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# Comparison of corrosion and antibacterial properties of Al alloy treated by plasma electrolytic oxidation and anodizing methods

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## Abstract

Plasma electrolyte oxidation (PEO) and anodizing coatings were produced on 7075 Al alloy and compared together. Surface and cross section morphology of the coatings were studied by field emission scanning electron microscope. Phase compositions of coatings were analyzed by the X-ray diffraction Technique. Tafel polarization and immersion tests were done in 3.5%wt NaCl solution to evaluate the corrosion properties of the coatings and substrate. The antibacterial activity of coatings was evaluated against *E. coli* bacterium. The PEO and anodized coatings had a completely different surface morphology and microstructure. The PEO coating was not affected by substrate surface features. Coatings cross sectional analysis showed that PEO coating had a dense barrier inner layer and a porous outer layer and it was less uniform in thickness than anodized coating. X-ray diffraction patterns of coatings demonstrated that PEO coating is mainly consisted of a crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase, while in the case of anodized coating no crystalline phase was observed which suggested that it composed of an amorphous phase. Corrosion resistance of 7075 Al alloy were improved after both coating treatments but PEO coating exhibited superior corrosion properties compared to anodized coating because of the crystalline barrier layer. Also, the presence of Silicon in PEO coating resulted in better antibacterial activity than anodized coating.

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## 1. Introduction

Aluminum and its alloys possess many characteristics, such as high strength to weight ratio, beautiful appearance, strong electrical and thermal conductivity, high ductility and a good processing performance. Hence, they have been widely applied in aviation and aerospace, medical equipment, food processing, storage equipment, kitchen utensils, transportation and public facilities [1-3]. But some disadvantages like low wear and corrosion resistance limits their efficiency. Therefore, corrosion resistance of Aluminium alloys needs to be improved and it is crucial for them to be antibacterial because of some of the mentioned applications. Thus, the production of hard, corrosion resistant and antibacterial ceramic coatings on aluminum components is of great interest.

In the past, a wide range of techniques have been investigated to produce protective coatings on aluminum components, such as chemical conversion coating, anodizing, plasma thermal spray, physical vapor deposition and plasma electrolytic oxidation [4-7]. Anodizing, a coating process which originated in the 1930s, is one of the most commonly used treatments for aluminum alloys because of the low cost and good mechanical properties. Anodizing is an electrochemical process, which makes use of the almost unique ability of amorphous alumina to develop a regular porous morphology, when it is usually formed in acidic electrolytes. These coatings protect against both corrosion and wear, provide keying layers for adhesive bonding, and form base layers for topcoats [8-10]. Also, some researchers produced antibacterial coatings on Al alloys by the anodizing process [11-13]. Despite the benefits, anodizing is carried out by the use of acidic electrolytes such as concentrated sulfuric acid, phosphoric acid and other salt solutions which cause environmental pollution. Moreover, anodized coatings have many cracks in their structure and cannot provide sufficient Fatigue properties [14].

Another coating method which is developed in the recent decade and can be a suitable alternative for conventional anodizing process is plasma electrolytic oxidation (PEO). PEO is a promising process which is used to improve corrosion properties of lightweight metals, because of the formation of a thick, dense and hard nanostructured ceramic coating. This technology is derived from conventional anodizing but uses environmental friendly alkaline solutions with higher PH as electrolyte [15, 16]. The process of PEO is carried out at voltages higher than the breakdown voltage of the gas layer covering the anode. Since the substrate alloy is connected to the positive pole of the power supply as anode, the gas layer consists of oxygen. Applying these high voltages leads to the formation of electrical discharges which passes through the gas layer. The coating formed on the substrate alloy consists of crystalline or amorphous phases formed at breakdown sites, which usually contains constituent species derived from the substrate and the applied electrolytes. Coatings produced by this method have good adhesion to the substrate but unfortunately, they are porous. Because of the porous layer when the coated sample is exposed to the aggressive environment, corrosive ions like  $Cl^-$  penetrate into the substrate through the pores and accordingly, the corrosion resistance of the coatings decreases. Several researches have been carried out on the effect of PEO parameters on corrosion and antibacterial properties in recent years [17-19], and few of them compared properties of PEO with Hard anodized (HA) coatings. Rama Krishna et al. [20] investigated the relative performance of PEO and HA coated AA 6061 under abrasion and erosion. They reported that MAO coated samples exhibited superior erosion and abrasive wear resistance compared to HA coated samples. Ugur Malayoglu et al. [21] compared the mechanical and tribological properties of PEO and HA coatings on 6082 aluminum alloy. Their results showed that PEO coating exhibited higher adhesion strength and wear resistance because of the crystalline gamma and alpha alumina phases present in PEO coating structure and these phases have higher hardness and elastic modulus values compared with amorphous phases in HA coating.

Recently Pietrogiovanni Cerchier et al. [22] incorporated Ag particles into the PEO coating on 7075 Al alloy to obtain antibacterial and corrosion resistant properties. They reported that the addition of Ag particles could improve antibacterial properties of PEO coating but it decreased the corrosion resistance of the coating compared with PEO (without silver) and anodizing coating. Since PEO coating of Al alloys is commonly carried out using silicate based electrolytes, thus, Silicon (Si) is one of the main elements in such coatings. The antibacterial effect of Si is well known in literature [23, 24]. But effect of Si on antibacterial properties of PEO coatings has not been studied. Therefore the main objective of this study is to investigate the effect of Si on the antibacterial activity of PEO coating. For this reason, a Si containing PEO coating was produced on 7075 Al alloy and its antibacterial and corrosion properties were evaluated and compared with the same properties of anodized coating. Because of the existence of Si in PEO coating, it's expected to show better antibacterial properties than anodized coating.

## 2. Materials and methods

### 2.1. Preparation of the samples

Rectangular specimens of Al 7075 alloy of size 2 cm × 1 cm × 0.1 cm were used as substrates. The samples were polished following a standard metallographic technique (finest paper with 2000 grit size) before the PEO and anodizing treatments and then degreased using alcohol in an ultrasound.

### 2.2. Preparation of the PEO and Anodized coatings

PEO coating was deposited in an alkaline electrolytic bath containing 10 g/l sodium silicate and 2 g/l potassium hydroxide. The treatment was performed maintaining the current constant, letting the potential free to vary. In detail, the current density was fixed at 0.14 A/cm<sup>2</sup> and the samples were treated in a duty cycle of 50% for 30 min.

The anodizing sample was chemically treated prior to anodizing as follows: 1) etching in 5 wt.% NaOH solution for 2 min; 2) cold water rinsing; 3) chemical polishing in 30 V% nitric acid at room temperature for 2 min; 4) cold water rinsing. The anodizing process was accomplished in an electrolyte consisting of 184 g/L sulphuric acid at a temperature of 10 °C for 10 min. Current density and duty cycle were maintained constant with values of 0.11 A/cm<sup>2</sup> and 50%, respectively.

Both anodizing and PEO processes were carried out with equipment consisting of a pulsed DC source with 10000 Hz modulation, a stirring and a cooling system.

### 2.3. Characterization of the coatings

The coated specimens were cross-sectioned, mounted in resin and polished by standard metallographic abrasive paper. Subsequently The microstructure of the cross-section and the surface of coatings was studied by FE-SEM (TESKAN-MIRA3). FE-SEM images of coatings Cross-section were analyzed by MIP software to measure mean values of coatings thicknesses. The semi quantitative chemical composition of the coatings were analyzed by an energy dispersive X-ray spectroscopy (C-MAX) incorporated into SEM after Au deposition by sputtering. The phase composition of coatings was analyzed by X-ray diffraction (Philips, CuK $\alpha$  radiation, 40 kV, 35 mA, 0.02\_/s scan rate).

### 2.4. Corrosion behaviour of the coatings

Corrosion resistance of the uncoated and PEO coated specimens was evaluated through potentiodynamic polarization techniques using a computer controlled PGS 2065 potentiostat. Tests were carried out using a standard three-electrode setup with the coated sample as working electrode, Pt as the counter electrode and saturated calomel electrode (SCE) as the reference. Unstirred 3.5 wt.% NaCl solution prepared with distilled water which was exposed freely to the atmosphere was used as the corrosive medium, then, all the electrodes were dipped in a beaker with three necks, which were full of 3.5 wt.% NaCl aqueous solution. Also, polarization tests were conducted over a potential range of -900 mV to -600 mV using the scan rate of 1 mV/s. Long term immersion tests of bare alloy and anodized and PEO samples were carried out in 3.5 wt.% NaCl solution (pH=7.0) for 7 days at room temperature.

### 2.5. Antibacterial characteristics of the coatings

*E. coli* (ATCC25922), which is used in most antibacterial assays as an indicator bacterium was selected as a test microorganism. Bacterial cultures were suspended in 5 mL tryptic soy broth (TSB) using a vortex mixer and developed in a shaking incubator at 37°C for 24 hours. The culture was kept in a shaking incubator for the duration of the experiments. All samples were sterilized in 70% ethanol, rinsed with sterile deionized boiling water and kept under ultraviolet light for 15 minutes on each side prior to the bacteria inoculation. The samples were placed in individual wells in a 2-well culture plate. Then, 1 mL of the aforementioned bacterial suspension was added to each

sample and incubated for 24 h at 37 °C. After the culture, the medium was collected to determine the viable counts of planktonic bacteria, and the values are expressed relatively to the volume of the medium (number of bacteria per mL). As an alternative to the OD595, colony-counting measurements were also performed. Five hours into the spectroscopy measurements, the bacteria strains were plated to yield an approximate concentration.

### 3. Results and discussion

#### 3.1. Coatings characterization

SEM images of coating surfaces depicted in Fig. 1 illustrate the different morphologies produced by these two coating techniques. Some microstructures including; preferential oxide growth and surface inclusions occurred on the coating surface prepared by the Anodizing process. Preferential oxide growth is resulted from different chemical reactivity of Al 7075 matrix and the second-phase existing in the Alloy, in other words, during the anodizing process, coating grow with different rates on the matrix and the second-phase, therefore, coating had a different thickness on these two regions and could be separately observed in FE-SEM images [25]. Before the anodizing process, a pretreatment comprising of degreasing and pickling apply on the surface of Al alloys which aims to make a chemically clean surface ready for anodizing. Localized corrosion, in the form of pits, occur during the pre-treatment solution exposure and these pits cause several inclusions on the coating surface which are showed in Fig. 1(a) [26]. In the case of PEO coating, several microstructures including pancakes, micropores and microcracks occurred on the ceramic coating surface, as illustrated in Fig. 1(b). A significant area on the surface was occupied by the pancake microstructures, which formed by the discrete localized microdischarge events and they are the result of cooling and deposition of the molten material on the surface. The discharge channels are the result of localized discharge and the micro-pores are possibly the result of gases escaping during the PEO process [16]. It should also be noted that some elongated pores can be observed between the pancakes which is formed by the incomplete combination of the pancake structures. Some micro-cracks appear on the coating surface. The cracks are usually

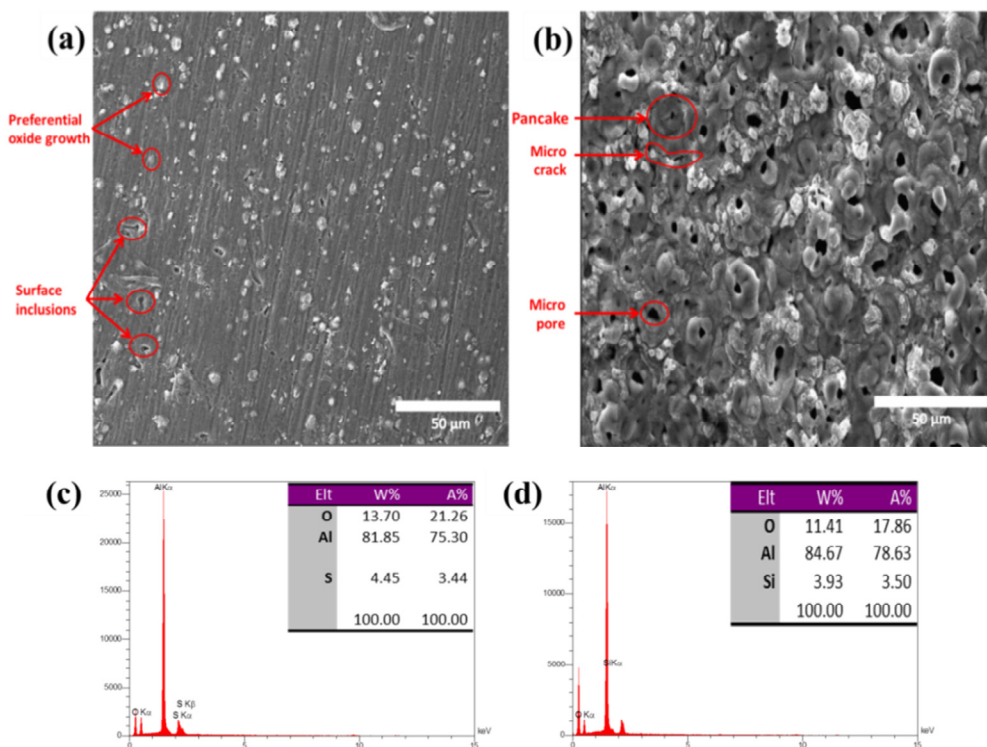


Fig. 1. FE-SEM images of surface microstructures and EDS spectra recorded on topmost surface of (a, c) anodized and (b, d) PEO coatings.

generated at the boundaries of the pancake structures or radially distributed around the central pores. The formation of the cracks is possibly related to the thermal stress resulting from the transient temperature fluctuations during PEO process. Despite of anodized coating, No trace of substrate (pits, scratches, etc.) is evident on the PEO coating surface. The elements of anodized coating are Al, O and S whereas The PEO coating is mainly composed of Al, O, and Si. In both coatings Al are from the alloy substrate, and the presence of S and Si suggests that the components of the electrolyte have been incorporated into the coating for the anodized and PEO coatings respectively.

Fig. 2 compares the SEM (back-scattered electron mode) and EDS elemental maps of the cross sections of anodized and PEO samples. In the anodized sample, the coating has a uniform thickness and it appears continuous, smooth and well-bonded coating–substrate interfaces. Moreover, it seems that the presence of a second phases in the Aluminum alloy did not affect the coating structure. Elements of Al, O and S are uniformly distributed throughout the coating. As compared to the anodized layer, PEO coating is non-uniform in thickness and consists of a typical two-layer structure with a porous outer layer and barrier inner layer. The reason behind the two-layer structure is due to the different transient temperature field of the outer layer and inner layer. Because of the periodical increasing and decreasing of surface temperature due to periodical plasma discharge, melting and solidification occurs in the outer layer repeatedly, leading to a porous structure. The transient temperature in the inner layer is lower than that the outer layer, therefore solidification occurs in the inner layer, leading to a compact crystalline structure. EDS elemental maps of the PEO coating showed that Al, O and Si elements were present in the coating but distribute non-uniformly in the coating. Al and O are more concentrated in the outer layer and also in the coating/substrate interface, but Si is only accumulated in the outer layer since it originates from the  $\text{SiO}_3^{2-}$  in the electrolyte, the mechanism of which is depicted in Fig.4 (c).

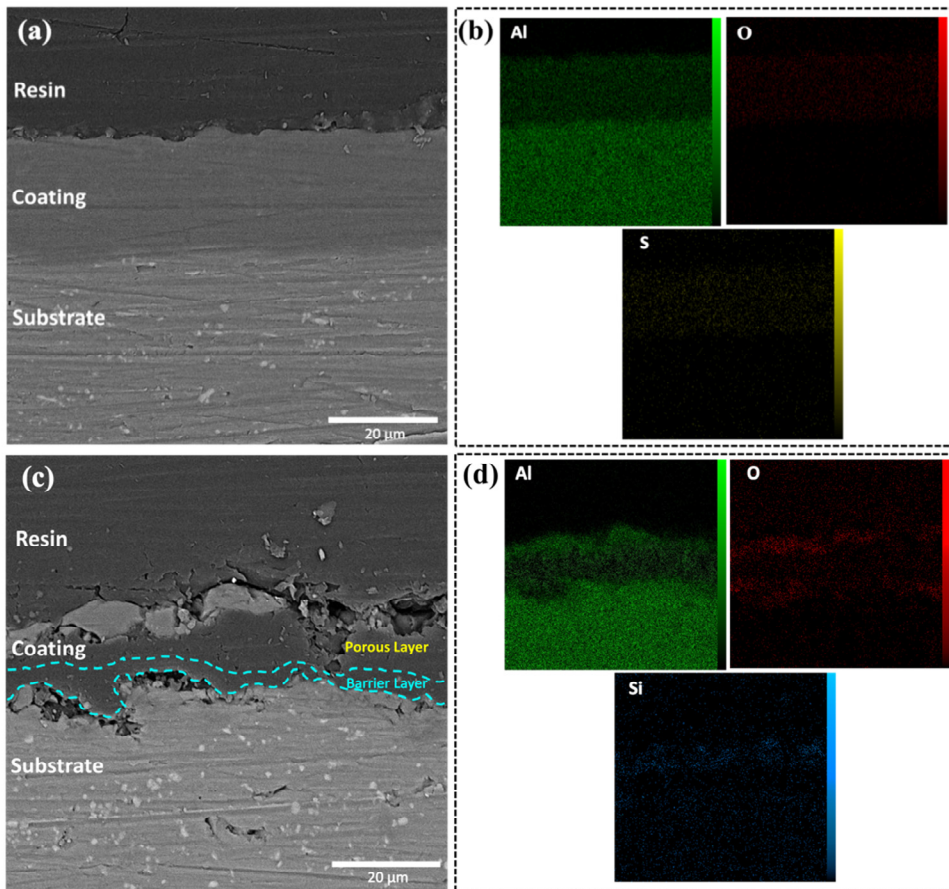


Fig.2. FE-SEM micrographs using back-scattered electron mode (BSE) and EDS elemental maps of polished cross sections of (a, b) anodized and (c, d) PEO samples.

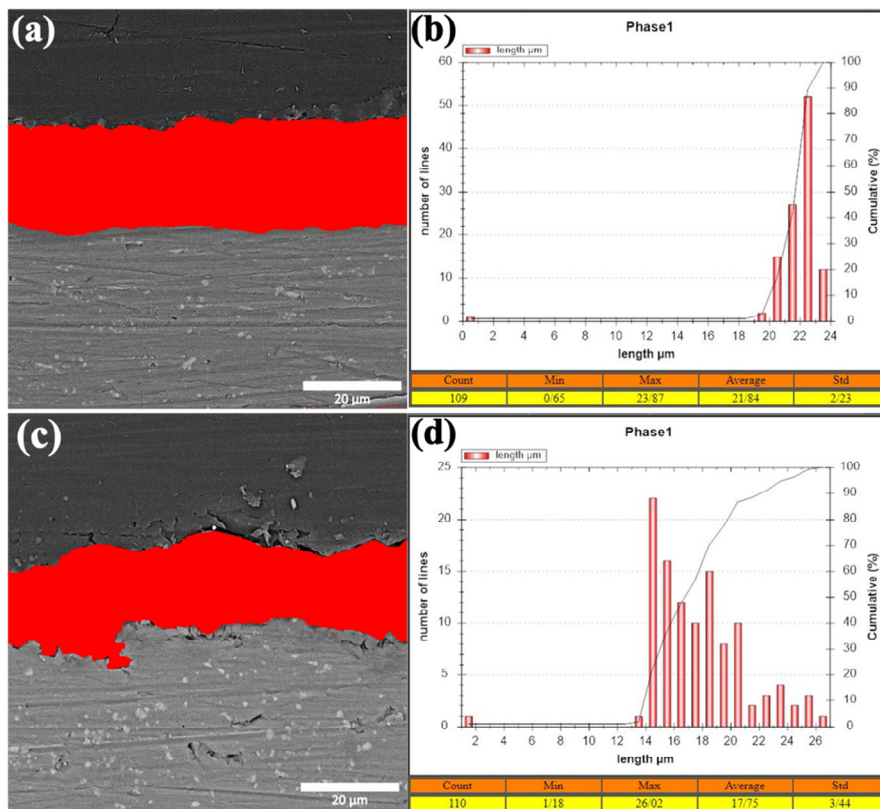


Fig. 3. Results of coating thickness measurement using MIP software. (a, b) anodized coating and (c, d) PEO coating.

To further compare the thickness of anodized and PEO composite coatings, we perform studies on the cross-sectional images of the coatings by MIP software (Fig. 3). The average thickness of anodizing and PEO coatings was 21.84 and 17.75 respectively. From Comparison of Fig. 3 (b) and (d) it can be found that the distribution of thickness values is more uniform along the anodized coating.

Fig.4 shows the X-ray diffraction patterns of samples coated by anodizing and PEO processes. The X-rays can easily penetrate through the coatings because of the porous structure of them, thus the diffraction peaks of substrate are strongly detected for both samples and it should be ignored. It can be seen that PEO coating consists mainly of  $\gamma$ - $\text{Al}_2\text{O}_3$  that is a common phase in PEO coatings of Al alloys. Because coating temperature can be raised up to thousands of kelvin in discharge areas during the PEO process, it causes the oxide layer to melt in these regions, so, The melted oxide layer is ejected from the channel and then objected to high cooling rates and exposed to immediate contact with surrounding cool electrolyte which promotes the formation of  $\gamma$  phase during solidification of alumina droplets. In the case of the anodized layer, only the peaks of substrate can be seen in pattern which indicates that this layer is probably composed of an amorphous phase. Although, it has been reported that either amorphous or crystalline barrier aluminum oxide can be made by anodizing, depending on the growth conditions, but formation of different kinds of amorphous phases is much more favorable and has been reported in numerous reports [27, 28]. The presence of such crystalline alumina phases can explain the higher hardness of the PEO coating than anodizing coating; which has been studied elsewhere [21].

### 3.2. Corrosion behavior of the coatings

The corrosion behaviour of anodized and PEO coatings and bare sample are evaluated through potentiodynamic polarization technique and the polarization curves are shown in "Fig. 5". Corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ), cathodic/anodic Tafel constants ( $\beta_c$  and  $\beta_a$ ), polarization resistance ( $R_p$ ) values

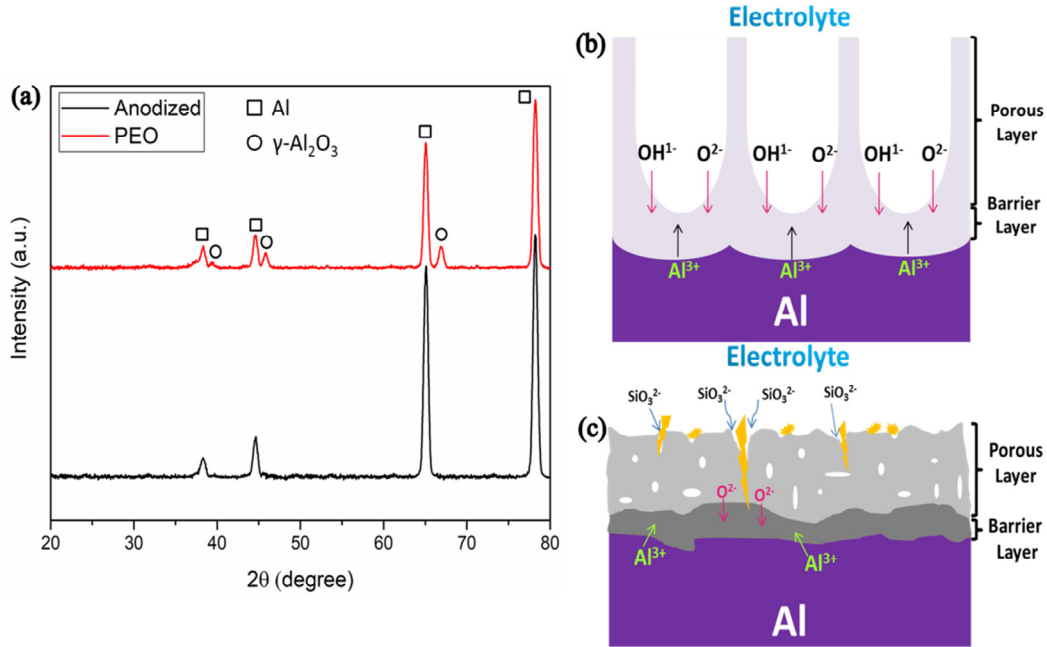


Fig. 4. (a) The XRD patterns of anodized and PEO coatings on 7075 Al alloy; growth mechanism of (b) anodized and (c) PEO coatings.

were determined from Stern-Geary equation [29]:

$$R_p = \frac{\beta_a \beta_c}{2.303 i_{corr} (\beta_a + \beta_c)} \quad (1)$$

and the results are presented in Table 1. These data clearly show that the corrosion resistance of the anodized and PEO coatings is evidently different. As seen from Fig. 5 and Table. 1, after both coating treatments, polarization curves move to a lower current density side and the corrosion current density is about 3 orders of magnitude smaller than the substrate for PEO samples. Also, both coated samples have a higher polarization resistance relative to the bare sample. It means that both coatings have considerably increased the corrosion resistance of Al 7075 alloy. PEO sample corrosion current density is about 2 times lower than the anodized one therefore the PEO sample has a lower corrosion rate. On the other hand, corrosion potential ( $E_{corr}$ ) of the Anodized sample is more active (-1.05V) when compared to the PEO (-0.78V) sample that suggest corrosion initiate easily in anodized sample, However, slope of anodic branch increases drastically after about 0.05 V from  $E_{corr}$  which indicates that the corrosion rate has decreased. This could be attributed to the sealing of small pores and cracks by corrosion products after initiation of corrosion. But this sudden increase in slope cannot be seen in the anodic branch of the PEO sample because of the size of the pores and cracks in the PEO coating is too large to be sealed by the corrosion products. It has been reported that both anodized and PEO coatings have a barrier dense layer in their structure that gives them

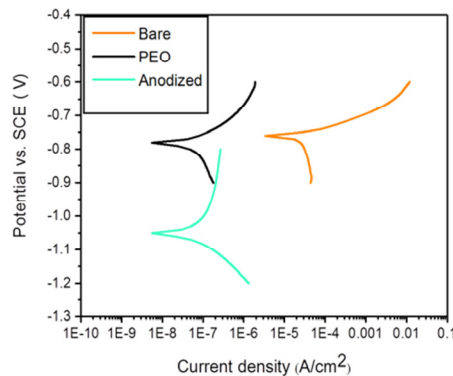


Fig. 5. Potentiodynamic polarization curves of the Bare, PEO and Anodized samples.

Table 1. The results obtained from tafel polarization tests of different samples in 3.5% NaCl medium.

Sample code	$E_{corr}(V)$	$I_{corr}(A.cm^{-2})$	$\beta_a (mV)$	$\beta_c (mV)$	$R_p (\Omega.cm^2)$	%F
Bare	-0.76	$2.98 \times 10^{-5}$	40	497	539	—
Anodized	-1.05	$1.16 \times 10^{-7}$	498	137	402183	0.13
PEO	-0.78	$6.42 \times 10^{-8}$	92	257	458212	1.19

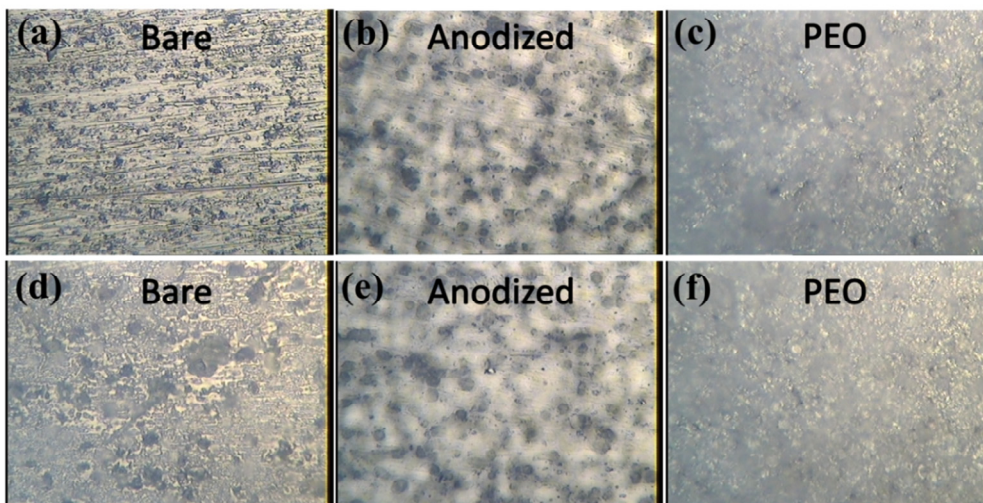


Fig. 6. Optical surface morphology of the Bare and coated samples. (a, b, c) before immersion and (d, e, f) after immersion in 3.5% NaCl solution for 7 days.

corrosion protective properties, However the thickness of the barrier layer can be increased to a maximum of  $1\mu m$  in anodizing coatings which is very small compared to the thickness of the barrier layer in the PEO coatings [8]. Also, as the XRD result showed, PEO coatings are composed of a crystalline phase whereas anodized coatings are usually amorphous; so, PEO coatings exhibited superior corrosion resistance. The porosity measurement of the derived coatings can be evaluated by the following equation, Eq. (2) [30]:

$$F = \left( \frac{R_{ps}}{R_{pc}} \right) \times 10^{-|\Delta E_{corr}/\beta_a|} \quad (2)$$

Where,  $F$  is the value of the coating porosity,  $R_{ps}$  and  $R_{pc}$  are the polarization resistance of the substrate and the coatings respectively.  $\Delta E_{corr}$  is the difference between corrosion potential of the coated sample and substrate.  $\beta_a$  is the anodic Tafel slope of the substrate. The measured porosity of the coatings was given in Table 1.

Fig. 6. shows the surface morphologies of the bare alloy, Anodized and PEO coatings after the immersion. A uniform corrosion can be seen on the surface of the bare sample after the immersion test but The surface of both coatings was not damaged by the immersion process, indicating that both the coating materials, are relatively stable in the neutral 3.5 wt.% NaCl solution. It should be noted that not all the PEO coatings are stable in NaCl solutions, it depends on the substrate and the electrolyte used to fabricate the coatings [31].

### 3.3. Antibacterial characteristics of the coatings

The antibacterial activity of anodized and PEO coatings was evaluated against *E. coli* bacterium. The antibacterial assessment of coatings was measured by different methods such as the zone of inhibition and growth curve. The Optical densities (OD) were measured and plotted as a function of time at regular intervals between 0 and 24 h for PEO and anodized samples (Fig. 7a). The increase in the cell mass of the organism is measured using a spectrophotometer. The spectrophotometer measures the turbidity or OD which is the amount of light absorbed



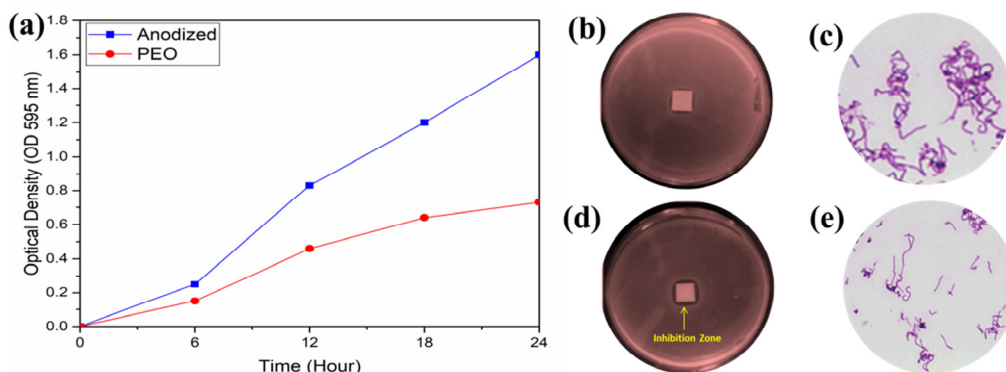


Fig. 7. (a) Growth curve of bacteria for anodized and PEO coatings after 24 h, the antibacterial activity of (b) anodized coating and (d) PEO coating for zone of inhibition, optical microscopy of bacteria morphology for (c) anodized and (e) PEO coating.

by a bacterial suspension. The degree of turbidity in broth cultures is directly related to the number of microorganism present, either viable or dead cells, and is a convenient and rapid method to measure the cell growth rate of an organism. Thus increasing the turbidity of the broth medium indicates an increase of the microbial cell mass. It is observed that PEO coating acts as an effective bactericides and there is an abrupt decrease of bacterial growth. Figs.7 (b) and (d) show the zone of inhibition of coatings. The inhibition zone of PEO coating displays 1.6 cm ( $16 \mu\text{g mL}^{-1}$ ) diameter of the inhibition zones, which has good antibacterial activity and a higher inhibition zone compared to the anodized coating. The optical microscope analysis Figs. 7 c and e advocate that the PEO coating has successfully controlled the growth of *E. coli* bacterium. These results show that the antibacterial activity of the PEO coating probably depends on the silicon (Si) in the chemical composition (see Fig. 1). According to the Figs.7 b and d, the antibacterial activity of Si element in PEO coating appears to be significantly greater on *E. coli* compared to sulfur (S) in anodized coating. The results are in accordance with the studies on antibacterial effects of Si reported in the literature. Recently, much research has been done on the properties of silicon as a new antibacterial agent. Jiang et al. [23] investigated the antibacterial efficiency of silicon-modified polyethylene against pathogenic bacteria. They showed that silicon have more antibacterial activity compared with that of the Ag-modified polyethylene. Wang et al. [24] measured the antibacterial efficiency of pDMAEMA modified silicon nanowire arrays against *Escherichia coli* and concluded that direct contact of the sharp edges of graphene with cell membrane leads to inactivation of bacteria. They showed that silicon nanowire array modified with quaternized pDMAEMA is a highly effective antibacterial material due to the high density of antibacterial polymer and consequently high bacterial adhesion and killing.

#### 4. Conclusion

The corrosion and antibacterial properties of plasma electrolytic oxidation and anodizing coatings on 7075 Al alloy were studied. Unlike anodized coating, PEO coating surface was not affected by substrate surface features (second phases, pits, scratches, etc.). Comparison of the coatings Cross sections indicated that the PEO coating had less uniformity and thickness and it had a two layer structure. EDS elemental maps of the coatings surfaces and cross sections revealed that Al, O and Si were present in the PEO coating, whereas anodized coating composed of Al, O and S elements. Both coating techniques improved the corrosion resistance of Al 7075 alloy but PEO coating exhibited further corrosion resistance which was attributed to its thick dense barrier layer and crystalline structure, while anodized coating composed of an amorphous phase. The presence of Si in the PEO coating caused better antibacterial properties compared to anodized coating.

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