Á.F.; Szabó, G.; Simó, Z.; Hórvölgyi, Z.; Albert, E.; Végh, A.G.; Zimányi, L.; Muresan, L.M. Chitosan coatings ionically cross-linked with ammonium paratungstate as anticorrosive coatings for zinc. *Eur. Polym. J.* **2019**, *118*, 205–212. [CrossRef]
- Szöke, Á.F.; Szabó, G.S.; Hórvölgyi, Z.; Albert, E.; Gaina, L.; Muresan, L.M. Eco-friendly indigo carmine-loaded chitosan coatings for improved anticorrosion protection of zinc substrates. *Carbohydr. Polym.* **2019**, *215*, 63–72. [CrossRef]
- Szöke, Á.F.; Szabó, G.S.; Hórvölgyi, Z.; Albert, E.; Végh, A.G.; Zimányi, L.; Muresan, L.M. Accumulation of 2-Acetylamino-5-mercapto-1,3,4-thiadiazole in chitosan coatings for improved anticorrosive effect on zinc. *Int. J. Biol. Macromol.* **2020**, *142*, 423–431. [CrossRef]
- Dabóczi, M.; Albert, E.; Agócs, E.; Kabai-Faix, M.; Hórvölgyi, Z. Bilayered (silica–chitosan) coatings for studying dye release in aqueous media: The role of chitosan properties. *Carbohydr. Polym.* **2016**, *136*, 137–145. [CrossRef]
- Cheng, B.; Wang, B.; Luo, M.; Yang, Y.; Zhitomirsky, I.; Shi, K. Patterned polypyrrole for reversible zinc anodes via electrochemical additive manufacturing. *Mater. Lett.* **2023**, *350*, 134963. [CrossRef]
- Taheri, N.N.; Ramezanzadeh, B.; Mahdavian, M. Application of layer-by-layer assembled graphene oxide nanosheets/polyaniline/zinc cations for construction of an effective epoxy coating anti-corrosion system. *J. Alloys Compd.* **2019**, *800*, 532–549. [CrossRef]
- Machado Oliveira, J.A.; Costa de Santana, R.A.; Neto de Oliveira, A.W. Electrophoretic deposition and characterization of chitosan-molybdenum composite coatings. *Carbohydr. Polym.* **2021**, *255*, 117382. [CrossRef] [PubMed]
- Avilez, H.V.R.; Casadiego, D.A.C.; Avila, A.L.V.; Perez, O.J.P.; Almodovar, J. Production of chitosan coatings on metal and ceramic biomaterials. *Chitosan Based Biomater.* **2017**, *1*, 255–293. [CrossRef]
- Carneiro, J.; Tedim, J.; Fernandes, S.C.M.; Freire, C.S.R.; Gandini, A.; Ferreira, M.G.S.; Zheludkevich, M.L. Chitosan as a smart coating for controlled release of corrosion inhibitor 2-mercaptobenzothiazole. *ECS Electrochem. Lett.* **2013**, *2*, C19–C22. [CrossRef]
- Roshan, S.; Dariani, A.A.S.; Mokhtari, J.J. Monitoring underlying epoxy-coated St-37 corrosion via 8-hydroxyquinoline as a fluorescent indicator. *Appl. Surf. Sci.* **2018**, *440*, 880–888. [CrossRef]
- Tian, X.-L.; Feng, C.; Zhao, X.-H.J. Corrosion monitoring effect of rhodamine-ethylenediamine on copper relics under a protective coating. *ACS Omega* **2020**, *5*, 21679–21683. [CrossRef]
- Mata, D.; Scharnagl, N.; Lamaka, S.; Malheiro, E.; Maia, F.; Zheludkevich, M.J. Validating the early corrosion sensing functionality in poly (ether imide) coatings for enhanced protection of magnesium alloy AZ31. *Corros. Sci.* **2018**, *140*, 307–320. [CrossRef]
- Sousa, I.; Quevedo, M.C.; Sushkova, A.; Ferreira, M.G.S.; Tedim, J. Chitosan Microspheres as Carriers for pH-Indicating Species in Corrosion Sensing. *Macromol. Mater. Eng.* **2019**, *305*, 1900662. [CrossRef]

28. Huhtamäki, T.; Tian, X.; Korhonen, J.T.; Ras, R.H.A. Surface-wetting characterization using contact-angle measurements. *Nat. Protoc.* **2018**, *13*, 1521–1538. [CrossRef]
29. Jagodzińska, S.; Pałys, B.; Wawro, D. *Progress on Chemistry and Application of Chitin and Its Derivatives*; Polish Chitin Society: Wałbrzych, Poland, 2021; Volume XXVI, pp. 89–100. [CrossRef]
30. European Pharmacopoeia 8.0: Wettability of Porous Solids Including Powders. 2014, Volume I, p. 2.9.45. Available online: <https://www.yaopinnet.com/yaodian/ep8.0-index.pdf> (accessed on 22 November 2023).
31. Stern, M.; Geary, A.L. Electrochemical polarization: I. A theoretical analysis of the shape of polarization curves. *J. Electrochem. Soc.* **1957**, *104*, 56.
32. Almadani, E.A.; Adress, H.M.; Moftah, H.M. Evaluate the Activation energy of Cresol Red by study the effect of U.V irradiation. *SSRG Int. J. Appl. Chem.* **2019**, *6*, 58–61. [CrossRef]
33. Abdollahi, Y.; Abdullah, A.H.; Zainal, Z.; Yusof, N.A. Photocatalytic Degradation of p-Cresol by Zinc Oxide under UV Irradiation. *Int. J. Mol. Sci.* **2012**, *13*, 302–315. [CrossRef] [PubMed]
34. Tsai, H.-S.; Wang, Y.-Z.; Lin, J.-J.; Lien, W.-F. Preparation and Properties of Sulfopropyl Chitosan Derivatives with Various Sulfonation Degree. *J. Appl. Polym. Sci.* **2010**, *116*, 1686–1693. [CrossRef]
35. Deslouis, C.; Duprat, M.; Tournillon, C. The kinetics of zinc dissolution in aerated sodium sulphate solutions. A measurement of the corrosion rate by impedance techniques. *Corros. Sci.* **1989**, *29*, 13–30. [CrossRef]
36. Yadav, A.P. Electrochemical Impedance Response of Zn and Galvanized Steel Corroding under Marine Atmospheric Environments. *J. Nepal Chem. Soc.* **2009**, *23*, 33–42. [CrossRef]
37. Cui, Z.; Xiang, Y.; Si, J.; Yang, M.; Zhang, Q.; Zhang, T. Ionic interactions between sulfuric acid and chitosan membranes. *Carbohydr. Polym.* **2008**, *73*, 111–116. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Corrosion Behavior of the Cu₂₄Zn₅Al Alloy in Sodium Sulfate Solution in the Presence of 1-Phenyl-5-mercaptotetrazole

Vojka Gardić ^{1,*}, Žaklina Z. Tasić ², Marija B. Petrović Mihajlović ², Milan B. Radovanović ²
and Milan M. Antonijević ²

¹ Minning and Metallurgy Institute Bor, Zeleni Bulevar 35, 19210 Bor, Serbia

² Technical Faculty in Bor, University of Belgrade, Vojske Jugoslavije 12, 19210 Bor, Serbia; ztasic@tfbor.bg.ac.rs (Ž.Z.T.); mpetrovic@tfbor.bg.ac.rs (M.B.P.M.); mradovanovic@tfbor.bg.ac.rs (M.B.R.); mantonijevic@tfbor.bg.ac.rs (M.M.A.)

* Correspondence: vojka.gardic@irmbor.co.rs; Tel.: +381-63-845-7818

Abstract: The results of this research on the electrochemical behavior of Cu₂₄Zn₅Al alloy in a 0.1 mol/dm³ sodium sulfate (Na₂SO₄) solution containing 1-phenyl-5-mercaptotetrazole (PMT) are presented in this paper. The influence of PMT concentration, chloride ion concentration, and pre-treatment were examined. The influence of pre-treatment was studied in terms of the effect of the immersion time of the electrode in the appropriate inhibitor solution. After selecting the optimal immersion time, its effect on the behavior of the Cu₂₄Zn₅Al alloy was tested in a 0.1 mol/dm³ solution of sodium sulfate in the presence of different concentrations of chloride ions. Research shown that with the increase of PMT concentration, the anodic current density around the corrosion potential decreases, indicating that PMT behaves as a corrosion inhibitor for Cu₂₄Zn₅Al alloy.

Keywords: Cu₂₄Zn₅Al; corrosion inhibitor; 1-phenyl-5-mercaptotetrazole; electrochemical measurement; sodium sulfate solution; azoles

1. Introduction

CuZnAl is one of the first shape memory alloys (SMAs) based on copper, which has found its commercial application [1]; for example, the devices of fire-preventing systems in underground pit, the damper for reducing vibration [2], fluid fitting system [3], automotive industry [4], various applications in engineering fields [5–7]. The primary benefit of CuZnAl alloys is that they can be produced using conventional metallurgical methods from relatively low-cost metals, which makes them more affordable compared to commercial shape memory alloys (SMAs) [8–11]. The transformation temperature of the binary alloy is typically too elevated for practical applications, and a third element (Zn) is usually incorporated to create a useful alloy [12]. Also, elevating the concentration of zinc enhances the corrosion resistance of the alloys. CuAlNi-based SMAs have also shown some advantages, but their use in biomedicine is problematic due to the fact that nickel is an allergen and due to the tendency of these alloys towards pitting corrosion [13].

Due to the application of SMA alloys in the fluid fitting system [3], an investigation of the corrosion behavior of SMA alloys in different environments is necessary.

The behavior of copper-based alloys in sodium sulfate solutions in the presence of halides has been the subject of investigation by some researchers. Majed et al. [14] investigated the behavior of brass in a sodium sulfate solution, with and without various halides. It was observed that the corrosion potential shifts toward lower values in a sodium sulfate solution with the presence of halide ions, compared to the corrosion potential of brass in a sodium sulfate solution. Also, it was found that the presence of iodide ions had the greatest influence on increasing the rate of brass corrosion.

Vrsalovic et al. [15] investigated the behavior of the CuAlNi shape memory alloy in sodium chloride solutions. The corrosion potential shift towards more negative values, with

increasing chloride ion concentration, was observed. No pitting corrosion was identified on the electrode surface as shown by the results obtained using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS) in a 0.1 wt.% sodium chloride (NaCl) solution. However, it was identified in NaCl solutions of concentrations higher than 0.1 wt.%. EDS analysis showed the presence of copper oxide on the electrode surface, with a small proportion of aluminum in the form of aluminum oxide. Many researchers have investigated the possibility of inhibiting the corrosion of copper and copper alloys. Inhibition of the corrosion process using some organic compounds containing N and/or S atoms has been particularly studied and explained by the fact that a bond with transition metals, such as copper, is easily formed through these atoms [16–19]. The effectiveness of inhibition can be ascribed to the adsorption process, i.e., the formation of a thin film of complexes on the copper surface, which was represented as an inhibitor–copper bond [20–23]. For these reasons, a large number of copper and copper alloy corrosion inhibitors from the group of azoles [16–18], amines [19–23], amino acids [24–26], and others have been investigated. The copper atom has an unoccupied d orbital, allowing it to form coordinate bonds with atoms that donate electrons [27].

Due to the application of CuZnAl alloys in the fluid fitting system [3], as well as various applications in engineering fields where the CuZnAl alloy can be exposed to various corrosion environments, it is necessary to test the effectiveness of the application of various corrosion inhibitors. In their research, Ye et al. [28] showed that the coordinative compound formed on the surface of copper in the presence of 1-phenyl-5-mercaptotetrazole (PMT) more efficiently inhibited the corrosion process of copper compared to the films formed in the presence of tetrazole (TTA), benzotriazole (BTA), hydroxy benzotriazole (HBTA), 2-mercaptobenzotriazole (MBT), 2-mercaptobenzimidazole (MBI), 2-aminopyrimidine (2-AP), imidazole (IBM), and chromate. In the presence of PMT, a film was formed on the surface of copper that can be best described as a composite structure Cu-PMT/Cu₂O/Cu. By measuring the weight loss in a solution of 1 mmol/dm³ sulfuric acid (H₂SO₄) in the presence of 5-mercapto-1-phenyltetrazole and without the presence of an inhibitor, it was found that the weight loss was reduced in the solution with the inhibitor. This can be related to the strong chemical bond of 5-mercapto-1-phenyltetrazole to the surface of copper [29].

The electron donating nitrogen atom and the properties of the -SH group have an important role in the process of adsorption [1]. The PMT molecule probably adsorbs via the -S or the coordinative bond of the -N atom from the tetrazole. Szocs et al. [30] evaluated the inhibitory properties of PMT in acidic sulfate solutions, in which PMT exhibited excellent inhibitory characteristics.

The aim of this study is to evaluate the corrosion behavior of the copper alloy Cu24Zn5Al in blank 0.1 mol/dm³ sodium sulfate, and in the presence of PMT as an inhibitor. Additionally, the electrochemical behavior of the copper alloy was investigated in 0.1 mol/dm³ sodium sulfate in the presence of different concentrations of chloride.

2. Materials and Methods

2.1. Materials

For the experimental investigations, a Cu24Zn5Al electrode was used as the working electrode, which was obtained by sealing a Cu24Zn5Al wire in a methyl methacrylate-based mixture. The electrode surface area was 0.5 cm². The chemical composition of the electrode was determined by measuring with an optical emission spectrometer (Spectro 20, Boschstrasse 10, Kleve, Germany) and is shown in Table 1.

Table 1. Chemical composition of the investigated alloy (wt.%).

Cu	Zn	Al	Fe	Other
70.91	24.00	5.02	0.05	0.02

All solutions were prepared from chemicals of analytical purity. The test solution was a 0.1 mol/dm³ sodium sulfate solution.

The influence of the inhibitor on the corrosion behavior of the copper alloy was investigated in solutions of different concentrations of 1-phenyl-5-mercaptotetrazole (PMT) as follows: 2.5×10^{-3} , 1×10^{-3} , 5×10^{-4} , 1×10^{-4} , and 1×10^{-5} mol/dm³ of PMT in a 0.1 mol/dm³ sodium sulfate solution.

The impact of chloride ions on the corrosion behavior of the copper alloy was investigated in a 0.1 mol/dm³ sodium sulfate solution with the following concentrations of Cl⁻: 5×10^{-2} , 1×10^{-2} , 1×10^{-3} , and 1×10^{-4} mol/dm³.

To investigate the effect of electrode immersion time in the inhibitor solution, a PMT solution with a concentration of 0.017 mol/dm³ was used, which was prepared by dissolving 3.0298 g of PMT in 1 dm³ of distilled water.

2.2. Methods

The samples of the investigated alloy were polished with alumina (Al₂O₃) with a coarseness of 1 µm, washed with distilled water, dried, and immersed in the appropriate solutions.

The electrochemical measurements were performed using a potentiostat that was directly connected to a computer via an AD card, with a three-electrode cell. The saturated calomel electrode (SCE) was used as the reference electrode, while a platinum electrode was utilized as the auxiliary electrode.

The open circuit potential was determined for 30 min, after which anodic polarization curves were recorded from the open circuit potential to approximately 1.0 V vs. SCE. The measurements were performed at a scan rate of 1 mV/s. Cyclic voltammograms were recorded from the corrosion potential to 1.0 V vs. SCE as well as from −1.0 V to 1.0 V vs. SCE, with scan rates of 10 mV/s. All measurements were performed at room temperature.

The electrochemical characteristics of Cu₂₄Zn₅Al alloy in a sodium sulfate solution with the addition of the investigated inhibitor, 1-phenyl-5-mercaptotetrazole, and chloride ions, were tested as follows:

- (A) Potentiodynamic polarization measurements (linear and cyclic voltammetry) were conducted in a 0.1 mol/dm³ sodium sulfate solution without and with the addition of various concentrations of the inhibitor (2.5×10^{-3} mol/dm³, 1×10^{-3} mol/dm³, 5×10^{-4} mol/dm³, 1×10^{-4} mol/dm³, 1×10^{-5} mol/dm³), as well as in 0.1 mol/dm³ sodium sulfate solutions containing various concentrations of chloride ions (5×10^{-2} mol/dm³, 1×10^{-2} mol/dm³, 1×10^{-3} mol/dm³, 1×10^{-4} mol/dm³).
- (B) The testing of the effect of the immersion time of the Cu₂₄Zn₅Al alloy in the 0.017 mol/dm³ PMT solution was conducted by allowing the Cu₂₄Zn₅Al electrode to stand in the solution for 15 min, 60 min, and 240 min, then rinsing with distilled water and immediately subjecting it to potentiodynamic polarization measurements (linear and cyclic voltammetry) in a 0.1 mol/dm³ sodium sulfate solution. After obtaining the optimal exposure time, the effect of chloride ions was examined by rinsing the Cu₂₄Zn₅Al electrode that was immersed for 60 min (optimal time) in the 0.017 mol/dm³ PMT solution with distilled water and immediately subjecting it to potentiodynamic polarization measurements (linear and cyclic voltammetry) in a 0.1 mol/dm³ sodium sulfate solution containing different concentrations of chloride ions (5×10^{-2} mol/dm³, 1×10^{-2} mol/dm³, 1×10^{-3} mol/dm³, 1×10^{-4} mol/dm³).

All tests were performed in duplicate.

3. Results and Discussion

3.1. Electrochemical Measurements

Influence of the Concentration of PMT

The electrochemical behavior of the Cu₂₄Zn₅Al alloy was investigated in a sodium sulfate solution with different concentrations of PMT (1×10^{-5} , 1×10^{-4} , 5×10^{-4} ,

1×10^{-3} , and 2.5×10^{-3} mol/dm³). The obtained results are shown in Figure 1 and Table 2.

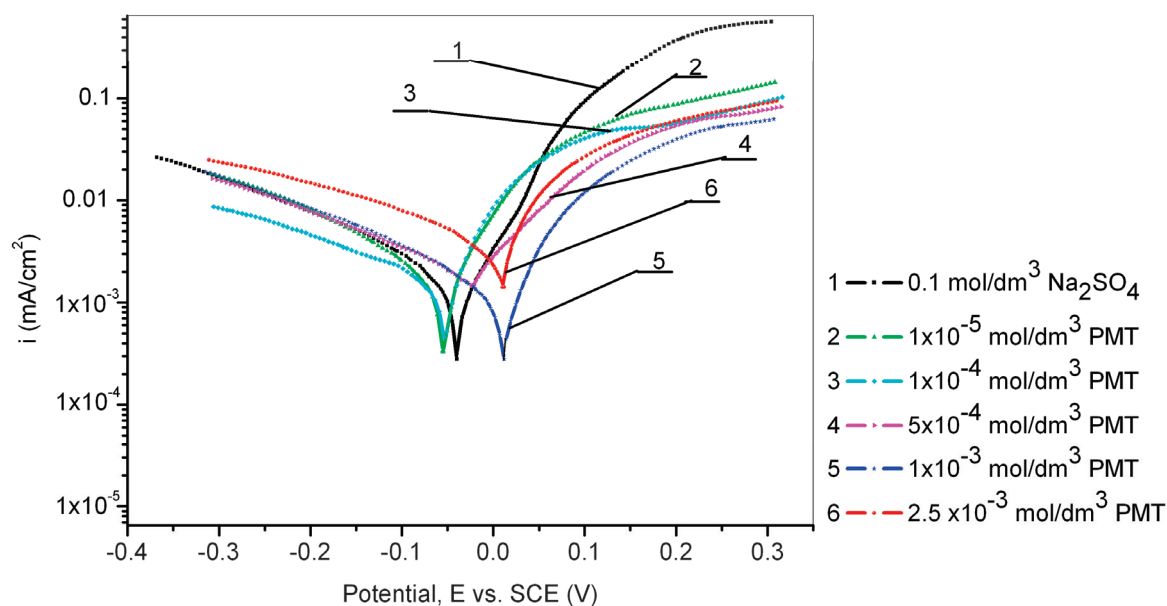


Figure 1. Potentiodynamic polarization curves of the Cu24Zn5Al alloy in 0.1 mol/dm³ sodium sulfate solution without and with the addition of various concentrations of PMT (scan rate 1 mV/s).

Table 2. Corrosion parameters of the Cu24Zn5Al alloy in 0.1 mol/dm³ Na₂SO₄ without and with the addition of various concentrations of PMT.

Parameters						
Inhibitor Concentration	OCP	E _{corr}	j _{corr}	β _c	β _a	IE
Unit						
mol/dm ³ PMT	V vs. SCE	V vs. SCE	μA/cm ²	V/dec	V/dec	%
/	−0.030	−0.040	4.7	−0.292	0.148	/
1×10^{-5}	−0.040	−0.054	2.1	−0.238	0.087	54.9
1×10^{-4}	−0.035	−0.054	1.9	−0.379	0.084	58.4
5×10^{-4}	−0.022	−0.020	2.0	−0.302	0.120	56.4
1×10^{-3}	0.012	0.018	1.6	−0.299	0.091	66.1
2.5×10^{-3}	0.010	0.011	2.4	−0.440	0.110	48.5

From Figure 1, it can be observed that the corrosion potential shifts towards positive values with the increase of PMT concentration in the solution [31]. Additionally, all current densities, obtained by the polarization of the Cu24Zn5Al alloy in the solution of sodium sulfate in the presence of different concentrations of PMT inhibitor, have lower values (curves 2, 3, 4, 5, and 6) than the current density obtained by polarization of the Cu24Zn5Al alloy in the solution of sodium sulfate without an inhibitor (curve 1) [1,31–33].

This fact indicates that the tested PMT has an inhibitory effect in the vicinity of the corrosion potential [31].

From Table 2, it can be seen that the OCP established on the Cu24Zn5Al alloy in the sodium sulfate solution in the presence of different concentrations of the PMT inhibitor depends on the concentration of the inhibitor. The obtained OCP of the Cu24Zn5Al alloy with PMT concentrations of 5×10^{-4} mol/dm³, 1×10^{-3} mol/dm³, and 2.5×10^{-3} mol/dm³

was more positive than the OCP of the alloy in the blank solution. In the presence of lower PMT concentrations, the OCP values were close to the OCP in the blank solution (Table 2). By comparing these values, it can be said that there is a shift in the OCP in the positive direction, which is consistent with the literature [24]. However, the OCP shift was less than 85 mV, indicating that PMT behaved as a mixed type [1,31,34].

The mechanism of inhibition relies on the creation of a polymer film consisting of Cu-PMT [28,35]. Through the dissolution of the relatively more electronegative zinc and aluminum, the copper content on the surface of the alloy increases, enabling the inhibitor to form a protective film that strongly attaches to the surface by reacting with Cu^+ ions [29,36].

The inhibition efficiency (IE) is calculated according to the following equation [1,37]:

$$\text{IE}(\%) = \frac{(j_{\text{corr}} - j_{\text{corr(inh)}})}{j_{\text{corr}}} \times 100 \quad (1)$$

where the symbols are:

j_{corr} —corrosion current density in the sodium sulfate solution without inhibitor ($\mu\text{A}/\text{cm}^2$);
 $j_{\text{corr(inh)}}$ —corrosion current density in the sodium sulfate solution with PMT ($\mu\text{A}/\text{cm}^2$).

The electrochemical corrosion parameters of Cu₂₄Zn₅Al alloy, such as open circuit potential (OCP), corrosion potential (E_{corr}), corrosion current density (j_{corr}), cathodic and anodic Tafel slopes (β_c and β_a), inhibition efficiency (IE), are summarized in Table 2. The values for E_{corr} , j_{corr} , β_c , and β_a were obtained based on the polarization curves shown in Figure 1.

The highest efficiency of corrosion inhibition for the Cu₂₄Zn₅Al alloy in 0.1 mol/dm³ sodium sulfate solution was achieved at a PMT concentration of 1×10^{-3} mol/dm³ [29,30]. Further, increase in the PMT concentration led to a diminution in the inhibition efficiency, which can be explained by the fact that an increase in the inhibitor concentration led to a faster formation of the protective layer on the alloy surface, causing the layer to become more porous and less compact, resulting in a reduced protective effect [29,30].

Figure 2 shows the results obtained by cyclic voltammetry from -1 V to 1 V vs. SCE for Cu₂₄Zn₅Al alloy in 0.1 mol/dm³ sodium sulfate solution in the presence of different concentrations of the PMT inhibitor (scan rate 10 mV/s).

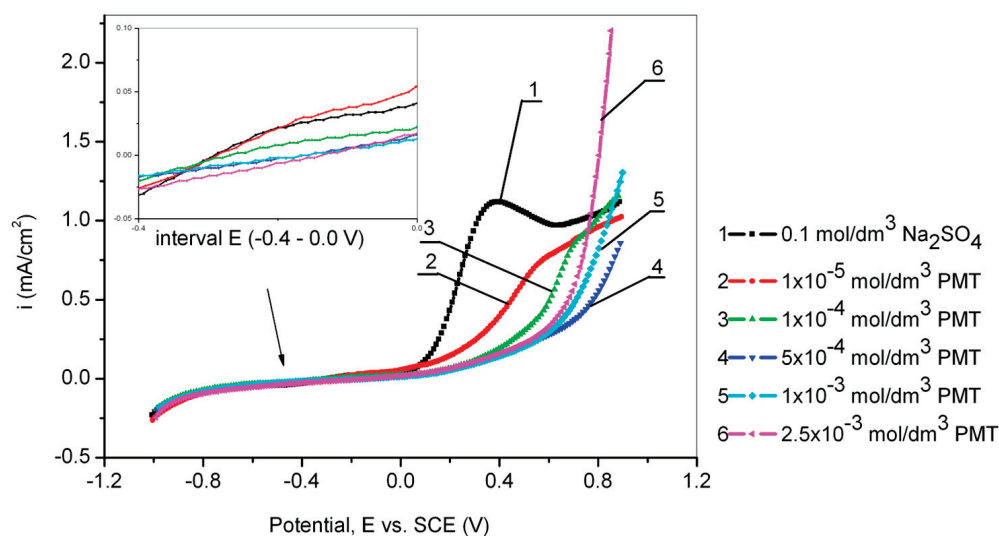


Figure 2. Anodic curves of the Cu₂₄Zn₅Al alloy in 0.1 mol/dm³ sodium sulfate solution without and with the addition of various concentrations of PMT obtained by cyclic voltammetry (scan rate 10 mV/s).

The results obtained by cyclic voltammetry from OCP to 1 V of Cu₂₄Zn₅Al alloy in a 0.1 mol/dm³ sodium sulfate solution in the presence of different concentrations of PMT inhibitor (scan rate 10 mV/s) are shown in Figure 3.

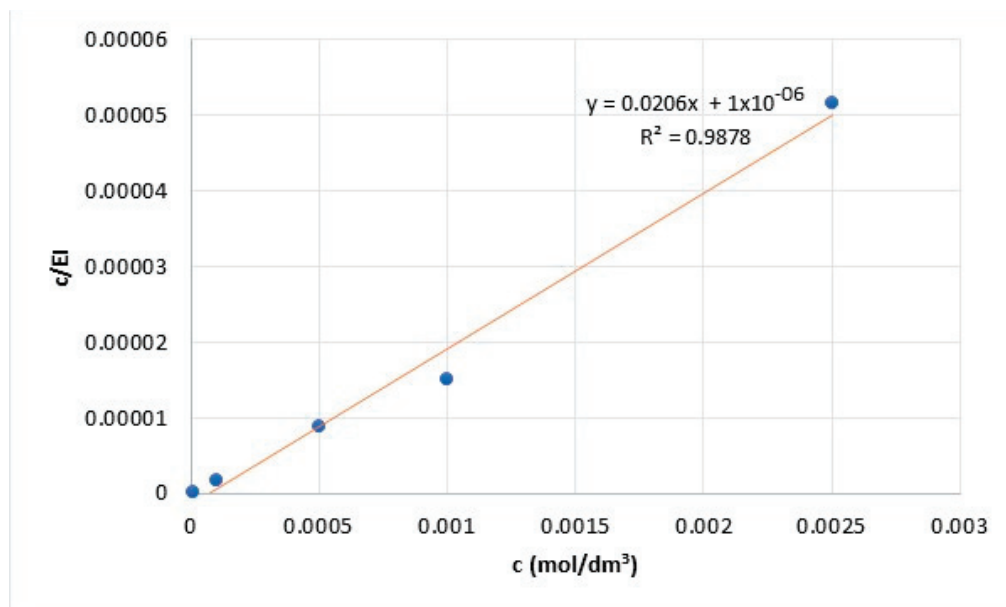


Figure 3. Langmuir adsorption isotherm model of PMT.

On some polarization curves (curves 1 and 2) in Figure 2, a peak originating from the formation of Cu₂O can be observed [38]. This peak is not present on the polarization curves 5 and 6 [38,39], due to the relatively rapid formation of a stable protective film of Cu-PMT, which completely prevents the formation of Cu₂O. The creation of the Cu₂O protective film in a neutral environment has been confirmed by other authors as well [40,41].

A slight increase in the corrosion current can also be observed in the polarization curves obtained from solutions containing inhibitors at potentials more positive than 0.4 V, compared to the increase in corrosion current obtained in the blank solution, as seen in Figure 2. This can be explained by the disruption of the compactness of the Cu-PMT protective film, which results in its damage [29]. At even higher potentials, greater than 0.5 V, the curve becomes steeper, which concurs with the research of Ye et al. [28], where it was found that complete destruction of the Cu-PMT protective film occurs at potentials greater than 0.6 V. At a potential of 0.8 V, there is a sudden increase in current density, indicating the onset of PMT oxidation in the solution [42,43]. Also, Figure 1 shows that the lowest current density value was obtained at a PMT concentration of 1×10^{-3} mol/dm³. Mihit et al. [44], conducted polarization measurements of brass in 0.2 mol/dm³ HNO₃ with and without the addition of PMT and concluded that the anodic current density decreased with increasing PMT concentration. The optimal inhibitor concentration was 1×10^{-3} mol/dm³. At the lowest PMT concentration and up to a potential of 0.3 V, the current density was the highest compared to the current densities in the polarization curves recorded in solutions with higher inhibitor concentrations, indicating that the formation of a protective film on the alloy surface in sodium sulfate solution at neutral pH was relatively slow and thin [28,45,46].

3.2. Adsorption Isotherm

Potentiodynamic polarization measurements provided results for the determination of adsorption mechanisms. The adsorption isotherm that best fits the obtained data was determined. Research results showed that PMT adsorption on the surface of Cu₂₄Zn₅Al

alloy can best be described by the Langmuir adsorption isotherm [47]. The Langmuir adsorption isotherm was formulated using the following relationships [1,38,44]:

$$\frac{IE}{1 - IE} = A \cdot c \cdot e^{\left(-\frac{\Delta G}{RT}\right)} = K \cdot C \quad (2)$$

where they are:

K—adsorptive equilibrium constant;

ΔG —the Gibbs free energy of adsorption (J/mol);

c—the concentration of PMT (mol/dm³);

IE—the inhibition efficiency (%).

Equation (2) can be represented as follows:

$$\frac{c}{IE} = \frac{1}{K} + c \quad (3)$$

The adsorption constant K can be expressed by the following equation:

$$K = \frac{1}{55.55} e^{\left(-\frac{\Delta G}{RT}\right)} \quad (4)$$

$$\ln K - \ln\left(\frac{1}{55.55}\right) = -\frac{\Delta G}{RT} \quad (5)$$

$$-\Delta G = \left(\ln K - \ln\left(\frac{1}{55.55}\right)\right) \times RT \quad (6)$$

where the symbols are:

R—the universal gas constant;

T—the thermodynamic temperature (293 K).

Based on Equation (2) and Figure 3 the adsorption constant K is calculated. Further, the Gibbs free energy of PMT adsorption in the sodium sulfate solution is calculated based on Equation (6). The calculated value of the Gibbs free energy of PMT adsorption in the sodium sulfate solution was $\Delta G = -43.44$ kJ/mol. The obtained value of the ΔG indicates spontaneous PMT adsorption on the surface of the Cu24Zn5Al alloy. Also, based on the value of the Gibbs free energy, it can be concluded that the chemisorption of the inhibitor occurs on the surface of the Cu24Zn5Al alloy in a neutral Na₂SO₄ solution [1,48–50].

3.3. The Effect of Chloride Ion Concentration

The electrochemical behavior of the Cu24Zn5Al alloy was investigated in a 0.1 mol/dm³ sodium sulfate solution containing various concentrations of chloride ions (1×10^{-4} , 1×10^{-3} , 1×10^{-2} , and 5×10^{-2} mol/dm³), and the obtained results are presented in Figure 4 and Table 3. Figure 4 shows that all recorded anodic currents of the Cu24Zn5Al alloy in solutions containing chloride ions are higher than the anodic current observed in sodium sulfate solutions without Cl[−] ions.

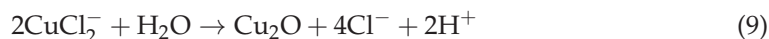
It was also observed that the OCP shifts in the negative direction with the increasing concentration of chloride ions.

The observed behavior of the Cu24Zn5Al alloy in 0.1 mol/dm³ Na₂SO₄ containing chloride ions can be explained through Reactions (7)–(19) that occur at the cathode and anode.

The cathodic reaction represents the reduction of dissolved oxygen according to the following reaction [1,37,50–53]:



The main anodic reaction of Cu₂₄Zn₅Al alloy in 0.1 mol/dm³ Na₂SO₄ containing chloride ions can be represented by the following equations [1,38,51–56]:



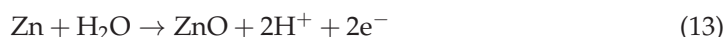
With prolonged immersion time in the solution containing dissolved oxygen copper, from the surface of the Cu₂₄Zn₅Al alloy, it oxidizes according to the following reactions [50–55]:



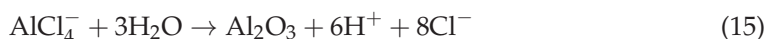
At the same time, the dezincification process takes place according to the following equation [50,51,54]:



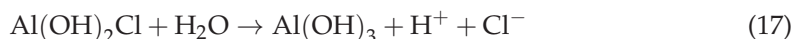
As well as the oxidation of zinc which can lead to passivation by the formation of a zinc oxide layer on the surface of the alloy according to the following equation [50,51,54]:



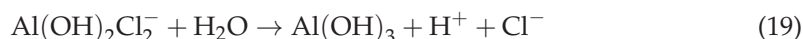
Due to the presence of aluminum as an alloy element, additional passivation occurs due to the dissolution of aluminum and the formation of an aluminum oxide layer on the surface of the alloy according to the following equations [50,51,53–55]:



The aluminum oxide film can protect the surface of the alloy from severe corrosion, but it also dissolves in chloride solutions, according to the following equations [51]:



or



The anodic reactions according to Equations (9), (13), (15)–(17) or (18), and (19) result in the release of hydrogen ions, which causes local acidity and further promotes surface dezincation [36] and dealumination reactions, leading to a potential shift in the negative direction and increased corrosion currents compared to the solution without chloride ions present [32].

According to this, the surface becomes enriched in copper content and Equations (8) and (9) become dominant.

The electrochemical corrosion parameters of Cu₂₄Zn₅Al alloy in a 0.1 mol/dm³ sodium sulfate solution containing various concentrations of Cl[−] ions are presented in Table 3. The values of E_{corr} , j_{corr} , β_c , and β_a were obtained based on the polarization curves shown in Figure 4.

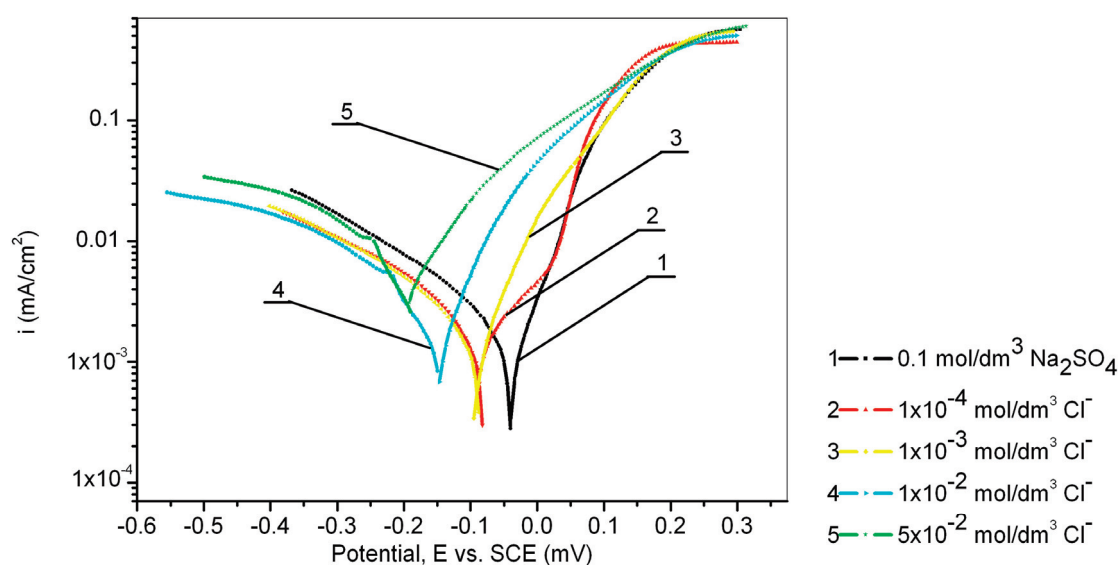


Figure 4. Potentiodynamic polarization curves of Cu24Zn5Al alloy in 0.1 mol/dm³ sodium sulfate solution with the addition of various concentration of chloride ions (scan rate 1 mV/s).

Table 3. Corrosion parameters of Cu24Zn5Al alloy in 0.1 mol/dm³ Na₂SO₄ in the presence of various concentrations of Cl[−] ions.

Parameters					
Concentration of Chloride Ions in 0.1 mol/dm ³ Na ₂ SO ₄	OCP	E _{corr}	j _{corr}	β _c	β _a
	Unit				
mol/dm ³ Cl [−]	V vs. SCE	V vs. SCE	μA/cm ²	V/dec	V/dec
/	−0.030	−0.040	4.7	−0.292	0.148
1 × 10 ^{−4}	−0.198	−0.082	2.9	−0.388	0.108
1 × 10 ^{−3}	−0.144	−0.090	3.5	−0.413	0.130
1 × 10 ^{−2}	−0.094	−0.144	4.5	−0.432	0.137
5 × 10 ^{−2}	−0.077	−0.200	11.8	−0.552	0.255

Based on the results presented in Table 3, it can be concluded that the presence of chloride ions at concentrations of 1 × 10^{−4} mol/dm³, 1 × 10^{−3} mol/dm³, and 1 × 10^{−2} mol/dm³ has an inhibitory effect, as the corrosion current obtained in these solutions is lower than that obtained in the 0.1 mol/dm³ sodium sulfate solution, while the concentration of chloride ions of 5 × 10^{−2} mol/dm³ has a significant influence on increasing the corrosion current of the Cu24Zn5Al alloy. The inhibitory effect of the present chloride ions has been confirmed by other authors as well [35,56,57].

3.4. The Influence of the Immersion Time of Cu24Zn5Al Alloy in a Solution of 0.017 mol/dm³ PMT

The influence of the immersion time was investigated by immersing the Cu24Zn5Al electrode in a 0.017 mol/dm³ PMT solution for a specific time (15 min, 60 min, and 240 min). Afterwards, the electrode was taken out, washed with distilled water and alcohol, and moved into an electrochemical cell where open circuit potential (OCP) was determined, followed by polarization testing in a sodium sulfate solution with a concentration of 0.1 mol/dm³. The results of these experiments are shown in Figure 5 and Table 4. Based on the recorded OCP values, it can be said that the OCPs after immersion in the inhibitor solution for 15 min, 60 min, and 240 min (−0.035 V, −0.045 V, and −0.035 V) were close to the OCP value of the electrode

obtained without the pretreatment (-0.030 V). This confirms the assertion that a Cu_2O film was formed on the surface of the copper alloy in a neutral medium [41], which has a similar role as the film formed during immersion in the PMT solution [58]. From Figure 6, it can be seen that the lowest current densities were obtained when the Cu24Zn5Al alloy was immersed in the inhibitor solution for 240 min. By analyzing the results shown in Figures 1 and 5, it can be concluded that the current densities in the case when the electrode was pretreated in the inhibitor solution for a period of 15 min do not differ significantly from the current densities when the Cu24Zn5Al alloy was in the solution of PMT. This also supports the claim that the Cu-PMT protective layer forms more slowly in neutral sodium sulfate solutions. However, the inhibition efficiency was higher with immersion times of 60 min and 240 min compared to the maximum inhibition efficiency value recorded in solutions with the inhibitor present. This observation supports the fact that the thickness of the Cu-PMT protective film formed on the surface of the alloy increases over time [30,50,59].

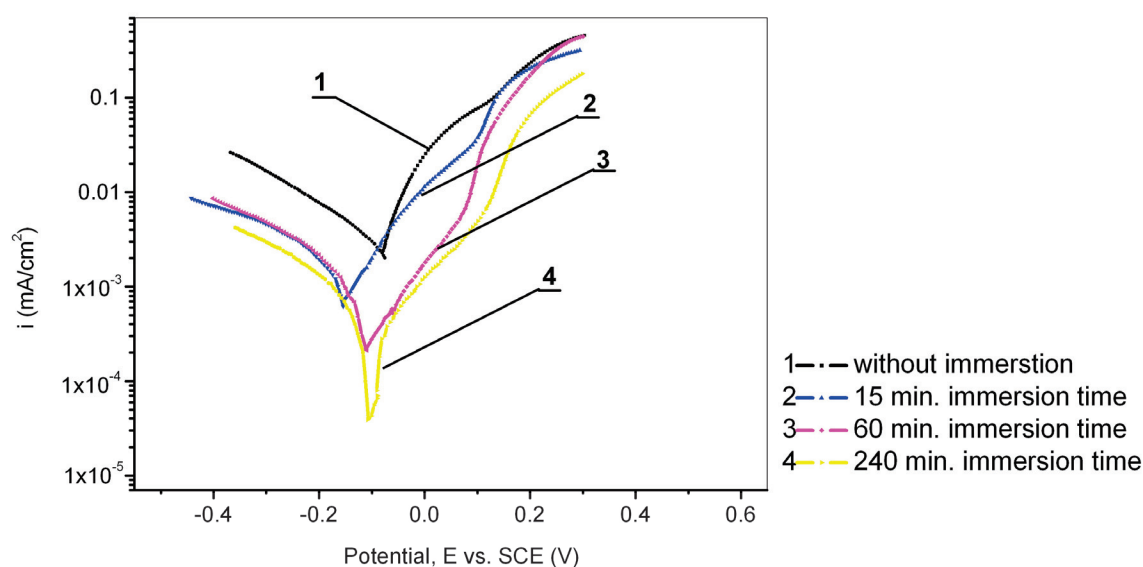


Figure 5. Potentiodynamic polarization curves of Cu24Zn5Al alloy in $0.1 \text{ mol/dm}^3 \text{ Na}_2\text{SO}_4$ solution: 1—without pretreatment, and with different immersion time of electrode in $0.017 \text{ mol/dm}^3 \text{ PMT}$: 2—15 min, 3—60 min, 4—240 min.

Table 4. Electrochemical parameters of Cu24Zn5Al alloy in $0.1 \text{ mol/dm}^3 \text{ Na}_2\text{SO}_4$ without and after pretreatment in a $0.017 \text{ mol/dm}^3 \text{ PMT}$ solution.

Immersion Time of Electrode in $0.017 \text{ mol/dm}^3 \text{ PMT}$ Solution	Parameters					
	OCP	E_{corr}	j_{corr}	β_c	β_a	IE
	Unit					
min	V vs. SCE	V vs. SCE	$\mu\text{A/cm}^2$	V/dec	V/dec	%
0	-0.030	-0.040	4.7	-0.292	0.148	/
15 min	-0.035	-0.157	1.9	-0.390	0.196	59.6
60 min	-0.045	-0.113	1.3	-0.341	0.144	72.3
240 min	-0.035	-0.105	0.9	-0.344	0.159	80.8

The OCP of Cu24Zn5Al alloy after 15 min, 60 min, and 240 min of immersion in the solution of sodium sulfate varies from -0.045 V to -0.035 V, which is close to the OCP value of Cu24Zn5Al alloy without immersion in the sodium sulfate solution, -0.030 V. The OCP of the Cu-PMT protective film is similar to the OCP of Cu24Zn5Al alloy in the sodium sulfate solution.

The inhibition efficiency (IE) is calculated according to the following equation:

$$IE(\%) = \frac{(j_{\text{corr}} - j_{\text{corr(immersion)}})}{j_{\text{corr}}} \times 100 \quad (20)$$

where they are:

j_{corr} —corrosion current density obtained in sodium sulfate solution without pretreatment ($\mu\text{A}/\text{cm}^2$);

$j_{\text{corr(immersion)}}$ —current density obtained in the sodium sulfate solution after pretreatment in the $0.017 \text{ mol}/\text{dm}^3$ PMT solution ($\mu\text{A}/\text{cm}^2$).

Electrochemical corrosion parameters of Cu24Zn5Al alloy such as open circuit potential (OCP), corrosion potential (E_{corr}), corrosion current density (j_{corr}), cathodic and anodic Tafel slopes (β_c and β_a), and inhibition efficiency (IE) are also shown in Table 4. The values for E_{corr} , j_{corr} , β_c , and β_a were obtained based on the polarization curves shown in Figure 5.

The effect of Cu24Zn5Al alloy immersing in a solution of $0.017 \text{ mol}/\text{dm}^3$ PMT can also be observed from Figure 6, which shows the results obtained by cyclic voltammetry from a potential of -1 V to 1 V (vs. SCE).

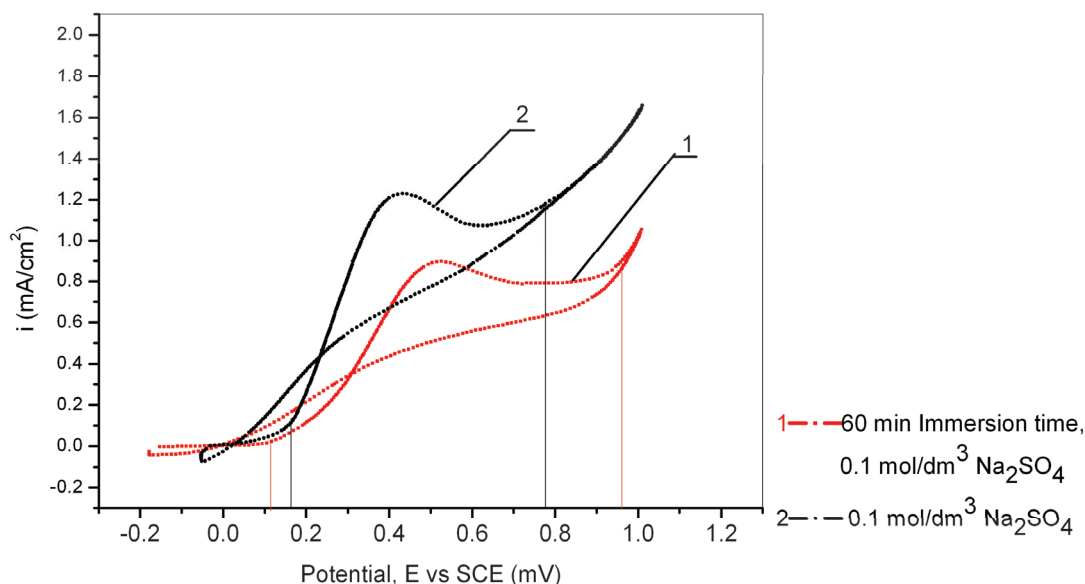


Figure 6. Cyclic voltametric curves of Cu24Zn5Al without pretreatment and with pretreatment of 60 min in $0.017 \text{ mol}/\text{dm}^3$ PMT solution (scan rate $10 \text{ mV}/\text{s}$).

Figure 6 clearly shows a shift of the peak originating from the formation of Cu_2O towards more positive potentials, as well as a decrease in anodic current densities obtained by recording the behavior of the Cu24Zn5Al alloy that had previously been allowed to stand for 60 min in $0.017 \text{ mol}/\text{dm}^3$ PMT solution. This clearly shows the formation of a protective Cu-PMT film on the surface of the alloy during its standing in a PMT solution with a concentration of $0.017 \text{ mol}/\text{dm}^3$ [58].

The inhibition efficiency (IE) is calculated according to the following equation:

$$IE(\%) = \frac{(A_{\text{corr}} - A_{\text{corr(immersion)}})}{A_{\text{corr}}} \times 100 \quad (21)$$

where they are:

A_{corr} —the area provided by integrated curve obtained in the sodium sulfate solution without pretreatment ($\text{mV mA}/\text{cm}^2$);

$A_{\text{corr(immersion)}}$ —the area provided by integrated curve obtained in the sodium sulfate solution after pretreatment in the 0.017 mol/dm^3 PMT solution ($\mu\text{A/cm}^2$).

The values for area under each peak are provided by integrating the curves in Figure 6 in range of potential from 0 mV to 1 mV and from 0 mV to 0.3 mV. Results are shown in Table 5.

Table 5. The inhibition efficiency (IE) of Cu24Zn5Al without pretreatment and with pretreatment of 60 min in 0.017 mol/dm^3 PMT solution in different range of potential.

Parameters			
Immersion Time of Electrode in 0.017 mol/dm^3 PMT Solution	Range of Potential	Obtained Area by Integrating	IE
min	V vs. SCE	mVmA/cm ²	%
0	0–1	0.911	/
60 min	0–1	0.576	36.77
0	0–0.3	0.069	/
60 min	0–0.3	0.027	60.87

We obtained the inhibition efficiency (IE) by integrating the curves in Figure 6 in range of potential from 0 mV to 0.3 mV confirm data for inhibition efficiency (IE) given in Table 4 and Figure 5.

The Effect of Chloride Ion Concentration

The electrochemical behavior of the Cu24Zn5Al alloy was tested in a 0.1 mol/dm^3 sodium sulfate solution containing various concentrations of chloride ions (1×10^{-4} , 1×10^{-3} , 1×10^{-2} , and $5 \times 10^{-2} \text{ mol/dm}^3$), and after 60 min of immersing in a 0.017 mol/dm^3 PMT solution. The results obtained are shown in Figure 7 and Table 5. As seen in Figure 7, an increase in the concentration of chloride ions leads to a shift in the potential of Cu24Zn5Al in the negative direction [32,60] after 60 min of immersion in a 0.017 mol/dm^3 PMT solution. The current density is higher in all solutions containing chloride ions in comparison to the current density in the sodium sulfate solution measured under the same conditions, but significantly lower than the current densities obtained by polarization in solutions with chloride ions of the same concentration, without 60 min of immersion in a 0.017 mol/dm^3 PMT solution. The results obtained in this way indicate the influence and importance of the process of immersing the alloy in the inhibitor solution.

The degree of corrosion current density reduction (%) is calculated according to the following equations:

$$S_{j_{\text{corr}}}(\%) = \frac{(j_{\text{corr}(\text{Na}_2\text{SO}_4)} - j_{\text{corr(immersion)}})}{j_{\text{corr}(\text{Na}_2\text{SO}_4)}} \times 100 \quad (22)$$

where they are:

$S_{j_{\text{corr}}}$ —the degree of corrosion current reduction (%);

$j_{\text{corr}(\text{Na}_2\text{SO}_4)}$ —corrosion current density obtained in sodium sulfate solution ($\mu\text{A/cm}^2$);

$j_{\text{corr(immersion)}}$ —current density obtained in the sodium sulfate solution without and with the presence of different concentrations of chloride ions, after the immersion time of 60 min in a solution of 0.017 mol/dm^3 PMT ($\mu\text{A/cm}^2$).

And

$$S_{j_{\text{corr}}}(\%) = \frac{(j_{\text{corr}(\text{Cl})} - j_{\text{corr(immersion)}(\text{Cl})})}{j_{\text{corr}(\text{Cl})}} \times 100 \quad (23)$$

where they are:

$S_{j_{\text{corr}}}$ —the degree of corrosion current reduction (%);

$j_{\text{corr(Cl)}}$ —corrosion current density obtained in sodium sulfatase solution with different concentrations of chloride ions ($\mu\text{A}/\text{cm}^2$);

$j_{\text{corr(immersion)(Cl)}}$ —current density obtained in sodium sulfate solution with different concentrations of chloride ions, and after the immersion time of 60 min in $0.017 \text{ mol}/\text{dm}^3$ PMT solution ($\mu\text{A}/\text{cm}^2$).

Electrochemical corrosion parameters of the Cu24Zn5Al alloy, such as open circuit potential (OCP), corrosion potential (E_{corr}), corrosion current density (j_{corr}), cathodic and anodic Tafel slopes (β_c and β_a), and corrosion current reduction efficiency (S) are presented in Table 6. The values for E_{corr} , j_{corr} , β_c , and β_a were obtained based on the polarization curves shown in Figure 7.

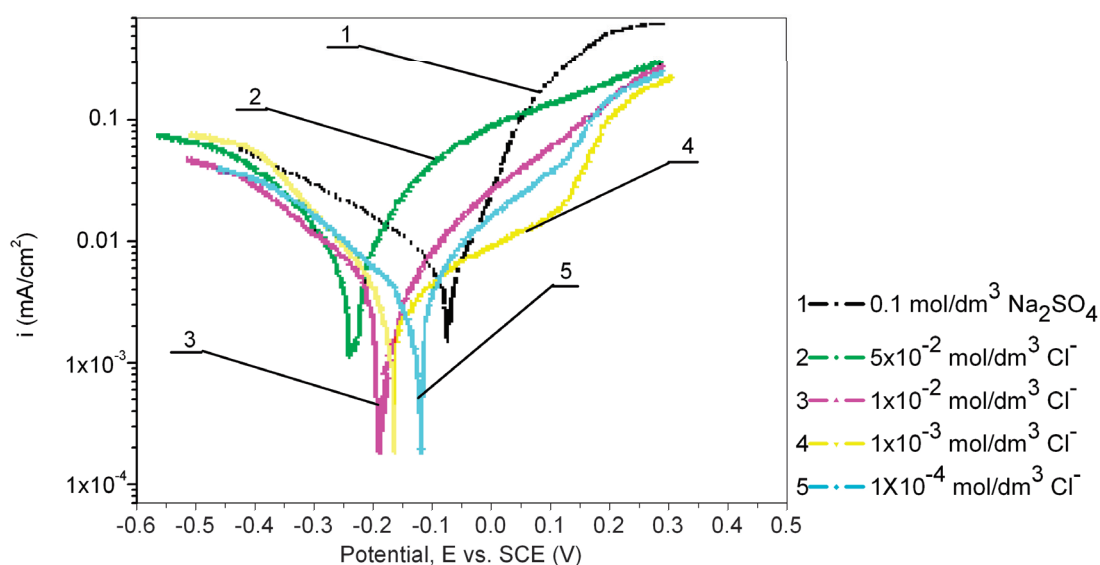


Figure 7. Potentiodynamic polarization curves of Cu24Zn5Al alloy in $0.1 \text{ mol}/\text{dm}^3 \text{ Na}_2\text{SO}_4$ in the presence of various chloride ions concentrations, after 60 min pretreatment in $0.017 \text{ mol}/\text{dm}^3$ PMT (scan rate $1 \text{ mV}/\text{s}$).

Table 6. Electrochemical corrosion parameters of the Cu24Zn5Al alloy in $0.1 \text{ mol}/\text{dm}^3 \text{ Na}_2\text{SO}_4$ without and with the presence of chloride ions, without and after 60 min immersion time in $0.017 \text{ mol}/\text{dm}^3$ PMT.

Parameters							
0.1 mol/dm ³ Na ₂ SO ₄ Containing Various Concentrations of Cl [−]	OCP	E _{corr}	j _{corr}	β _c	β _a	IE	
Unit							
mol/dm ³ Cl [−]	V vs. SCE	V vs. SCE	μA/cm ²	V/dec	V/dec	%	%
Without immersion in 0.017 mol/dm ³ PMT							
/	−0.030	−0.040	4.7	−0.292	0.148	/	/
After 60 min immersion time in 0.017 mol/dm ³ PMT							
/	−0.045	−0.113	1.3	−0.341	0.144	72.3	/
1 × 10 ^{−4}	−0.082	−0.128	2.7	−0.234	0.116	42.6	6.90
1 × 10 ^{−3}	−0.076	−0.181	3.3	−0.207	0.249	29.8	7.14
1 × 10 ^{−2}	−0.077	−0.198	4.1	−0.255	0.268	12.8	7.87
5 × 10 ^{−2}	−0.073	−0.248	9.8	−0.275	0.219	n/a	16.95

Based on the results presented in Table 6, it can be concluded that by immersing the Cu₂₄Zn₅Al alloy in a 0.017 mol/dm³ PMT solution, there is an additional influence on the reduction of the corrosion current density compared to the results presented in Table 3, which shows the electrochemical corrosion parameters of the Cu₂₄Zn₅Al alloy in a 0.1 mol/dm³ sodium sulfate solution with varying concentrations of chloride ions, without prior immersing.

4. Conclusions

Polarization measurements have shown that with the increase of the PMT concentration, the anodic current density around the corrosion potential decreases, indicating that PMT behaves as a corrosion inhibitor for the Cu₂₄Zn₅Al alloy.

The investigation that involved immersing the alloy in a 0.017 mol/dm³ inhibitor solution suggests the formation of a protective layer (Cu-PMT).

The presence of chloride ions in the tested solutions has an impact on the corrosion behavior of the Cu₂₄Zn₅Al alloy, causing a negative shift in the corrosion potential and an increase in the current density as the concentration of chloride ions rises.

The investigation that involved immersing the alloy in a 0.017 mol/dm³ inhibitor solution and testing it in sodium sulfate solutions with different concentrations of chloride indicates the formation of a protective layer (Cu-PMT), as the current densities measured in chloride solutions with prior immersion of the alloy in the inhibitor solution are lower than those measured in chloride solutions of the same concentrations without immersion in the inhibitor solution.

Author Contributions: Conceptualization, V.G. and M.M.A.; methodology, M.M.A.; validation, Ž.Z.T., M.B.P.M. and M.B.R.; investigation, V.G.; resources, V.G.; data curation, M.B.P.M. and M.B.R.; writing—V.G.; visualization, Ž.Z.T.; supervision, M.M.A.; project administration, M.B.P.M. and M.B.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by the Ministry of Science and Technological Development and Innovations of the Republic of Serbia, Grant No. 451-03-47/2023-01/200052.

Data Availability Statement: Data availability is not applicable to this article as no new data were created or analysed in this study.

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

References

1. Fateh, A.; Aliofkhazraei, M.; Rezvanian, A.R. Review of corrosive environments for copper and its corrosion inhibitors. *Arab. J. Chem.* **2020**, *13*, 481–544. [CrossRef]
2. Liu, H.X.; Si, N.C.; Xu, G.F. Influence of process factors on shape memory effect of CuZnAl alloys. *Trans. Nonferrous Met. Soc. China* **2006**, *16*, 1402–1409. [CrossRef]
3. Guerioune, M.; Amiour, Y.; Bounour, W.; Guellati, O.; Benaldjia, A.; Amara, A.; Chakri, N.E.; Ali-Rachedi, M.; Vrel, D. SHS of Shape Memory CuZnAl Alloys. *Int. J. Self-Propagating High-Temp. Synth.* **2008**, *17*, 41–48. [CrossRef]
4. Jani, J.M.; Leary, M.; Subic, A.; Gibson, M.A. A review of shape memory alloy research, applications and opportunities. *Mater. Des.* **2014**, *56*, 1078–1113. [CrossRef]
5. De Filippo, B.; Brotzu, A.; Natali, S. Corrosion Behavior of Cu-Zn-Al Shape Memory Alloy in Controlled Environments. *AIP Conf. Proc.* **2020**, 2257, 020013. [CrossRef]
6. Cubela, D. Shape Memory Alloys. *Masinstvo* **2002**, *2*, 83–92.
7. Huang, W. Shape Memory Alloys and their Application to Actuators for Deployable Structures. Ph.D. Dissertation, Department of Engineering University of Cambridge, Cambridge, MA, USA, 1998.
8. Subramanian, A. Fatigue Behavior of Copper Zinc Aluminum Shape Memory Alloys. Master's Thesis, The Faculty of Graduate Studies, University of Manitoba, Winnipeg, MB, Canada, 1998.
9. Agnihotri, R.; Bhardwaj, S. Synthesis and Characterization of CuZnAl Based Shape Memory Alloys and to Optimize Behavior on Different Properties by Varying Weight Percentage. *Int. J. Mater. Sci. Eng.* **2016**, *4*, 229–234.
10. Wang, Y.; Jing, T.; Peng, H.; He, W.; Yan, J.; Wang, S.; Li, N.; Wen, Y. Re-examination of martensitic stabilization in Cu-based shape memory alloys Part I. Identification of occurrence stage and degree of martensitic stabilization in CuZnAl alloys. *J. Alloys Compd.* **2022**, *913*, 165276. [CrossRef]

11. Alaneme, K.K.; Okotete, E.A.; Oluwafemi, A.; Inyang, U. Assessment of the mechanical behaviour of thermally aged B and Fe modified CuZnAl shape memory alloys. *Rev. De Metal.* **2019**, *55*, 1–8. [CrossRef]
12. Sampath, V. Improvement of Shape-Memory Characteristics and Mechanical Properties of Copper-Zinc-Aluminum Shape-Memory Alloy with Low Aluminum Content by Grain Refinement. *Mater. Manuf. Process.* **2006**, *21*, 789–795. [CrossRef]
13. Sathish, S.; Mallik, U.S.; Raju, T.N. Corrosion Behavior of Cu-Zn-Ni Shape Memory Alloys. *J. Miner. Mater. Charact. Eng.* **2013**, *1*, 49–54. [CrossRef]
14. Majed, R.A.; Elia, S.M.; Fadhel, Z.; Mohamed, D. Effect of Halogen Ions on the Corrosion of Brass in Na₂SO₄ Solution. *Eng. Technol. J.* **2010**, *28*, 1386–1395.
15. Vrsalović, L.; Ivanić, I.; Čudina, D.; Lokas, L.; Kožuh, S.; Gojić, M. The Influence of Chloride Ion Concentration on the Corrosion Behavior of the CuAlNi Alloy. *Tech. Bull.* **2017**, *11*, 67–72.
16. Qafsaou, W.; Blanc, C.; Peabeare, N.; Shhiri, A.; Mankowski, G. Study of different triazole derivative inhibitors to protect copper against pitting corrosion. *J. Appl. Electrochem.* **2000**, *8*, 959–966. [CrossRef]
17. Lalitha, A.; Ramesh, S.; Rajeswari, S. Surface protection of copper in acid medium by azoles and surfactants. *Electrochim. Acta* **2005**, *51*, 47–55. [CrossRef]
18. Gomma, G.K. Effect of azole compounds on corrosion of copper in acid medium. *Mater. Chem. Phys.* **1998**, *56*, 27–34. [CrossRef]
19. Warraky, A.A.E. The effect of sulphide ions on the corrosion inhibition of copper in acidic chloride solutions. *Anti-Corros. Methods Mater.* **2003**, *50*, 40–46. [CrossRef]
20. Ehteshamzade, M.; Shahrabi, T.; Hosseini, M.G. Inhibition of copper corrosion by self-assembled films of new Schiff bases and their modification with alkanethiols in aqueous medium. *Appl. Surf. Sci.* **2006**, *252*, 2949–2959. [CrossRef]
21. Ma, H.; Chen, S.; Niu, L.; Zhao, S.; Li, S.; Li, D. Inhibition of copper corrosion by several Schiff bases in aerated halide solutions. *Appl. Electrochem.* **2002**, *32*, 65–72. [CrossRef]
22. Sherif, E.M.; Park, S.M. Inhibition of copper corrosion in acidic pickling solutions by N-phenyl-1,4-phenylenediamine. *Electrochim. Acta* **2006**, *51*, 4665–4673. [CrossRef]
23. Lisac, E.S.; Brnada, A.; Mance, A.D. Secondary amines as copper corrosion inhibitors in acid media. *Corros. Sci.* **2000**, *42*, 243–257. [CrossRef]
24. Matos, J.B.; Pereira, L.P.; Agostinho, S.M.L.; Barcia, O.E.; Cordeiro, G.G.O.; D'Elia, E. Effect of cysteine on the anodic dissolution of copper in sulfuric acid medium. *J. Electroanal. Chem.* **2004**, *570*, 91–94. [CrossRef]
25. Zhang, D.; Gao, L.; Zhou, G. Inhibition of copper corrosion in aerated hydrochloric acid solution by amino-acid Compounds. *J. Appl. Electrochem.* **2005**, *35*, 1081–1085. [CrossRef]
26. Scendo, M. The effect of purine on the corrosion of copper in chloride solutions. *Corros. Sci.* **2007**, *49*, 373–390. [CrossRef]
27. Subramanian, R.; Lakshminarayanan, V. Effect of adsorption of some azoles on copper passivation in alkaline medium. *Corros. Sci.* **2002**, *44*, 535–554. [CrossRef]
28. Ye, X.R.; Xin, X.Q.; Zhu, J.J.; Xue, Z.L. Coordination compound films of 1-phenyl-5-mercaptotetrazole on copper surface. *Appl. Surf. Sci.* **1998**, *135*, 307–317. [CrossRef]
29. Szocs, E.; Vastag, G.; Shaban, A.; Kalman, E. Electrochemical behavior of an inhibitor film formed on copper surface. *Corros. Sci.* **2005**, *47*, 893–908. [CrossRef]
30. Szocs, E.; Vastag, G.; Shaban, A.; Konczos, G.; Kalman, E. Investigation of copper corrosion inhibition by STM and EQCM techniques. *J. Appl. Electrochem.* **1999**, *29*, 1339–1345. [CrossRef]
31. Pi, J.; Chen, M.; Chen, T.; Wang, Q.; Cheng, S.; Fu, C. Corrosion inhibition effect of 1-phenyl-5-mercaptotetrazole on nickel-aluminum bronze in seawater: A combined experimental and theoretical study. *Colloids Surf. A Physicochem. Eng. Asp.* **2023**, *666*, 131354. [CrossRef]
32. Altaf, F. Effect of Inhibitors on the Corrosion of Copper and its Alloys by Using Electrochemical Impedance Spectroscopy and Cyclic Voltammetry. Ph.D. Thesis, Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan, 2013.
33. Wang, J.L.; Wu, Y.G.; Liu, J. Effectiveness of Corrosion Inhibitors on Bronze and Cast Iron with Prefilming Treatment. *Int. J. Electrochem. Sci.* **2013**, *8*, 4631–4640. [CrossRef]
34. Al-Otaibi, M.S.; Al-Mayouf, A.M.; Khan, M.; Mousa, A.A.; Al-Mazroa, S.A.; Alkhatlan, H.Z. Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media. *Arab. J. Chem.* **2014**, *7*, 340–346. [CrossRef]
35. Hrimla, M.; Bahsis, L.; Laamari, M.R.; Julve, M.; Stiriba, S.E. An Overview on the Performance of 1,2,3-Triazole Derivatives as Corrosion Inhibitors for Metal Surfaces. *Int. J. Mol. Sci.* **2022**, *23*, 16. [CrossRef] [PubMed]
36. Mihit, M.; Laarej, K.; El Makarim, H.A.; Bazzi, L.; Salghi, R.; Hammouti, B. Study of the inhibition of the corrosion of copper and zinc in HNO₃ solution by electrochemical technique and quantum chemical calculations. *Arab. J. Chem.* **2010**, *3*, 55–60. [CrossRef]
37. Rao, B.V.A.; Reddy, M.N. Formation, characterization and corrosion protection efficiency of self-assembled 1-octadecyl-1H-imidazole films on copper for corrosion protection. *Arab. J. Chem.* **2017**, *10*, S3270–S3283. [CrossRef]
38. Radovanović, M. Influence of Organic Inhibitors on Corrosion Behavior of Brass in Sodium Sulfate Solution. Ph.D. Thesis, University of Belgrade—Technical Faculty Bor, Bor, Serbia, 2012.
39. Antonijević, M.M.; Milic, S.M. Electrochemical behavior of Cu₂₄Zn₅Al alloy in alkaline medium in the presence of chloride ions and benzotriazole. *Mater. Chem. Phys.* **2009**, *118*, 385–391. [CrossRef]
40. Huković, M.M.; Babić, R.; Paić, I. Copper corrosion at various pH values with and without the inhibitor. *J. Appl. Electrochem.* **2000**, *30*, 617–624. [CrossRef]

41. Benzbiria, N.; Zertoubi, M.; Azzi, M. Oxygen reduction reaction kinetics on pure copper in neutral sodium sulfate solution. *SN Appl. Sci.* **2020**, *2*, 2101. [CrossRef]
42. Gardic, V.; Gupta, V.; Antonijevic, M. Corrosion behaviour of Cu₂₄Zn₅Al alloy in a sodium tetraborate solution in the presence of 1-phenyl-5-mercaptotetrazole. *Indian J. Chem. Technol.* **2014**, *21*, 350–358.
43. Kozlica, D.K.; Kokalj, A.; Milosev, I. Corrosion inhibition of copper and aluminium by 2-mercaptobenzimidazole and octylphosphonic acid—Surface pre-treatment and method of film preparation. *Electrochim. Acta* **2022**, *431*, 141154. [CrossRef]
44. Mihit, M.; Ellssami, S.; Bouklah, M.; Bazzi, L.; Hammouti, B.; AitAddi, E.; Salghi, R.; Kertit, S. The inhibited effect of some tetrazolic compounds towards the corrosion of brass in nitric acid solution. *Appl. Surf. Sci.* **2006**, *252*, 2389–2395. [CrossRef]
45. Kozlica, D.K.; Ekar, J.; Kovač, J.; Milošev, I. Roles of Chloride Ions in the Formation of Corrosion Protective Films on Copper. *J. Electrochem. Soc.* **2021**, *168*, 031504. [CrossRef]
46. Kozlica, D.K.; Kokalj, A.; Milosev, I. Synergistic effect of 2-mercaptobenzimidazole and octylphosphonic acid as corrosion inhibitors for copper and aluminium—An electrochemical, XPS, FTIR and DFT study. *Corros. Sci.* **2021**, *182*, 109082. [CrossRef]
47. Kokalj, A. On the use of the Langmuir and other adsorption isotherms in corrosion inhibition. *Corros. Sci.* **2023**, *2017*, 111112. [CrossRef]
48. Yu, P.; Liao, D.M.; Luo, Y.B.; Chen, Z.G. Studies of Benzotriazole and Tolytriazole as Inhibitors for Copper Corrosion in Deionized Water. *Corrosion* **2003**, *59*, 314–318. [CrossRef]
49. Wang, X.; Li, W.; Tan, B.; Wang, F.; Du, H.; Liu, R.; Han, X.; Zhang, S. Corrosion inhibition effect of benzimidazole and two derivatives on copper in alkaline environments: Experimental and theoretical analyses. *J. Mol. Liq.* **2023**, *390*, 122985. [CrossRef]
50. Yin, M.; Li, Z.; Xiao, Z.; Pang, Y.; Li, Y.; Shen, Z. Corrosion behavior of Cu-Al-Mn-Zn-Zr shape memory alloy in NaCl solution. *Trans. Nonferrous Met. Soc. China* **2021**, *31*, 1012–1022. [CrossRef]
51. Nady, H.M.; El-Rabiei, M.M.; Badawy, W.A. Stability of Some Copper Ternary Alloys in Chloride Solutions Polluted by Sulfide Ions. *Chem. Process Eng. Res.* **2014**, *20*, 35–44.
52. Feng, Y.; Teo, W.K.; Siow, K.S.; Tag, K.L.; Hsieh, A.K. The Corrosion Behaviour of Copper in Neutral Tap Water. Part I: Corrosion Mechanisms. *Corros. Sci.* **1996**, *38*, 369–385. [CrossRef]
53. Gudić, S.; Vrsalović, L.; Radeljić, A.; Oguzie, E.E.; Ivanić, I.; Kožuh, S.; Gojić, M. Comparison of Corrosion Behavior of Copper and Copper Alloys in Aqueous Chloride Solution. *Chem. Ind. Chem. Eng. Q.* **2021**, *27*, 383–394. [CrossRef]
54. Nady, K.; El-Rabiei, M.M.; El-Hafez, G.M.A.; Tribo, J.B. Electrochemical Stability of Cu–10Al–10Zn, Cu–10Al–10Ni, and Cu–10Ni–10Zn Ternary Alloys in Simulated Physiological Solutions. *J. Bio Tribo-Corros.* **2016**, *2*, 28. [CrossRef]
55. Shaik, M.A.; Syed, K.H.; Golla, B.R. Electrochemical behavior of mechanically alloyed hard Cu-Al alloys in marine environment. *Corros. Sci.* **2019**, *153*, 249–257. [CrossRef]
56. Brotzu, A.; Filippo, B.D.; Natali, S.; Zortea, L. Corrosion behavior of Shape Memory Alloy in NaCl environment and deformation recovery maintenance in Cu-Zn-Al system. *Frat. Ed Integrità Strutt.* **2022**, *62*, 64–74. [CrossRef]
57. Ding, Y.; Zhao, R.; Qin, Z.; Wu, Z.; Wang, L.; Liu, L.; Lu, W. Evolution of the Corrosion Product Film on Nickel-Aluminum Bronze and Its Corrosion Behavior in 3.5 wt % NaCl Solution. *Materials* **2019**, *12*, 209. [CrossRef] [PubMed]
58. Al-Mobarak, N.A.; Khaled, K.F.; Hamed, M.N.H.; Abdel-Azim, K.M. Employing electrochemical frequency modulation for studying corrosion and corrosion inhibition of copper in sodium chloride solutions. *Arab. J. Chem.* **2011**, *4*, 185–193. [CrossRef]
59. Khaitia, Z.; Othman, A.A.; Morena, M.S.; Bernarda, M.C.; Joireta, S.; Suttera, E.M.M.; Viviera, V. Corrosioninhibitionofcopperin-neutralchloridemediabyanoveldervative of 1,2,4-triazole. *Corros. Sci.* **2011**, *53*, 3092–3099. [CrossRef]
60. Yanga, J.; Zenga, y.; Zhua, M.; Liub, L.; Mengc, Y.; Chena, Y.; Maod, S. Study on effect of chloride and temperature on corrosion behavior of CoCrFeMnNi high entropy alloy. *Int. J. Electrochem. Sci.* **2023**, *18*, 100132. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Corrosion Behaviour Modelling Using Artificial Neural Networks: A Case Study in Biogas Environment

María Jesús Jiménez-Come *, Francisco Javier González Gallero , Pascual Álvarez Gómez and Jesús Daniel Mena Baladés

Escuela Técnica Superior de Ingeniería de Algeciras, Universidad de Cádiz, 11202 Algeciras, Spain; javier.gallero@uca.es (F.J.G.G.); pascual.alvarez@uca.es (P.Á.G.); jesusdaniel.mena@uca.es (J.D.M.B.)

* Correspondence: mariajesus.come@uca.es

Abstract: The main objective established in this work was to develop a model based on artificial neural networks (ANNs) to predict the corrosion status of stainless steel involved in biogas production, analyzing the influence of the material composition and the breakdown potential value. To achieve this objective, an ANN model capable of predicting the corrosion status of the material without the need to perform microscopic analysis on the material surface was proposed. The applicability of the corrosion models was verified via the experimental data considering different factors such as stainless steel composition, biogas environments simulated by artificial solution, temperature, surface finish, and the breakdown potential of the passive layer of stainless steel obtained from electrochemical tests. The optimal prediction performance shown by the model in terms of specificity and sensitivity values were 0.969 and 0.971, respectively, obtaining an accuracy of 0.966. Furthermore, analyzing the influence of the breakdown potential on corrosion modelling, an alternative model was presented capable of predicting the corrosion status automatically, without the need to resort to electrochemical tests for new conditions. The results demonstrated the utility of this technique to be considered in design and maintenance planning tasks for stainless steel structures subjected to localized corrosion in biogas production.

Keywords: biogas; corrosion modelling; artificial neural network; stainless steel; electrochemical tests

1. Introduction

In recent decades, the increasing energy requirements, in addition to the need to face the consequences of climate change, have encouraged looking for alternative renewable energy sources [1]. The International Energy Agency has estimated that global energy demand will increase by two to three times in this century. With the aim to reduce global warming, in addition to transforming pollutant waste into a valuable resource, the production of bioenergy has become a viable alternative to obtain more cost-effective and less polluting economic activity. It is estimated that the global bioenergy demand will increase by 20% in 2050 [2]. This bioenergy is represented mostly by biogas, bioethanol, and bioelectricity. Biogas is considered a versatile renewable energy source that can replace fossil fuels in power and heat production. It is obtained via anaerobic digestion of organic wastes, offering significant advantages over other types of bioenergy. The use of biodigesters to produce and store biogas via anaerobic digestion can be considered an environmentally friendly technology [3]. Biodigesters are tanks used for energy and biogas production. Raw biogas consists of 60–65% of methane, 30–35% of carbon dioxide, and small percentages of water vapour, H₂, H₂S, and other impurities [4]. The presence of hydrogen sulphide and other impurities in the production process may cause corrosion, leading to the deterioration of appliances and engines involved in biogas production [5].

Corrosion is considered one of the most critical issues in industrial processes [6]. It can be defined as the degradation of metal or alloy in contact with the environment, reducing

its durability. For most applications, it is possible to select materials that show excellent corrosion resistance; however, their costs are often prohibitive. In practice, it is usual to select materials that corrode slowly under uniform corrosion. Nevertheless, a significant proportion of corrosion failures occur due to localized corrosion, which results in failure in a much shorter time. The increasing price of energy encourages the development of cost-effective design solutions for biogas production. In this context, although concrete has been a widely used material in the manufacture of biodigesters, the reduction or even the elimination of corrosion in these tanks is difficult even when special coating is applied. In order to solve these disadvantages, stainless steel has become a suitable option for this application due to its great corrosion resistance, among other factors [7,8].

The high corrosion resistance of stainless steel is explained by the formation of the passive film on the material surface that protects it from aggressive environments. Chromium is the principal element in the composition of stainless steel responsible for the formation of the passive layer. Moreover, other alloying elements may appear in the chemical composition of the alloy, primarily nickel or molybdenum, improving the resistant behaviour of the material. According to the chemical composition, different grades of stainless steel can be obtained with different mechanical, physical, and chemical properties. The chemical composition of the alloy and its surface finish are factors that may have an influence on the corrosion behaviour of the material depending on the environmental conditions [9].

Over the past 50 years, different corrosion studies have concluded that corrosion costs can be estimated to be 3–4% of each nation's gross domestic product (GDP) [10]. These estimated costs do not consider individual safety or environmental consequences such as incidents, accidents, or outages, among others. Several industries have exposed that via adequate corrosion management, significant cost savings can be achieved [11]. In this context, electrochemical techniques have become a widely used tool in the study of corrosion behaviour [12]. The application of polarization techniques, both potentiostatic and dynamic methods, has been very successful in studying the phenomena involved in the corrosion process. However, in order to understand the behaviour of materials in different environmental conditions, a large number of experimental tests must be carried out. Moreover, the application of electrochemical methods to study the corrosion behaviour of material may influence the corrosion reaction of the samples, and they may not be capable of identifying localized corrosion accurately since these tests often require microscopic analysis of the material surface [13]. This can be tedious and lead to possible undesirable errors, including subjectivity in the experimental results. In order to solve these drawbacks and to improve precision, save time in the evaluation, and eliminate human error, the use of artificial intelligence-based models has been proposed by many researchers. In recent years, the adoption of machine learning in modelling real engineering problems was built on its ability to understand the interrelationships between real input and output data. The potential of these techniques to predict material properties has been reported in scientific literature [14–19]. Among the different techniques proposed in the literature, Artificial Neural Networks (ANNs) have become a promising tool that offers great computational power even when a small experimental dataset is considered [20]. In the literature, different models based on ANNs have been presented to model corrosion behaviour.

Pintos et al. [21] developed an ANN model to model atmospheric corrosion processes of carbon steel. The proposed model was compared against a classical regression model to predict the corrosion rate of this material. Diaz et al. [22] proposed an ANN model for the prediction of corrosion damage under different climatological and pollution conditions. The number of neurons in the input layer was defined according to the number of meteorological variables considered in the experimental procedure, whereas the output layer had one unit corresponding to the cumulated penetration. The authors concluded that the presented methodology based on ANNs was an efficient tool for corrosion process modelling from experimental data. These authors continued their studies in [23], where they presented an ANN-based methodology to predict corrosion damage of atmospheric corrosion problems for carbon steel expressed in terms of corrosion penetration. The authors used

the model to analyze the relevance of meteorological and pollution factors on corrosion behaviour. Silva et al. [24] applied an ANN to analyze the corrosion defects in pipelines with the aim of finding out the influence of the geometry of the defects on the pipe pressure capacity. Kenny et al. [25] developed an ANN model to analyze the factors that influence the atmospheric corrosion of carbon steel, copper, and aluminum. The authors considered the following as inputs for modelling the meteorological data in addition to local pollution: temperature, solar radiation, relative humidity, precipitation, time of exposure, time of wetness, wind velocity, chloride ions, sulphur compounds, and dustfall. According to the results, the authors concluded that the proposed ANN model could be considered as a good corrosion estimator to predict corrosion rates of the materials. Halama et al. [26] designed a model based on ANN for the assessment of atmospheric corrosion of carbon steel under local geographical conditions, considering climatic conditions (temperature and relative humidity) in addition to pollutant concentrations and precipitation. In that work, the objective was to construct an ANN model that operates with numerous time-dependent parameters predicting related corrosion mass losses accurately. Lin et al. [27] employed the ANN model to predict atmospheric corrosion rates of carbon steel subjected to general and coastal industrial zones. The model was used to determine the most significant factors in corrosion behaviour for the different environments. Tran et al. [28] proposed an ANN model to model atmospheric corrosion in tropical climate conditions. Different meteorological and chemical factors were considered as inputs for modelling, whereas the output provided by the model was related to the atmospheric corrosion rate of carbon steel. Kim et al. [29] used an ANN model to examine the oxidation resistance of Ni-based superalloys, analyzing the effect of the elements to define the optimum composition of the alloy. Zhu et al. [30] presented an ANN model to study the corrosion of carbon steel in reinforced concrete. The authors considered different physical and chemical parameters, including pH, corrosion potential, breakdown potential, and temperature, in addition to cement composition, concrete porosity, and water/cement ratio. They demonstrated the utility of the proposed model to evaluate the corrosion behaviour of materials. Wang et al. [31] presented a model based on ANN as a novel non-destructive testing method of corrosion. According to the electrochemical laboratory tests, the authors predicted the corrosion current density of the gas pipeline accurately. Li et al. [32] proposed an ANN corrosion model to predict the corrosion rate of Q345R steel, considering different factors as input variables: MDEA concentration, total amine concentration, pH, conductivity, and solution type, whereas the target value was defined as the corrosion rate. Soomro et al. [33] applied an ANN to predict the integrity of damaged oil and gas pipelines, considering temperature, pH, pressure, and velocity as input characteristics, whereas Li et al. [34] proposed an ANN for quantitative modelling of corrosion degradation prediction of offshore oil pipelines.

Although there are numerous applications in which neural network-based techniques have been successfully implemented in energy fields [35–37], no studies focused on localized corrosion modelling of stainless steel in biogas environments have been found in the literature. This work presents the application of the ANN model to predict the corrosion status of different grades of stainless steel in biogas environments. The proposed model was also applied to analyze the influence of different factors that may affect the corrosion behaviour of stainless steel subjected to these environments. The validity of the model was evaluated with the experimental data set obtained from electrochemical tests in addition to the microscopic analysis of the tested sample. In the experimental procedure, the polarization curves were carried out to assess the localized corrosion resistance of different stainless steel grades, namely pitting [38,39] and crevice [40] corrosion since they are the most important corrosion forms in biogas production [41,42].

In this study, the use of the ANN model allows us to determine the corrosion state of the sample under different conditions simulating biogas environments. Based on our experience in corrosion modelling [43,44], different ANN model configurations were proposed to achieve the established objectives:

Objective 1—To develop an ANN model capable of predicting the corrosion state of stainless steel involved in biogas production without the need for microscopic analysis of the analyzed sample after electrochemical tests.

In this case, three configurations were developed:

MODEL 1: In this case, the ANN model was presented to predict the pitting corrosion status of stainless steel considering data related to the properties of the material (stainless steel composition and surface finish), data obtained from the electrochemical test (breakdown potential of the passive layer) and those data related to the environment to which the material may be exposed in biogas production (temperature and the type of artificial solution). All these data were considered as inputs for the ANN model, while the output was defined by the pitting corrosion status of the sample: 1 for the patterns that suffer pitting corrosion under the conditions analyzed in each case and 0 for those patterns that resist the attack.

MODEL 2: In this case, the model was presented to predict crevice corrosion status. Similar to the previous model, the input variables were defined by the properties of the material (stainless steel composition and surface finish), data obtained from the electrochemical test (breakdown potential of the passive layer) and data related to the environment to which the material may be exposed in biogas production (temperature and the type of artificial solution). However, the output in this case corresponded to the state of crevice corrosion of the sample under study: 1 for the patterns that suffer crevice corrosion and 0 otherwise.

MODEL 3: It was presented as a global model to predict the pitting or crevice corrosion state of the material. In this case, the experimental data used in Model 1, in addition to the data used to develop Model 2, were considered. An additional input variable related to the type of corrosion to be evaluated was included, namely pitting or crevice corrosion. In this way, the input data presented to the model for each pattern were defined by the composition of the stainless steel, surface finish, breakdown potential value obtained from electrochemical tests, temperature, and type of artificial solution, in addition to the type of corrosion that was intended to be predicted (pitting or crevice corrosion). For this model, the output was defined by the corrosion status of the sample under study: 1 for samples that suffered corrosion and 0 otherwise.

The advantage of the proposed models to achieve Objective 1 is that all the models were developed to predict the corrosion status of the stainless steel involved in biogas production without the need to perform microscopic analysis of the material surface after electrochemical tests. This fact avoids adding subjectivity to the results since the optical analysis of the surface depends on the experience of the analyst and may be confusing.

Objective 2—To analyze the effect of PREN (Pitting Resistance Equivalent Number) as an input for corrosion behaviour modelling instead of considering the concentration of the alloying elements in the material.

In this case, MODEL 4, the composition of the material expressed as a percentage of the alloying elements that took part in the composition of the material was replaced by PREN, reducing the number of inputs that were considered in the ANN model.

Objective 3—To analyze the influence of the breakdown potential value obtained from electrochemical techniques in the corrosion modelling of stainless steel in biogas production.

In this case, a new configuration for the ANN model was proposed: MODEL 5. This configuration allowed predicting the corrosion status of stainless steel automatically, without the need to resort to electrochemical tests or microscopic analysis of stainless steel. This can be considered a great advantage in terms of cost savings since it allows knowing, in advance, the corrosion resistance of the material for new environmental conditions related to biogas production automatically.

2. Materials and Methods

With the aim to evaluate the susceptibility of different grades of stainless steel to suffer localized corrosion in biogas production, electrochemical tests were carried out in

two different solutions simulating biogas environments. The composition of the different stainless steel grades analyzed is collected in Table 1.

Table 1. Stainless steel composition for experimental tests.

Stainless Steel Grade	Cr (%)	Mo (%)	N (%)	Mn (%)	Ti (%)	Nb (%)
EN 1.4404	16.71	2.018	0.038	1.291	0.016	0.016
EN 1.4462	22.892	3.279	0.1619	1.397	0.034	0.011
EN 1.4482	19.94	0.223	0.1374	4.016	0.025	0.006
EN 1.4003	11.45	0.01	0.0115	0.547	0.015	0.006
EN 1.4571	16.801	2.066	0.0134	1.578	0.301	0.008
EN 1.4509	18.492	0.051	0.0235	0.43	0.148	0.393
EN 1.4521	18.555	1.999	0.024	0.507	0.127	0.416
EN 1.4318	17.744	0.089	0.144	1.258	0.002	0.007

The polarization curves for each sample in different environmental conditions simulating biogas environments were obtained according to ASTM standards: “Convention applicable to electrochemical measurements in corrosion testing” and “Making potentiostatic and potentiodynamic anodic polarization measurements” [45]. The electrochemical tests were carried out in a flat cell for both the pitting and the crevice corrosion analysis, where the temperature was controlled at a constant value by a thermostatic bath (Figure 1b). The test equipment consisted of a potentiostat (EG&G PARC model 263) connected to a computer with the software “Power suite 2.58”. The solution was stirred during the test to homogenize its composition. Two different temperatures were analyzed: 35 °C representing the mesophilic conditions and 50 °C corresponding to thermophilic ones. With the aim to ensure reproducibility in the experimental results, each condition was tested three times. The composition of each artificial solution (AS), representing the biogas environment, is collected in Table 2.

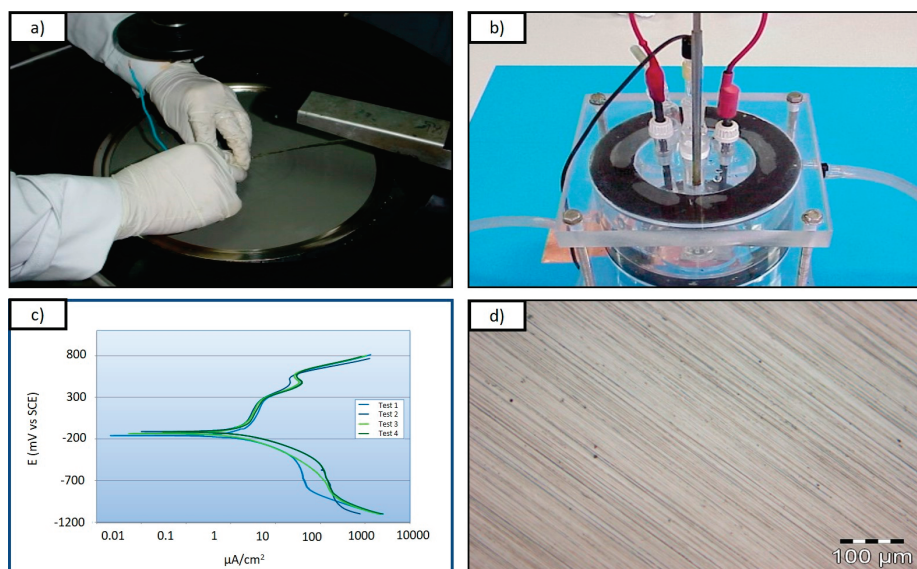


Figure 1. Experimental procedure of stainless steel EN 1.4462: (a) polishing, (b) electrochemical cell design, (c) potentiodynamic curves, (d) microscopic analysis.

Table 2. Artificial solutions conditions.

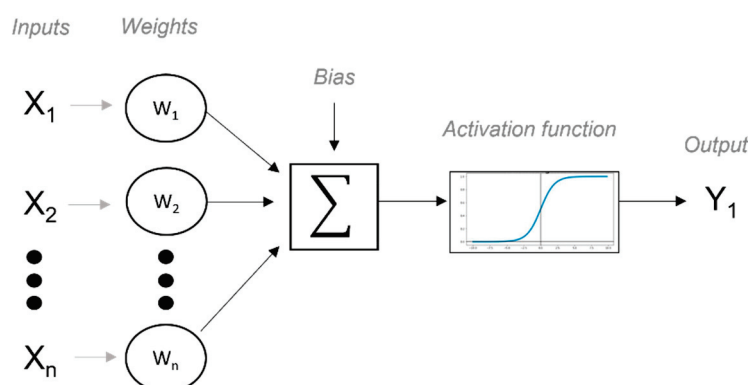
Reagent	g/L	AS 1	AS 2
Sodium Sulphate, Na_2SO_3	12.67	X	X
Ammonium Chloride, NH_4Cl	69.81	X	X
Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$	15.13	X	X
Sodium Acetate Trihydrate, $\text{NaCH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$	17.06	X	X
Hydrogen chloride, HCl , from FeCl_2 desulfuration	7.31	--	X
pH range		8.2–8.5	6.6–7.2

During the experimental procedure, to obtain a comparative assessment of the corrosion resistance of the different grades of stainless steel, the breakdown potential was evaluated for each condition according to the polarization curve obtained from the electrochemical test of each sample according to the environmental conditions. This potential is defined as the potential at which current density suffers an abrupt increase (Figure 1c). Many authors determine this potential as the value of potential corresponding to $100 \mu\text{A}/\text{cm}^2$ at the polarization curve [46]. After the electrochemical test, each sample was analyzed under a microscope to confirm whether it had suffered a localized corrosion attack, see Figure 1d. Therefore, each sample was defined according to the experimental conditions tested: types of artificial solution, temperature, chemical composition of the alloy, surface finish, breakdown potential, and finally, the localized corrosion status. In this way, the experimental database was obtained considering the most relevant factors involved in biogas production that may have an influence on stainless steel durability. This data set was used to develop ANN models to predict the corrosion behaviour of the different grades of stainless steel when they are exposed to the environmental conditions involved in the biogas production process.

2.1. Methodology

Artificial Neural Networks are considered a powerful machine learning technique for modelling real problems, including function approximation and classification problems that cannot be described with traditional mathematical models [47].

The fundamental unit in the ANN architecture is called a neuron or node that mimics the properties of biological neurons. Although there are many different types of ANNs, all of them consist of a set of neurons connected between them. Each unit receives inputs and produces the output based on a mathematical operation. In this case, the input entering the unit is weighted, and a bias is added to its value after passing through the activation function. A structural model is shown in Figure 2.

**Figure 2.** Mathematical model of an artificial neuron.

The structural type of the ANN model proposed in this study was the multilayer feedforward network, see Figure 3. This structure consists of multiple layers of neurons

where each neuron in the first layer receives the input while the neurons in the last layer provide the output. The layer between the input and the output is referred to as the hidden layer. All neurons in the input layer are connected to all neurons in the hidden layer, and so on to the output layer.

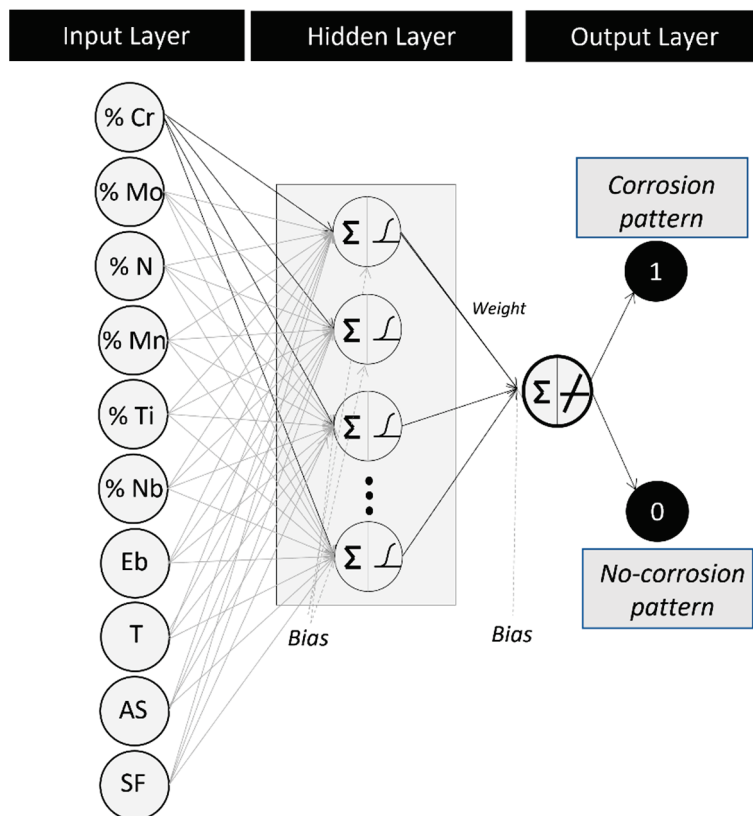


Figure 3. Structure for the proposed ANN model (Model 1) to predict the pitting corrosion status of stainless steel in biogas production. The input variables considered in this case were alloy composition, Eb (breakdown potential of passive layer), Temperature, AS (type of artificial solution simulating biogas environment), and SF (surface finish of the material).

ANNs technique uses a perceptron to classify a set of patterns of different classes that are linearly separable in the input space. However, the classification fails when non-separable data are presented to the model. In order to solve this drawback, a back-propagation algorithm is introduced [48]. It consists of a supervised learning method that considers the desired output value to train the model. This algorithm is used for backward propagation errors in feed-forward networks. According to the evaluated error, the weights of the network are updated. The algorithm can be considered as a recursive process that continues until a satisfactory performance is achieved.

For ANN models, a critical step is to find the optimal structure since there is no systematic method to determine it. The network incorporated in this study used a two-layer feed-forward network with one hidden layer, as depicted in Figure 3. The number of units in the input layer was specified by the number of parameters considered in each case, as shown in the results section, whereas the number of units in the output layer was specified according to the different corrosion statuses: 1 for corrosion samples and 0, otherwise. Moreover, the selection of the optimal number of hidden layers was made, knowing that those models with one hidden layer can solve most of the non-linear functions in real problems [49].

The optimal ANN structure is defined according to the number of neurons in each hidden layer, the number of hidden layers, the activation function, the learning algorithm and training parameters. Related to the activation functions, they were selected according

to the type of layer: the activation function applied in the hidden layer of the multilayer network presented in this study was the sigmoid transfer function since it is the most commonly used function for this layer, whereas the linear transfer function is generally employed in the final layer of a multilayer network with backpropagation. For the learning stage, the Levenberg–Marquardt training algorithm, based on the minimization of the sum of square error, was applied [50]. This algorithm was introduced by Levenberg in 1944 and then rediscovered by Marquardt. It was applied to train the model due to its speed to converge as well as its stability.

For the training stage, the input and output values were normalized to fall in a certain range to increase the convergence ability of the network, improving the training process of the ANN model. Training a neural network that can generalize well to new data is a challenging problem. One of the problems to avoid in the training stage is overfitting. Overfitting occurs when the model classifies those patterns that are presented in the training set correctly. However, the network fails when patterns that have not been used for training are presented to the model.

One method for avoiding overfitting is an early learning-stopping mechanism. In this case, the original data is divided into three subsets: the training set, the validation set, and the test set. The training set is used to adjust the parameters of the network. Out of the patterns that make up the training set, 25% of the data is not used for training and is set aside to form the validation set. This set is used to provide an unbiased evaluation of a model fit tuning model hyperparameters. The validation test determines when overfitting occurs. Finally, the test dataset is used to provide the generalization of the model. In this work, with the aim to avoid overfitting, the experimental data set was divided randomly into three subsets according to the 5-fold cross-validation method for the training stage. The model was trained on the training set and evaluated on the validation set to determine when overfitting occurs. This step is repeated until the optimal values for the ANN model are found. Once the optimal configuration is defined, the classification performance of the model is measured based on the test set, the independent set that has not been presented to the network before. The test set was applied to assess the behaviour of the model to predict the corrosion status of stainless steel. This process was implemented in MATLAB[®], 2021. It was repeated 20 times with the different configurations proposed for the ANN model to determine the optimal number of neurons in the hidden layer since too few units in the hidden layer may result in underfitting, whereas too many hidden neurons may lead to overfitting, consuming more time for training the model. The steps for the design of the ANN models are represented in Figure 4.

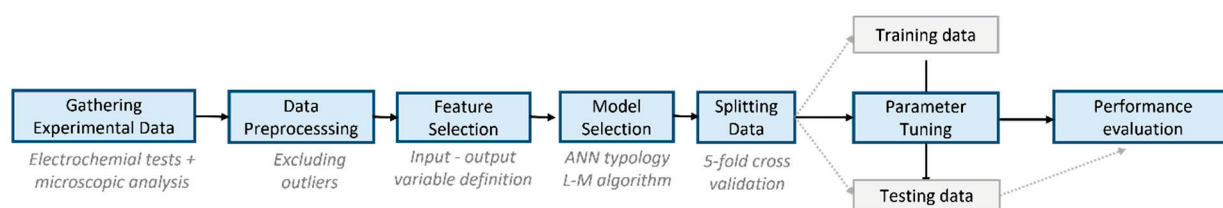


Figure 4. Methodology proposed to model the corrosion behaviour of stainless steel in biogas environments.

2.2. Classification Performance of ANN Models

Confusion matrix has been commonly used to evaluate the classification performance of the classification models. In this case, the accuracy of the model is measured based on the comparison between the target value and the output provided by the model. For a classifier and a pattern considered, there are four possible outcomes: true positive, true negative, false positive, and false negative. True positive is a correct classification result (the number of corrosion patterns that have been classified correctly by the model). A false positive is an incorrect result; this means those original no-corrosion patterns have been incorrectly classified by the model as corrosion patterns. The possible outcomes of a classification model are collected in the confusion matrix shown in Table 3.

Table 3. Confusion matrix for corrosion modelling.

	Target Status	
	Positive (Corrosion Pattern)	Negative (No-Corrosion Pattern)
Classification results		
Positive	TP (True Positive)	FP (False Positive)
Negative	FN (False Negative)	TN (True Negative)

According to the confusion matrix, the classification performance of the model can be evaluated according to the following equations:

$$Precision = TPR = \frac{TP}{TP + FP} \quad (1)$$

$$Accuracy = \frac{TP + TN}{TP + FP + TN + FN} \quad (2)$$

According to Lemeshow and Hosmer [51], the classification models can be divided into the following four categories based on accuracy results:

- Fail classifier: $0.5 \leq \text{Accuracy} < 0.6$;
- Poor Classifier: $0.6 \leq \text{Accuracy} < 0.7$;
- Fair Classifier: $0.7 \leq \text{Accuracy} < 0.8$;
- Good Classifier: $0.8 \leq \text{Accuracy} < 0.9$;
- Excellent Classifier: $0.9 \leq \text{Accuracy} \leq 1.0$.

3. Results and Discussion

In the study, the main objective was to develop ANN models capable of predicting the corrosion state of different stainless steel grades in biogas environments since localized corrosion can be considered one of the most critical problems in the maintenance of biodigestors used in biogas production. This work focused on pitting and crevice corrosion modelling since they are the two types of localized corrosion that can cause more dangerous damage to the material, affecting its durability. In this section, the results obtained for the different cases proposed in this work are shown in addition to the influence analysis of the parameters considered in the experimental procedure on corrosion modelling.

3.1. Localized Corrosion Behaviour Modelling: Results from OBJECTIVE 1

Three different ANN models were developed to predict the corrosion status of stainless steel used in biogas production. The most relevant characteristics of each ANN model proposed are shown in Table 4. In this case, Model 1 was developed for pitting corrosion modelling; Model 2 was presented to model crevice corrosion behaviour; and Model 3 was proposed to model both corrosion types.

Table 4. Structure of the proposed ANN model to model localized corrosion of stainless steel in biogas production. The inputs variables considered in this case were: alloy composition, Eb (breakdown potential of passive layer), Temperature, AS (type of artificial solution simulating biogas environment), and SF (surface finish of the material).

Identity	Corrosion Type	Input Neurons	Output Neurons:
Model 1	Pitting	10 units: %Cr, %Mo, %N, %Mn, %Ti, %Nb, Eb, T, AS, SF	2 units: 1: corrosion pattern 0: no-corrosion pattern

Table 4. Cont.

Identity	Corrosion Type	Input Neurons	Output Neurons:
Model 2	Crevice	10 units: %Cr, %Mo, %N, %Mn, %Ti, %Nb, Eb, T, AS, SF	2 units: 1: corrosion pattern 0: no-corrosion pattern
Model 3	Pitting and Crevice	11 units: %Cr, %Mo, %N, %Mn, %Ti, %Nb, Eb, T, AS, SF, corrosion type (pitting or crevice)	2 units: 1: corrosion pattern 0: no-corrosion pattern

For each case, the number of neurons in the input layer was determined by the number of factors considered in the experimental procedure, whereas the number of neurons in the output layer was defined as a function of the corrosion state: 1 for corrosion patterns and 0 for no-corrosion patterns. For all the models, different numbers of hidden neurons were considered to determine their optimal configurations, from 1 to 15 hidden neurons.

For all cases, the key challenge was to define the optimal structure for the ANN models proposed. In this study, the backpropagation algorithm was applied. The classification performance was validated by comparing the real corrosion status of the original samples with the predictive status provided by the model. As it was indicated previously, the performance of the models was tested by using 5-fold cross validation. This process was repeated 20 times.

The classification performance of Model 1 proposed to predict the pitting corrosion status of stainless steel in a biogas environment is collected in Figure 5 in terms of precision and accuracy.

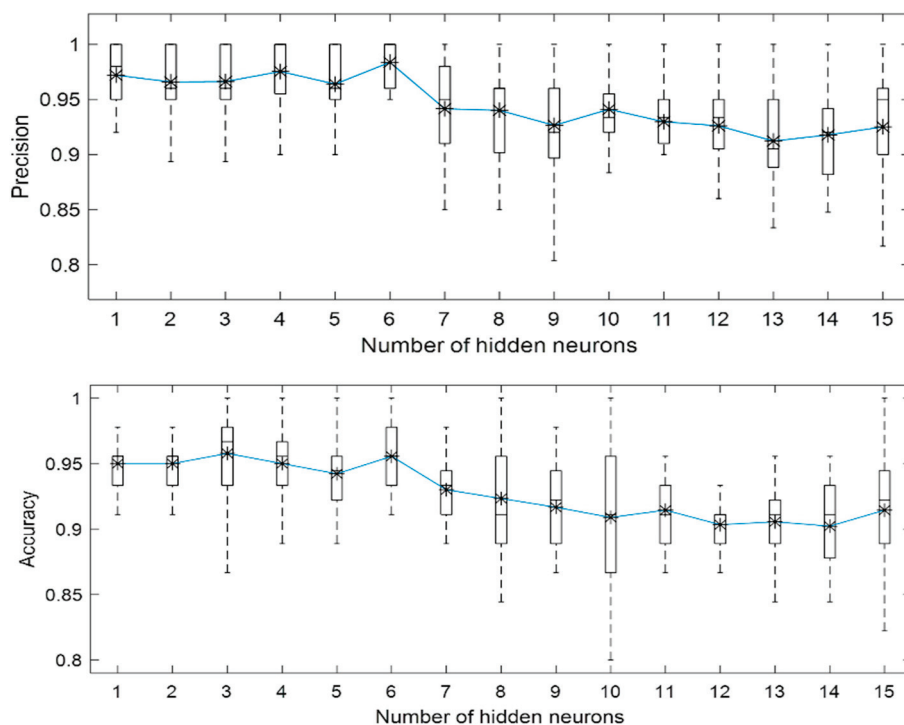


Figure 5. Influence of the number of hidden neurons in ANN models on precision and accuracy results for Model 1. Mean values (20 repetitions) for each case are pointed out with an asterisk.

According to Figure 5, it is observed that the maximum precision value reached by MODEL 1 to predict the pitting corrosion status of stainless steel in a biogas environment was 0.984 using six neurons in the hidden layer. In terms of accuracy, the maximum value reached by Model 1 was 0.958 with three hidden neurons. As can be seen in Figure 5, as

the number of hidden units increased, the model showed a worse performance for both indices: precision and accuracy.

Similar behaviour was obtained for Model 2, which proposed to predict the crevice corrosion status of stainless steel. In this case, the results are shown in Figure 6. According to the figure, the maximum values reached in terms of precision and accuracy were 0.971 and 0.949, respectively. In this case, the optimal structure of the ANN model was obtained by considering three neurons in the hidden layer.

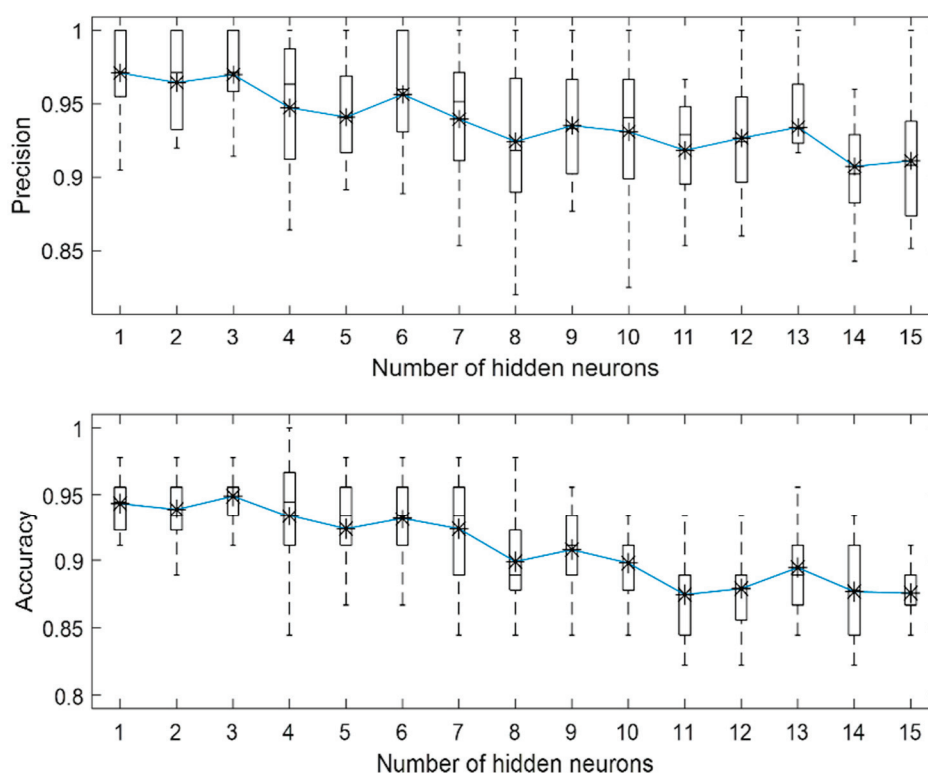


Figure 6. Influence of the number of hidden neurons in ANN models on precision and accuracy results (Model 2). Mean values for each case are pointed out with an asterisk.

According to the results collected in Figures 5 and 6, the proposed models can be used effectively to determine the corrosion status of both types of attack: pitting (Model 1) and crevice corrosion (Model 2). In this case, the behaviour is similar for both proposed cases, and the capability to predict the corrosion status in terms of precision and accuracy reached maximum values of 0.97 and 0.95, respectively. However, in order to develop a model with greater predictive capacity, a new scenario is proposed (Model 3). In this case, both types of localized corrosion are considered together in the same data set. As shown in Table 4, when Model 3 was proposed, a new input variable was included in the ANN model compared with the previous models. This new input corresponded to the type of corrosion analyzed for each pattern: pitting or crevice corrosion. The results obtained for this model are shown in Figure 7. As shown in the figure, the maximum precision and accuracy values obtained for Model 3 are 0.968 and 0.966, respectively. It is observed that, as in the previous cases, an increase in the number of hidden neurons led to a worse classification performance.

In order to compare the prediction performance for each model (Model 1, Model 2 and Model 3) and to determine the optimal configuration for the proposed models, it is useful to resort to the ROC (receiver operator characteristic) space [52]. In this graphic, the performance of different classification models can be compared. An ROC space is a two-dimensional graph in which the true positive rate (TPR) is plotted against the false positive rate (FPR) for each model. In the ROC space, the better configurations are those

located in the upper left corner since these points represent models with high true positive rates and low false positive rates.

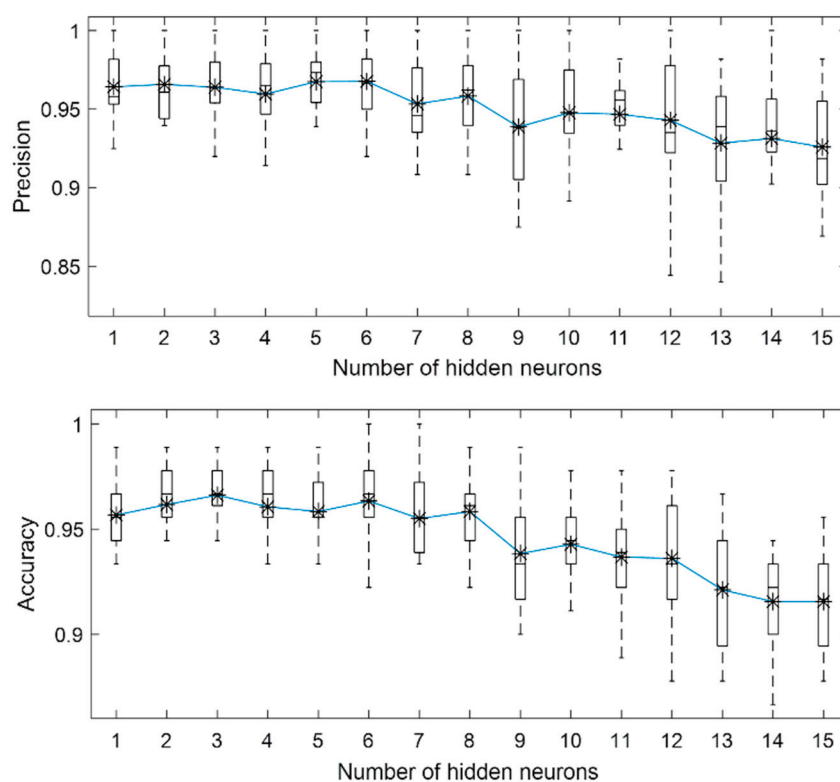


Figure 7. Influence of the number of hidden neurons in ANN models on precision and accuracy results (Model 3). Mean values for each case are pointed out with an asterisk.

Given a model, TPR is the proportion of positive patterns correctly classified by the model over the total number of positive patterns, whereas FPR represents the proportion of incorrectly classified negative patterns over the total number of negative patterns, as shown in the following equations:

$$TPR = \frac{TP}{TP + FN} \quad (3)$$

$$FPR = 1 - \frac{TN}{TN + FP} \quad (4)$$

According to Figure 8, it is observed that the different configurations proposed for Model 1 stood out for their specificity values, while for Model 2, its different configurations with different numbers of hidden units stood out for its sensitivity values. Furthermore, according to Figure 8, Model 3 showed the best classification performance. This model, considering both types of localized corrosion, outperformed single models: Model 1 and Model 2. In this case, for Model 3, the optimal configuration was obtained when three hidden units were considered in the ANN structure since this is the configuration that is located closest to the upper left corner of ROC space. In this case, specificity values ($1 - FPR$) of 0.969, sensitivity (TPR) of 0.971 and accuracy of 0.966 are obtained. Based on these values and according to Lemeshow and Hosmer, Model 3 can be defined as an excellent classifier since the accuracy was greater than 0.9. These results showed the usefulness of considering the proposed Model 3 to predict the behaviour against localized corrosion (pitting and crevice) for the different types of stainless steels evaluated in biogas environments. In this case, the model presented the advantage of being able to predict when the material will suffer the attack of localized corrosion (pitting or crevice) without

the need to perform microscopic analysis after the electrochemical test. This allowed for automation of part of the process, reducing subjectivity in the results.

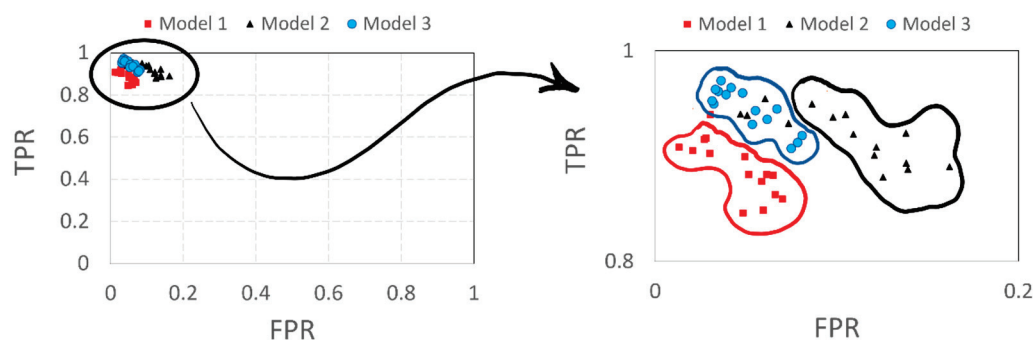


Figure 8. ROC graph for the different configurations of Model 1, Model 2, and Model 3.

Once the optimal configuration for the ANN model to predict localized corrosion status has been defined, an analysis of the influence of the different factors considered in this study could be developed.

3.2. Influence of PREN on Corrosion Modelling of Stainless Steel in Biogas Production

The previous models presented in this study considered, among the input variables, six variables related to the composition of the stainless steel: %Cr, %Mo, %N, %Mn, %Ti, and %Nb. Among the alloying elements, those that increase the resistance to pitting and crevice corrosion are molybdenum and chromium. Based on Mo and Cr content, among other alloying elements, a formula expressed as pitting resistance equivalent number (PREN) can be defined. PREN provides a qualitative method to predict the susceptibility of stainless steel to suffer pitting corrosion. This number is calculated using an empirical formula on the basis of the weight content of Nitrogen (N), Chromium (Cr), and Molybdenum (Mo) of stainless steel.

$$\text{PREN} = 1 \times \% \text{Cr} + 3.3\% \times \text{Mo} + 16\% \times \text{N} \quad (5)$$

According to this expression, a new model is proposed. In this case, the number of inputs in the ANN model was reduced in order to improve the prediction performance of the model since an excessive number of input variables can lead to a poor-quality model. For this reason, Model 4 considered as inputs six factors: PREN (related to the chemical composition of the stainless steel), surface finish, breakdown potential value obtained from electrochemical tests, temperature, the type of artificial solution simulating biogas environment in addition to the type of corrosion that is intended to be predicted (pitting or crevice corrosion). For this model, the output was defined by the corrosion status of the sample under study: 1 for samples that suffered corrosion and 0 otherwise. Table 5 collects the structure proposed for this model.

Table 5. Structure of the proposed ANN model to model localized corrosion of stainless steel in biogas production (MODEL 4).

Identity	Corrosion Type	Input Neurons	Output Neurons:
Model 4	Pitting and Crevice	6 units: PREN, Eb, T, AS, SF, corrosion type (pitting or crevice)	2 units: 1: corrosion pattern 0: no-corrosion pattern

The results obtained from Model 4, as a function of the number of hidden neurons, are shown in the Figure 9:

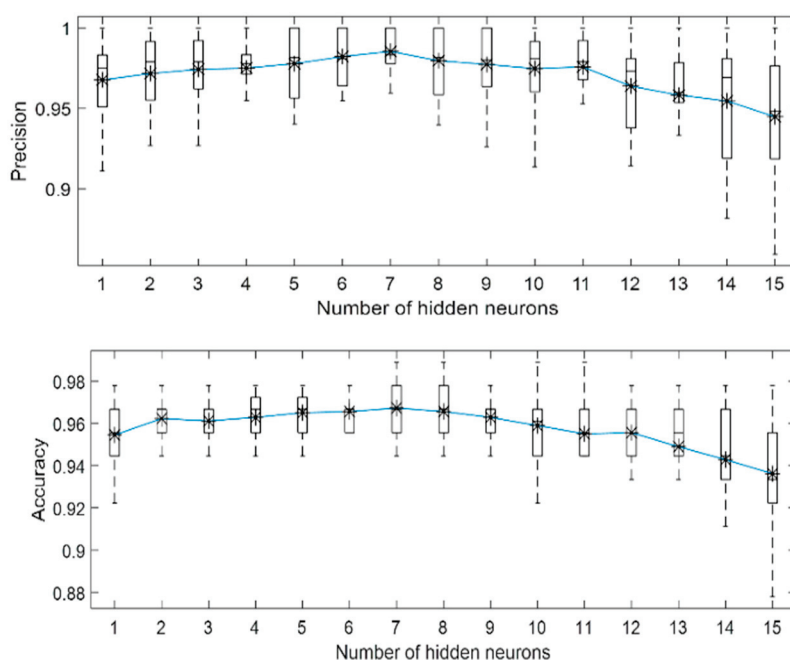


Figure 9. Influence of the number of hidden neurons in ANN models on precision and accuracy results (Model 4). Mean values for each case are pointed out with an asterisk.

Analyzing the results obtained for Model 4, it is observed that for the proposed configurations of the ANN model, greater precision and accuracy values were achieved compared to Model 3. In this case, reducing the number of input variables in the model (six inputs instead of eleven used in Model 3) improved the classification performance of the ANN model to predict the corrosion status of stainless steels in biogas environments.

The maximum precision and accuracy values obtained by the model were 0.985 and 0.967, respectively, using seven neurons in the hidden layer. In this case, an excessive number of hidden neurons led to poor classification performance. Comparing these results with those obtained for Model 3, it can be concluded that considering PREN allowed obtaining a more accurate model. Furthermore, according to Lemeshow and Hosmer, Model 4 can be defined as an excellent classifier since the accuracy value was greater than 0.9.

3.3. Influence of Breakdown Potential on Corrosion Modelling of Stainless Steel in Biogas Production

Finally, the objective was to analyze the influence of the breakdown potential of the passive layer obtained from the polarization curve on the classification performance. MODEL 5 was proposed, and its characteristics are specified in Table 6. In this case, the breakdown potential value was not considered an input variable. Compared with the previously proposed models, this approach had the advantage that it allowed us to determine the corrosion status of stainless steel automatically, with no need to carry out electrochemical tests or the microscopic analysis of the material surface. In this case, the model was trained considering as input variables the following ones: stainless steel composition, temperature, type of artificial solution simulating biogas environment, surface finish of the material under study, and the type of localized corrosion (pitting or crevice corrosion).

The results for Model 5, in terms of precision and accuracy, are shown in Figure 10:

According to Figure 10, the maximum precision and accuracy values reached for the different configurations proposed for Model 5 were 0.907 and 0.902, respectively. In this case, the optimal configuration was obtained when three neurons were considered in the hidden layer. These results demonstrated that the model showed a good capability to predict the corrosion status of stainless steel for this application automatically. However, the results related to precision and accuracy values were much lower than those obtained for Model 3, where the breakdown potential value was considered an input in the ANN model.

This fact emphasizes the importance of considering the breakdown potential value of the passive layer to model the corrosion behaviour of stainless steel in biogas environments.

Table 6. Structure of the proposed ANN model to model localized corrosion of stainless steel in biogas production (MODEL 5).

Identity	Corrosion Type	Input Neurons	Output Neurons:
Model 5	Pitting and Crevice	10 units: %Cr, %Mo, %N, %Mn, %Ti, %Nb, T, AS, SF, corrosion type (pitting or crevice)	2 units: 1: corrosion pattern 0: no-corrosion pattern

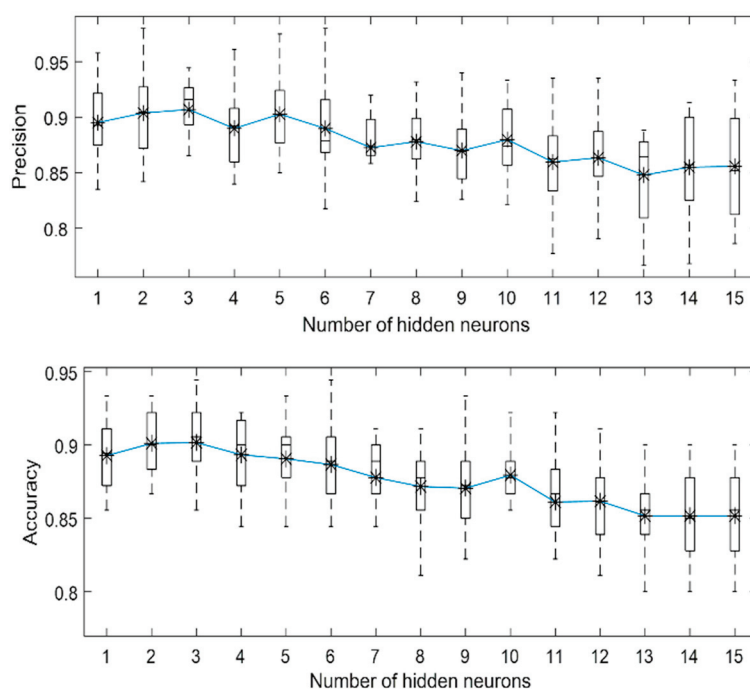


Figure 10. Influence of the number of hidden neurons in ANN models on precision and accuracy results (Model 5). Mean values for each case are pointed out with an asterisk.

Figure 11 depicts the results obtained from Model 5 using three neurons in the hidden layer. This figure shows the corrosion status predicted by the model under different conditions simulating biogas environments. In this case, following the experimental procedure, the corrosion state predicted by the model will be determined based on the artificial solution (AS₁ or AS₂), the thermal conditions (mesophilic or thermophilic), and the surface finish. In this case, the corrosion state is represented considering a pitting attack (P) or crevice attack (C). Cases in which the model predicts that the material will not undergo corrosion are shown in black, while cases in which the model predicts that the material will experience corrosion are shown in red. Furthermore, for those cases in which the corrosion state predicted by the model matches the one obtained experimentally, the box is coloured green, while in cases where they do not match, orange is used. While the graph represents the case for three grades of stainless steel (EN 1.4462, EN 1.4404, and EN 1.4521), the model is applicable to any alloy composition of stainless steel within the studied range.

EN 1.4462			
	No polishing		#600# grain polishing
AS ₁ mesophilic	P	C	P C
AS ₁ thermophilic	P	C	P C
AS ₂ mesophilic	P	C	P C
AS ₂ thermophilic	P	C	P C

EN 1.4404			
	No polishing		#600# grain polishing
AS ₁ mesophilic	P	C	P C
AS ₁ thermophilic	P	C	P C
AS ₂ mesophilic	P	C	P C
AS ₂ thermophilic	P	C	P C

EN 1.4521			
	No polishing		#600# grain polishing
AS ₁ mesophilic	P	C	P C
AS ₁ thermophilic	P	C	P C
AS ₂ mesophilic	P	C	P C
AS ₂ thermophilic	P	C	P C

Figure 11. Corrosion behaviour predicted by the model under different conditions simulating biogas environments, considering different artificial solutions (AS1 or AS2), thermal conditions (mesophilic or thermophilic), and the surface finish. In this case, the corrosion state is represented considering a pitting attack (P) or crevice attack (C). Corrosion cases are represented with red letters, while no-corrosion cases are indicated with black letters.

4. Conclusions

In order to minimize the impact of corrosion on the durability of stainless steel structures used in biogas production, different models based on ANN were proposed in this study.

The main objective was to develop an ANN model capable of predicting the corrosion state of stainless steel involved in biogas production. The two most important types of localized corrosion that can affect stainless steel in this type of application were analyzed: pitting and crevice corrosion. The variables considered to model corrosion behaviour were those related to the composition of the material, the breakdown potential of the passive layer obtained from electrochemical tests and the conditions to which the material may be exposed in biogas production (temperature and type of artificial solution simulating the biogas environmental conditions). Different configurations were proposed, concluding the following aspects:

The proposed ANN model presented in this work to predict the corrosion status of the material after electrochemical tests with no need to analyze the material surface microscopically, MODEL 3, showed high classification performance. In this case, the precision and accuracy values obtained were 96.8% and 96.6%, respectively. These values demonstrated the usefulness of Model 3 to predict the corrosion status of the material without resorting to microscopic analysis of its surface and thus reducing the subjectivity in the results. However, the proposed model was not completely automatic; as for new experimental conditions, it was necessary to know the value of the breakdown potential from electrochemical tests since it was defined as input to the model. In order to obtain an automatic model to predict corrosion status, Model 5 was proposed, excluding the

breakdown potential value as input for modelling. In this case, the corrosion behaviour of stainless steel could be predicted automatically for new exposure conditions without the need to perform electrochemical tests for the new samples. However, the precision (90.7%) and accuracy (90.2%) of the model decreased compared with Model 3. This result demonstrated the importance of considering the breakdown potential of the passive layer to model corrosion behaviour in biogas environments.

In addition, the composition of the stainless steel considered as input to model corrosion behaviour can be represented by PREN. This index is calculated based on the percentage of the alloying elements. In this way, when PREN was considered as input for modelling, the number of input variables was reduced, improving the classification performance. In this case, for Model 4, the maximum values for precision and accuracy were 98.5% and 96.7%, respectively.

These results showed that ANN-based models could be shown as a useful tool in the design of biodigester since they predict the corrosion behaviour of stainless steel accurately depending on the environmental conditions to which the material will be exposed in biogas production. Therefore, the model allows for selecting the correct grade of stainless steel in biogas production based on the environmental conditions to which it will be exposed.

Author Contributions: M.J.J.-C.: Writing—Review and Editing, Methodology, Software, Formal analysis, Supervision. F.J.G.G.: Conceptualization, Writing—Review and Editing, Methodology. P.Á.G.: Data Curation, Resources. J.D.M.B.: Resources, Validation. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Universidad de Cádiz, grant number, 52004195.

Data Availability Statement: The raw/processed data required to reproduce the above findings cannot be shared at this time as the data also form part of an ongoing study.

Acknowledgments: The authors gratefully acknowledge the financial support provided by the Projects funded by the University of Cadiz (52004195). It has been developed with the support of the European project “Innovative and competitive solutions using stainless steel and adhesive bonding in biogas. (BiogaSS)”, developed partly in ACERINOX EUROPA S.A.U.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this work.

References

1. Cesaro, A.; Belgiorno, V. Combined Biogas and Bioethanol Production: Opportunities and Challenges for Industrial Application. *Energies* **2015**, *8*, 8121–8144. [CrossRef]
2. Guo, M.; Song, W.; Buhain, J. Bioenergy and biofuels: History, status, and perspective. *Renew. Sustain. Energy Rev.* **2015**, *42*, 712–725. [CrossRef]
3. Angelidaki, I.; Treu, L.; Tsapekos, P.; Luo, G.; Campanaro, S.; Wenzel, H.; Kougias, P.G. Biogas upgrading and utilization: Current status and perspectives. *Biotechnol. Adv.* **2018**, *36*, 452–466. [CrossRef] [PubMed]
4. Weiland, P. Biogas production: Current state and perspectives. *Appl. Microbiol. Biotechnol.* **2010**, *85*, 849–860. [CrossRef] [PubMed]
5. Zhang, Y.; Kawasaki, Y.; Oshita, K.; Takaoka, M.; Minami, D.; Inoue, G.; Tanaka, T. Economic assessment of biogas purification systems for removal of both H₂S and siloxane from biogas. *Renew. Energy* **2021**, *168*, 119–130. [CrossRef]
6. Koch, G.H.; Brongers, M.P.H.; Thompson, N.G.; Virmani, Y.P.; Payer, J.H. *Corrosion Costs and Preventive Strategies in the United States*; FHWA: Washington, DC, USA, 2001.
7. Bo, T.; Zhu, X.; Zhang, L.; Tao, Y.; He, X.; Li, D.; Yan, Z. A new upgraded biogas production process: Coupling microbial electrolysis cell and anaerobic digestion in single-chamber, barrel-shape stainless steel reactor. *Electrochem. Commun.* **2014**, *45*, 67–70. [CrossRef]
8. Ruiz, D.; Miguel, G.S.; Corona, B.; Gaitero, A.; Domínguez, A. Environmental and economic analysis of power generation in a thermophilic biogas plant. *Sci. Total. Environ.* **2018**, *633*, 1418–1428. [CrossRef]
9. Bao, L.; Li, K.; Zheng, J.; Zhang, Y.; Zhan, K.; Yang, Z.; Zhao, B.; Ji, V. Surface characteristics and stress corrosion behavior of AA 7075-T6 aluminum alloys after different shot peening processes. *Surf. Coat. Technol.* **2022**, *440*, 128481. [CrossRef]
10. Shekari, E.; Khan, F.; Ahmed, S. Economic risk analysis of pitting corrosion in process facilities. *Int. J. Press. Vessel. Pip.* **2017**, *157*, 51–62. [CrossRef]
11. NACE International. *International Measures of Prevention, Application, and Economics of Corrosion Technologies Study 2012*; NACE International: Houston, TX, USA, 2012.

12. Chen, Z.; Gao, L.; Koleva, D.A. Evaluating the stray current corrosion of steel rebar in different layouts. *Measurement* **2022**, *196*, 111217. [CrossRef]
13. Ma, C.; Wang, Z.; Behnamian, Y.; Gao, Z.; Wu, Z.; Qin, Z.; Xia, D.-H. Measuring atmospheric corrosion with electrochemical noise: A review of contemporary methods. *Measurement* **2019**, *138*, 54–79. [CrossRef]
14. Sanni, O.; Adeleke, O.; Ukoba, K.; Ren, J.; Jen, T.-C. Application of machine learning models to investigate the performance of stainless steel type 904 with agricultural waste. *J. Mater. Res. Technol.* **2022**, *20*, 4487–4499. [CrossRef]
15. Hao, J.-Z.; Xu, S.-A.; Xu, J.-J.; Cao, H.-L.; Miao, H. Modeling and optimization of the corrosion resistance of Cr-free and Cr-based chemical conversion coatings on nickel foil by artificial neural network and response surface method. *Mater. Today Commun.* **2023**, *36*, 106858. [CrossRef]
16. Akbarzadeh, S.; Akbarzadeh, K.; Ramezanzadeh, M.; Naderi, R.; Mahdavian, M.; Olivier, M.-G. Corrosion resistance enhancement of a sol-gel coating by incorporation of modified carbon nanotubes: Artificial neural network (ANN) modeling and experimental explorations. *Prog. Org. Coat.* **2023**, *174*, 107296. [CrossRef]
17. Moses, A.; Chen, D.; Wan, P.; Wang, S. Prediction of electrochemical corrosion behavior of magnesium alloy using machine learning methods. *Mater. Today Commun.* **2023**, *37*, 107285. [CrossRef]
18. Kumari, P.; Halim, S.Z.; Kwon, J.S.-I.; Quddus, N. An integrated risk prediction model for corrosion-induced pipeline incidents using artificial neural network and Bayesian analysis. *Process Saf. Environ. Prot.* **2022**, *167*, 34–44. [CrossRef]
19. Woldehellasse, H.; Tesfamariam, S. Data augmentation using conditional generative adversarial network (cGAN): Application for prediction of corrosion pit depth and testing using neural network. *J. Pipeline Sci. Eng.* **2023**, *3*, 100091. [CrossRef]
20. Duan, Y.; Ma, L.; Qi, H.; Li, R.; Li, P. Developed constitutive models, processing maps and microstructural evolution of Pb-Mg-10Al-0.5B alloy. *Mater. Charact.* **2017**, *129*, 353–366. [CrossRef]
21. Pintos, S.; Queipo, N.V.; de Rincón, O.T.; Rincón, A.; Morcillo, M. Artificial neural network modeling of atmospheric corrosion in the MICAT project. *Corros. Sci.* **2000**, *42*, 35–52. [CrossRef]
22. Díaz, V.; López, C.; Rivero, S. Low carbon steel corrosion damage prediction in rural and urban environments. *Rev. De Met.* **2003**, *39*, 188–193. [CrossRef]
23. Díaz, V.; López, C. Discovering key meteorological variables in atmospheric corrosion through an artificial neural network model. *Corros. Sci.* **2007**, *49*, 949–962. [CrossRef]
24. Silva, R.; Guerreiro, J.; Loula, A. A study of pipe interacting corrosion defects using the FEM and neural networks. *Adv. Eng. Softw.* **2007**, *38*, 868–875. [CrossRef]
25. Kenny, E.D.; Paredes, R.S.C.; de Lacerda, L.A.; Sica, Y.C.; de Souza, G.P.; Lázaris, J. Artificial neural network corrosion modeling for metals in an equatorial climate. *Corros. Sci.* **2009**, *51*, 2266–2278. [CrossRef]
26. Halama, M.; Kreislova, K.; Van Lysebettens, J. Prediction of Atmospheric Corrosion of Carbon Steel Using Artificial Neural Network Model in Local Geographical Regions. *Corrosion* **2011**, *67*, 065004-1–065004-6. [CrossRef]
27. Lin, H.-T.; Lo, C.-M.; Lin, M.-D. Application of Artificial Neural Networks on Predicting Corrosion Rates of Carbon Steel in Taiwan Industrial Zones. *Adv. Intell. Syst. Res.* **2017**, *132*, 278–282. [CrossRef]
28. Tran, N.-L.; Nguyen, T.-H.; Phan, V.-T.; Nguyen, D.-D. A Machine Learning-Based Model for Predicting Atmospheric Corrosion Rate of Carbon Steel. *Adv. Mater. Sci. Eng.* **2021**, *2021*, 6967550. [CrossRef]
29. Kim, H.-S.; Park, S.-J.; Seo, S.-M.; Yoo, Y.-S.; Jeong, H.-W.; Jang, H. Regression analysis of high-temperature oxidation of Ni-based superalloys using artificial neural network. *Corros. Sci.* **2021**, *180*, 109207. [CrossRef]
30. Zhu, Y.; Macdonald, D.D.; Qiu, J.; Urquidí-Macdonald, M. Corrosion of rebar in concrete. Part III: Artificial Neural Network analysis of chloride threshold data. *Corros. Sci.* **2021**, *185*, 109438. [CrossRef]
31. Wang, C.; Li, W.; Xin, G.; Wang, Y.; Xu, S.; Fan, M. Novel method for prediction of corrosion current density of gas pipeline steel under stray current interference based on hybrid LWQPSO-NN model. *Measurement* **2022**, *200*, 111592. [CrossRef]
32. Li, Q.; Wang, D.; Zhao, M.; Yang, M.; Tang, J.; Zhou, K. Modeling the corrosion rate of carbon steel in carbonated mixtures of MDEA-based solutions using artificial neural network. *Process Saf. Environ. Prot.* **2021**, *147*, 300–310. [CrossRef]
33. Soomro, A.A.; Mokhtar, A.A.; Kurnia, J.C.; Lashari, N.; Lu, H.; Sambo, C. Integrity assessment of corroded oil and gas pipelines using machine learning: A systematic review. *Eng. Fail. Anal.* **2022**, *131*, 105810. [CrossRef]
34. Yang, J.; Li, R.; Chen, L.; Hu, Y.; Dou, Z. Research on equipment corrosion diagnosis method and prediction model driven by data. *Process Saf. Environ. Prot.* **2022**, *158*, 418–431. [CrossRef]
35. Entezari, A.; Aslani, A.; Zahedi, R.; Noorollahi, Y. Artificial intelligence and machine learning in energy systems: A bibliographic perspective. *Energy Strat. Rev.* **2023**, *45*, 101017. [CrossRef]
36. Akhshik, M.; Bilton, A.; Tjong, J.; Singh, C.V.; Faruk, O.; Sain, M. Prediction of greenhouse gas emissions reductions via machine learning algorithms: Toward an artificial intelligence-based life cycle assessment for automotive lightweighting. *Sustain. Mater. Technol.* **2022**, *31*, e00370. [CrossRef]
37. Kaab, A.; Sharifi, M.; Mobli, H.; Nabavi-Pelesaraei, A.; Chau, K.-W. Combined life cycle assessment and artificial intelligence for prediction of output energy and environmental impacts of sugarcane production. *Sci. Total. Environ.* **2019**, *664*, 1005–1019. [CrossRef]
38. Ryan, M.P.; Williams, D.E.; Chater, R.J.; Hutton, B.M.; McPhail, D.S. Why stainless steel corrodes. *Nature* **2002**, *415*, 770–774. [CrossRef]
39. Sedriks, A.J. *Corrosion of Stainless Steel*; John Wiley & Sons: Hoboken, NJ, USA, 1996.

40. Vargel, C. Crevice Corrosion. In *Corrosion of Aluminium*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 267–271. [CrossRef]
41. Blackwood, D.J.; Lim, C.S.; Teo, S.L.; Hu, X.; Pang, J. Macrofouling induced localized corrosion of stainless steel in Singapore seawater. *Corros. Sci.* **2017**, *129*, 152–160. [CrossRef]
42. Mele, C.; Bozzini, B. Localised corrosion processes of austenitic stainless steel bipolar plates for polymer electrolyte membrane fuel cells. *J. Power Sources* **2010**, *195*, 3590–3596. [CrossRef]
43. Jiménez-Come, M.J.; Martín, M.d.I.L.; Matres, V.; Baladés, J.D.M. The use of artificial neural networks for modelling pitting corrosion behaviour of EN 1.4404 stainless steel in marine environment: Data analysis and new developments. *Corros. Rev.* **2020**, *38*, 339–353. [CrossRef]
44. Jiménez-Come, M.J.; Turias, I.J.; Ruiz-Aguilar, J.J. A two-stage model based on artificial neural networks to determine pitting corrosion status of 316L stainless steel. *Corros. Rev.* **2016**, *34*, 113–125. [CrossRef]
45. ASTM International. *Annual Book of ASTM Standards*; American Society for Testing & Materials: West Conshohocken, PA, USA, 2004.
46. Deng, B.; Jiang, Y.; Gong, J.; Zhong, C.; Gao, J.; Li, J. Critical pitting and repassivation temperatures for duplex stainless steel in chloride solutions. *Electrochim. Acta* **2008**, *53*, 5220–5225. [CrossRef]
47. White, H. Learning in Artificial Neural Networks: A Statistical Perspective. *Neural Comput.* **1989**, *1*, 425–464. [CrossRef]
48. Rumelhart, D.E.; Hinton, G.E.; Williams, R.J. Learning representations by back-propagating errors. *Nature* **1986**, *323*, 533–536. [CrossRef]
49. Lippmann, R. An introduction to computing with neural nets. *IEEE Assp Mag.* **1987**, *4*, 4–22. [CrossRef]
50. Lourakis, M.I.A. A brief description of the Levenberg-Marquardt algorithm implemented by levmar. *Found. Res. Technol.* **2005**, *11*, 1–6.
51. David, W.H.; Stanley, L. *Applied Survival Analysis*; Elsevier Science Inc.: New York, NY, USA, 2000. [CrossRef]
52. Fawcett, T. An Introduction to ROC analysis. *Pattern Recogn. Lett.* **2006**, *27*, 861–874. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

MDPI AG
Grosspeteranlage 5
4052 Basel
Switzerland
Tel.: +41 61 683 77 34

Metals Editorial Office
E-mail: metals@mdpi.com
www.mdpi.com/journal/metals



Disclaimer/Publisher's Note: The title and front matter of this reprint are at the discretion of the Guest Editor. The publisher is not responsible for their content or any associated concerns. The statements, opinions and data contained in all individual articles are solely those of the individual Editor and contributors and not of MDPI. MDPI disclaims responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.



Academic Open
Access Publishing

mdpi.com

ISBN 978-3-7258-5516-2