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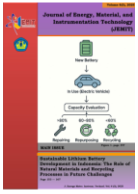

Analysis of Aluminium Alloy 6061 Material Coating with the Addition of Malonic Acid Additive in the Plasma Electrolytic Oxidation Method to Improve Corrosion Resistance Properties

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Abstract

Aluminum alloy 6061 is extensively used in structural and engineering applications due to its favorable strength-to-weight ratio, good mechanical properties, and inherent corrosion resistance. However, it remains vulnerable to localized corrosion, especially in chloride-rich environments. This study investigates the effect of malonic acid (MA) as an organic additive in the Plasma Electrolytic Oxidation (PEO) process to enhance the corrosion resistance of aluminum alloy 6061. The experimental results indicate that the presence of MA reduces plasma initiation time, stabilizes discharge behavior, and facilitates the formation of a denser and more uniform oxide layer. Surface morphology analysis reveals that PEO coatings with MA exhibit finer porosity and a thicker structure, contributing to improved barrier properties. XRD characterization confirms the presence of stable crystalline phases such as mullite and andalusite in the MA-enhanced coatings. Electrochemical testing via Tafel polarization shows a significant reduction in corrosion current density (3.899 × 10^{-7} A/cm²) and corrosion rate (0.642 mm/year), alongside a more positive corrosion potential (−2.616 V) in the MA-treated samples. When compared to traditional corrosion inhibitors, both organic (e.g., imidazole-based compounds) and inorganic (e.g., $CaCO_3$ and SiO_2), the PEO + MA method demonstrates superior long-term corrosion resistance and structural stability. These findings highlight the potential of malonic acid as an effective additive for optimizing the PEO process in demanding environmental conditions.

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Abstrak

Paduan aluminium 6061 banyak digunakan dalam aplikasi struktural dan rekayasa karena rasio kekuatan terhadap beratnya yang tinggi, sifat mekanik yang baik, dan ketahanan korosi yang melekat. Namun, material ini tetap rentan terhadap korosi lokal, terutama di lingkungan yang kaya klorida. Penelitian ini mengkaji pengaruh asam malonat (MA) sebagai aditif organik dalam proses Plasma Electrolytic Oxidation (PEO) untuk meningkatkan ketahanan korosi paduan aluminium 6061. Hasil eksperimen menunjukkan bahwa penambahan MA mempercepat waktu inisiasi plasma, menstabilkan perilaku pelepasan plasma, dan mendorong pembentukan lapisan oksida yang lebih padat dan seragam. Analisis morfologi permukaan menunjukkan bahwa lapisan PEO dengan MA memiliki porositas yang lebih halus dan struktur yang lebih tebal, yang berkontribusi pada peningkatan sifat penghalang. Karakterisasi XRD mengonfirmasi keberadaan fase kristalin stabil seperti mullite dan andalusite pada lapisan yang mengandung MA. Uji elektrokimia menggunakan polarisasi Tafel menunjukkan penurunan signifikan pada densitas arus korosi (3,899 × 10^{-7} A/cm²) dan laju korosi (0,642 mm/tahun), serta pergeseran potensial korosi ke arah yang lebih positif (−2,616 V) pada sampel yang diproses dengan MA. Jika dibandingkan dengan metode inhibitor korosi konvensional, baik organik (misalnya senyawa berbasis imidazol)

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maupun anorganik (seperti $CaCO_3$ dan SiO_2), metode PEO + MA menunjukkan ketahanan korosi jangka panjang dan stabilitas struktural yang lebih unggul. Temuan ini menyoroti potensi asam malonat sebagai aditif efektif untuk mengoptimalkan proses PEO dalam kondisi lingkungan yang ekstrem.

1. Pendahuluan

Aluminum alloys are widely used in various structural and functional components due to their high strength-to-weight ratio, good thermal and mechanical properties, and inherent corrosion resistance (Sieber et al., 2018). Among these, 6061 aluminum alloy is one of the most commonly used, particularly in aerospace, automotive, and marine industries. This is due to its excellent formability, weldability, and high thermal conductivity (Pillai et al., 2018). However, aluminum alloys remain susceptible to localized corrosion, especially when exposed to acidic or chloride-containing environments. Such corrosion can significantly reduce the service life and reliability of the material (Dzhurinskiy et al., 2021).

To enhance corrosion resistance, several surface treatment methods have been developed, including anodizing, chemical conversion coatings, and Plasma Electrolytic Oxidation (PEO). Among these, PEO is considered a promising technique, as it produces a hard, adherent oxide layer on the surface of light metals such as aluminum, magnesium, and titanium (Huang, 2019). The PEO process involves high-voltage micro-discharges that form oxide layers with superior wear and corrosion resistance compared to conventional anodizing (Fernández-López et al., 2024). Despite these advantages, PEO coatings have a major drawback—porosity. The porous structure of the oxide layer allows aggressive ions to penetrate through the coating and cause corrosion at the metal surface (Pillai et al., 2018). Therefore, many studies have focused on reducing porosity and improving the protective properties of PEO coatings. These efforts include optimizing process parameters and adding inorganic or organic additives to the electrolyte solution (Sieber et al., 2018; Casanova et al., 2022).

Recent research has explored the use of organic acids as electrolyte additives in PEO processes to enhance coating performance. Organic compounds such as citric acid, phytic acid, and lactic acid have been shown to regulate plasma discharge behavior and produce more uniform coatings with better corrosion resistance (Casanova et al., 2022). One organic acid that has received increasing attention is malonic acid ($HOOC–CH_2–COOH$). This dicarboxylic acid functions as a chelating agent and has the potential to influence oxide layer formation and structure during the PEO process. Several studies have reported the positive effects of incorporating malonic acid into the electrolyte. Poznyak et al. (2021) demonstrated that malonic acid can interact with aluminum ions during PEO, resulting in a denser oxide layer with lower porosity and improved corrosion resistance. Yin et al. (2019) found that adding malonic acid to a silicate-based electrolyte modified the discharge behavior and led to a smoother, less porous coating surface. Similarly, Lee et al. (2020) reported that malonic acid enhanced coating compactness and reduced current fluctuations during PEO, which are often associated with coating defects.

Although these studies indicate the promising potential of malonic acid, the effect of its concentration on PEO coating characteristics, particularly on 6061 aluminum alloy, is not yet fully understood. Furthermore, few studies have systematically investigated the relationship between malonic acid concentration and coating performance in corrosive environments containing chlorides.

2. Research Methods

2.1 Materials and Equipment

The equipment used in this study includes a grinding machine, abrasive paper, digital caliper, hot air stream, analytical balance, measuring cup, beaker, spatula, stirrer, hot plate magnetic stirrer, graphite, DC power supply, camera, water cooling system, optical microscope, X-ray Diffraction equipment, FESEM-EDS equipment, coating thickness gauge and Amtek Parstat 4000 A. The materials used include aluminum alloy 6061, electrolyte solution (KOH and Na_2SiO_3), malonic acid additive, aquades and corrosive solution (NaCl).

2.2 Sample Preparation

Aluminum Alloy 6061 material is cut with a rectangular dimension of 3 x 4 cm. Next, the sample drilling process is carried out with a hole diameter of 5 mm. Then, the sample grinding process uses abrasive paper with grit #600, #800, #1000 and #2000.

2.3 Solution Preparation

Electrolyte solution is used as an electrochemical medium in this study. The solution was made with and without 1 gr/L of additive. The first solution, dissolving KOH of 6.172 gr/L (0.11 M) and Na_2SiO_3 of 15 gr/L (0.124 M) in 1 liter of Aquades. while the second solution, dissolving KOH of 6.172 gr/L (0.11 M), Na_2SiO_3 of 15 gr/L (0.124 M) and malonic acid additive of 1 gr/L (0.0096 M) in 1 liter of Aquades.

2.4 Experimental Setup

The experimental setup for the Plasma Electrolytic Oxidation (PEO) process consists of a reaction chamber containing an electrolyte solution, with and without additive, where a 6061 aluminum alloy sample serves as the anode. A graphite electrode is used as the cathode, and both electrodes are immersed in the electrolyte. A DC power supply is connected to the system to generate a plasma discharge, which facilitates the oxidation process on the aluminum surface. To ensure temperature uniformity and control, a hot magnetic plate stirrer is used to continuously stir the electrolyte. An air-cooling system is applied to regulate the hot temperature, preventing excessive heat. The electrode spacing is carefully maintained to optimize plasma formation and coating quality. After the oxidation process, the coated sample is rinsed using aquades and dried using a hot air stream.

2.5 Characterization

To understand the characteristics of materials that have undergone specific treatments, various characterization methods are used to analyze crystal structure, surface morphology, elemental composition, and the thickness of protective layers. The following are the characterization techniques that were conducted:

- X-Ray Diffraction (XRD) is used to identify crystal phases and crystal structures in materials, especially after certain treatments such as coating or oxidation. To process XRD data, the HighScore application is used, which aims to process and analyze X-ray diffraction (XRD) data. Its main functions include phase removal, peak adjustment, background subtraction, profile analysis, and quantitative analysis of crystalline materials.
- Field Emission Scanning Electron Microscopy - Energy Dispersive Spectroscopy (FESEM-EDS) allows high-resolution surface morphology analysis and identifies the elemental composition of the material.
- Thickness Measurement is used to measure the thickness of the protective layer to ensure uniformity and effectiveness of protection against corrosion.

2.6 Performance Test

Tafel polarization test, which is used to determine the corrosion rate and electrochemical behavior of a material in an aggressive environment. In this study, a corrosive solution was used as a corrosion test medium. This solution was prepared by dissolving 3.5% NaCl in 1 liter of distilled water. It was designed to have a high corrosion rate to test the corrosion resistance of PEO coating materials. To process the Tafel polarization data, the VersaStudio application is used, which aims to process Tafel polarization test data, allowing for accurate extraction of key corrosion parameters such as corrosion potential (E_{corr}) and corrosion current density (I_{corr}), which are important for evaluating the corrosion resistance of materials.

A detailed flowchart of the experimental procedure is presented in **Figure 1**.

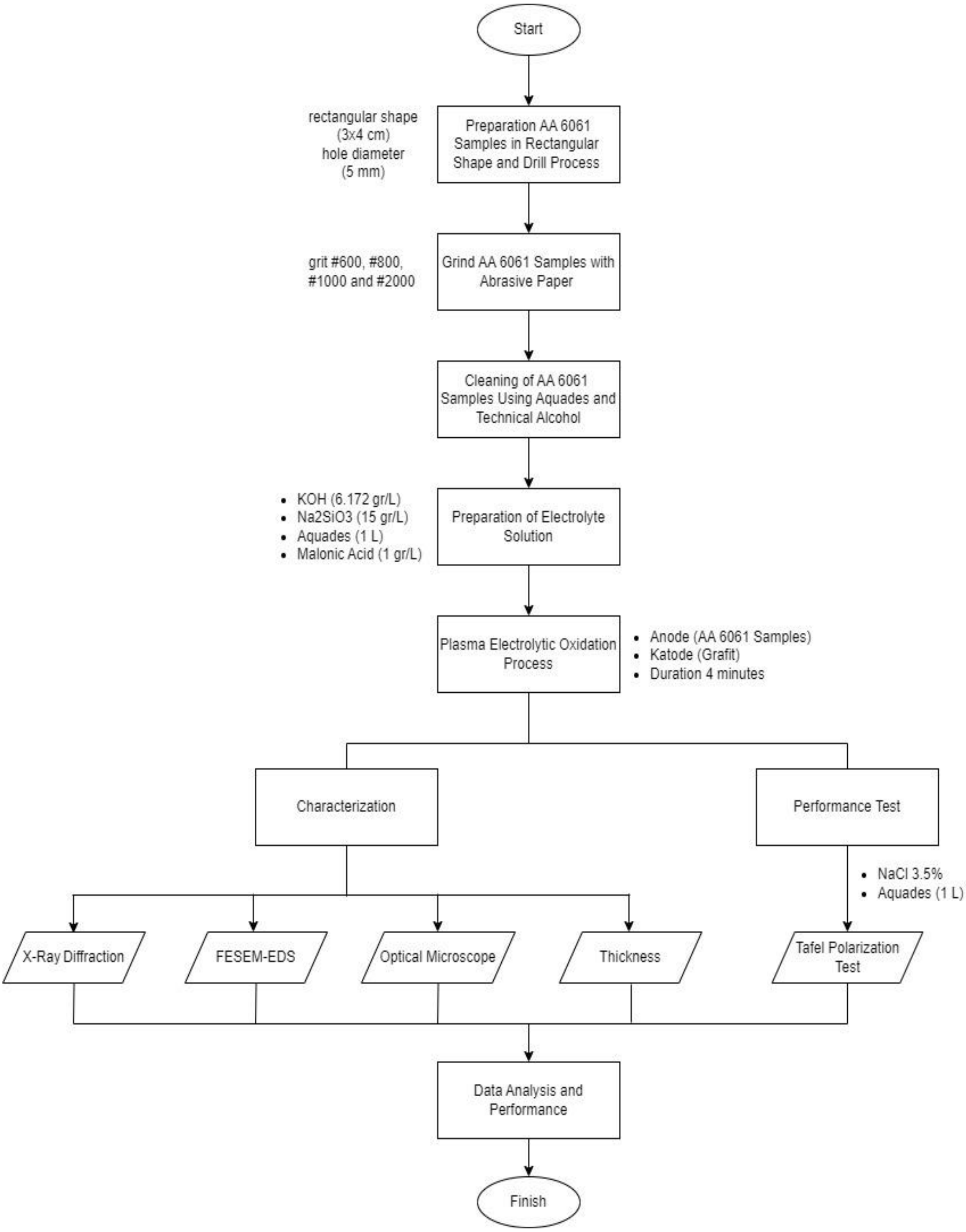
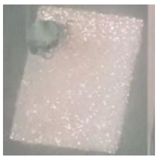
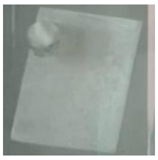
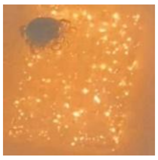
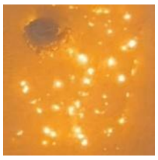


Figure 1. Research flowchart

3. Results and Discussions

The Plasma Electrolytic Oxidation (PEO) process is a high-voltage electrochemical treatment that generates micro-discharge plasma to form a protective oxide layer on metal surfaces. The experimental data obtained for Aluminum 6061 alloy reveals a significant influence of malonic acid (MA) as an electrolyte additive on plasma initiation, stability, and discharge behavior. From **Table 1** the plasma formation time in the PEO without additive sample is delayed, occurring at 2 minutes and 40 seconds, while in the PEO with 1 g/L MA sample, plasma initiates significantly earlier at 1 minute and 15 seconds. This substantial reduction in plasma initiation time suggests that MA lowers the breakdown voltage by enhancing electrolyte conductivity and modifying the dielectric properties of the growing oxide layer. The earlier plasma formation in the MA-containing sample indicates more efficient charge transfer, leading to a quicker onset of the micro-discharge process. This finding aligns with the voltage-time data, where the voltage in the MA sample increases more rapidly compared to the control.

Table 1. Plasma Formation and Spark Intensity During the Plasma Electrolytic Oxidation (PEO) Process with and without Additive

No	Sample	Plasma	Minute 1	Minute 2	Minute 3	Minute 4
1	PEO without additive	 2 m 40 s				
2	PEO with additive	 1 m 15 s				

Further analysis of the plasma emission patterns over time reveals differences in plasma uniformity and intensity between the two samples. In the PEO without additive sample, the initial plasma discharges are weak and sporadic, with a notable increase in intensity after the third minute. This delayed intensification suggests a gradual charge accumulation process due to the lower conductivity of the electrolyte, resulting in irregular and less controlled discharge events. By contrast, in the PEO with MA sample, plasma discharges appear more uniformly distributed from the second minute, indicating that the additive plays a role in regulating discharge behavior. The more stable plasma activity throughout the process suggests a better-controlled oxidation reaction, which is essential for forming a dense and uniform oxide layer.

By the third and fourth minutes, the plasma emissions in the control sample become more intense but also increasingly erratic, potentially leading to localized overheating, excessive melting, and surface roughness. This uncontrolled plasma activity can contribute to the formation of an uneven oxide layer with porous or brittle regions. Conversely, in the MA-containing sample, plasma discharges remain consistently distributed, suggesting that the additive helps maintain a controlled oxidation process, likely resulting in a smoother and more homogeneous oxide coating. The observed differences in plasma behavior reinforce the hypothesis that MA improves the overall efficiency of the PEO process by enhancing electrolyte conductivity and stabilizing plasma emissions. This controlled plasma behavior can lead to higher-quality oxide coatings with improved structural integrity and performance. These findings align with prior research on organic additives in PEO, demonstrating their role in tailoring plasma characteristics and influencing oxide layer formation. The addition of MA, therefore, presents a promising approach for optimizing PEO coatings, particularly in applications requiring enhanced surface properties such as wear resistance and corrosion protection.

The voltage-time data in **Table 2** and **Figure 2** reveal distinct electrochemical behaviors between PEO processes conducted with and without malonic acid (MA). In the PEO without additive sample, the voltage increases gradually, reaching the breakdown voltage at approximately 160 seconds, indicating low electrolyte conductivity and inefficient charge transfer. This slow voltage rise suggests the formation of a less conductive intermediate oxide layer, delaying plasma initiation and leading to weaker, sporadic discharges. These factors contribute to the formation of a porous and less uniform oxide layer, consistent with plasma visualization observations.

In contrast, the PEO with MA sample exhibits a much steeper voltage rise, with breakdown occurring at 75 seconds, less than half the time required in the control sample. This indicates enhanced charge transfer efficiency, improved ionic mobility, and optimized electrolyte dielectric properties due to MA. The earlier plasma onset results in a more controlled and uniform plasma discharge regime, promoting the formation of a denser and more compact oxide layer. Additionally, the stabilized voltage in the MA sample remains higher than in the control sample, suggesting stronger, more evenly distributed discharges that contribute to a more durable coating.

The higher stabilized voltage further implies that the oxide layer formed in the MA sample has superior dielectric properties, which could enhance mechanical strength and corrosion resistance. This finding aligns with previous research showing that organic additives influence oxide growth kinetics, phase composition, and coating performance. Additionally, the shorter breakdown time in the MA sample indicates improved process efficiency, making MA a promising additive for optimizing PEO treatments in similar electrolyte systems. Overall, these results highlight MA's critical role in accelerating plasma initiation, enhancing electrolyte conductivity, and promoting uniform oxide growth. The improved electrochemical behavior in the MA-containing system demonstrates its potential for optimizing PEO coatings, offering superior surface properties for industrial applications.

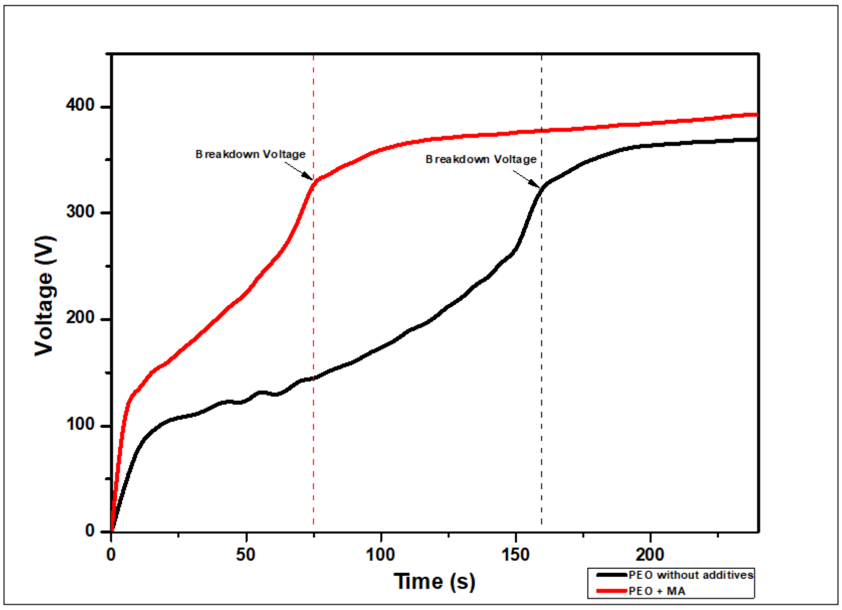


Figure 2. Comparison of Voltage-Time Graphs for PEO Samples with and without Additive MA

Table 2. Comparison of Voltage Changes Over Time for PEO with and without Additive

PEO without Additive		PEO with Additive	
Time (s)	Voltage (V)	Time (s)	Voltage (V)
30	110.65	30	183.38
60	126.91	60	253.82
90	158.45	90	349.31
120	201.80	120	368.82
150	264.66	150	374.24
180	349.31	180	378.57
210	363.40	210	385.07
240	368.82	240	393.75

In **Figure 3**, the surface morphology of the PEO layers with and without the addition of the MA additive is shown under a magnification of x15,000. For the PEO sample without additives, the surface of the layer appears smooth and flat with a few large protrusions, indicating that the oxide layer formed is very thin and not highly porous. However, with the addition of MA, the surface of the layer undergoes significant changes, showing an increase in large protrusions and greater porosity.nFor the PEO without additives, the particle size distribution shows that most particles range from 0.3 to 0.4 μm. The pores formed are relatively larger and fewer in number, indicating that the layer formed is thin and has limited area to interact with corrosive agents. This condition reduces its ability to provide optimal protection against corrosion.

However, with the addition of the MA additive, a shift in the pore size distribution is observed, now more concentrated around sizes of 0.05 to 0.08 μm. The pores formed become more uniform and smaller compared to PEO-M0, although this particle size distribution is larger, indicating that the layer is becoming more porous with a greater surface area. The increase in the number of smaller and more uniform pores enhances the strength of the oxide layer, improving its resistance to the penetration of corrosive agents. A denser and more uniform layer also helps to improve the material's corrosion resistance, as it prevents deeper penetration by corrosive substances that could damage the underlying aluminum substrate. Thus, the addition of MA improves the corrosion resistance of the material by creating an oxide layer that is more resistant to environmental degradation.

The reduction in pore size when using MA additive can be attributed to the adsorption behavior of organic acids on the substrate surface. Organic molecules like mandelic acid, which possess functional groups such as –OH and –COOH, adsorb onto the metal surface during the early stages of the PEO process. This adsorption forms a protective layer that modifies the local electric field and suppresses the formation of intense plasma discharges, leading to a "soft plasma" regime. The soft plasma discharges result in less localized energy release, producing coatings with smaller and more uniformly distributed pores. This behavior has been widely observed in coatings formed with other organic additives, such as glycerol, phytic acid, citric acid, and sodium benzoate. These additives help form an electrochemical double layer (EDL) that absorbs part of the discharge energy and reduces the temperature and intensity of the micro-arcs. Consequently, the growth of large discharge channels is suppressed, resulting in smaller pore formation (0.05–0.08 μm) compared to the wider channels formed without the additive (0.3–0.4 μm).

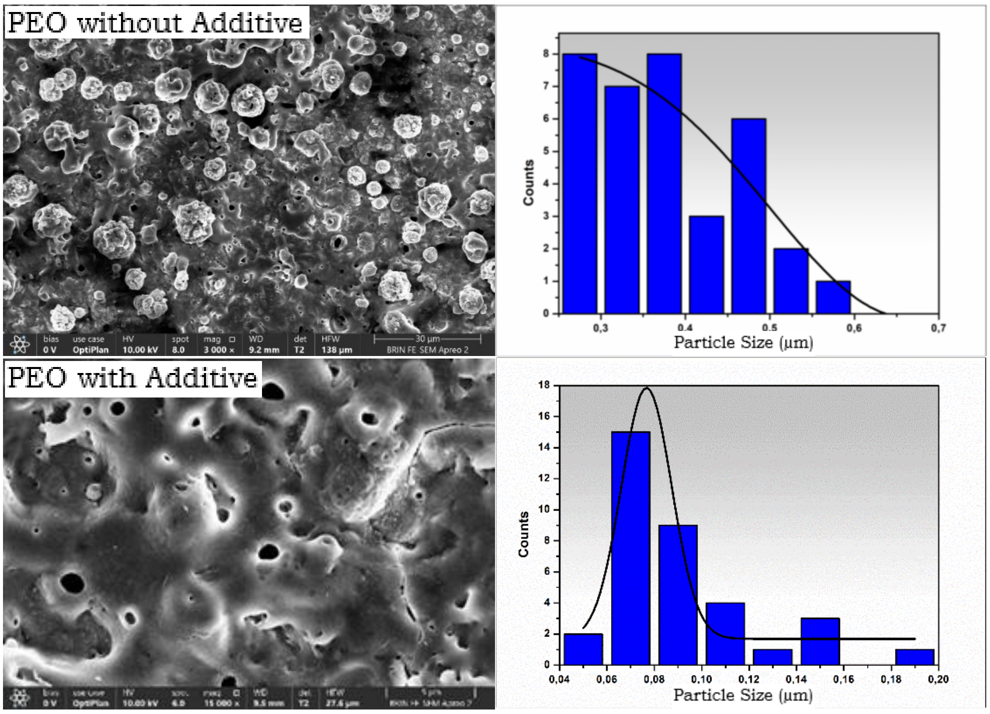


Figure 3. Surface Layer Morphology of PEO Samples with and without Additive MA

Additionally, as noted by Casanova et al., the inclusion of small-molecule organic acids like acetates in the electrolyte enhances plasma suppression and promotes short-lived and well-distributed discharges, contributing to finer surface morphology with reduced roughness and smaller pores.

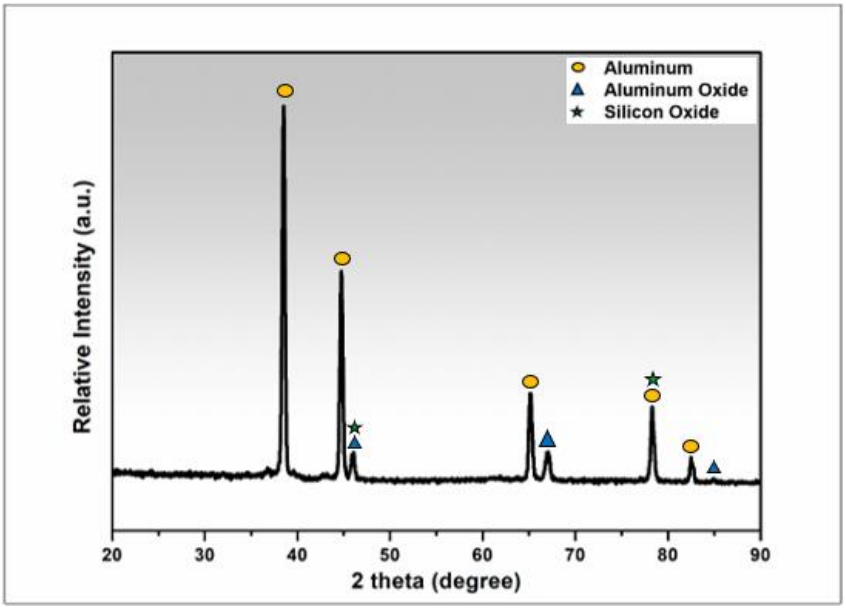


Figure 4. Elemental Composition from the XRD Pattern of the PEO Sample Without Additives

Table 3. Elemental Composition of the PEO Sample Without Additives

Component	**Chemical Formula**	**Mineral Name**	**Crystal System**	**Density (g/cm³)**	**Unit Cell Volume ($10^{-30}m^3$)**	**RIR**	**SemiQuant%**
Aluminum	Al	Aluminum, syn	cubic	2.70	66.42	4.10	61
Aluminum oxide (gamma)	Al_2O_3	-	cubic	3.66	61.63	1.09	17
Silicon oxide	SiO_2	Stishovite	Tetragonal	4.36	45.76	1.95	22

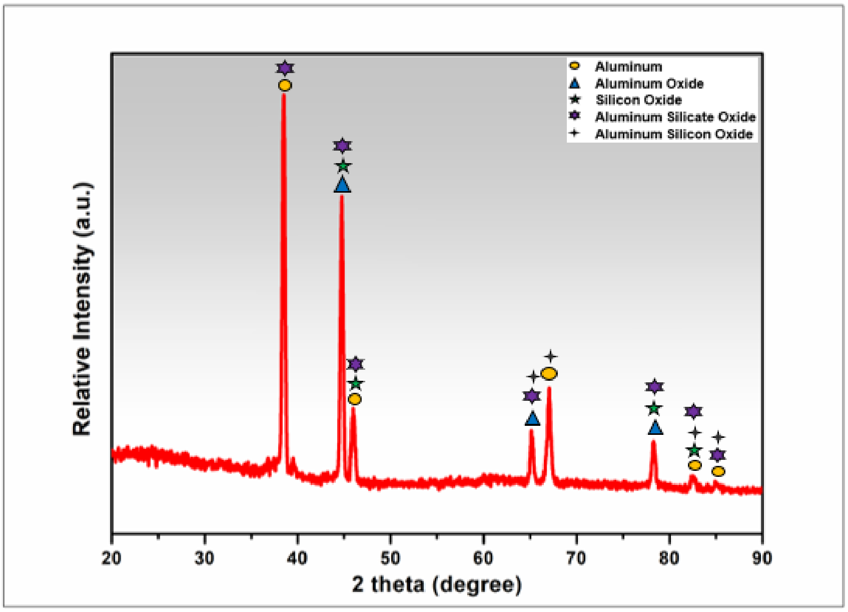


Figure 5. Elemental Composition from the XRD Pattern of the PEO Sample with Additives

Table 4. Elemental Composition of the PEO Sample with Additives

Component	Chemical Formula	Mineral Name	Crystal System	Density (g/cm^3)	Unit Cell Volume $(10^{-30}m^3)$	RIR	SemiQuant%
Aluminum	Al	Aluminum,	cubic	2.70	66.42	4.10	4
Aluminum oxide (gamma)	Al_2O_3	-	cubic	3.66	61.63	1.09	3
Silicon oxide	SiO_2	Quartz	Hexagonal	2.52	118.90	2.87	25
Aluminum Silicate Oxide	$Al_2(SiO_4)O$	Andalusite	Orthorhombic	3.12	342.23	0.73	6
Aluminum Silicon oxide	$Al_{5.65}Si_{0.35}O_{9.175}$	Mullite, syn	Orthorhombic	2.98	171.87	0.79	62

In the PEO sample without additives, as shown in **Figure 4** and **Table 3**, the main phases identified are aluminum (Al) with a cubic crystal structure (Ref. 01-085-1327) and alumina (Al_2O_3) in its gamma crystallization form. A small amount of silicon dioxide (SiO_2) (Ref. 01-086-2333) was also detected. The alumina phase plays a crucial role in forming a protective oxide layer on the aluminum surface, acting as a physical barrier against the penetration of corrosive agents. This significantly improves the corrosion resistance by preventing further oxidation and also contributes to increased surface hardness, providing mechanical resistance against wear. However, the oxide layer formed in the PEO process without additives remains relatively simple in structure, which may not provide optimal protection under highly corrosive or extreme environmental conditions.

Significant changes in the crystalline structure and oxide layer composition were observed in the PEO sample processed with the addition of malonic acid (MA), as shown in **Figure 5** and **Table 4**. In this condition, new aluminosilicate phases such as andalusite (Ref. 39-376) and mullite (Ref. 00-015-0776) were detected. The presence of mullite is particularly important due to its excellent thermal stability and superior corrosion resistance. The formation of these phases results directly from the complex interaction between MA and the PEO process. The addition of MA alters the plasma discharge behavior, promoting the formation of a more uniform and denser oxide layer. This is consistent with the findings of Kaseem and Dikici (2021), who reported that organic additives containing –OH and –COOH functional groups tend to adsorb on the metal surface, modifying the local electric field and suppressing the intensity of plasma discharges. This leads to a more controlled and structured oxide growth process.

Moreover, as supported by Casanova et al. (2022), the addition of organic acids into the PEO electrolyte influences the plasma evolution and enhances the resulting oxide morphology. In this case, MA likely forms transient metal-organic complexes with Al^{3+} and Si^{4+} ions, which decompose within the plasma discharge channels to act as precursors for mullite formation. Mullite, a compound formed from the reaction between Al_2O_3 and SiO_2, requires high-temperature plasma and an alkaline environment—conditions that are facilitated by the presence of organic additives. The formation of mullite and andalusite results in a denser, more thermally stable, and corrosion-resistant oxide structure, offering better protection against aggressive ion infiltration and thermal or mechanical stress.

Overall, the addition of MA in the PEO process significantly enhances the corrosion resistance of aluminum. The resulting oxide layer is not only thicker and denser but also composed of complex crystalline phases with superior chemical and thermal stability compared to pure alumina. This reduces the risk of localized corrosion such as pitting and extends the service life of the material in harsh operating environments. Furthermore, the improved mechanical strength and adhesion of the oxide layer to the substrate indicate that MA is an effective and promising additive for enhancing the performance of plasma electrolytic oxidation coatings on aluminum-based materials.

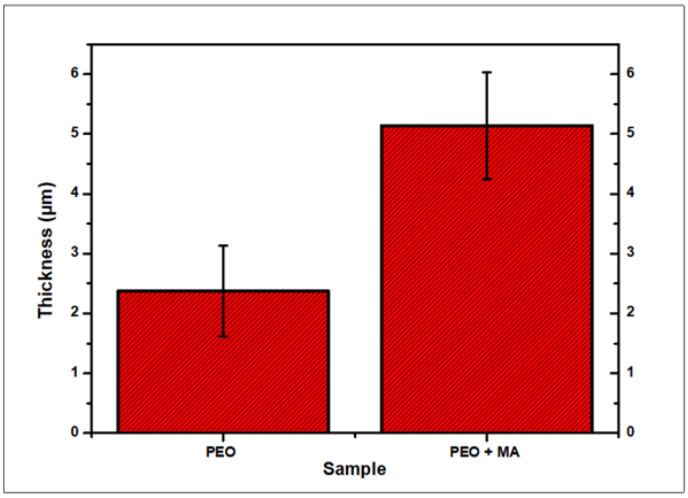


Figure 6. Comparison of Coating Thickness on PEO and PEO + MA Samples

The oxide layer thickness measurements validate the findings from plasma visualization and voltage-time curve analyses, emphasizing the significant role of malonic acid (MA) in the Plasma Electrolytic Oxidation (PEO) process. As shown in **Figure 6**, the PEO sample without additives produces an oxide layer with an average thickness of 2.37 ± 0.76 µm, whereas the sample treated with 1 g/L MA results in a significantly thicker layer of 5.14 ± 0.89 µm. This increase confirms that MA enhances plasma discharge behavior, improves electrolyte conductivity, and facilitates more uniform and sustained oxidation, leading to the development of a thicker and denser oxide layer.

The effect of MA on the oxidation process can be attributed to its ability to stabilize micro-discharges, reduce the breakdown voltage, and improve dielectric properties, which promotes controlled and sustained plasma activity. This controlled environment minimizes surface defects such as cracks and melting zones while increasing layer uniformity and compactness. These characteristics lead to improved mechanical performance, corrosion resistance, and wear protection. Although minor thickness variations still occur due to the stochastic nature of plasma discharges, the overall improvement in thickness and uniformity in the MA-treated sample demonstrates its effectiveness as a performance-enhancing additive in PEO coatings.

To further contextualize these findings, it is useful to compare them with coating thicknesses achieved by other surface engineering techniques. For instance, Li et al. (2019) developed a two-layer sol-gel derived silica-titania coating on Q235 carbon steel using spray deposition, achieving a coating thickness of 35 ± 3 µm. This thick film provided excellent barrier properties, although it required a more complex deposition process involving multiple layers and fillers. In contrast, Ramos et al. (2019) used a sol-gel method to deposit alumina films, but the resulting coatings were much thinner—approximately 55–85 nm—due to limitations inherent in dip-coating and thermal treatment techniques. Similarly, Vera et al. (2014) applied anodic oxidation to produce TiO_2 films with thicknesses ranging from 23 to 54 nm, depending on the treatment voltage and electrolyte conditions.

In comparison, the PEO method combined with MA strikes a balance between process simplicity and coating performance, achieving a moderate yet significant oxide layer thickness (~5 µm) with enhanced mechanical and anticorrosive properties. While sol-gel and anodic oxidation techniques offer excellent control over surface chemistry and nanostructure, they generally produce much thinner coatings, which may be inadequate for applications requiring robust barrier properties in aggressive environments. Thus, the incorporation of MA in the PEO process not only improves coating characteristics but also positions the method as a versatile and scalable solution for high-performance surface protection.

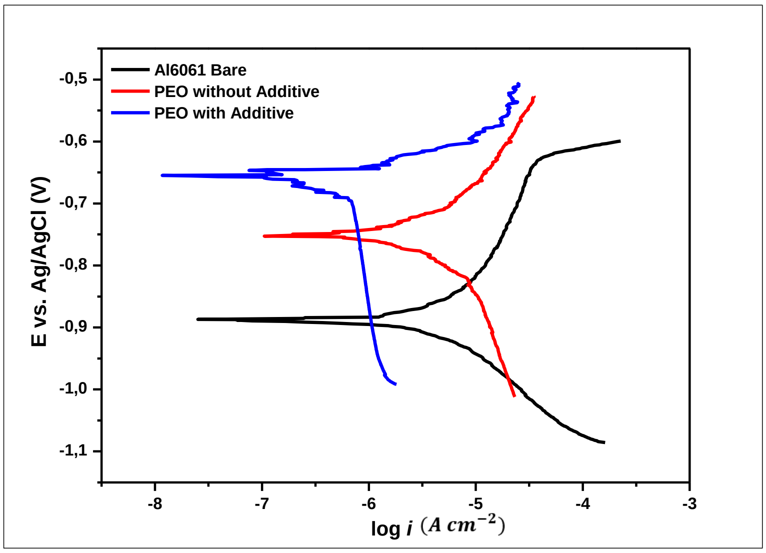


Figure 7. Potentiodynamic Tafel Polarization Curve of each sample

Table 5. Electrochemical Parameters obtained by the Tafel plot of each sample

Sample	$E_{corr}(V)$	$I_{corr}(A/cm^2)$	$\beta_a\ (V/dec)$	$\beta_c\ (V/dec)$	*Corrotion Rate* (mpy)
Al 6061 Bare	-3.519	$6.330\text{x}10^{-6}$	0.491	- 0.491	8.140
PEO without Additive	-3.001	$3.957\text{x}10^{-6}$	0.783	- 0.783	6.524
PEO with Additive	-2.616	$3.899\text{x}10^{-7}$	0.770	- 0.377	0.642

Based Based on the potentiodynamic polarization curves **Figure 7** and electrochemical parameters obtained from Tafel extrapolation **Table 5**, the corrosion resistance of the aluminum alloy 6061 samples shows significant variation depending on the application of Plasma Electrolytic Oxidation (PEO) and the inclusion of malonic acid (MA) as an organic additive. The uncoated Al 6061 sample exhibits the poorest corrosion resistance, with the highest corrosion rate of 8.140 mm/year, a high corrosion current density (I_{corr} = 6.330 × 10^{-6} A/cm^2), and the most negative corrosion potential (E_{corr} = –3.519 V). These values indicate severe susceptibility to electrochemical degradation in chloride-rich environments, highlighting the inadequacy of the bare aluminum surface in aggressive media.

In contrast, the PEO-coated sample without MA shows a moderate improvement in corrosion resistance, with a reduced corrosion current density (I_{corr} = 3.957 × 10^{-6} A/cm^2) and a lower corrosion rate of 6.524 mm/year. The shift in corrosion potential to a more positive value (E_{corr} = –3.001 V) suggests the formation of a protective oxide layer. However, this improvement is limited by the presence of microstructural defects—such as pores and cracks—typically found in untreated PEO coatings. These flaws act as diffusion pathways for corrosive ions, thus compromising the long-term integrity of the coating. A significant enhancement is observed in the PEO sample treated with 1 g/L of malonic acid. This sample shows the lowest corrosion current density (I_{corr} = 3.899 × 10^{-7} A/cm^2) and the most positive corrosion potential (E_{corr} = –2.616 V), corresponding to a drastically reduced corrosion rate of 0.642 mm/year. The superior corrosion performance is attributed to the ability of MA to stabilize plasma discharges, enhance electrolyte conductivity, and promote the growth of a thicker, more compact, and uniform oxide layer with fewer structural defects. Furthermore, XRD analysis reveals the formation of thermodynamically stable crystalline phases, including mullite ($3Al_2O_3{\cdot}2SiO_2$) and andalusite (Al_2SiO_5), in the PEO + MA sample. These aluminosilicate phases offer excellent barrier properties due to their dense structures and high resistance to ionic diffusion. According to Zhang et al. (2018), mullite-based coatings are especially effective at impeding chloride ion ingress, thereby drastically lowering corrosion rates. This structural transformation, enabled by the interaction between MA and the plasma environment, enhances the long-term durability of the coating.

To evaluate the effectiveness of this method, it is important to compare it with alternative corrosion protection strategies involving organic and inorganic corrosion inhibitors. Organic inhibitors such as 4-ethylpyridine (EP) and imidazole derivatives have shown inhibition efficiencies above 85% in acidic media, as reported by Chopda (2023). Similarly, Leguta et al. (2021) found that imidazolium-based ionic liquids can reach up to 98% inhibition efficiency through surface adsorption and electron donation mechanisms. While effective, these inhibitors typically require continuous replenishment or immersion in controlled environments, limiting their long-term applicability. Inorganic inhibitors, on the other hand, such as $CaCO_3$ nanoparticles (Bolzoni et al., 2022) and SiO_2-based sol-gel coatings, offer physical barrier properties that slow down corrosive ion diffusion. However, these coatings often suffer from mechanical limitations such as cracking under thermal stress or require complex fabrication methods. Despite their advantages, the corrosion protection offered by these inorganic systems remains vulnerable in harsh environments.

Compared to these approaches, the PEO + MA method stands out by offering a permanent, integrated coating system that combines chemical passivation, microstructural optimization, and crystalline phase stability. Unlike molecular inhibitors that may degrade or leach out over time, the PEO + MA coating is embedded in the metal matrix, providing long-term corrosion resistance without the need for retreatment. Electrochemical data further supports this claim, showing that the corrosion current density in the PEO + MA sample is at least one order of magnitude lower than in systems using traditional organic or inorganic inhibitors. In conclusion, the integration of malonic acid into the PEO process significantly outperforms both conventional organic and inorganic inhibitor strategies. It offers a scalable, efficient, and durable solution for improving corrosion resistance in aluminum alloys, particularly in applications exposed to aggressive chloride environments.

4. Conclusion

In This study confirms the effectiveness of incorporating malonic acid (MA) as an organic additive in the Plasma Electrolytic Oxidation (PEO) process for enhancing the surface and corrosion resistance properties of 6061 aluminum alloy. The addition of MA significantly improves plasma discharge behavior, reduces breakdown voltage, and promotes the formation of a denser and more uniform oxide layer. Structural analysis reveals the formation of thermally stable and chemically resistant crystalline phases such as mullite and andalusite, contributing to improved barrier properties.Compared to traditional PEO coatings and conventional corrosion inhibitors—both organic (e.g., imidazole derivatives and ionic liquids) and inorganic (e.g., $CaCO_3$ and SiO_2-based films)—the PEO+MA approach demonstrates superior and more durable corrosion protection. The significant reduction in corrosion current density and rate, combined with increased oxide layer thickness and reduced porosity, highlights the enhanced protective performance of this method. Overall, the use of malonic acid in PEO presents a promising and scalable solution for advanced surface engineering, offering robust, long-term protection against corrosion in aggressive environments, with potential applications in automotive, aerospace, and marine industries.

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