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Electron Donor-Induced Electrochemical Reduction in Vanadate Anions to Enhance the Electrochemical Performance of Plasma Electrolytic Oxidation Layers

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Abstract: Despite the increasing interest in enhancing the electrochemical stability of Al alloys through protective coatings, the role of electron donor agents during coating formation remains poorly understood in terms of morphological control and anticorrosion properties in aqueous environments. In this context, 1H-Benzotriazole (BTA) was utilized as a proof of concept to regulate the in situ reactive integration of V_2O_5 into the alumina layer via the plasma electrolytic oxidation of a 6061 Al alloy. BTA played a crucial role in chemically incorporating V_2O_5 into the alumina coating by supplying electrons to VO_3^- ions, facilitating their reduction. The quantity of BTA added to the electrolyte was found to influence defect morphology and concurrently enhance the chemical incorporation of V_2O_5 . Notably, corrosion measurements revealed that the less porous hybrid film formed with higher corrosion resistance was associated with the utilization of increased concentrations of BTA. These findings highlight the potential of BTA in modifying the structure and improving the ability of alumina coatings to resist corrosion, enabling advanced applications in protecting Al alloys from corrosion.

Keywords: electron donor; plasma electrolytic oxidation (PEO); vanadate reduction; V_2O_5 ; corrosion



Citation: Kaseem, M.; Fattah-alhosseini, A.; Dikici, B. Electron Donor-Induced Electrochemical Reduction in Vanadate Anions to Enhance the Electrochemical Performance of Plasma Electrolytic Oxidation Layers. *Metals* **2024**, *14*, 606. <https://doi.org/10.3390/met14060606>

Academic Editors: Rastko Vasilic and Nebojša Nikolić

Received: 11 March 2024

Revised: 9 May 2024

Accepted: 18 May 2024

Published: 21 May 2024



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1. Introduction

Plasma electrolytic oxidation (PEO) is a wet-coating approach that is favored for modifying the compounds and surface structure of various metallic materials. It enables the production of thick, hard, and strongly adherent coatings on valve metals, such as Mg, Al, and Ti, as well as their alloys [1]. The coatings fabricated by PEO are primarily influenced by the conditions associated with the electrolyte and processing parameters [2–6]. Among all the processing variables, the electrolyte's role has been noted to considerably alter the structure of the coatings, thus affecting their protective characteristics [7]. To date, various inorganic-containing electrolytes have been investigated for their benefits in generating oxide layers on the surfaces of light metals. These electrolytes include silicate, aluminate, phosphate, and borate, each with different chemical additives [8–11].

Incorporating metallic oxide particles into the PEO coating via electrochemical and electrophoretic mechanisms has been highlighted as an efficient method for boosting their protective attributes [12]. Numerous particles, including SiO_2 , ZrO_2 , MoO_2 , WO_3 , TiO_2 , CeO_2 , VO_2 , and V_2O_5 , were integrated into coatings applied on Al and its alloys [13–22]. Among them, it was stated that the inclusion of V_2O_5 particles would be beneficial to boost the anticorrosive performance of Al alloys. For example, Kwon et al. [21] documented

that the introduction of V_2O_5 into the coating layer of Al alloy led to decreased porosity and enhanced electrochemical stability. These particles, being more electrochemically inert, create barriers against corrosive ions, thus impeding corrosion. In another work, the anticorrosive properties of PEO-coated Al alloy were improved by incorporating V_2O_5 nanoparticles [22].

On the other hand, incorporating organic additives, such as alcohols, organic acid salts, organic amides, and aromatics, into electrolytes during the PEO process was found to be an effective method to enhance the performance of the coatings [1]. Benzotriazole (BTA) functions as an effective corrosion inhibitor via the formation of a protective layer on metal surfaces [23,24]. This layer serves as a protective barrier, preventing corrosion by shielding the metal from environmental factors. Widely used due to its versatility, BTA is a cost-effective solution in various industries for enhancing metal corrosion resistance. Kaseem et al. [24] showed that the surface modification of an Al alloy via PEO with phosphate and BTA additives led to a reduction in micropore size, thereby limiting the infiltration of aggressive species during corrosion tests.

In earlier investigations, the predominant focus in research on the electrochemical functions of chemical additives in PEO-induced metal oxide formation was on incorporating V_2O_5 . This incorporation entailed two distinct pathways: the initial one involved incorporating V_2O_5 through the direct addition of V_2O_5 nanoparticles or utilizing vanadate salts. As far as our understanding extends, there is a notable absence of reports delving into the potential impacts of organic agents on the level of incorporation of V_2O_5 into the alumina layer. One of the additives that could potentially influence the performance of the PEO coatings is capable of donating electrons during the oxidation process. This capability could contribute to modulating the electrochemical reactions occurring at the alloy–electrolyte interface [25,26]. BTA, as a common electron donor agent, is expected to initiate the plasma-assisted electrochemical reduction in vanadate ions (VO_3^-) present in the electrolyte. In the present study, an Al alloy underwent PEO treatment in vanadate electrolytes containing varying concentrations of BTA. The resulting hybrid films, primarily composed of V_2O_5 and Al_2O_3 , were characterized in terms of their structure and composition, and a corrosion assessment.

2. Experimental Procedures

2.1. Fabrication of Hybrid Films

In this study, 6061 Al alloy sheets measuring 25 mm × 20 mm × 2 mm were employed as substrates. Before the PEO process, the samples underwent mechanical grinding with emery papers up to #2400 grit, ultrasonic cleaning in pure ethanol, and drying in warm air. To fabricate the hybrid film through PEO, the Al alloy served as the anode, while a stainless-steel net acted as the cathode. A sequence of PEO processes was carried out using alkaline–phosphate electrolytes with varying concentrations of 1H-benzotriazole ($C_6H_5N_3$) BTA (soluble organic compound), while keeping the NH_4VO_3 (soluble salt) concentration consistent. The process was performed for 3 min at a current density of 100 mA/cm² and a frequency of 60 Hz using an AC power supply (ACP 1010, Gunpo, Republic of Korea), as outlined in Table 1.

Table 1. Composition of electrolytes with the variation BTA concentration used for hybrid films.

Sample	KOH (g/L)	Na ₃ PO ₄ (g/L)	BTA (g/L)	NH ₄ VO ₃ (g/L)	pH	Conductivity (mS/cm)
0BTA	6	6	0	3	12.2	18.6
3BTA	6	6	3	3	12.1	18.7
5BTA	6	6	5	3	11.9	18.8
7BTA	6	6	7	3	11.7	18.9

2.2. Characterization

Surface structures of the hybrid films were observed using field emission-scanning electron microscopy (FE-SEM, HITACHI S-4800, Hitachi, Tokyo, Japan) linked with an energy-dispersive X-ray spectroscopy detector (EDS, Horiba Inc., Kyoto, Japan). Before SEM observation, the samples were subjected to a platinum (Pt) sputtering process to enhance their conductivity and improve imaging quality. The size and fraction of micropores were measured via SEM observations taken from at least ten different areas for each condition, aided by image analysis software (version 1.47 for Windows, 64 bit, free software, National Institutes of Health, Bethesda, MD, USA). Surface roughness assessments (AFM, ToscaTM Analysis, Anton Paar, Graz, Austria) were performed by taking measurements five times longitudinally and five times laterally across each specimen's surface. The outcomes are expressed as the arithmetic mean roughness (R_a). Constituent compounds were identified via X-ray diffraction (XRD, RIGAKU, D-MAX 2500, Tokyo, Japan) in a scanning range of 20 to 90 degrees with a step size of 0.05 degrees. The hybrid films also underwent a thorough examination through X-ray photoelectron spectroscopy (XPS, VG Microtech, ESCA 2000, VG Microtech, London, UK) to confirm the correlation between BTA and the incorporation of V_2O_5 .

2.3. Corrosion Tests

The corrosion assessments were performed in a 3.5 wt.% NaCl electrolyte to simulate the salinity of typical seawater. Potentiodynamic polarization (PDP) tests were carried out over the range of -250 to $+400$ mV relative to the open-circuit potential (OCP) at a scan rate of 1 mV/s, while electrochemical impedance spectroscopy (EIS) tests were conducted in the frequency range of 10^6 to 0.1 Hz with an AC amplitude of 10 mV over the OCP. All corrosion measurements were performed after stabilizing the OCP for 1 h using a Gamry Potentiostat, Interface 1010, Philadelphia, PA, USA. The experiments were conducted at least five times to guarantee the acquisition of highly precise data.

3. Results and Discussion

3.1. BTA Concentration and Voltage Relationship

The voltage–time plots depicted in Figure 1 illustrate the formation of oxide layers in an alkaline–phosphate–vanadate electrolyte with varying concentrations of BTA. Regardless of the BTA concentrations, the curves exhibit three distinct regions, denoted as regions I, II, and III.

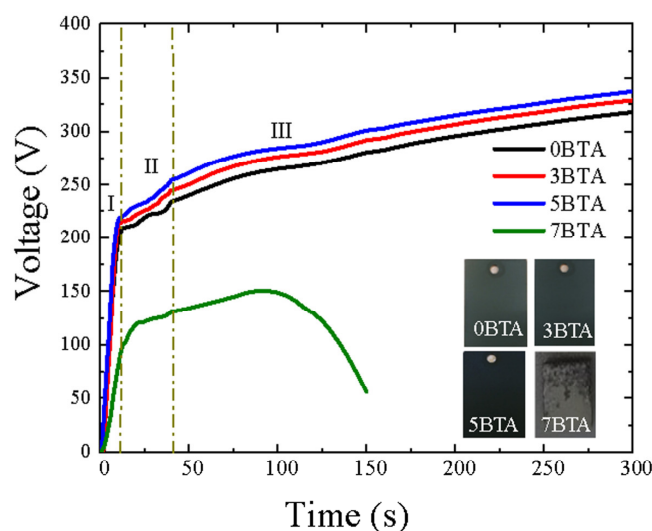


Figure 1. Voltage–time curves observed during the PEO process of 6061 Al alloy in an alkaline–phosphate–vanadate electrolyte with different concentrations of BTA. The inset displays the color variation among the coated samples, namely 0BTA, 3BTA, 5BTA, and 7BTA samples.

At the onset, in region I, a rapid and sharp linear rise in voltage is observed across all samples, which could be ascribed to the swift formation of a thin passive layer across the entire sample surface [27–29]. The breakdown potential is the voltage threshold at which dielectric breakdown occurs in the barrier film during the PEO process. This signifies the point where the barrier film, originally functioning as a resistor to current flow, undergoes breakdown at regions of lower resistance. This transition is marked by the appearance of spark discharges on the surface of the substrate. These spark discharges indicate the initiation of a localized breakdown, marking the transition from uniform barrier film growth to the onset of PEO.

As depicted in Figure 1, the breakdown voltage experiences variations based on the content of BTA in the electrolyte. The breakdown voltage values were ~208 V, ~214 V, ~217 V, and ~100.1 V for 0BTA, 3BTA, 5BTA, and 7BTA samples, respectively. Following the breakdown voltage and during the growth of the PEO coating (region II), the rate of voltage increment diminishes, showing a slower increase with a reduced slope across all samples until the completion of the PEO process. Since the conductivity of the electrolytes remained nearly identical and was unaffected by the concentration of BTA, the variations in breakdown voltage values can be attributed to the increased incorporation of vanadium oxides (as will be proven later) facilitated by higher BTA concentrations. This outcome aligns with the observations made by Tang et al. [30], who found a relationship between the breakdown voltage and the melting point of oxide elements located at the interface of the anode and electrolyte. Thus, it was proposed that the inclusion of nanoparticles with elevated melting points could potentially increase the breakdown voltage.

In stage III, there was a consistent upward trend in the voltage of the 3BTA and 5BTA samples compared to the 0BTA sample, indicating the coating's augmented resistance to dielectric breakdown. This pattern was characterized by the uniform advancement of the hybrid film across all electrolyte conditions [31]. Nonetheless, an unusual behavior surfaced in the 7BTA sample towards the conclusion of stage III, marked by a substantial drop in voltage, suggesting a partial inhibition of coating growth [32]. Therefore, the opportunity to conduct a microstructural and electrochemical analysis of the surface of the 7BTA sample was not pursued. The observed outcome is likely due to the increasing concentration of BTA, acknowledged as a weak electrolyte, wherein a notable portion of BTA particles may not completely dissociate within the electrolyte solution, thereby disturbing ionic equilibrium and interactions between the electric field and BTA particles [33]. On the other hand, the coating colors of samples with 0BTA, 3BTA, and 5BTA concentrations displayed varying degrees of darkness, with the darkness intensifying as the BTA concentration increased (see inset in Figure 1), ultimately resulting in the 5BTA sample having a black appearance.

3.2. Morphology of the Hybrid Films

Figure 2a,d,g depict the surface morphologies of 0BTA, 3BTA, and 5BTA specimens produced via PEO in electrolytes with varying contents of BTA. Plasma activity during the PEO process is responsible for the creation of a porous structure on the surface of 0BTA, 3BTA, and 5BTA samples [34–36].

Moreover, some cracks were observed on the 0BTA sample, arising from the swift solidification of molten oxides upon contact with the cold electrolyte. Pore size and porosity level calculations were conducted for the 0BTA, 3BTA, and 5BTA samples, and the outcomes are detailed in Table 2.

Table 2. The correlation between BTA concentration and the porosity and pore size of the oxide layers produced on 6061 Al alloy through the PEO process.

Sample	0BTA	3BTA	5BTA
Pore size (μm)	1.28 ± 0.42	1.13 ± 0.35	0.87 ± 0.29
Porosity (%)	13.57 ± 2.20	11.98 ± 3.07	6.815 ± 2.56

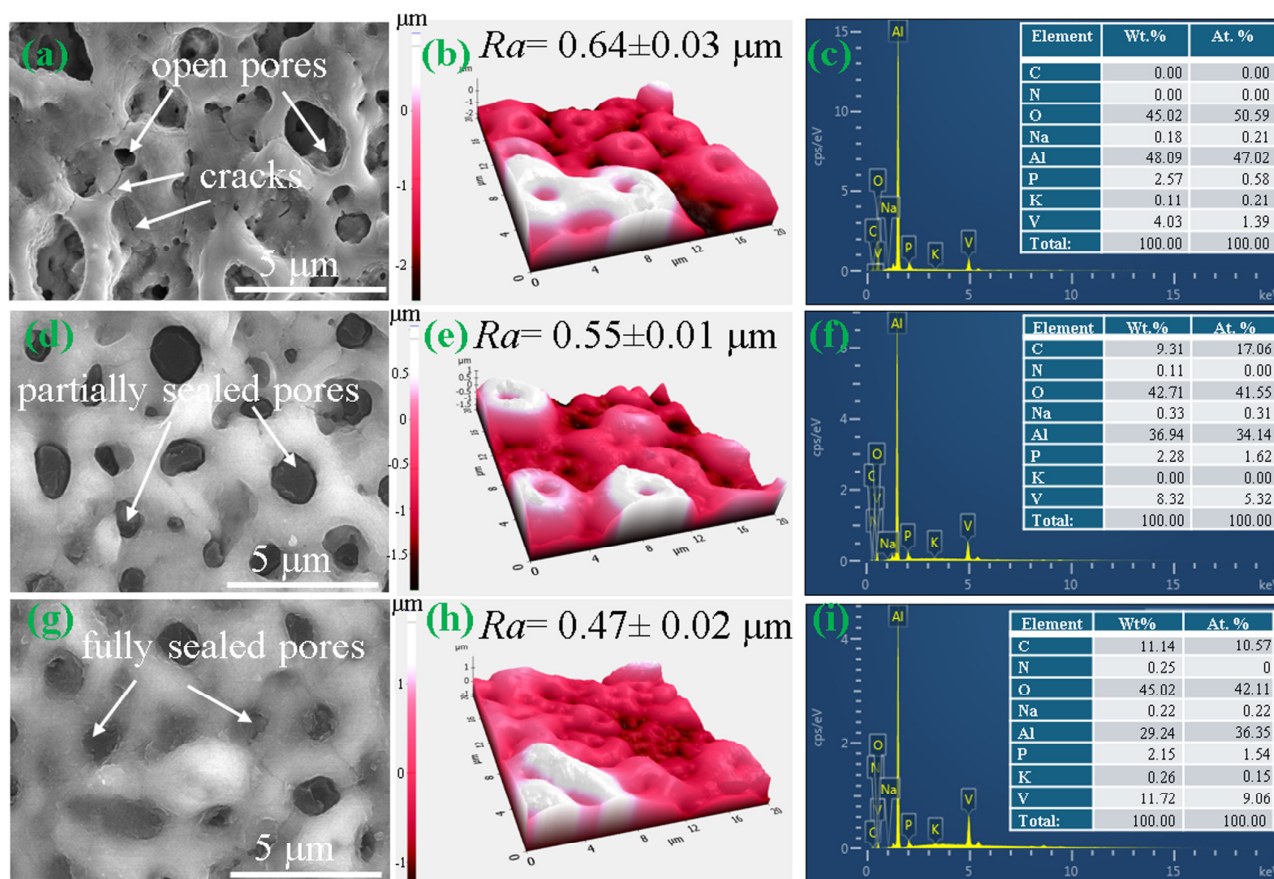


Figure 2. SEM images, AFM results, and the corresponding EDS analysis conducted on the surfaces of the coated samples, where (a–c) 0BTA, (d–f) 3BTA, and (g–i) 5BTA.

The introduction of BTA resulted in a decrease in both pore size and porosity, with the 5BTA sample, made in an electrolyte with 5 g/L of BTA, exhibiting the smallest average pore size ($\sim 0.87 \mu\text{m}$) and the lowest porosity ($\sim 6.81\%$). According to the AFM findings depicted in Figure 2b,e,h, the R_a values for 0BTA, 3BTA, and 5BTA samples were approximately 0.64 ± 0.03 , $0.55 \pm 0.01 \mu\text{m}$, and $0.47 \pm 0.02 \mu\text{m}$, respectively. This indicates that incorporating BTA in the electrolyte during PEO results in a reduction in R_a values within the oxide films. The reduced surface roughness noticed in the 5BTA samples could be linked to the significant collapse of plasma bubbles, which is likely impeded during the adsorption of BTA molecules. The EDS area findings presented in Figure 2c,f,i show the existence of Al, O, P, K, Na, and V elements in all specimens, while C and traces of N elements were detected in samples coated with electrolytes containing BTA (3BTA and 5BTA). The existence of Al was linked to the Al alloy substrate, whereas the presence of other elements stemmed from the electrolyte solution. Given that BTA in the electrolyte was the sole source of C and N, it was confirmed that BTA successfully participated in plasma-assisted electrochemical reactions. With 5 g/L of BTA present in the electrolyte, the 5BTA sample displayed higher levels of the V element compared to other samples, indicating the induced integration of V-containing compounds (presumably V_2O_5 , as subsequently verified). Hence, the inclusion of BTA in the electrolyte substantially fostered the development of the hybrid film and the assimilation of V oxide. This observation aligns with the EDS mapping shown in Figure 3, unveiling the consistent dispersion of V and O throughout the hybrid film.

Figure 4a–c present cross-sectional morphologies of the 0BTA, 3BTA, and 5BTA samples. The average thickness was found to be consistent ($9.15 \pm 1.20 \mu\text{m}$) across the 0BTA, 3BTA, and 5BTA samples. This indicates that the addition of BTA had minimal impact on the thickness of the samples, likely because they were exposed to identical current

densities for a brief duration [37]. The coating layers of each sample revealed a dual structure consisting of inner and outer layers. Remarkably, the inner layer exhibited greater density despite its thinner dimensions compared to the porous outer layer. Interestingly, the compactness of the hybrid films was significantly increased in the 3BTA and 5BTA samples compared to the 0BTA sample. This increase is attributed to the favorable influence of V_2O_5 incorporation facilitated by the addition of BTA, potentially impeding the formation of micropores. The EDS point analyses conducted at different positions (Figure 4d), such as 1 and 2 from the 0BTA sample, 3 and 4 from the 3BTA sample, and 5 and 6 from the 5BTA sample, showed a notable trend: the incorporation of the V element tended to increase with an increase in the content of BTA. The denser coating layer enriched with stable V_2O_5 in the 5BTA sample would offer promising protection against substrate corrosion.

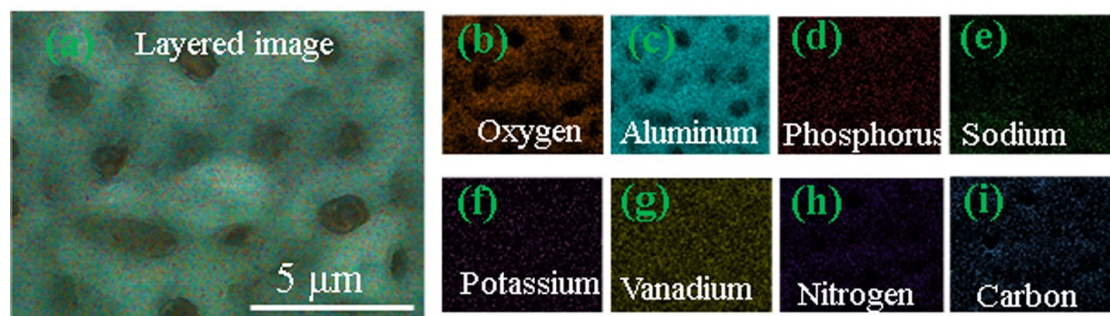


Figure 3. EDS mappings conducted on the surface of the 5BTA sample, as depicted in Figure 2g. The mappings include (a) the EDS layered image, (b) oxygen, (c) aluminum, (d) phosphorus, (e) sodium, (f) potassium, (g) vanadium, (h) nitrogen, and (i) carbon.

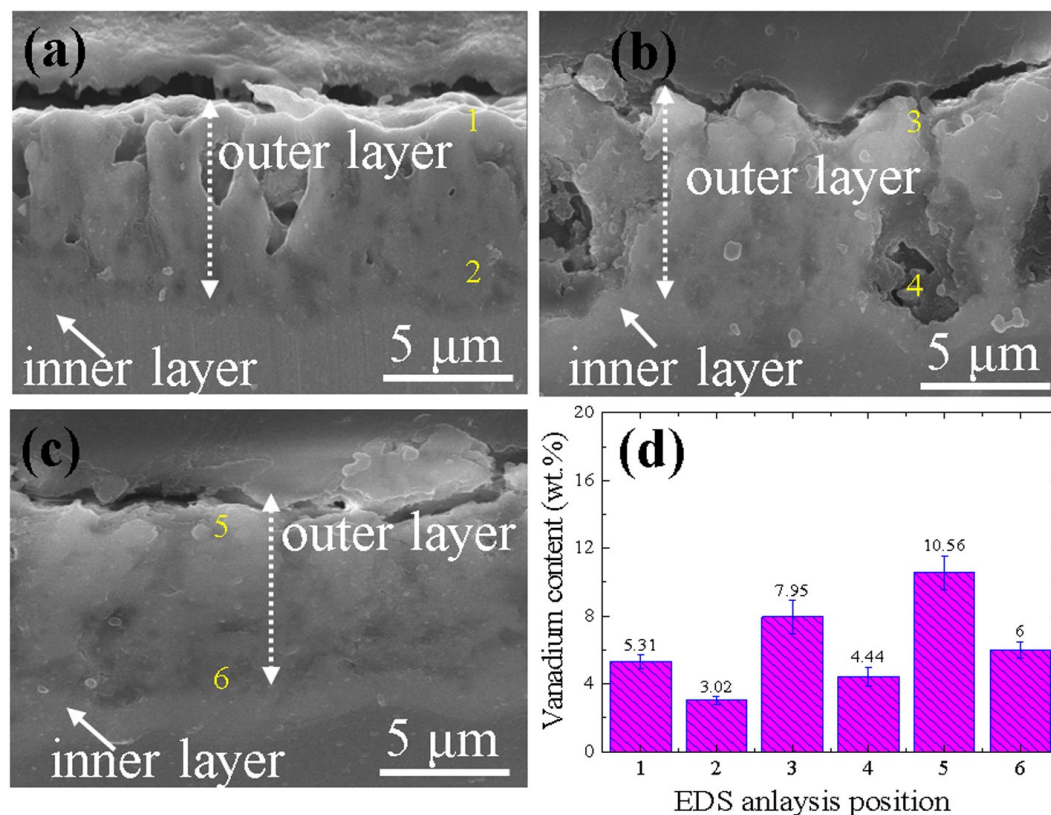


Figure 4. Cross-sectional images of the (a) 0BTA sample, (b) 3BTA sample, and (c) 5BTA sample. (d) shows the variation in the wt.% content of vanadium element at points 1 and 2 from the 0BTA sample, points 3 and 4 from the 3BTA sample, and points 5 and 6 from the 5BTA sample.

3.3. Compositional Analysis

XRD patterns of 0BTA, 3BTA, and 5BTA specimens resulting from the oxidation of the substrate specimens in BTA-containing electrolytes are presented in Figure 5a. γ - Al_2O_3 , α - Al_2O_3 , AlPO_4 , α - Al_2O_3 , and V_2O_5 were identified across all samples. Moreover, peaks originating from the Al substrate were detected in all samples, likely owing to X-ray infiltration through micro-pores within the hybrid films. Notably, the intensities of V_2O_5 -related peaks in the 3BTA and 5BTA samples exceeded those in the 0BTA sample, suggesting the potential influence of BTA in promoting the amount of V_2O_5 that was incorporated into the hybrid film. No carbon-containing compounds were detected in the 3BTA and 5BTA samples, possibly indicating either the decomposition of BTA under plasma conditions or its incorporation in amorphous forms [38].

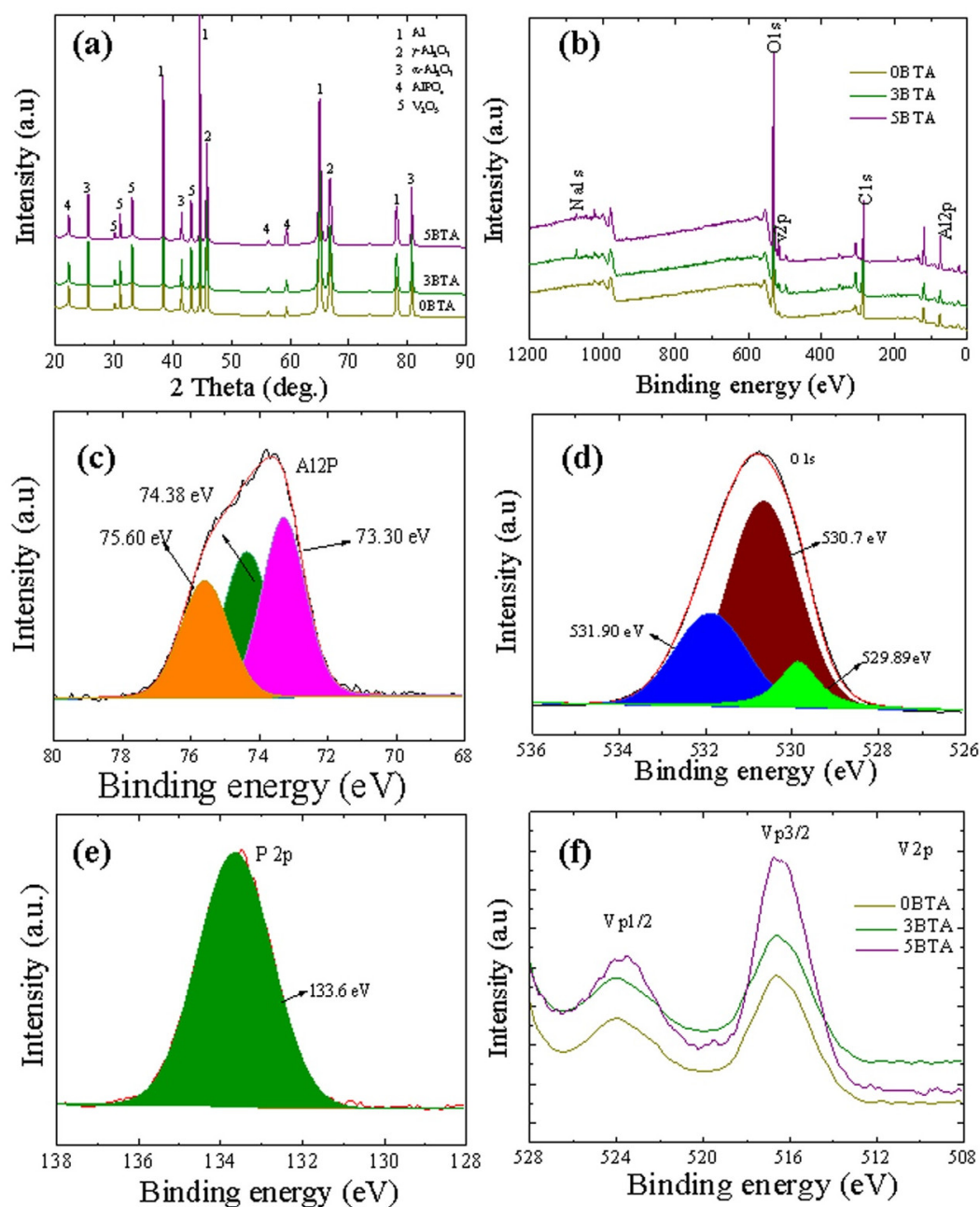
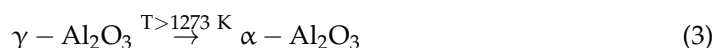
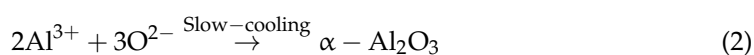


Figure 5. (a) XRD patterns of the 0BTA, 3BTA, and 5BTA samples. (b) Wide scan spectra of 0BTA, 3BTA, and 5BTA samples. (c–f) The high-resolution spectra of Al2p, O1s, P2p, and V2p for the 5BTA sample.

XPS analysis verified the chemical composition of the 0BTA, 3BTA, and 5BTA samples, as illustrated in the XPS survey spectra presented in Figure 5b. Across all samples, the hybrid films demonstrated a consistent composition, comprising Al, O, Na, K, P, V, and C, consistent with the EDS analysis findings depicted in Figure 2. Given the marginal disparities in the XPS spectra of the hybrid films, the high-resolution spectra of Al 2p, O 1s, P 2p, and V 2p elements are only presented for the 5BTA samples in Figure 5c–f. Specifically, the Al2p spectrum reveals three peaks, corresponding to α -Al₂O₃, γ -Al₂O₃, and AlPO₄, with binding energies of approximately 74.38, 73.30, and 75.60 eV, respectively [39]. The lowered critical free energy characteristic of the γ -Al₂O₃ phase leads to the rapid cooling of molten oxides upon interaction with the electrolyte, facilitating the nucleation and subsequent solidification of the γ -Al₂O₃ phase. Conversely, a slower cooling rate favors the formation of the more enduring α -Al₂O₃ phase. Under optimal temperature conditions, the metastable γ -Al₂O₃ phase can transfer into the stable α -Al₂O₃ phase (Equations (1)–(3)). The O1s spectra fit Al₂O₃, V₂O₅, and AlPO₄ corresponding to ~530.7, ~529.89 and ~531.9 eV, respectively [40].

In the deconvoluted spectrum of P2p shown in Figure 5e, a solitary peak is noticed at ~133.6 eV, corresponding to AlPO₄. In Figure 5b, the high-resolution spectra of V2p, ranging from ~512 eV to ~528 eV, are examined. Specifically, the peak at approximately 523.9 eV corresponds to V2p1/2, while the one at around 516.58 eV is associated with V2p3/2, consistent with the earlier results [41]. It is interesting to note that the V2p1/2 and V2p3/2 peaks were significantly higher for the 5BTA sample compared to the 0BTA and 3BTA samples. This suggests the more substantial incorporation of V₂O₅ in the BTA sample, consistent with the results obtained from EDS analyses and the XRD patterns presented in Figures 1–3.



3.4. Electrochemical Behavior

The micro-pores on the surface of the PEO coating layer provide a short-circuit path for the easier infiltration of the corrosion medium into the inner region, close to the substrate [42,43]. This infiltration leads to a change in the local pH [44], which decreases the energy barrier of the electrical double layer against electrochemical corrosion. Consequently, the dissolution of the oxide coating is triggered [45], leading to surface degradation and a reduction in the overall endurance of the coating in a corrosive environment.

To explore how variations in BTA concentration influence the corrosion tendencies of 0BTA, 3BTA, and 5BTA samples, PDP curves are depicted in Figure 6a. A comparative analysis of their results with those of the uncoated substrate was conducted. The E_{corr} and i_{corr} were calculated using the Tafel extrapolation method, whereas the Stern–Geary equation was used to determine the values of polarization resistance (R_p) (Equation (4)). In this equation, β_a and β_c represent the Tafel slopes (anodic and cathodic), respectively [46]. Table 3 summarizes the results obtained from these investigations.

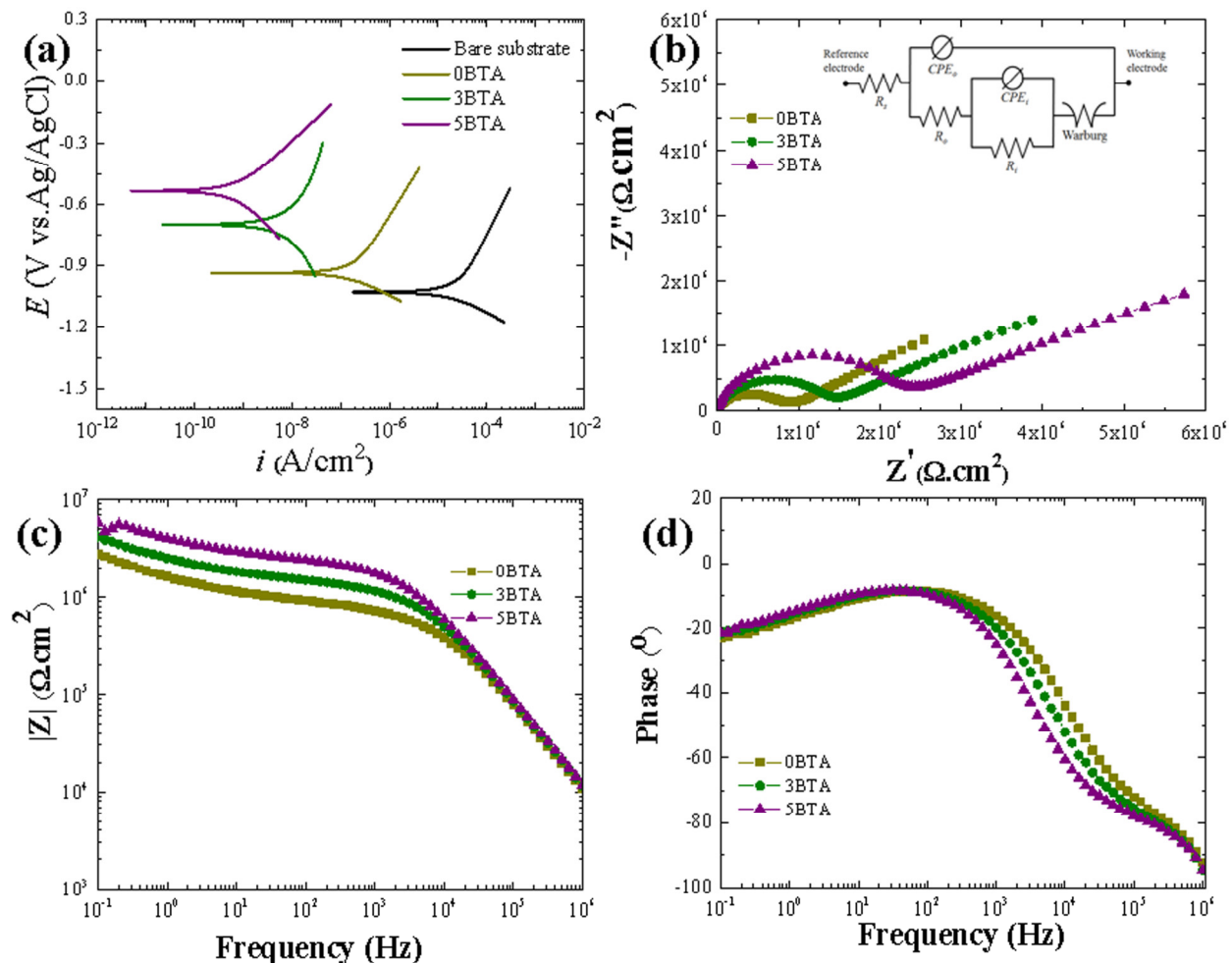
$$R_p = \frac{\beta_a \cdot \beta_c}{2.303 i_{corr} (\beta_a + \beta_c)} \quad (4)$$

A positive E_{corr} and/or a low i_{corr} , indicating a low corrosion rate, typically signify excellent corrosion resistance in a standard polarization curve [47,48].

In Figure 6a, there is a clear trend where the PDP curves move towards more positive potentials and reduced current densities as the BTA content increases from 0 to 5 g/L. The E_{corr} of the 0BTA sample shifted in a nobler direction, from −0.94 to −0.53 V Ag/AgCl, upon treatment with 5 g/L of BTA in the solution, as depicted in Figure 6a and Table 3.

Table 3. PDP parameters of the bare substrate and hybrid films after 1 h immersion in 3.5 wt.% NaCl electrolyte.

Sample	E_{corr} (V vs. Ag/Ag/Cl)	i_{corr} (A/cm ²)	β_a (V/Decade)	$ \beta_c $ (V/Decade)	R_p (Ω cm ²)
Substrate	−1.02	2.14×10^{-5}	0.25	0.13	1.74×10^3
0BTA	−0.94	1.31×10^{-7}	0.34	0.11	2.75×10^5
3BTA	−0.71	4.00×10^{-9}	0.25	0.27	1.41×10^7
5BTA	−0.53	6.04×10^{-10}	0.19	0.24	7.62×10^7

**Figure 6.** (a) PDP tests of the 0BTA, 3BTA, and 5BTA samples. (b) Nyquist plots, (c) Bode impedance plots, and (d) Bode phase plots. The inset in Figure 6b shows the circuit model used for fitting the impedance results.

As commonly recognized, E_{corr} correlates with the thermodynamic aspect, reflecting the susceptibility of the coating to corrosion, and is influenced solely by the composition of the PEO coatings [1,43]. Therefore, we hypothesized that the incorporation of V_2O_5 into the alumina coating might be responsible for the shift in E_{corr} values towards nobler potentials upon PEO treatment in a solution with a BTA additive. Additionally, the 5BTA sample displayed the smallest i_{corr} value compared to the other samples. The results showed a decrease of three orders of magnitude in comparison to the 0BTA sample, roughly one order below the 3 BTA sample. This result suggests the 5BTA sample offers better protection for the Al alloy substrate than the other samples. This difference shows that the 5BTA sample exhibits enhanced corrosion resistance, as also evidenced by its higher R_p value. The

improved corrosion protection observed in the 5BTA sample can be attributed to its smaller pore size and reduced porosity, which result from the higher level of V_2O_5 incorporation compared to the 0BTA and 3BTA samples. V_2O_5 particles exhibit high chemical stability in neutral electrolytes, such as 3.5 wt. % NaCl solution. The increased presence of V_2O_5 in the 5BTA sample effectively hinders the transportation of corrosive ions toward the substrate during the corrosion test.

Figure 6b provides insights into the corrosion mechanism through EIS analysis, showcasing Nyquist plots that predominantly display resistive–capacitive characteristics, forming (partial) semi-circular patterns that are inversely linked to the coating dissolution kinetics. Furthermore, the EIS characteristics can be further elucidated through Bode plots (Figure 6c), illustrating impedance values alongside phase angles compared to frequency, contributing to a comprehensive understanding of the corrosion dynamics. In qualitative terms, the impedance modules are in line with the outcomes of the PDP tests, signifying a notable improvement in the anticorrosive properties of the hybrid film with the inclusion of BTA in the electrolyte. Notably, the 5BTA sample displays a superior performance, attributed to the optimal incorporation of V_2O_5 . Moreover, the impedance characteristics of the PEO layer diverge from those of the 5BTA sample at lower frequencies. This indicates that the degree of V_2O_5 integration has a notable impact on the electrochemical behavior. In a quantitative approach, the EIS responses of samples can be likened to the behavior of circuit components, producing the parameter values systematically detailed in Table 4. Employing Equivalent Electrical Circuit (EEC) modeling enables the disentanglement of various processes occurring in the working electrode. The assigned EEC for all samples' layers is illustrated as an inset in Figure 6b. In this configuration, R_s denotes the resistance of the corrosive solution; R_o and CPE_o indicate the capacitive and resistive properties of the porous outer film. Meanwhile, R_i and CPE_i denote the corresponding parameters of the dense inner film [49].

Table 4. Outcomes of the EIS examinations on the 0BTA, 3BTA, and 5BTA specimens submerged in a 3.5 wt.% NaCl electrolyte.

Sample	R_s (Ωcm^2)	R_o (Ωcm^2)	$CPE-n_{pore}$	$CPE-Y_o$ ($S.s^n.cm^{-2}$)	R_i (Ωcm^2)	$CPE-n_i$	$CPE-Y_i$ ($S.s^n.cm^{-2}$)	W ($S^*S^{1/2}$)
0BTA	20.12	7.11×10^5	0.91	5.77×10^{-11}	3.47×10^6	0.49	7.54×10^{-10}	1.00×10^{-6}
3BTA	20.07	4.63×10^6	0.94	6.91×10^{-11}	5.01×10^7	0.51	3.68×10^{-11}	2.08×10^{-6}
5BTA	19.89	8.81×10^6	0.98	1.00×10^{-12}	9.33×10^7	0.52	4.00×10^{-11}	4.57×10^{-6}

To address the variation in time constants across the non-uniform surface of the plasma-modified PEO layer, CPE is employed instead of a conventional capacitor. As outlined in Table 4, the values of R_i exceed those of R_o , irrespective of the electrolyte composition, which can be ascribed to the free-defective structure of the inner layer. The values of R_o demonstrated an increase with the increase in BTA concentration to 5 g/L. The extent of the improvement in the values of R_o depends on the amount of V_2O_5 that is incorporated into the hybrid; thus, the 5BTA sample exhibited the highest R_o value in comparison to the 0BTA and 3BTA samples. Moreover, the high value of R_i in 5BTA, in comparison to the counterparts' values in other samples, suggests that the incorporation of V_2O_5 is not only localized in the outer part of the hybrid film but also extends to the inner layer of the film. On the other hand, the parameters of the CPE (Y and n) are correlated with the structure of the hybrid films. A higher value of Y suggests that a larger area is exposed to the corrosive solution, while a higher value of n indicates better uniformity of the oxide layer [50]. The value of Y_o in the 0BTA sample exceeded that of the other samples, implying that a larger area is exposed to Cl^- ions, aligning with the SEM results in Figure 2, where 0BTA had the largest micropore size. The low value of n_o in the 0BTA sample also indicated a rougher surface, consistent with AFM results in Figure 2b. In contrast, the 5BTA

sample featured a lower value of Y_0 and a higher value of n_o , affirming the uniformity observed in the sample in Figure 2.

Figure 7 shows the surface morphologies of the 0BTA, 3BTA, and 5BTA samples after electrochemical corrosion testing in 3.5 wt% NaCl solution. The coatings on all samples exhibited partial damage, characterized by corrosion pits. The surfaces of the 3BTA and 5BTA samples were less affected, displaying a typical PEO morphology. Increasing the BTA concentration to 5BTA resulted in fewer pits appearing on the surface, which could be attributed to the smaller micro-pore size and increased incorporation of V_2O_5 into the oxide layer. This result confirms that the corrosion resistance of the Mg alloy was significantly enhanced by the incorporation of V_2O_5 facilitated by the addition of BTA.

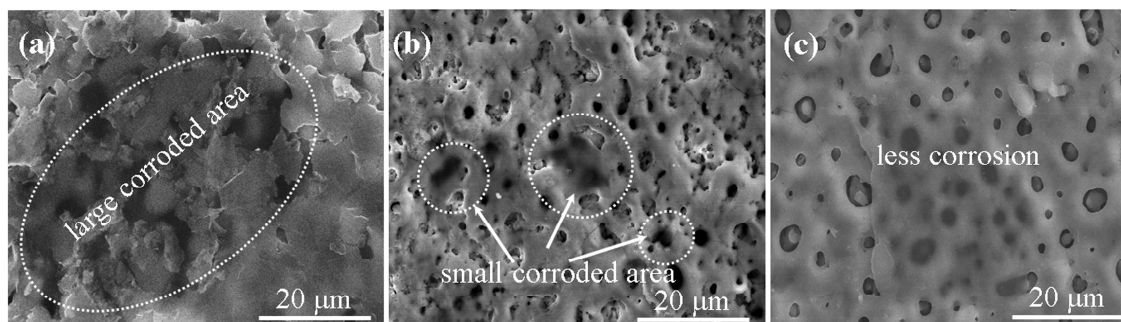


Figure 7. Surface morphologies showing the levels of degradation by corrosion on the surface of (a) 0BTA, (b) 3BTA, and (c) 5BTA.

3.5. EIS Evaluation for a Long Period of Immersion

To evaluate the corrosion resistance of coatings exposed to a NaCl solution, EIS measurements were conducted over 96 h. The results for 0BTA, 3BTA, and 5BTA samples are shown in Figure 8. Throughout the immersion period, 0BTA exhibited inferior corrosion resistance compared to 3BTA and 5BTA, evident in the smaller capacitive loop diameters in Nyquist plots and decreased impedance modulus at low frequencies, particularly from 24 to 96 h. The more porous structure of 0BTA facilitated the quicker diffusion of corrosive ions, leading to higher corrosion rates. Despite the reduction in capacitive loop diameters in Nyquist plots for 5BTA over time, their corrosion resistance remained superior, attributed to V_2O_5 particles reducing pore size and inhibiting the infiltration of corrosive anions into the substrate. This superiority was also reflected by the higher impedance values obtained at lower frequencies in Bode impedance plots. Furthermore, in all samples, at least two time constants can be identified from the phase angle plots shown in Figure 8c,f,i.

The impedance responses of each sample were analyzed using the equivalent circuit model depicted in Figure 6b. The parameter values derived from these models are provided in Tables S1–S3. Notably, the 5BTA sample consistently exhibited the highest R_o and R_i values throughout the immersion period. While the R_i values for the 0BTA and 3BTA samples sharply decreased with increasing immersion time, those for the 5BTA sample remained largely unchanged, suggesting that significant protection against erosion for the inner layer of the Al alloy was achieved by the PEO coating containing 5BTA in the electrolyte.

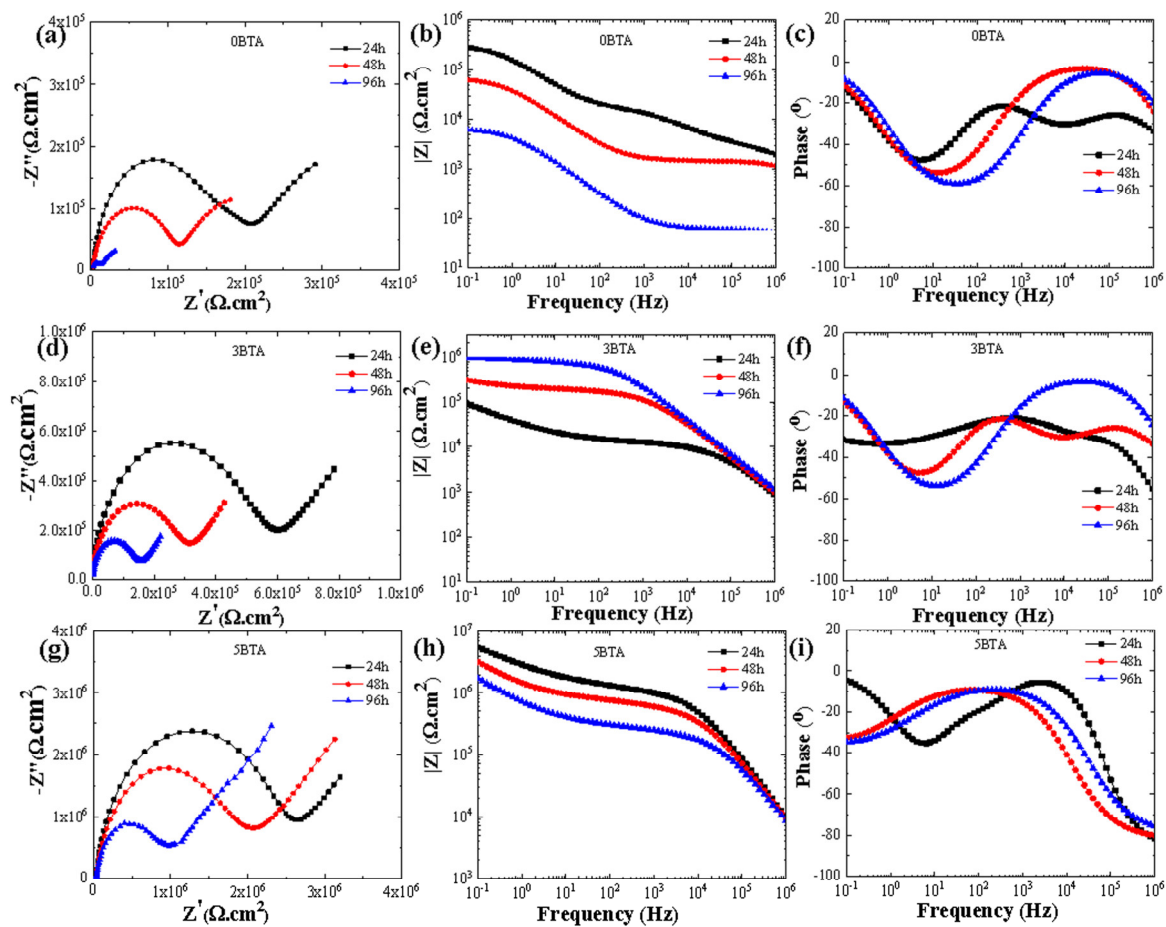
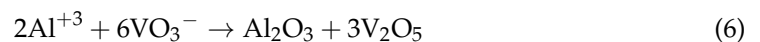


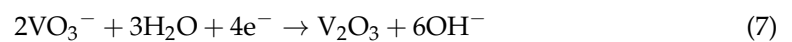
Figure 8. Nyquist and bode plots obtained for the 0BTA, 3BTA, and 5BTA samples at different immersion times, where (a–c) 0BTA, (d–f) 3BTA, and (g–i) 5BTA.

3.6. Incorporation Mechanism of the Particles

Figure 9 depicts a schematic illustration detailing the mechanism underlying the role of BTA in the PEO process. The NH_4VO_3 salt initially dissociates into NH_4^+ and VO_3^- ions initially (Equation (5)). As the electrolyte infiltrates the pores and cools down, it reacts with the molten flux to generate V_2O_5 , as illustrated by Equation (6):



However, when BTA is introduced into the electrolyte solution, its role as an electron donor significantly alters the mechanism. BTA facilitated the reduction in VO_3^- species present in the electrolyte solution. This reduction process involves the transfer of electrons from BTA to the VO_3^- species, leading to the conversion from a higher oxidation state (V^{5+}) to lower oxidation states, such as V^{3+} in the form of V_2O_3 (Equation (7)). On the other hand, it is worth mentioning that the addition of BTA to the strongly alkaline electrolyte alters the behavior of vanadium species present in the electrolyte. BTA acts as a complexing agent and electron donor, affecting the speciation and reactivity of vanadium ions. Specifically, BTA can form complexes with vanadium ions, such as VO_4^{3-} and HVO_4^{2-} , and facilitate reduction reactions, leading to changes in the oxidation states of vanadium species during the PEO process.



Since the XPS results did not show V_2O_3 , it is suggested that all V_2O_3 subsequently reacts with oxygen in the electrolyte environment to yield V_2O_5 (Equation (8)).

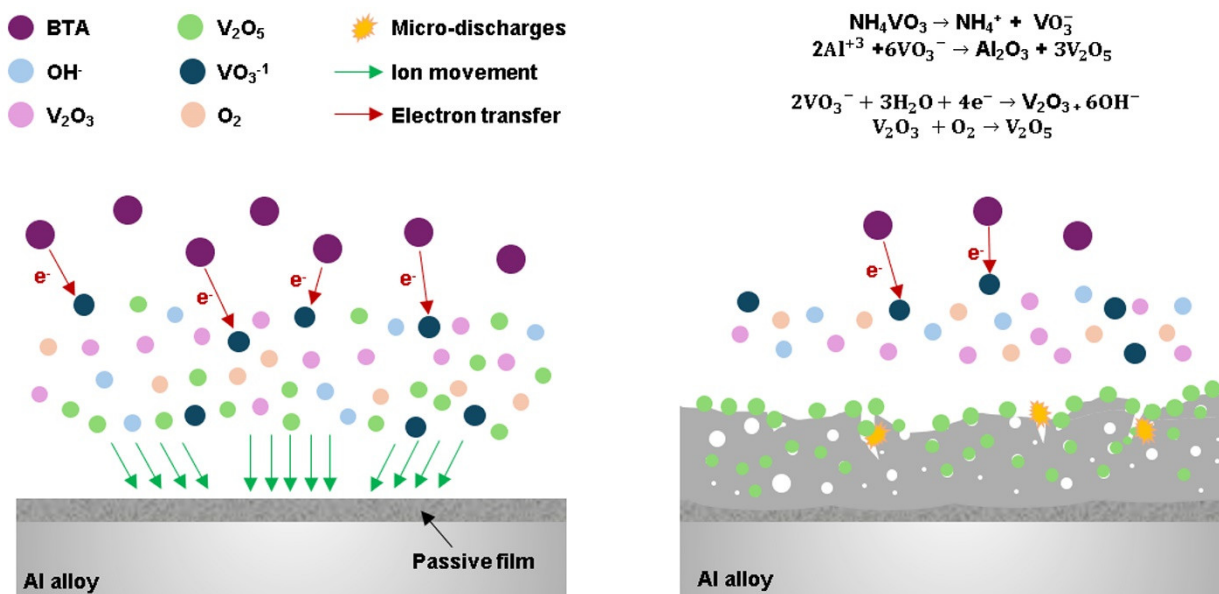


Figure 9. The mechanism underlying the role of BTA in facilitating the incorporation of V_2O_5 into the alumina layer.

This leads to the enhanced incorporation of V_2O_5 into the coating. The increased availability of reduced VO_3^- species facilitated by BTA caused the formation of a denser hybrid film. Comparing the effects of using 3 g/L versus 5 g/L of BTA, distinct outcomes were observed. While both concentrations contributed to improved protective properties compared to the case without BTA, the experiment using 5 g/L of BTA notably outperformed its 3 g/L counterpart. The higher concentration of BTA accelerated reduction reactions, resulting in increased V_2O_5 incorporation and the formation of a denser oxide layer. Therefore, two factors likely contribute to the enhanced chemical stability observed in the 5BTA sample. Firstly, its less porous structure could substantially limit the movement of corrosive anions towards the substrate, thereby improving the corrosion protection properties of the Al alloy. This denser layer offers superior corrosion protection compared to the 3BTA sample. Secondly, the incorporation of stable oxides, such as V_2O_5 , could effectively inhibit the penetration of corrosive anions into the Al alloy substrate. Thus, the choice of BTA concentration significantly impacts the efficiency of the PEO method in enhancing the stability of aluminum alloy coatings in NaCl solution.

4. Conclusions

In this study, our focus centered on the successful integration of V_2O_5 into the Al_2O_3 film made on an Al alloy, achieved through a one-step PEO process, where BTA molecules played a substantial role as the electron donor. The breakdown phenomenon inherent to the PEO surface modification process facilitated the electrochemical reduction in NH_4VO_3 , leading to the incorporation of a substantial amount of V_2O_5 into the Al_2O_3 layer, a phenomenon catalyzed by the presence of BTA. The electron-donating capabilities of BTA were instrumental in enhancing the reduction in VO_3^- species, resulting in the more efficient integration of V_2O_5 into the coating. Notably, the 5BTA sample exhibited a reduction in porosity and surface roughness compared to its counterpart samples, namely 0BTA and 3BTA. This improvement in structural characteristics can be attributed to the role of BTA in

promoting the more controlled and effective incorporation of V_2O_5 . Consequently, electrochemical measurements affirmed that the hybrid film made in the presence of 5 g/L BTA demonstrated superior anticorrosive properties. This superiority was primarily attributed to the sealing effect of V_2O_5 particles, whose activation tendency was found to be higher at increased concentrations of BTA. Thus, the observed structural and corrosion resistance improvements underscore the synergistic influence of BTA in optimizing the incorporation mechanism of V_2O_5 , enhancing the performance of the Al alloy coating.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met14060606/s1>, Table S1: Outcomes of the EIS examinations on the 0BTA specimen submerged in a 3.5 wt.% NaCl electrolyte for different immersion time. Table S2: Outcomes of the EIS examinations on the 3BTA specimen submerged in a 3.5 wt.% NaCl electrolyte for different immersion time. Table S3: Outcomes of the EIS examinations on the 5BTA specimen submerged in a 3.5 wt.% NaCl electrolyte for different immersion time.

Author Contributions: Conceptualization, M.K.; Methodology, M.K.; Investigation, M.K.; Writing—original draft, M.K., A.F.-a. and B.D.; Writing—review & editing, M.K., A.F.-a. and B.D.; Funding acquisition, M.K. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Research Foundation of Korea (NRF), funded by the Korean government (MSIT; No. 2022R1A2C1006743).

Data Availability Statement: The raw/processed data required to reproduce these findings are not readily available because the data are part of an ongoing study. Requests to access the datasets should be directed to the corresponding authors.

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

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