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## Short Communication

# Enhanced the Electrochemical Stability of Al-Zn-Mg Alloy Through the Dual Incorporation of ZrO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> into the Alumina Layer

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## Abstract

This study explores the impact of direct and indirect incorporation of metallic oxide particles namely ZrO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> on the corrosion behavior of the alumina layer obtained by the plasma electrolytic oxidation of Al-Zn-Mg alloy. To achieve this goal, plasma electrolytic oxidation coating was formed in an alkaline-aluminate-ZrO<sub>2</sub> electrolyte, without and with NH<sub>4</sub>VO<sub>3</sub>. The morphological analysis reveals a porous structure influenced by gas bubble discharge and rapid cooling, featuring micropores, oxide nodules, and cracks. The incorporation of V<sub>2</sub>O<sub>5</sub> particles is observed to decrease surface roughness and enhance the compactness of the oxide layer. The X-ray diffraction patterns reveal the presence of γ-Al<sub>2</sub>O<sub>3</sub>, α-Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and V<sub>2</sub>O<sub>5</sub> particles exclusively in the sample coated in the electrolyte with NH<sub>4</sub>VO<sub>3</sub>. Potentiodynamic polarization and impedancetests in a 3.5 wt.% NaCl solution revealed enhanced corrosion resistance, attributed to reduced micro-defects through V<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> incorporation.

**Keywords:** Al alloy, plasma electrolytic oxidation, V<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub>, corrosion

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## 1 INTRODUCTION

Aluminum and its alloys are well-recognized for their excellent structural properties in various industries, including aircraft, architecture, transportation, and manufacturing, thanks to features such as low density and high mechanical strength. Despite these advantages, the limited surface hardness and corrosion resistance of Al alloys have restricted their extensive application<sup>[1]</sup>. The advent of plasma electrolytic oxidation (PEO) has become a notable surface engineering technology, generating significant interest. PEO oxide coatings exhibit remarkable corrosion protection properties<sup>[2-7]</sup>. The properties of

oxide films produced through PEO are significantly impacted by factors such as the chemical composition of the electrolyte and electrical parameters, including current density, frequency, and current mode<sup>[8-12]</sup>. Recent research has underscored the potential for substantial improvement in corrosion resistance, particularly in demanding environments where micro-arc-induced pores are only partially filled. This enhancement is achieved through the incorporation of stable metal oxides like V<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, CeO<sub>2</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> as secondary particles into the oxide layer. For instance, Arunnellaiappan et al.<sup>[13]</sup> demonstrated a noteworthy enhancement in the corrosion resistance of Al-Zn-Mg alloy through the

introduction of  $\text{CeO}_2$ , as evidenced by potentiodynamic polarization experiments. Bahramian et al.<sup>[14]</sup> found that the inclusion of  $\text{TiO}_2$  particles in the oxide coating, formed in an alkaline-silicate solution, elevated the corrosion resistance of an Al-Zn-Mg alloy. In a separate study, Xiang et al.<sup>[15]</sup> observed that the addition of potassium fluorozirconate salts to an alkaline electrolyte facilitated the integration of  $\text{ZrO}_2$  into oxide layers, thereby improving the corrosion characteristics of the 6063 Al alloy. Fatimah et al.<sup>[16]</sup> successfully incorporated  $\text{SiO}_2$  and  $\text{ZrO}_2$  particles into the PEO coating formed on 6061Al alloy. They reported that electrophoresis is the primary mechanism influencing the incorporation of these particles into the coating layer.

Additionally,  $\text{V}_2\text{O}_5$  particles were incorporated into the electrolyte during the PEO processing of Al alloys to induce dark hues and enhance the electrochemical stability of the resulting coatings<sup>[17-19]</sup>. For example, Kwon et al.<sup>[17]</sup> demonstrated enhanced electrochemical stability and reduced porosity in 6061 Al alloy by incorporating  $\text{V}_2\text{O}_5$  particles into the coating. These particles, known for their electrochemical inertness, created a more effective barrier against corrosive chlorine ions, thereby inhibiting corrosion. Similarly, Kaseem et al.<sup>[19]</sup> improved the compactness and electrochemical stability of Al alloy by introducing  $\text{V}_2\text{O}_5$  nanoparticles into the coating, utilizing an alkaline-phosphate electrolyte. While past studies primarily focused on the incorporation of single particles, our study aims to integrate both  $\text{V}_2\text{O}_5$  and  $\text{ZrO}_2$  particles into the  $\text{Al}_2\text{O}_3$  oxide film formed on Al-Zn-Mg alloy through PEO. This will be achieved using an electrolyte containing  $\text{NH}_4\text{VO}_3$  metallic salt and  $\text{ZrO}_2$  powder. To the best of our knowledge, this is the first instance of incorporating  $\text{ZrO}_2$  and  $\text{V}_2\text{O}_5$  particles into the alumina layer produced via PEO treatment of Al-Zn-Mg alloy. In this study, we successfully fabricated  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$ - $\text{V}_2\text{O}_5$  oxide layers on Al-Zn-Mg alloy using the PEO process with an alkaline-aluminate electrolyte containing  $\text{ZrO}_2$  and  $\text{NH}_4\text{VO}_3$ . The characteristics of the resulting oxide layers were analyzed in terms of structure, composition, and corrosion behavior.

## 2 MATERIALS AND METHODS

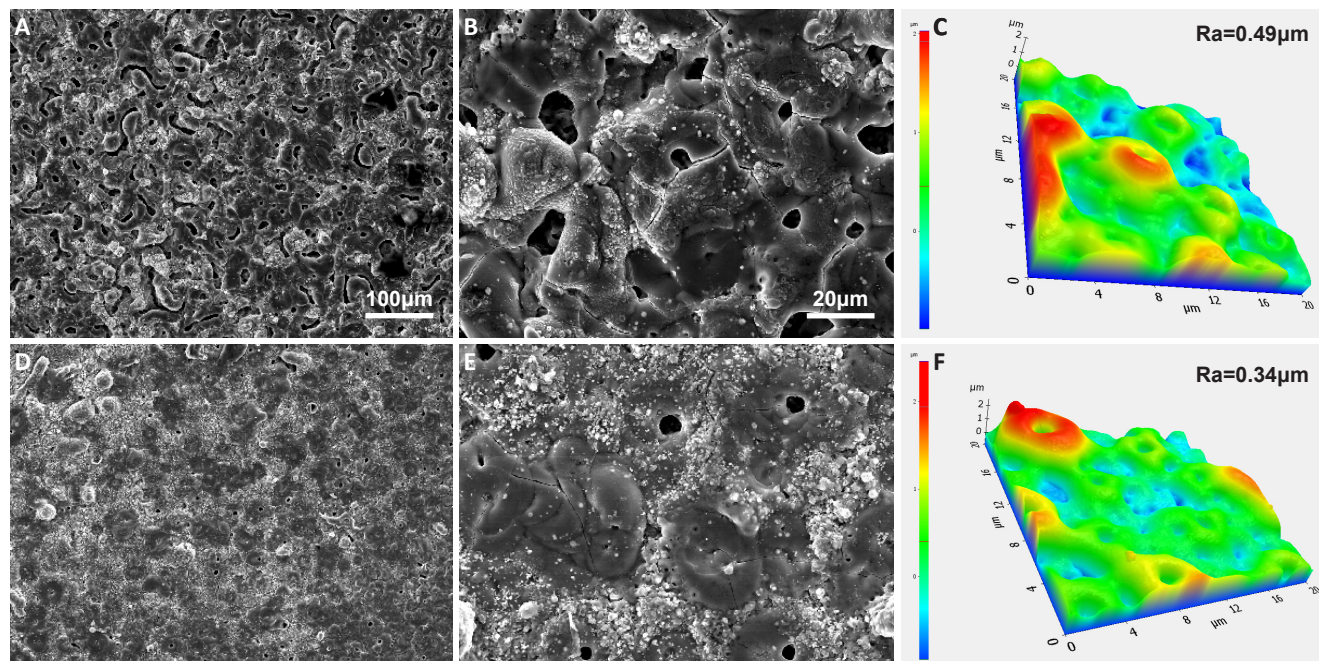
The material under investigation in this study is an Al-Zn-Mg alloy (7075 alloy) with the following chemical composition: 5.1% Zn, 2.2% Mg, 1.2% Cu, 0.3% Fe, 0.2% Si, 0.2% Cr, 0.2% Mn, with the remaining balance being Al in weight percent. Before the PEO treatment, the specimens underwent grinding and polishing using abrasive paper, followed by degreasing with pure acetone. Two electrolytes, designated as Bath A (6g/L KOH + 4g/L  $\text{NaAlO}_2$  + 2gr of  $\text{ZrO}_2$  nanoparticles) and Bath B (6g/L KOH + 4g/L  $\text{NaAlO}_2$  + 2g/L  $\text{ZrO}_2$  + 3gr  $\text{NH}_4\text{VO}_3$ ), were employed in the PEO process. The concentration of  $\text{ZrO}_2$  nanoparticles was adjusted to 3g to prevent particle agglomeration, a phenomenon

that may occur at higher concentrations. The PEO procedures were conducted for 180 seconds at a frequency of 60Hz and a current density of 100mA/ $\text{cm}^2$  under alternating current conditions. Throughout the PEO process, the temperature of the electrolytes was maintained at 288 K. Surface and cross-sectional morphologies of the oxide layer were analyzed using a Scanning Electron Microscope (SEM-HITACHI, S-4800) equipped with an energy-dispersive spectrometer (EDS). Additionally, atomic force microscopy (AFM-3D surface profiler, Contour GT-K 3D) was employed in ambient air to measure mean surface roughness (Ra) using a 10 nm radius silicon tip in contact mode. The thickness of the oxide layer was measured using an eddy-current tester (Minitest 2100, Electrophysik, Germany), with a minimum of 10 measurements conducted on each side of the sample. X-ray diffraction (XRD) was conducted using a RIGAKU D-MAX 2500 instrument with a step size of  $0.05^\circ$  and a scan range of 30 to  $90^\circ$  to identify the component phases. The chemical compositions of the PEO-coated oxides were analyzed using X-ray photoelectron spectroscopy (XPS, VG Microtech, ESCA2000). The corrosion resistance of the oxide films was assessed through potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) in a 3.5% NaCl solution, with the sample serving as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum plate as the counter electrode. The potentiodynamic polarization tests were conducted within a range from -0.25 to -0.4V vs. open circuit potential (OCP) at a scan rate of 1mV/s, with the samples immersed in the corrosive solution for 1h to achieve OCP stabilization. EIS measurements were conducted over a frequency range from  $10^6\text{Hz}$  to 0.1Hz, with data sampled at intervals of 10 points per decade, using a 10mV rms amplitude. To ensure data accuracy, these tests were repeated three to four times.

## 3 RESULTS AND DISCUSSION

### 3.1 Morphology of the Coating

The surface properties of the oxide coating formed on the Al-Zn-Mg alloy after 180 seconds in Baths A and B are depicted in [Figure 1](#). Both oxide films exhibit distinctive porous architectures characterized by micro-pores and oxide nodules resulting from gas bubble discharge through discharge channels during intense arcing. Surface cracks appear in both samples because of the rapid cooling of oxide clusters upon contact with the electrolyte held at 288K<sup>[20]</sup>. As shown in [Figure 1A](#) and [1B](#), the sample from Bath A exhibits more noticeable cracks compared to the sample from Bath B. In contrast, it is evident from [Figure 1D](#) and [1E](#) that the oxide layer produced in Bath B exhibits lower porosity and smaller pore size compared to its counterparts in Bath A. The varied surface morphologies of the oxide coatings in Baths A



**Figure 1. SEM images showing surface morphologies (lower and higher magnification) and the corresponding AFM results of the oxide layers formed on Al-Zn-Mg alloy via PEO in (A-C) Bath A and (D-F) Bath B.**

and B would be ascribed to differences in electrolyte content and other electrochemical reactions during the PEO process, leading to the incorporation of V-based compounds in the majority of micropores and cracks. The AFM results in Figure 1C and 1F show that the surface roughness values of the PEO coatings obtained in Baths A and B were  $\sim 0.49\mu\text{m}$  and  $\sim 0.34\mu\text{m}$ , respectively. This suggests that the oxide layer's surface roughness in Bath B was somewhat lower than that in Bath A. The observed variation in surface roughness between the coatings obtained in Baths A and B is attributed to the incorporation of  $\text{V}_2\text{O}_5$  nanoparticles, as will be elucidated later. The formation of micropores during the PEO process, attributed to the implosion of gas bubbles, plays a crucial role in determining surface roughness and is closely associated with electrical transport behavior<sup>[21,22]</sup>. Upon incorporating  $\text{V}_2\text{O}_5$  into the oxide layer, there is a notable decrease in the electric resistivity compared to the case of the oxide layer in Bath A<sup>[23]</sup>. This reduction in resistivity signifies improved electrical conductivity, leading to the effective consumption of high energy generated from plasma discharges in the development of a surface with lower roughness. The intricate interplay between gas bubble dynamics, electrical properties, and surface morphology underscores the influence of  $\text{V}_2\text{O}_5$  incorporation on the characteristics of the oxide coatings obtained in Bath B. Examination of the EDS data provided in Table 1 highlights discernible differences in the compositions of oxide films obtained from Baths A and B. Although the oxide film obtained from Bath B contains elements such as Al, O, and Zr, it has a distinct composition compared to that observed in Bath A. In addition, the presence of V elements

in Bath B can also be attributed to the incorporation of V compounds because of the addition of  $\text{NH}_4\text{VO}_3$  additive in the electrolyte. On the other hand, the average thickness was calculated to be  $7.54\pm 0.1\mu\text{m}$  and  $7.33\pm 0.2\mu\text{m}$ , for the samples made in Bath A and Bath B, respectively. This suggests that the impact of  $\text{V}_2\text{O}_5$  on the thickness of oxide layers was negligible. This observation can be attributed to the consistent application of a constant current density of  $100\text{mA}/\text{cm}^2$  across both samples for a duration of 180s<sup>[24]</sup>.

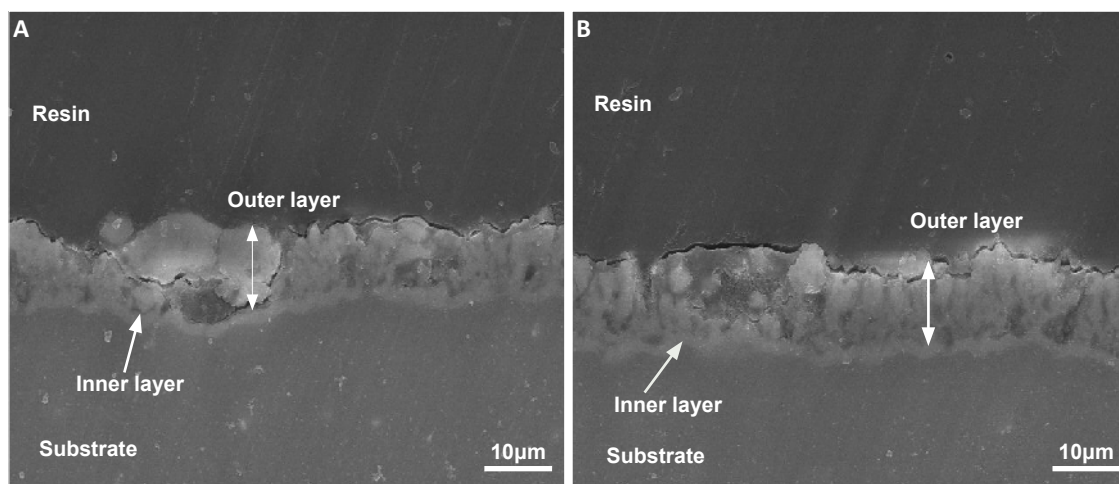
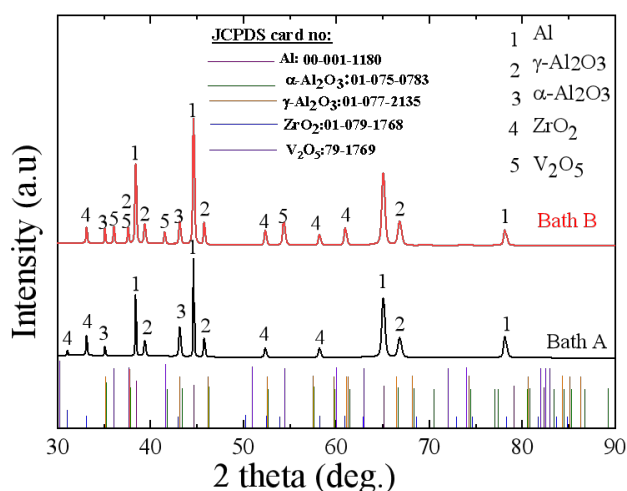
Figure 2 presents the cross-sectional images of the oxide films formed in Baths A and B. Both coatings were composed of an outer porous layer and an inner layer (as marked by arrows), and the thickness of the coating layers was approximately identical ( $\sim 7.4\pm 0.3\mu\text{m}$ ) which was nearly identical to the results calculated by the eddy-current tester. In addition, the sample coated in Bath A exhibited a rough surface with relatively coarse pores and some cracks, as shown in Figure 2A. In contrast, Figure 2B indicated that the sample coated in Bath B had a relatively uniform compact microstructure with fewer micropores, which was consistent with the surface images in Figure 1.

### 3.2 Composition of the Coating and the Mechanism of Incorporation

Figure 3 depicts the XRD patterns of oxide films formed on an Al-Zn-Mg alloy in Baths A and B. The oxide film produced in Bath A predominantly comprises  $\gamma\text{-Al}_2\text{O}_3$  (JCPDS card no: 01-077-2135),  $\alpha\text{-Al}_2\text{O}_3$  (JCPDS card no: 01-075-0783), Al (JCPDS card no: 00-001-1180) phases, and  $\text{ZrO}_2$  (JCPDS card no: 01-079-1768).

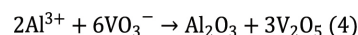
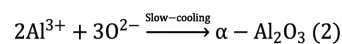
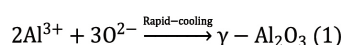
**Table 1. Composition of the oxide layers formed on Al-Zn-Mg alloy via PEO in Baths A and B detected through EDS**

Sample	Al (wt.%)	O (wt.%)	Zr (wt.%)	V (wt.%)
Bath A	43.36±3.42	48.15±4.67	8.49±7.75	-
Bath B	38.21±2.75	49.37±4.89	5.97± 0.61	6.45± 0.63

**Figure 2. SEM images showing the cross-sectional images the oxide layers formed on Al-Zn-Mg alloy via PEO in (A) Bath A and (B) Bath B.****Figure 3. XRD results of the oxide layers formed on Al-Zn-Mg alloy via PEO in Baths A and B.**

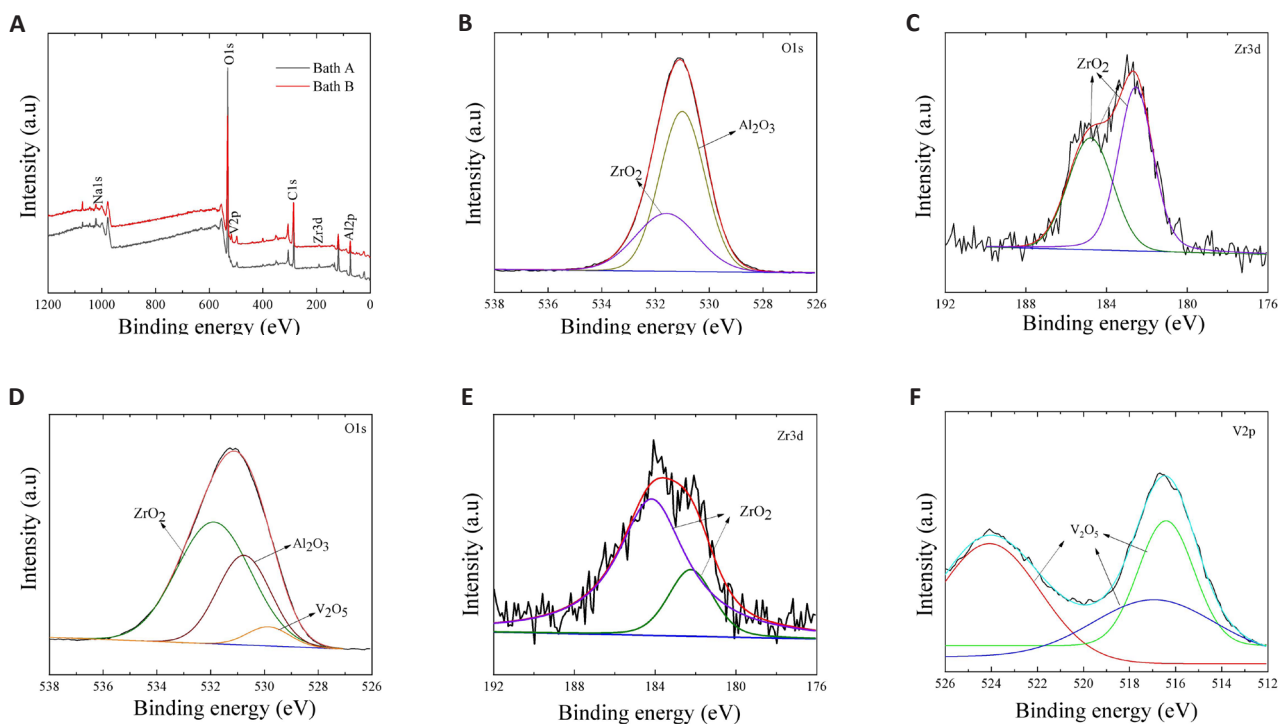
According to Equation 1 and Equation 2,  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\gamma$ - $\text{Al}_2\text{O}_3$  are formed through the counter migration of  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  within the oxide layer, depending on the cooling rates.

The presence of tetragonal-structured  $\text{ZrO}_2$  in the XRD patterns indicates the successful incorporation of  $\text{ZrO}_2$  into the oxide films during the PEO process. Through the electrochemical anodic reaction (Equation 4),  $\text{V}_2\text{O}_5$  (JCPDS card no: 79-1769) is formed<sup>[25]</sup>. The electrochemical processes during PEO can be succinctly described as follows:



To investigate the chemical nature, composition, and oxidation states of Al, O, Zr, and V in the samples, XPS measurements were utilized. The full-range XPS spectral analysis of the oxide films produced in Baths A and B is presented in Figure 4A. Both samples exhibit the presence of Al, O, and Zr, with the additional detection of V in the coating obtained from Bath B. Notably, there are no significant differences in the fundamental elements observed between both samples, except for the inclusion of V in the sample obtained from Bath B. The Al, O, and Zr elements are attributed to the oxidation of the Al alloy substrate in an alkaline-aluminate electrolyte solution containing  $\text{ZrO}_2$  nanoparticles.

The individual spectra of O1s and Zr3d in the coating from Bath A, and O1s, Zr3d, and V2p in the coating from Bath B, are displayed in Figure 4B-F. In Figure 4B, the O1s spectrum of the oxide film from Bath A fits well with  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ , corresponding to binding energies of 530.9 and 531.9eV, respectively. Deconvolution of Zr3d (Figure 4C) reveals two peaks at approximately 184.8 and 182.4eV, indicative of Zr-O bonding in  $\text{ZrO}_2$ <sup>[26]</sup>. In contrast, the O1s spectrum of the Bath B coating (Figure 4D) exhibits three peaks at 530.9, 531.9, and 529.6eV, attributed to  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{V}_2\text{O}_5$ , respectively. Similarly, the Zr3d spectrum of the Bath B coating (Figure 4E) shows two peaks at around 184.8 and 182.4eV, indicating  $\text{ZrO}_2$  incorporation. The



**Figure 4. XPS results of the oxide layers formed on Al-Zn-Mg alloy via PEO in Baths A and B.** A: XPS full scan of the oxide layers made from Baths A and B. B and C: High-resolution XPS spectra of O1s (B) and Zr3d (C) spectra on the surface of the sample obtained from Bath A. D-F: O1s (D), Zr3d (E), and V2p (F) spectra on the surface of the sample coated in Bath B.

presence of  $V_2O_5$  in the Bath B coating is confirmed by the V2p peak (Figure 4F), which splits into two peaks at approximately 517 and 525eV, corresponding to V 2p 3/2 and V 2p 1/2, respectively. Fitting analysis reveals three peaks at 517, 517.4, and 524.3eV, characteristic of  $V_2O_5$  [27,28].

Figure 5 illustrates a proposed mechanism for the incorporation of  $ZrO_2$  and  $V_2O_5$  particles, based on the structural morphologies and composition of the oxide layers.  $ZrO_2$  particles dispersed in the electrolyte would exhibit a negative zeta potential [28]. This negative surface charge facilitated the electrophoretic migration of the  $ZrO_2$  particles toward the anode surface during the PEO process. The incorporation of  $ZrO_2$  particles into the oxide layer occurred due to localized melting induced by the high-temperature conditions generated during plasma arcing. Consequently, the assimilation of  $ZrO_2$  can be primarily attributed to the combined effects of electrophoresis and physical mixing (Figure 5A). In Bath B, the incorporation of  $ZrO_2$  followed the same mechanism described in Bath A. In addition, the inclusion of  $NH_4VO_3$  powders in the electrolyte results in the efficient incorporation of  $V_2O_5$  particles, a fact suggested in the XRD diagrams by the separate peaks corresponding to  $V_2O_5$  compounds. In this case, the incorporation of  $V_2O_5$  particles occurs through a series of plasma-assisted electrochemical reactions (Figure 5B).  $VO_3^-$  ions are generated by ionizing  $NH_4VO_3$  metallic salt in the electrolyte (Equation 3), and, propelled by the strong electric field created during PEO, these

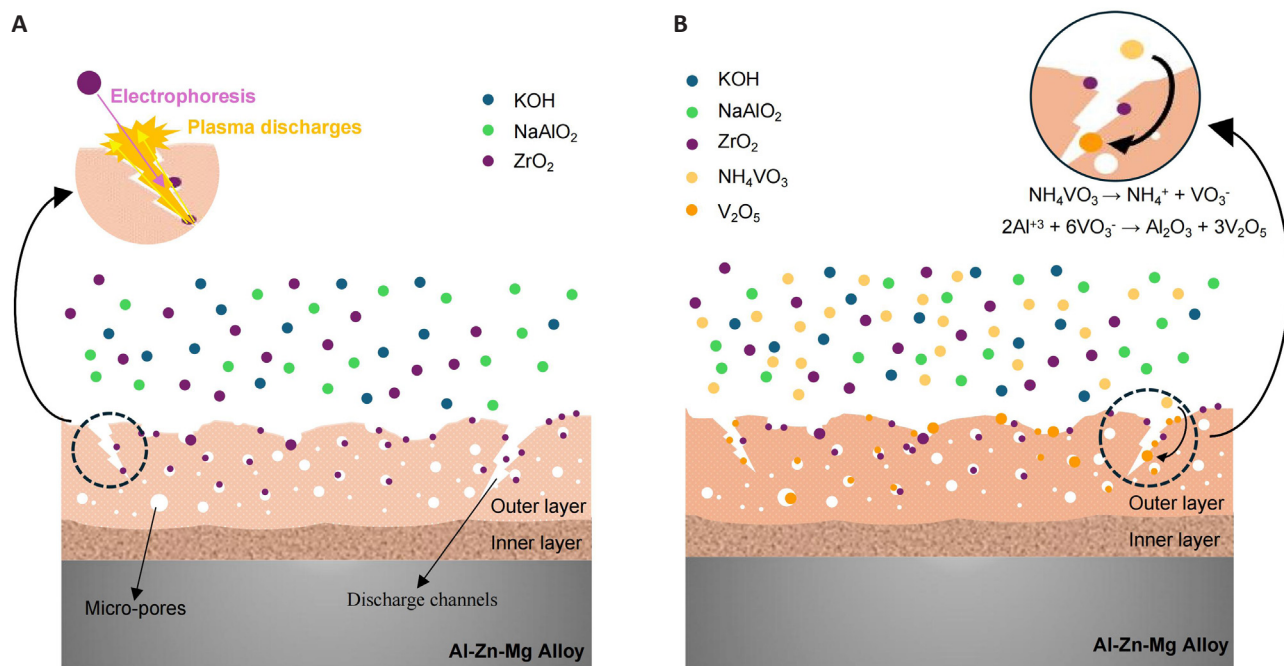
ions migrate towards the anode surface, where they react with  $Al^{3+}$  ions to form  $V_2O_5$  particles according to Equation 4.

### 3.3 Corrosion Behavior of the Coatings

Potentiodynamic polarization curves in a 3.5 wt.% NaCl solution were presented in Figure 6A to assess the corrosion resistance of the substrate and the oxide layers formed in Baths A and B. The corrosion potential ( $E_{corr}$ ) and corrosion current density ( $i_{corr}$ ) were calculated using the Tafel extrapolation method, while polarization resistance values ( $R_p$ ) were determined using the Stern-Geary equation (Equation 5).

$$R_p = \frac{\beta_a \cdot \beta_c}{2.303 i_{corr} (\beta_a + \beta_c)} \quad (5)$$

In this equation,  $\beta_a$  and  $\beta_c$  represent the anodic and cathodic Tafel slopes, respectively [29]. Table 2 summarizes the results obtained from these investigations. Irrespective of the coating type, both samples treated in Baths A and B demonstrated superior corrosion resistance compared to the untreated substrate. The bare substrate exhibited the most negative  $E_{corr}$ , the largest  $i_{corr}$ , and the lowest  $R_p$ , indicating significantly poorer corrosion resistance in comparison to the coated samples. However, compared with samples exposed in Bath A, the  $E_{corr}$  of the oxide layer developed in Bath B showed a substantial shift to a more positive zone (-0.642 V vs. Ag/AgCl). Furthermore, the  $i_{corr}$  for the oxide layers in Bath B was two orders of magnitude lower than that in Bath A,



**Figure 5. Schematic illustration for the incorporation mechanism of  $ZrO_2$  and  $V_2O_5$  particles into  $Al_2O_3$  layer where (A) Bath A and (B) Bath B.**

indicating that the sample coated in Bath B had a much-reduced corrosion rate. This difference shows that the sample in Bath B has improved corrosion resistance, reflected by a higher value of  $R_p$ , which may be related to the alteration of the surface structure of the oxide coating caused by the incorporation of  $V_2O_5$ .

For comparison, the  $i_{corr}$  values of different oxide films formed on Al alloys via PEO were collectively plotted, considering the types of secondary particles incorporated into the oxide layer, as depicted in Table 3<sup>[13-16,30,31]</sup>. In Table 3, it is evident that, regardless of variations in electrolyte and electrical parameters, the oxide layer formed in Bath B, following the current strategy, consistently demonstrated the lowest  $i_{corr}$  values compared to other investigated cases. This was observed even under shorter coating times and conditions of medium current density during the coating formation. This leads to the conclusion that the incorporation of  $ZrO_2$  and  $V_2O_5$  particles into the oxide layer represents an effective method for enhancing the corrosion resistance of Al alloy via PEO.

EIS assessments were also performed in a 3.5 wt.% NaCl solution after a 1h immersion, aiming to elucidate the role of  $V_2O_5$  within the coating obtained from Bath B. The impedance spectra, featured in both Nyquist and Bode configurations, are presented in Figure 6B and 6C for detailed examination. In Figure 6B (Nyquist plot), a semi-circular feature was evident, notably more pronounced in the oxide layer derived from Bath B compared to those from Bath A. Additionally, the Nyquist plots displayed linear behavior with a 45° inclination at low-frequency regions, indicating

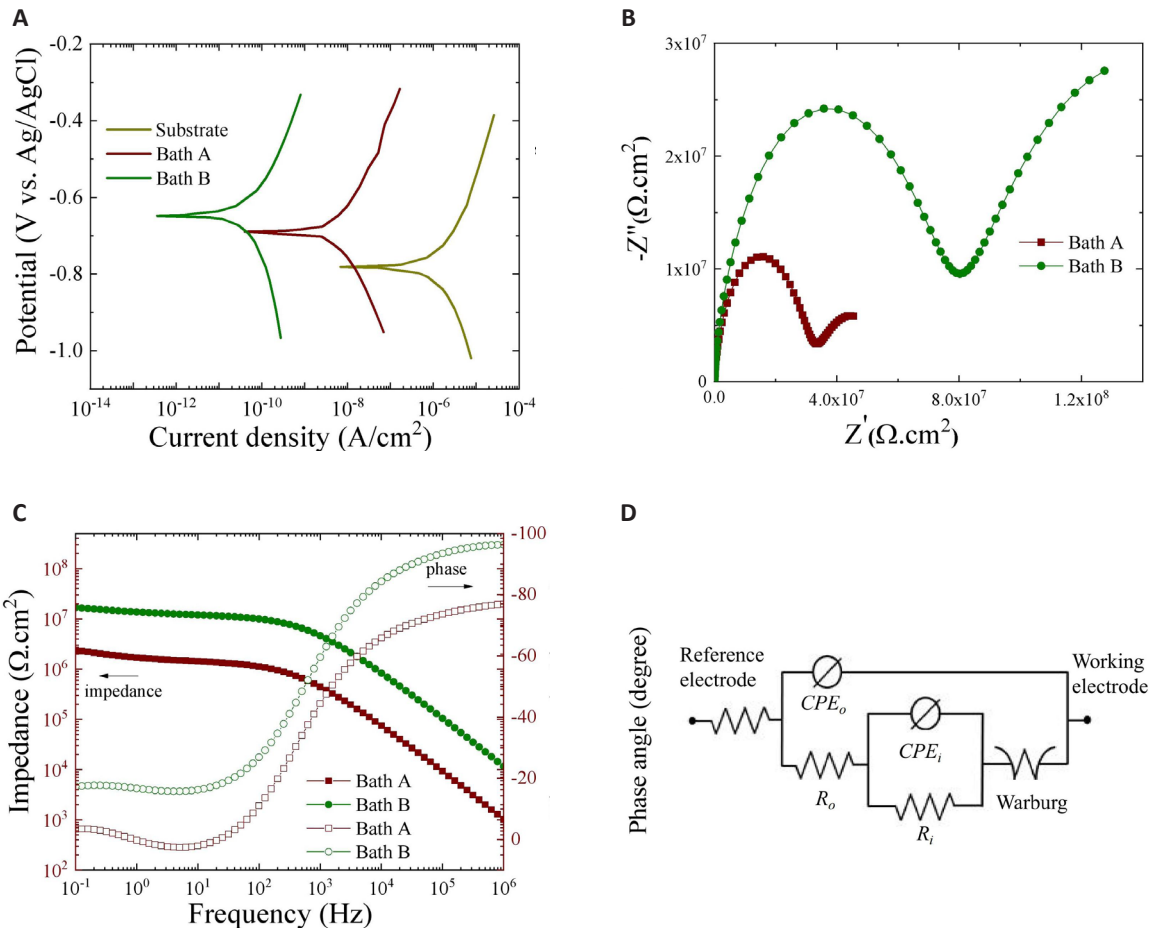
potential ion diffusion and corrosion product migration within the coating-substrate interface during the corrosion test<sup>[32,33]</sup>. Moreover, the impedance modulus  $|Z|$  at the low frequency region (0.1 Hz) serves as an indicator of the overall resistance of the oxide layers<sup>[34]</sup>. In Figure 6C, the oxide layer produced in Bath B demonstrated a higher  $|Z|$  compared to its Bath A counterpart, suggesting enhanced corrosion resistance in the former. This enhancement is primarily attributed to the incorporation of  $V_2O_5$ , which effectively fills structural defects within the PEO coating, consequently obstructing micro-pores and amplifying the impedance response of the oxide layer.

The EIS data was interpreted through the utilization of equivalent circuits as illustrated in Figure 6D, with the respective values of circuit elements outlined in Table 4. Within the proposed circuit models,  $R_s$ ,  $R_o$ , and  $R_i$  delineate the resistances of the corrosive solution, outer, and inner layers, while  $CPE_o$  and  $CPE_i$  signify the constant phase elements corresponding to the outer and inner layers, respectively. Additionally, a Warburg element ( $W$ ) was incorporated in series with  $R_i$  to simulate the mass-transport diffusion of  $Cl^-$  ions through the oxide layers.

As evident from Table 4, the values of  $R_o$  and  $R_i$  for the oxide layer produced in Bath B surpassed those of Bath A. This suggests that the corrosion resistance of the oxide layers improved with the integration of  $V_2O_5$  into the coating. Additionally, irrespective of the electrolyte concentration,  $R_i$  exceeded  $R_o$ , likely owing to the denser structure of the inner layer, with Bath B exhibiting higher  $R_i$  values compared to those from

**Table 2. Results of Potentiodynamic Polarization Tests of the Bare Substrate and the Oxide Layers Immersed in a 3.5 wt.% NaCl Solution for 1h**

Sample	$E_{corr}$ (V)	$i_{corr}$ (A/cm <sup>2</sup> )	$\beta_a$ (V/decade)	$\beta_c$ (V/decade)	$R_p$ ( $\Omega$ cm <sup>2</sup> )
Substrate	-0.780	$5.92 \times 10^{-7}$	0.155	-0.151	$5.61 \times 10^4$
Bath A	-0.694	$3.10 \times 10^{-9}$	0.153	-0.160	$1.10 \times 10^7$
Bath B	-0.642	$2.95 \times 10^{-11}$	0.169	-0.149	$1.17 \times 10^9$

**Figure 6. Corrosion results of the substrate, and the oxide layers formed via PEO in Baths A and B.** A-C: (A) Potentiodynamic polarization curves of the bare substrate and the oxide layers formed on Al-Zn-Mg alloy via PEO in Baths A and B (B and C) Nyquist and Bode plots of the oxide layers formed on Al-Zn-Mg alloy via PEO in Baths A and B where (B) Nyquist plots and (C) Bode plots. D: The equivalent circuit model used for fitting EIS results.

Bath A. This behavior is likely due to the advantageous effects of ZrO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> incorporation, which contribute to blocking micro-pores. Additionally, these particles exhibit strong chemical stability in neutral electrolytes like 3.5 wt.% NaCl solution, impeding the transport of corrosive ions toward the substrate during corrosion testing. Previous studies have shown that either ZrO<sub>2</sub><sup>[35,36]</sup> or V<sub>2</sub>O<sub>5</sub><sup>[17,18]</sup> nanoparticles can act as corrosion inhibitors by replacing water molecules at the surface/coating interface. The reduced porosity and smaller size of micro-pores observed in the oxide layer formed in Bath B compared to Bath A can be attributed to the incorporation of V<sub>2</sub>O<sub>5</sub>, leading to improved corrosion resistance. On the other hand, Table 4 revealed also higher values of  $n_o$  and  $n_i$  in Bath B compared to Bath A, suggesting a smoother coating/substrate interface facilitated by V<sub>2</sub>O<sub>5</sub> integration which was in good

agreement with the roughness results shown in Figure 1. Meanwhile, CPE-Y<sub>0</sub> represents the dielectric behavior at the electrolyte/coating interface<sup>[34]</sup>, with the Bath A sample exhibiting a higher CPE-Y<sub>0</sub> value than its Bath B counterpart.

## 4 CONCLUSION

The incorporation of ZrO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> into the oxide layer of an Al-Zn-Mg alloy through PEO has yielded significant insights into the composition and corrosion resistance of the resulting coatings. Both oxide films contained elements Al, O, and Zr, while the V element was detected only in the oxide film obtained from Bath B due to the presence of the NH<sub>4</sub>VO<sub>3</sub> additive. The introduction of V<sub>2</sub>O<sub>5</sub>, facilitated by NH<sub>4</sub>VO<sub>3</sub> metallic salt ionization, and ZrO<sub>2</sub>, integrated through electrophoresis and physical mixing, has played a pivotal role in

**Table 3. Studies Reported by Previous Researchers about the Influence of Inorganic and Organic Additives on the Surface Properties of PEO Coatings Formed on Al Alloys**

Substrate	Type of additive	additive content (g/L)	PEO conditions	$I_{corr}$ (A/cm <sup>2</sup> )	Highlights	Ref.
AA7075	CeO <sub>2</sub>	4	Current density: 150mA/cm <sup>2</sup> Electrolyte: alkaline-silicate electrolyte Coating time: 10min	$1.25 \times 10^{-10}$	Incorporation of CeO <sub>2</sub> nanoparticles increased also the adhesion strength of the coating-substrate system	[13]
AA7075	TiO <sub>2</sub>	4	Current density: 150mA/cm <sup>2</sup> Alkaline-silicate electrolyte Coating time: 60min	$1.5 \times 10^{-7}$	Microhardness increased with rising nanoparticle concentration.	[14]
6063 Al alloy	ZrO <sub>2</sub>	2	Current density: 5,10, 15, 20A/cm <sup>2</sup> Alkaline-silicate electrolyte Coating time: 18min	$6.688 \times 10^{-8}$	The PEO coating at 15A/dm <sup>2</sup> had superior microstructure and thickness, with fewer defects	[15]
6061 Al alloy	SiO <sub>2</sub> /ZrO <sub>2</sub>	2.5 of each SiO <sub>2</sub> and ZrO <sub>2</sub>	Current density: 130mA/cm <sup>2</sup> Alkaline-phosphate electrolyte Coating time: 10min	$8.21 \times 10^{-10}$	Porosity decreased by about 2.62% with either SiO <sub>2</sub> or ZrO <sub>2</sub> nanoparticles and by 7.61% with both.	[16]
7075 Al alloy	CNT	150 mL/L	Current density: 150mA/cm <sup>2</sup> Alkaline-silicate-fluoride electrolyte Coating time: 10min	$8.33 \times 10^{-10}$	Adding CNTs reduced pore size and oxide layer fraction in the electrolyte	[30]
7075 Al alloy	ZrO <sub>2</sub>	2	Current density: 100mA/cm <sup>2</sup> Alkaline-silicate-molybdate electrolyte Coating time: 5min	$6.95 \times 10^{-10}$	MoO <sub>2</sub> particles were added through Na <sub>2</sub> MoO <sub>4</sub> salt decomposition, while ZrO <sub>2</sub> particles were included via electrophoresis and physical mixing with molten Al <sub>2</sub> O <sub>3</sub> oxides.	[31]
Al-Zn-Mg	NH <sub>4</sub> VO <sub>3</sub>	3	Current density: 100mA/cm <sup>2</sup> Alkaline-aluminate-ZrO <sub>2</sub> electrolyte Coating time: 3min	$295 \times 10^{-11}$	Introducing V <sub>2</sub> O <sub>5</sub> via NH <sub>4</sub> VO <sub>3</sub> ionization and ZrO <sub>2</sub> through electrophoresis and physical mixing has helped reduce structural flaws in the oxide layer.	This work

**Table 4. Results of EIS Tests of the Oxide Layers Immersed in a 3.5 wt.% NaCl Solution for 1h**

Sample	$R_s$ (Ωcm <sup>2</sup> )	$R_o$ (Ωcm <sup>2</sup> )	$CPE-n_o$	$CPE-Y_o$ (S.s <sup>n</sup> .cm <sup>-2</sup> )	$R_i$ (Ωcm <sup>2</sup> )	$CPE-n_i$	$CPE-Y_i$ (S.s <sup>n</sup> .cm <sup>-2</sup> )	W (S*S <sup>1/2</sup> )
Bath A	17.54	$6.21 \times 10^5$	0.79	$5.77 \times 10^{-8}$	$5.23 \times 10^6$	0.48	$1.02 \times 10^{-6}$	$7.83 \times 10^{-6}$
Bath B	17.62	$8.24 \times 10^6$	0.81	$4.01 \times 10^{-9}$	$4.11 \times 10^7$	0.45	$3.01 \times 10^{-7}$	$2.00 \times 10^{-6}$

mitigating structural flaws within the oxide layer. Potentiodynamic polarization tests have underscored the superior corrosion resistance of the coating from Bath B, indicating a substantial shift to a more positive  $E_{corr}$  and a remarkably lower  $i_{corr}$  compared to Bath A. This difference highlights the enhanced corrosion protection

afforded by the altered surface structure resulting from the incorporation of V<sub>2</sub>O<sub>5</sub>. The comprehensive study has demonstrated that the dual incorporation of ZrO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> particles into the alumina layer not only influences the composition and morphology of the oxide layer but also significantly enhances the corrosion resistance of



the coated Al-Zn-Mg alloy. These findings hold promise for advancing the development of protective coatings for aluminum alloys, showcasing the potential of particle incorporation to tailor surface properties and improve overall performance.

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## Conflicts of Interest

The authors declare that they have no conflict of interest.

## Author Contribution

Kaseem M contributed to conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, validation, visualization, writing – original draft, writing – review & editing. Fattah-alhosseini A contributed to formal analysis, writing – original draft, writing – review & editing.

## Abbreviation List

AFM, Atomic force microscopy  
EDS, Energy-dispersive spectrometer  
EIS, Electrochemical impedance spectroscopy  
OCP, Open circuit potential  
PEO, Plasma electrolytic oxidation  
XPS, X-ray photoelectron spectroscopy  
XRD, X-ray diffraction

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