Atomic layer deposition of TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} thin films for the electrochemical study of corrosion protection in aluminum alloy cans used in beverage

V M Dias\textsuperscript{1,2}, W Chiappim\textsuperscript{3}, M A Fraga\textsuperscript{2}, H S Maciel\textsuperscript{1,4}, F R Marciano\textsuperscript{5} and R S Pessoa\textsuperscript{1,5,7}

\textsuperscript{1} Laboratório de Plasmas e Processos, Instituto Tecnológico de Aeronáutica, 12228-900, São José dos Campos, SP, Brazil
\textsuperscript{2} Laboratório de Nanotecnologias e Processos a Plasma, Universidade do Vale do Paraíba, 12244-000, São José dos Campos, SP, Brazil
\textsuperscript{3} i3N, Departamento de Física, Universidade de Aveiro, Campus Universitário de Santiago, Aveiro, 3810-193, Portugal
\textsuperscript{4} Instituto de Ciência e Tecnologia, Universidade Federal de São Paulo, São José dos Campos 12231-280, SP, Brazil
\textsuperscript{5} Instituto Científico e Tecnológico, Universidade Brasil, 08230-030, São Paulo, SP, Brazil
\textsuperscript{6} Universidade Federal do Piauí, 64049-530, Teresina, PI, Brazil
\textsuperscript{7} Author to whom any correspondence should be addressed. E-mail: mafraga@ieee.org, rspessoa@ita.br and wcj@ua.pt

Keywords: thin films, atomic layer deposition, titanium dioxide, aluminum oxide, electrochemical impedance spectroscopy

Abstract

Titanium dioxide (TiO\textsubscript{2}) and aluminum oxide (Al\textsubscript{2}O\textsubscript{3}) thin films, with thicknesses around 100 nm, were grown on commercial pure- and resin-coated Al substrates using the atomic layer deposition (ALD). A comprehensive and comparative study of corrosion protection was carried out by linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) measurements for a set of six samples: two reference samples (Al-bare and Al-resin), and four ALD coated samples (Al-TiO\textsubscript{2}, Al-Al\textsubscript{2}O\textsubscript{3}, Al-resin-TiO\textsubscript{2}, and Al-resin-Al\textsubscript{2}O\textsubscript{3}). The LSV and EIS results display good mutual agreement, indicating a higher protection efficiency of all ALD-coated samples after immersion in NaCl. When compared to Al-bare, all ALD coated samples (TiO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3}) showed a corrosion inhibition enhancement factor of 99%. Besides, our results demonstrated that Al-resin+Al\textsubscript{2}O\textsubscript{3} has 24.95\% and 33.40\% more corrosion inhibition than Al-Al\textsubscript{2}O\textsubscript{3} and Al-resin, respectively. EIS data were fitted by an equivalent electric circuit (EEC). The Nyquist and Bode plots from the experiments showed that ALD films are a potential candidate for altering/improving commercial resin-coated Al cans.

1. Introduction

Aluminum alloys (Al) are extensively used in the food packaging industry as they have the requirements for food and beverage preservation, such as protection from external light and gas barrier [1]. Their commercial and industrial appeal is because of its versatility, lightness, low cost, post-consumer recycling, and corrosion resistance [1–8]. However, when Al cans are exposed to beverages such as beer and soft drinks, which contain carbonates, acid, and chlorides, the corrosion resistance of Al is affected, and the packaging is modified [4, 9].

The corrosion resistance of Al in aqueous solutions is attributed to a passive layer of oxide on its surface [3]. Upon exposure to an acidic or alkaline medium, especially chloride-containing media, the protective oxide layer is damaged, and Al becomes susceptible to corrosion [4]. Different types of Al alloys have been developed in recent decades to improve the properties of Al in relation to their use applications [4]. Although these alloys have a relatively high natural resistance to corrosion, they are susceptible to localized forms of corrosion, especially pitting and intergranular corrosion [4].

For beverage storage applications, the most crucial function of protective coatings is to prevent the interaction between the metal packaging material and the beverage. Nevertheless, adhesion failures can occur during the covering and filling processes, promoting the formation of pits and consequently initiating the corrosion process when in contact with the beverage [9]. The types of coatings commonly used are organic...
paints, enamel, passive oxide film, and combinations of these systems, which are expected to be chemically inert, resistant to mechanical or thermal stresses, and free from cracks and potholes, and must provide protection against corrosive attacks [10].

To reduce the corrosion effect, some types of resins are used as protective coatings. The first resin is used as the coating was the bisphenol A (BPA). Used since the 1950s, BPA has still been one of the resin grades widely applied to metal packing today in several countries [9]. However, it has been observed that BPA can migrate during the corrosion process and interact, even at low levels, with the stored beverage, causing product quality loss or contamination. At certain levels of human exposure to BPA, the end consumer may have health problems in the brain, prostate gland in fetuses, lactating, and children [11–13].

Therefore, corrosion of Al cans and food packaging plays a crucial role in economic and health issues. The prevention of corrosion of Al and its alloys using environmentally friendly protective coating has been an important area of research, especially for the food industry. Overcoming corrosion in Al packaging requires the use of new technologies for the deposition of protective layers that are friendly to human health and the environment, besides being resistant to deterioration.

In this context, the atomic layer deposition (ALD) technique emerges as one of the most promising technologies for the conformal growth of protective layers through gas-phase repetitions, forming layers of inorganic material [14, 15]. This technique is based on a repeated series of self-limiting surface reactions for a well-controlled deposition of inorganic layers with nanoscale thickness control, excellent adhesion, and uniformity, avoiding pinholes and cracks in the coatings [16–18]. Due to these attributes, ALD has established itself as a strong competitor for the growth of anti-corrosion protection coatings on metals, as demonstrated by studies in copper [19–22], low alloy steel [23, 24], stainless steel [25–28], silver [29, 30], and aluminum [31–33].

Although ALD is a disruptive technology widely used for research and development, it suffers due to the low deposition rate, which is in the range of 100 to 300 nm h$^{-1}$ [34]. Another limitation is the low pressure of operating, which require a vacuum system. This limits it to laboratory testing only and is prohibitively expensive for use in industry. As a modern alternative to reduce deposition time, spatial ALD (that operating in atmospheric pressure) increases the deposition rate by more than ten times (3600 nm h$^{-1}$) [34]. Spatial ALD eliminates the traditional pulse and purge process and can replace it with: (i) samples which pass through fixed precursor nozzles, arranged so that the film grows when passing through the nozzles (figure 1(a)). On the other hand, the carousel ALD (that operating in low pressure), which exposes the samples to a specific precursor based in the rotation of a lot of substrates (figure 1(b)), is an alternative to accelerating the application of ALD technology in the industry.

![Figure 1. Illustration of the ALD tools applied to the production line in the industry: (a) spatial ALD and (b) carousel ALD with fixed precursors nozzles.](image-url)
Another obstacle, which is the high cost of the ALD tool, soon it will not be a problem, due to the large number of reactor manufacturers that have been increasing rapidly and will help to reduce prices. Therefore, research and development in conventional ALD in laboratories of research applied to industrial issues are necessary because, in a few years, the ALD technique will be cheaper, faster, and ready for consolidation in the industry, as aforementioned. Thus, the industry will have as reference the previously validated studies in the research laboratories that will help them to implement this technique on an industrial scale.

Some laboratories and research centers have been studying ALD of oxides films, like aluminum oxide (Al2O3) and titanium oxide (TiO2), which are the most widely considered and applied materials for protection against packaging corrosion [35]. Recently, these oxide coatings have been shown to make it possible to increase the shelf life of polymers and cardboard packaging [36–38].

However, due to the lack of studies on corrosion of commercial beverage cans, this work is focused on the evaluation of the electrochemical behavior of ALD Al2O3 and TiO2 thin films grown by ALD on resin-coated aluminum cans used in beverages and soft drinks. As a benchmark and to better comparison with the literature, we used the aluminum-bare coated with Al2O3 and TiO2 grown in the same conditions of the deposition for the samples early mentioned. All substrates were evaluated in a neutral to alkaline pH environment in NaCl solution.

Spectroscopy ellipsometry was used to measure the thickness uniformity of the TiO2 and Al2O3 thin films on the substrates, for confirmed the amorphous phase of the films was used the grazing incidence x-ray diffraction (GIXRD). The concern with maintaining the amorphous phase, mainly for TiO2 films, is due to the anatase phase shows problems during nucleation, leading to high porosity [19]. This behavior occurs because the crystalline TiO2 presents boundaries, causing diffusion of species, which promotes surface corrosion [25]. One way to overcome high porosity is to produce amorphous TiO2 thin films [35]. To evaluate the corrosion barrier efficiency, linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) measurements were performed. Moreover, the EIS results were discussed using specific equivalent electrical circuits (EEC) in order better to discuss the metal corrosion process on each substrate type.

In order to guarantee the reproducible nature of coatings and electrochemical data, each set of samples has five replicas, which was grown and analyses in the same conditions, to obtain an average in all measurements.

2. Experimental

2.1. Substrate preparation and film deposition

Commercial aluminum cans coated with resin (~3 μm) and uncoated (polished of 4–5 μm) (AA3104 alloy, Latapack-Ball, Jacareí, Brazil) were cut into pieces of 1 × 1 cm² and divided into the following set: (i) aluminum bare (Al-bare or control); (ii) aluminum coated with commercial resin (Al-resin); (iii) aluminum coated with TiO2 (Al-TiO2); (iv) aluminum coated with Al2O3 (Al-Al2O3); (v) aluminum coated with commercial resin plus TiO2 (Al-resin-TiO2); and (vi) aluminum coated with commercial resin plus Al2O3 (Al-resin-Al2O3). It is important to note that each set has five replica samples, which was grown in the same conditions.

Prior to deposition, distilled water and isopropyl alcohol (98%, Sigma-Aldrich, São Paulo, Brazil) were used to clean the samples, and nitrogen (N2) gas was used for drying. To prepare the metal oxide thin films, we use a commercial TFS-200 ALD system (Beneq Oy, Espoo, Finland) operating in thermal mode at a temperature of 100 °C. Sammelselg et al [39] demonstrated that for process temperatures around 100 °C, the best anticorrosive coatings were obtained. For the growth of TiO2 and Al2O3 coatings, titanium tetrachloride - TiCl4 (99.95%, Sigma-Aldrich, São Paulo, Brazil) and trimethylaluminum—TMA (Sigma-Aldrich, São Paulo, Brazil) was used as a metallic precursor, respectively, deionized water (H2O) as oxidant, and high purity N2 (99.999%, White Martins, Jacareí, Brazil) as a purge gas. Here the nominal thicknesses was 100 nm. One cycle for the ALD-TiO2 film consisted of a 0.25 s TiCl4 precursor pulse, 2 s N2 purge, 0.25 s H2O pulse, and 2 s N2 purge. While for the ALD-Al2O3 film, the cycle consisted of a 0.15 s TMA precursor pulse, 0.75 s N2 purge, 0.15 s H2O pulse, and 0.75 s N2 purge. These are optimal ALD cycle time conditions investigated in previous studies [40–45]. Liquid TiCl4, TMA, and deionized water were kept in stainless steel reservoirs at 21 °C. Needle valves were used to adjust the precursor vapor flow injected to the ALD chamber by the action of the precursor vapor pressure only. Before deposition, the base pressure of the reaction chamber was less than 10⁻⁷ mbar, while during deposition, the working pressure was maintained at 1 mbar through insert 300 sccm N2.

2.2. Spectroscopy ellipsometry and GIXRD

Ellipsometry is a well-known technique to obtain the thickness of thin films. This characterization was performed ex situ phase-modulated in ellipsometer UVISEL Jobin Yvon (Horiba, Kyoto, Japan) to measure the thickness uniformity of the TiO2 and Al2O3 on Al-bare, Al-resin samples in the spectral range 0.75 to 6.5 eV with
a step of 50 meV at an incident angle of 70°. The thickness was calculated using the values measured in each set of samples grown in the same conditions and repeated in each replica in more than one location.

The amorphous phase was proved by grazing incidence x-ray diffraction (GIXRD) (XRD 6000, Shimadzu, Kyoto, Japan). GIXRD diffractograms were obtained at room temperature in a goniometer using a copper target of CuKα radiation of 1.5418 Å, θ from 10° to 80°, at a scanning speed of 0.02° s⁻¹, a voltage of 40 kV, and a current of 30 mA. These studies were carried out at an incidence angle of 0.29°.

2.3. Electrochemical analysis
EIS and LSV were performed on Al-bare, Al-resin and ALD-coated samples to determine charge-transfer resistances in order to evaluate the electrochemical porosity and corrosion resistance of the coatings [46, 47]. These measurements were conducted with an Autolab potentiostat/galvanostat model 320N (Metrohm Autolab B.V., Herisau, Switzerland) controlled by Nova 2.0 software (Metrohm Autolab B.V., Herisau, Switzerland). A standard three-electrode electrochemical cell (Metrohm Autolab B.V., Herisau, Switzerland) filled with 250 ml of 0.5M NaCl solution (electrolyte, pH = 7.0) was used in electrochemical experiments. To prepare this solution, deionized water and sodium chloride reagent (purity ≥ 99%, Synth, Diadema, São Paulo) were used. In the setup, saturated Ag/AgCl (3M KCl) (Metrohm Autolab B.V., Herisau, Switzerland) was used as reference electrode, pure platinum coated wire (Metrohm Autolab B.V., Herisau, Switzerland) as counter electrode, and each analyzed sample as working electrode. Here, the working electrode area of 0.78 cm² was delimited by a Viton O-ring and its backside was worn in order to improve the ohmic contact. Initially, the open circuit potential (OCP) was measured for 60 min to reach the potential of equilibrium. After the stability of the potential the EIS measurements were performed in the frequency range from 100 kHz to 0.1 Hz with a sinusoidal signal of 10 mV. According to Grossi et al [48], usually the sinusoidal signal is used in the range of 10 to 100 mV. All electrochemical experiments were conducted at room temperature and the Kramers-Kronig routine was used to ensure linearity, causality and stability of the system during measurements [49]. The EIS data were modeled using an equivalent electric circuit (EEC) and these models allow comparison of the charge-transfer resistance ($R_p$) of the different coatings. To fitting EIS data, we used the Nova 2.0 software package and EEC models (these models are demonstrated and discussed in section 3.3). Immediately after the EIS tests, the LSV measurements was performed in open circuit potential (OCP) from −1.9 to −0.90 V at a sweep rate of 1 mV s⁻¹. To obtain the corrosion current ($i_{corr}$, A cm⁻²) and the corrosion potential ($E_{corr}$/V SCE), LSV curves and Tafel plots were used; being the $i_{corr}$, the current obtained from intercept of tangent lines on cathodic and anodic branches of Tafel plots in $E_{corr}$ (this potential corresponds to the zero transition current between the cathodic and anodic branches) [50].

Polarization resistance ($R_p$) was calculated by means of the Stern-Geary equation [35, 47]:

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

where $b_a$ and $b_c$ are the slopes of the anodic and cathodic branches of the Tafel plot, respectively, and $i_{corr}$ the corrosion current of coated sample. In order to obtain better accuracy in the data, each measurement made on a given set of samples was repeated on the replicas and was obtained an average deviation on measurement below 5%.

3. Results and discussion
3.1. Thickness and amorphous phase
Figure 2 shows the thin film thickness values with an average of the 98 ± 4 nm for TiO₂, and 100 ± 4 nm for the Al₂O₃, both films was grown on aluminum bare, and aluminum coated with commercial resin. The average thickness was calculated by measuring three different points in each sample, and this procedure was repeated for the all replicas. Therefore, the final thickness showed for each set of samples is an average of 15 measurements. Figure 2 also shows the diffractograms of GIXRD, and as can be seen, all films are amorphous, which is by the literature [40, 41]. The incident angle 0.29° was chosen due the reduction of the reflections from the substrate [41, 45]. This characterization is fundamental to show that the TiO₂ thin films are not crystalline, and thus we can avoid a low anticorrosive efficiency. The TiO₂ film in the crystalline anatase phase has high porosity and diffusion of species that promote surface corrosion, therefore limiting the application in this area [19, 25, 35]. Therefore, we were able to ensure that all films under the proposed deposition conditions are in the amorphous phase and are excellent candidates for the corrosion barrier.
3.2. LSV analysis

LSV tests were used to investigate the corrosion resistance of the coatings after immersion in NaCl solution. Figure 3 shows the LSV polarization curves for all investigated samples and table 1 summarizes the kinetic corrosion parameters. It is worth highlighting which the polarization curve of the Al-bare measured has a corrosion potential equal to $-1.42 \text{ V/SCE}$. This value is similar to other works, with a fluctuation due to specific conditions, such as (i) native oxide, (ii) polarization, (iii) electrical parameters and (iv) electrolyte concentration [31, 51].

According to Mirhashemihaghigi et al [31] and Härkönen et al [52] in neutral or alkaline environment, the cathodic reaction can be the reduction of dissolved oxygen and/or the reduction of water. The shape of the polarization curve of Al-bare, indicated that the cathodic reaction was limited by water reduction [31, 52]. A characteristic anodic plateau was observed from $-1.42$ to $-0.90 \text{ V/SCE}$ that shows a passive domain due to the presence of a native oxide on the Al-bare [31]. The shape of the polarization curve of Al-TiO$_2$, Al-resin and Al-resin + Al$_2$O$_3$ presented the same behavior observed in Al-bare. On the other hand, the polarization curves of Al-resin-TiO$_2$, and Al + Al$_2$O$_3$ presented a shape that indicated that the cathodic reaction was limited by oxygen reduction and the anodic reaction by charge transfer across the interface [51–54]. The $R_p$ was obtained from the slope of the curve close to the $E_{corr} \pm 30 \text{ mV}$.

Figure 2. GIXRD diffractogram for amorphous TiO$_2$ and Al$_2$O$_3$ films grown on aluminum bare, and aluminum coated with commercial resin using TiCl$_4$ and TMA precursor in thermal ALD. The thicknesses $d_{TiO_2} = 98 \pm 4 \text{ nm}$, and $d_{Al_2O_3} = 100 \pm 4 \text{ nm}$ was performed by ellipsometry.

Figure 3. LSV polarization curves of all samples investigated in the 0.5M NaCl electrolyte with pH ranging from neutral to alkaline at a sweep rate of 1 mV s$^{-1}$ in the voltage range of $-1.9$ to $-0.9 \text{ V}$. It was obtained an average deviation of measurement below 5%. The error bar is not shown in the graph, but the errors of the parameters are shown in table 1.
$R_p (\Omega \cdot \text{cm}^2)$ for the Al-bare presented the value of $(1.53 \pm 0.05) \times 10^5$ and $i_{\text{corr}} (\text{A.cm}^2)$ $(3.3 \pm 0.5) \times 10^{-7}$ in accordance with the literature [31]. Mirhashemihaghighi et al [31] showed a cathodic shift related to the increase in the thickness of the Al$_2$O$_3$ on the Al. This shift from 10 to 50 nm occurs with a shift in the corrosion potential from $-1.37$ to $-1.56 \text{ V/SCE}$. Our results for the (100 nm)-Al$_2$O$_3$ corroborate with this cathodic shift; as can be seen in figure 3 and table 1, the corrosion potential is $-1.62 \pm 0.05 \text{ V/SCE}$.

<i>Table 1. Kinetic corrosion parameters inferred from the polarization curves using Tafel plots and equation (1). Where $E_{\text{corr}}$ is the corrosion potential, $i_{\text{corr}}$ is the corrosion current, $R_p$ is the charge-transfer resistance. A = Al-bare, B = Al-resin, C = Al-TiO$_2$, D = Al-Al$_2$O$_3$, E = Al-resin-TiO$_2$, and F = Al-resin-Al$_2$O$_3$.</i>

| Sample | $E_{\text{corr}}$ (V/SCE) | $i_{\text{corr}}$ (A/cm$^2$) | $R_p$ (\text{\Omega cm}^2) | $b_0$ (mV.dec$^{-1}$) | $b_1$ (mV.dec$^{-1}$) |
|--------|---------------------------|-----------------------------|-----------------------------|------------------------|------------------------|
| A      | $-1.42$ $\pm 0.05$       | $3.3 \pm 0.5$               | $1.53 \pm 0.05$            | $8 \pm 8$              | $182 \pm 184$          |
|        | $x 10^{-7}$               |                             | $x 10^5$                   |                        |                        |
| B      | $-1.47$ $\pm 0.05$       | $6.9 \pm 0.5$               | $6.86 \pm 0.05$            | $5 \pm 5$              | $444 \pm 464$          |
|        | $x 10^{-1}$               |                             | $x 10^9$                   |                        |                        |
| C      | $-1.35$ $\pm 0.05$       | $2.4 \pm 0.5$               | $5.41 \pm 0.05$            | $5 \pm 5$              | $547 \pm 647$          |
|        | $x 10^{-9}$               |                             | $x 10^7$                   |                        |                        |
| D      | $-1.62$ $\pm 0.05$       | $2.5 \pm 0.5$               | $7.73 \pm 0.05$            | $5 \pm 5$              | $908 \pm 868$          |
|        | $x 10^{-1}$               |                             | $x 10^9$                   |                        |                        |
| E      | $-1.38$ $\pm 0.05$       | $5.2 \pm 0.5$               | $2.32 \pm 0.05$            | $6 \pm 6$              | $521 \pm 589$          |
|        | $x 10^{-10}$              |                             | $x 10^4$                   |                        |                        |
| F      | $-1.65$ $\pm 0.05$       | $1.9 \pm 0.5$               | $1.03 \pm 0.05$            | $8 \pm 8$              | $928 \pm 872$          |
|        | $x 10^{-11}$              |                             | $x 10^{10}$                |                        |                        |

The lower passive current shows the high sealing property of the ALD coatings that decrease the dissolution of aluminum substrate. A decrease of between two to four orders of magnitude was observed in the $i_{\text{corr}}$ for coated samples (table 1). This behavior occurred in all samples analyzed. This is related to the excellent sealing properties of the ALD TiO$_2$ and Al$_2$O$_3$ films on bare and resin-coated samples, indicating that the electrochemical response is connected to the interfacial reactions between the coating and the substrate exposed to the electrolyte. A decrease in corrosion activity was observed in the descending order: Al-TiO$_2$, Al-resin + TiO$_2$, Al-resin, Al-Al$_2$O$_3$ and Al-resin-Al$_2$O$_3$.

Another parameter that corroborates with the lower corrosion activity is the $R_p$, which is higher for samples Al-TiO$_2$, Al-resin + TiO$_2$, Al-resin, Al-Al$_2$O$_3$ and Al-resin-Al$_2$O$_3$ in comparison with the commercial Al-bare substrates.

In theory, the corrosion activity in the sample of Al-resin + TiO$_2$ should be higher when compared to the sample of Al-resin. However, we observed an inverse behavior, and this is repeated for the sample replicas. This unexpected effect in sample Al-resin + TiO$_2$ may be related to: (i) some inhomogeneity in Al substrate; (ii) defects in the resin coating resulting from the spray deposition process; (iii) pitting originated by pinholes or craters due to morphological fluctuation in resin+TiO$_2$ film; or (iv) a sum of the three problems. However, more studies are needed to better explain this result.

Al-resin + Al$_2$O$_3$, Al + Al$_2$O$_3$, and Al-resin presented a cathodic shift in comparison with the Al-bare. According to Garrigues et al [55], the cathodic shift observed in $E_{\text{corr}}$ is related to the adsorption of chlorine ions ($\text{Cl}^-$). Therefore, lower adsorption of $\text{Cl}^-$ on Al-bare + TiO$_2$ and Al + TiO$_2$ in comparison with the Al-bare is...
associated with the anodic shift. This behavior is consistent with the higher coating sealing that decreases the sites available for the Cl⁻ adsorption [31]. On the order hand, the cathodic shift observed in Al-resin + Al₂O₃, Al + Al₂O₃, and Al-resin samples indicate effects besides than Cl⁻ adsorption. Mirhashemihaghighi et al [31] proposed that the higher density and thickness of the coating hindered the access of the oxygen and water in the interface film/substrate, which result in a cathodic shift of Ecorr. Carbonini et al [51], showed a cathodic shift of Ecorr in case of hindered access of oxygen to the interface. They tested aluminum in deaerated and aerated NaCl, thus corroborated with the proposal of Mirhashemihaghighi et al [31]. Ambat et al [56], showed that with a local pH increase at the interface at the end of channel defects promotes the water reduction (2H₂O + e⁻ → H₂ + 2OH⁻) and increase the cathodic reaction. As a consequence of a higher OH⁻, Lee et al [57] showed a decrease of the Ecorr related with the increase of OH⁻ in the electrolyte.

These behaviors suggest a complete to partial blocking in the pores, and pits of the Al-bare and Al-resin coated with ALD films, which leads to lengthening the diffusion path of corroding species through the film towards the aluminum surface [58]. Thus, decreasing the corrosion activity.

According to Bahari et al [46], the corrosion inhibition enhancement factor is defined by the percentage difference between the polarization resistance of the coated and uncoated sample, as shown in equation (2):

\[ \delta_i(\%) = \left( \frac{R_{p_{film}} - R_{p_{bare}}}{R_{p_{film}}} \right) \times 100 \]

Equation (2) compares the samples with film and the bare sample, but we can expand this equation and compare the samples with coatings with each other to obtain a corrosion inhibition relationship between the films, for example Al-resin + Al₂O₃ versus other films (δ₂(%)%), and Al-Al₂O₃ versus other films (δ₃(%)%):

\[ \delta_2(\%) = \left( \frac{R_{p_{Al2O3}} - R_{p_{film}}}{R_{p_{Al2O3}}} \right) \times 100, \]

and

\[ \delta_3(\%) = \left( \frac{R_{p_{Al2O3}} - R_{p_{film}}}{R_{p_{Al2O3}}} \right) \times 100 \]

As can be seen, in table 2 the corrosion inhibition for the coated samples in relation with the Al-bare are excellent, and shows high enhancement with δ₂(%) above 99% for all coated samples studied.

However, a real comparison between the coatings shows which Al-resin + Al₂O₃ has 24.95 and 33.40% more corrosion inhibition compared to Al-Al₂O₃ and Al-resin, respectively. This enhancement suggests that the ALD Al₂O₃ sealed the resin and Al-bare, improving the corrosion resistance. On the other hand, despite the excellent corrosion inhibition of the ALD TiO₂ compared with the Al-bare, when compared with Al₂O₃, the efficiency is lower. This better Rp, and consequently, better corrosion inhibition for the Al₂O₃ in comparison with TiO₂, is in agreement with Daubert et al [35] and Fusco et al [47], which grow the thin films by ALD on copper bare.
3.3. Electrochemical impedance spectroscopy

3.3.1. Nyquist plot and equivalent electric circuits

The EIS analyzes were done to better clarify the corrosion protection mechanism of the different coatings grown on Al substrate. Here, the analyzes were performed in the frequency range from 100 kHz to 0.1 Hz with a sinusoidal signal of 10 mV after the samples were immersed in the NaCl solution. Figure 4 shows the equivalent electric circuits (EECs) using to fit the EIS data. Figure 4(a) shows the EEC used to fitted the EIS data for the Al-bare. Orazem and Tribollet [59] and Mirhashemihaghighi et al [22, 31] discussed previously this simplified Randle circuit model and showed the parallel combination of the cathodic and anodic Faradic responses at OCP. To explain the non-ideal capacitive behavior of the system was used the $Q_1$ (constant phase element (CPE)), this non-ideal capacitive behavior is due to the native oxide layer on the Al-bare.

Figure 4(b) shows the EEC used to fitted the EIS data for Al-resin + Al$_2$O$_3$, Al-resin + TiO$_2$, and Al-TiO$_2$, and Al-Al$_2$O$_3$ samples. This EEC has been commonly used to fitting EIS data in porous electrode coated or a defective electrolyte interface and has recently been applied in the inert layer on metals [25, 35, 47, 60–63] As we cannot prove or deny the existence of two or more capacitive loop (time constants) for the coated samples (as an exception the Al-TiO$_2$ sample), we chose to use the model shown in figure 4(b) instead of using Randle’s simplified model (figure 4(a)). $Q_1$ represents the CPE of the thin film, $R_1$ is the electrolyte resistance, $R_2$ represents the resistance of the films or the pores, being the resistance of ion-conducting paths developed in the coating. It worth highlighting that these paths may be physical pores filled with electrolyte [64], $Q_2$ represents the double-layer capacitance (metal-solution interface), and $R_3$ represents the charge transfer reaction that represents the interface resistance.

According to Brug et al [65] the CPE expression for the impedance is:

$$Z_{CPE} = \frac{1}{Q.(j\omega)^n}$$  \hspace{1cm} (5)

where $Q$ ($\Omega^{-1}.cm^{-2}.s^n$) is the CPE coefficient and $n$ (unitless) is the CPE exponent, both are independent of frequency, $j$ is the imaginary unit, $\omega$ is the angular frequency (rad/s). The CPE coefficient deviation from the unit indicates an ideal capacitance of Q.

Figure 5 shows the complex plane (Nyquist) plots measured at OCP used to fit the EIS data. All EECs show possible electrochemical processes that occur at the electrolyte interface of a conductor with or without a coating.

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*Figure 4. Equivalent electric circuits used to fit the EIS measurements at OCP. (Q indicates a constant phase element (CPE), and R indicates a resistor): (a) EEC used for the bare substrate, and (b) EEC used for the coated substrates.*
containing porosity [22, 31, 57–63]. In addition, these models allow to compare the effective porosity and charge-transfer resistance ($R_p$) obtained by LSV. It worth highlighting that the equivalent values of the $R_p$ in EIS is the sum of all resistances present in the EECs. For oxide-coated metals, the models exhibit capacitor and resistance behavior, as shown in figure 5.

Table 3 shows some significant parameters calculated by EEC. The fitting results show values of $n$ tending to 1. This demonstrates a physical behavior of the CPE acting as a capacitor, for both, thin-film ($Q_1$) and metal-solution interface ($Q_2$). Another parameter that has values higher for coated samples in comparison with Al-bare is the $R_p$, which indicates an increase of the corrosion resistance when we include the coverage onto the Al-bare. The high electrical insulating property of all coverages suggests that rarely occurs anodic oxidation on the surface. On the other hand, the anodic reaction occurs among the pores of coverage, the electrolyte, and the Al surface [46]. These physical parameters corroborate with the capacitive-resistive behavior proposed in EEC models.

Figure 5 shows the one capacitive loop (time constant) in high frequency for the bare sample, which confirms a protective native oxide thin film on Al-bare [66, 67]. This behavior was observed to Mirhashemihaghigi et al [31] on aluminum in NaCl aqueous solution with the value of capacitance in the same order of magnitude of the value shows in table 3. It was observed in the Nyquist graph one capacitance loop for the Al-resin + TiO$_2$, which is attributed to the ideality of the coatings in inhibited the corrosion [68]. In the case of Al-TiO$_2$ was observed a
tendency of two capacitance loop, which is attributed to the non-inhibition of corrosion [69]. This second loop is related to the penetration of the electrolyte through the coating filled the pores leading to the appearance of additional looping as a response in the EIS plot [70]. Nyquist plots for Al-resin + Al2O3, Al-Al2O3, and Al-resin showed a higher global impedance into a broad range of frequency of capacitive response, which indicates a blocking electrode behavior [31]. As can be seen in Nyquist plots, the radius of the semicircle tends to infinity values, and this behavior is attributed to a lower current measured for the aforementioned samples, and this behavior leads to higher resistance (as shown in table 3). As demonstrated to LSV measurements, the cathodic $R_p$ ($R_2 + R_3$) fitted by EEC for EIS data presents values that increase in the following order: Al-TiO2, Al-resin+TiO2, Al-resin, Al-Al2O3, Al-resin+Al2O3. The values of $R_p$ showed in table 3 are comparable with the values presented in table 1. Despite the different regimes used in LSV and EIS, the results are in concordance. The values obtained for n (table 3) above 0.9 reveals that the EEC fitted very well all curves, and indicated that the coatings have high-quality.

3.3.2. Bode plots

A qualitative analysis of the EIS measurements was performed using magnitude and phase Bode plots (figure 6). The ratio between the amplitude of alternating voltage and current as a function of frequency is represented in the Bode magnitude plot. The Bode phase plot represents the phase difference between alternating voltage and current as a function of frequency, regardless of the amplitude of both. According to the literature [39, 57], Bode phase plots can be used to describe the capacitive, resistive and capacitive-resistive junction of the system for a specific frequency range. Therefore, in the −90 degree line, there is a capacitive behavior of the sample. At another extreme, at 0 degrees, the response is resistive. Between these values, the response is mixed, i.e. capacitive-resistive.

As can be seen in figure 6, the coated samples show a higher impedance than Al-bare. According to Matero et al [25], as a characteristic of high performance and good quality of coatings, the broad region of capacitive frequency stands out, with phase angles close to 90°. In addition to these results corroborating with the LSV data (tables 3 and 4), they agree with the literature [21, 22, 31].

The proper choice of EEC for the EIS data adjustment is verified due to the agreement between the values obtained from the LSV and EIS data.

The present work shows that all coatings have a corrosion inhibition enhancement factor above 99% when compared to the Al-bare substrate. However, when comparing the different coverings, we observed that Al-resin-Al2O3 and Al-Al2O3 have a better quality compared to the other films. The various methods of electrochemical characterization confirm that the films grown by ALD are suitable for increased corrosion resistance and show that ALD-alumina coatings have a better sealing property, which corroborates the results of the literature [19–22, 31–33].

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**Figure 6.** Bode phase and magnitude plot of the sample (a) Al-bare, (b) Al-resin, (c) Al-TiO2, (d) Al-resin-TiO2, (e) Al-Al2O3, and (f) Al-resin-Al2O3. Points and black lines correspond to raw measured and fitted data, respectively. The error bar is not shown in the graph, but the errors of the parameters are shown in table 3.
4. Conclusions

The electrochemical behavior of ALD amorphous TiO$_2$ and Al$_2$O$_3$ thin films (approx. 100 nm thick) grown on commercial pure- and resin-coated Al substrates in 0.5M NaCl solution (electrolyte, pH $\approx 7.0$) was investigated using EIS and LSV measurements. Both techniques allowed the extraction and comparison of corrosion parameters for the six different samples evaluated (Al-bare, Al-resin, Al-TiO$_2$, Al-Al$_2$O$_3$, Al-resin-TiO$_2$, and Al-resin-Al$_2$O$_3$). All ALD coated samples have a corrosion inhibition enhancement factor above 99% when compared to the Al-bare substrate. Al-resin-Al$_2$O$_3$ and Al-Al$_2$O$_3$, and Al-resin samples have a cathodic shift in the corrosion potential in LSV data (compared with Al-bare), which indicates higher corrosion resistance. This corroborated by the lower corrosion current (of the order of $10^{-11}$ A.cm$^{-2}$) and higher polarization resistance (of the order $10^9$--$10^{10}$ $\Omega$.cm$^2$) measured for these samples. Overall, our results indicate that ALD oxides films have greater protection efficiency on coated and uncoated samples. Therefore, ALD thin films is a probable candidate for the exchange of commercial resin or to block the contact between the resin and beverage.

Acknowledgments

The financial support of the Brazilian agency program FAPESP/MCT/CNPq-PRONEX (grant no. 2011/50773-0), and Brazilian agencies FAPESP (grant no. 2018/01265-1, 2016/17826-7, and 14/18139-8) and CNPq (grant no. 303818/2018-2 and no. 437921/2018-2) is gratefully acknowledged.

Author Contributions

Conceptualization, V D, F M, and R P; methodology, V D, F M, and R P; formal analysis, V D, W C, R P, and M F; investigation, V D, F M, R P; resources: F M, H M, M F, and R P; writing—original draft, V D, R P, and W C; writing—review & editing, V D, W C, R P, M F; supervision, F M, and R P; funding acquisition, F M, H M, R P, and M F.

ORCID iDs

W Chiappim https://orcid.org/0000-0003-2615-2216
M A Fraga https://orcid.org/0000-0001-6976-8550
R S Pessoa https://orcid.org/0000-0001-7600-9747
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