



## OPTIMIZATION AND CHARACTERIZATION OF ANATASE FORMED ON ANODIZED TITANIUMIN MIXED ACIDS

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### ABSTRACT

Titanium (Ti) is widely used in dental and orthopedic implants because of its good biocompatibility and high corrosion resistance. Titanium oxide ( $\text{TiO}_2$ ) has shown to exhibit strong physicochemical bonding between Ti implant and living bone because of its ability to induce bone-like apatite in a body environment. Ti is always coated by an oxide surface layer of 1.5-10 nm thickness.  $\text{TiO}_2$  crystalline structures; anatase and rutile present several distinctive features, such as photocatalytic behaviour, superhydrophilicity and biocompatible properties. Anodic oxidation is used to modify the surface of commercially pure titanium (Cp-Ti) in a mixed acids electrolyte in order to maximize and characterize the  $\text{TiO}_2$  (anatase) crystalline phase. In the present work, thick films of the anatase polymorph of  $\text{TiO}_2$  were formed on Ti-Cp foil under potentials 150V-190V at current densities 40 and 60 mA/cm<sup>2</sup> for 10 min. Multiple characterization techniques were used. Glancing angle X-ray diffraction (GAXRD) is used to obtain crystalline phases, field emission scanning electron microscope (FESEM) is used to obtain surface images and water contact angle (WCA) is used to obtain the wettability of the oxide surface. According to GAXRD results the intensity of the major peak increased with increasing applied voltage and current density. Molar concentration of  $\text{H}_3\text{PO}_4$  has an inverse impact on the crystallinity, thus the peak intensity. Anatase peaks decreased at all voltages when  $\text{H}_3\text{PO}_4$  concentration increased. An increase in  $\text{H}_2\text{SO}_4$  molarity results in higher crystallinity. A predominance of anatase is noticed at all cases. This means that the amount and/or crystallinity of anatase are/is influenced with these parameters. FESEM images observed porous structure in which pore size increases with applied voltage (150-190 V) at current density of 60 mA/cm<sup>2</sup>. Surface morphology depends on the electrolyte composition. Surface morphology have porous surface which resulted from local film breakdown. WCA results of the coated samples have shown to be more hydrophobic at higher voltages while observed to be more hydrophilic at higher molarity. The increase of anatase crystalline with increasing molarity could be related to the more wettability, an exception for the less wettability for sample surfaces produced at 2 M  $\text{H}_2\text{SO}_4$ /0.1 M  $\text{H}_3\text{PO}_4$  at 60 mA/cm<sup>2</sup> could be due to the rutile presence according to GAXRD results.

**Keywords:** titanium, anodic oxidation, anatase, surface modification, water contact angle.

### INTRODUCTION

Titanium (Ti) is widely used in dental and orthopedic implants because of its good biocompatibility and high corrosion resistance (Adell *et al.*, 1990; van Steenberghe *et al.*, 1990). Titanium oxide ( $\text{TiO}_2$ ) has shown to exhibit strong physicochemical bonding between Ti implant and living bone because of its ability to induce bone-like apatite in a body environment (Hazan, Brener and Oron, 1993). Ti is always coated by an oxide surface layer of 1.5-10 nm thickness, which forms spontaneously upon exposure to air and atmospheric water vapour (Sul *et al.*, 2001; Diamanti and Peddefferi, 2007).  $\text{TiO}_2$  may present both amorphous and crystalline structures, depending on process parameters. Crystalline oxides, that is, anatase and rutile, present several distinctive features, such as photocatalytic behaviour, superhydrophilicity and biocompatible properties (Diamanti and Peddefferi, 2007). Anodic oxidation is used to modify the surfaces and properties of Ti and aluminium owing to the resultant mechanical properties, corrosion resistance, non-biototoxicity, and biocompatibility (Abdullah and Sorrell, 2007). Anodic oxidation of Ti allows the controlled production of a protective oxide surface layer much thicker than that formed naturally. These coatings may be dense or porous, amorphous or crystalline, depending on the conditions, such as electrolyte type, solution

concentration, and applied potential (Jäeggi *et al.*, 2005). The electrolytes most commonly used to anodise Ti are sulphuric and phosphoric acids (Diamanti and Peddefferi, 2007).

This work focuses on the evaluation of the effects of titanium anodic oxidation in a  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  mixture electrolyte on the formation of  $\text{TiO}_2$  crystal (anatase) phases in the oxide layer; the impact of process parameters modification will be studied, in order to maximize and characterize the achievement of anatase crystalline.

### EXPERIMENTAL METHOD

#### Sample preparation

Commercially-pure Ti (Cp-Ti) foils of dimensions 25 mm x 10 mm x 0.5 mm were wet hand-polished using 1200 grit (~1  $\mu\text{m}$ ) abrasive paper, followed by immersion in an ultrasonic bath with acetone, rinsing with distilled water, and drying with compressed air.

#### Anodization

Anodic oxidation was done in an electrochemical cell containing ~0.4 L aqueous solutions of  $\text{H}_3\text{PO}_4$  (Q-rec, 85 wt %). The anode and cathode were Ti foil and the anodizing was done with a programmable power supply (Gen 750W/1500W, TDK-Lambda). The anodized foils



were cleaned by dipping in distilled water and then dried in still air. The associated experimental parameters are shown in Table-1.

**Table-1.** Parameters used for anodic oxidation in  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  mixture electrolyte.

Parameters	Value
Temperature ( $^{\circ}\text{C}$ )	25
Electrolyte concentration (Molar) $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$	0.5/0.1
	0.5/0.3
	1/0.1
	2/0.1
DC Voltage (V)	150-190
Current density ( $\text{mA}/\text{cm}^2$ )	40, 60
Duration (min)	10

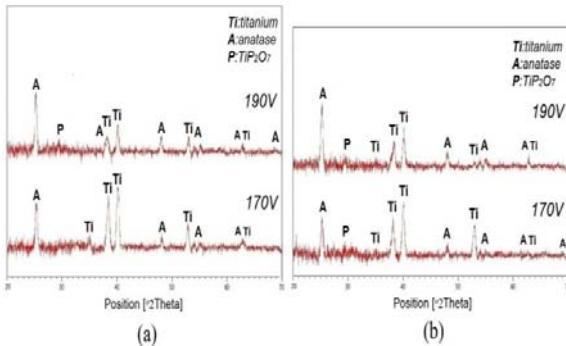
### Characterization

The mineralogical compositions of the films were determined using (1) Glancing angle X-ray diffraction (GAXRD: PANalytical X'Pert<sup>3</sup> Powder), (2) the microstructures were examined using a field emission scanning electron microscope (FESEM, Joel JSM-7600F) at an accelerating voltage of 20 kV, (3) the hydrophilicity of the film surface were tested with Water Contact Angle (WCA, Ramé-Hart instrument Co).

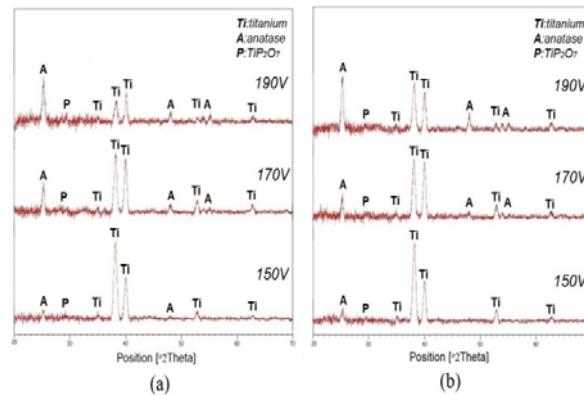
## RESULTS AND DISCUSSION

### X-ray diffraction

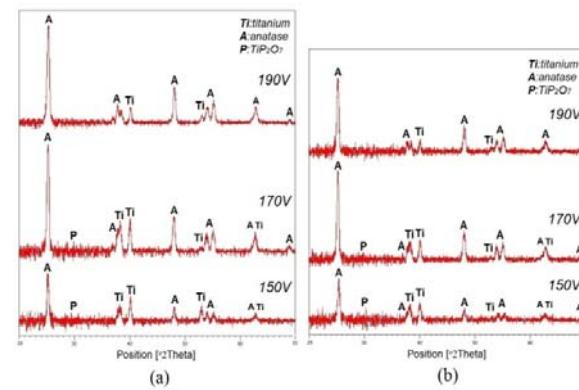
XRD spectra of anodised films in 0.5M  $\text{H}_2\text{SO}_4/0.1\text{M H}_3\text{PO}_4$  (Figure-1), 0.5M  $\text{H}_2\text{SO}_4/0.3\text{M H}_3\text{PO}_4$  (Figure-2), 1M  $\text{H}_2\text{SO}_4/0.1\text{M H}_3\text{PO}_4$  (Figure-3) and 2M  $\text{H}_2\text{SO}_4/0.1\text{M H}_3\text{PO}_4$  (Figure-4) under voltages (150-190 V (a)) at current density (40  $\text{mA}/\text{cm}^2$ ) and voltages (150-190 V (b)) at current density (60  $\text{mA}/\text{cm}^2$ ) respectively.



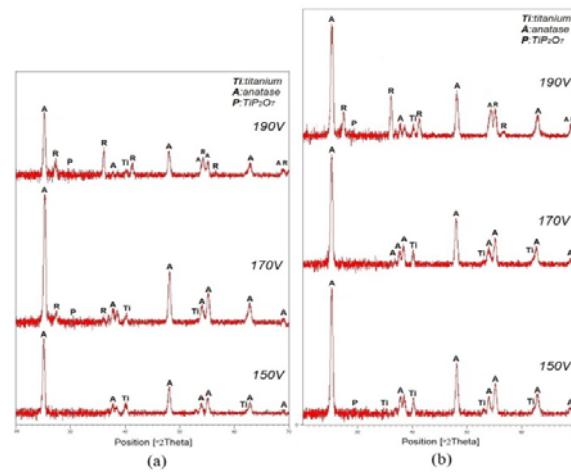
**Figure-1.** XRD spectra of anodized films in 0.5M  $\text{H}_2\text{SO}_4/0.1\text{M H}_3\text{PO}_4$ , (a) (170, 190 V) at current density (40  $\text{mA}/\text{cm}^2$ ) and (b) (170, 190 V) at current density (60  $\text{mA}/\text{cm}^2$ ).



**Figure-2.** XRD spectra of anodized films in 0.5M  $\text{H}_2\text{SO}_4/0.3\text{M H}_3\text{PO}_4$ , (a) (150-190 V) at current density (40  $\text{mA}/\text{cm}^2$ ) and (b) (150-190 V) at current density (60  $\text{mA}/\text{cm}^2$ ).



**Figure-3.** XRD spectra of anodized films in 1M  $\text{H}_2\text{SO}_4/0.1\text{M H}_3\text{PO}_4$ , (a) (150-190 V) at current density (40  $\text{mA}/\text{cm}^2$ ) and (b) (150-190 V) at current density (60  $\text{mA}/\text{cm}^2$ ).



**Figure-4.** XRD spectra of anodized films in 2M  $\text{H}_2\text{SO}_4/0.1\text{M H}_3\text{PO}_4$ , (a) (150-190 V) at current density (40  $\text{mA}/\text{cm}^2$ ) and (b) (150-190 V) at current density (60  $\text{mA}/\text{cm}^2$ ).

**Table-2.** Parameters used for anodic oxidation in  $H_2SO_4/H_3PO_4$  mixture electrolyte.

	<b>Current Work</b>	<b>Diamanti et al. (2011)</b>	<b>Abdullah (2010)</b>
Analytical Method	GAXRD	XRD	XRD
Experimental Conditions			
Solution	0.5/0.1 0.5/0.3 1/0.1 2/0.1	0.5/0.25	1.5/0.3
Potential (V)	150-190	100-200	90-180
Current Density ( $mA/cm^2$ )	40,60	80	5
Time (Min)	10	Few minutes	50
Anatase threshold	-	100 V	90 V

The following mineralogical results are observed:

The films from Figure-1 to Figure-3 consist of anatase and  $TiP_2O_7$  crystallines, and amorphous titania, according to diffraction peaks of anatase standard spectrum ( $TiO_2$ , JCPDS card #84-1286) and the peaks voltages (170, 190 V) contain anatase,  $TiP_2O_7$  and rutile( $TiO_2$ , JCPDS card #75-1753) crystallines.

In general, the intensity of the major peak increased with increasing applied voltage and current density. Molar concentration of  $H_3PO_4$  has inverse impact on the crystallinity, thus the peak intensity. This is clear in Figure-1 and Figure-2, where anatase peaks decreased at all voltages when  $H_3PO_4$  increased from 0.1 M to 0.3 M. An increase in  $H_2SO_4$  molarity results in higher amount of crystallinity, which is observed in Figure-2, Figure-3 and Figure-4, where anatase peaks grows higher at higher voltages. Rutile is formed alongside anatase at solution mixture with very high  $H_2SO_4$  concentration (2 M) at higher voltages (170, 190 V) at 40 and 60  $mA/cm^2$ . A predominance of anatase is noticed at all cases. This means that the amount and/or crystallinity of anatase are/is influenced with these parameters. Previous study have shown that films anodized in  $H_2SO_4$  electrolyte obtain anatase and rutile crystallines at potentials (120 V-140 V) (Saleh and Abdullah, 2015a) and anatase with amorphous  $TiO_2$  at potentials (200 V-350 V) in  $H_3PO_4$  electrolyte(Saleh and Abdullah, 2015b). Which confirm that slower crystallization in  $H_3PO_4$  than in  $H_2SO_4$ .A similar study by (Kern, Michler and Jäggi, 2005) have also concluded that for a given potential the crystallization is found more progressed in  $H_2SO_4$  than in  $H_3PO_4$ .

The different parameters with respect to anatase crystalline are obtained in Table-3. Anodization of sample under (150 V, 40  $mA.cm^2$  at 0.5 M  $H_2SO_4/0.1 M H_3PO_4$ ) could not be performed due to no electrical conductivity at low molar concentration and voltage, therefore samples (150 V at 40 and 60  $mA.cm^2$  at 0.5 M  $H_2SO_4/0.1 M H_3PO_4$ ) was not included in this comparison.

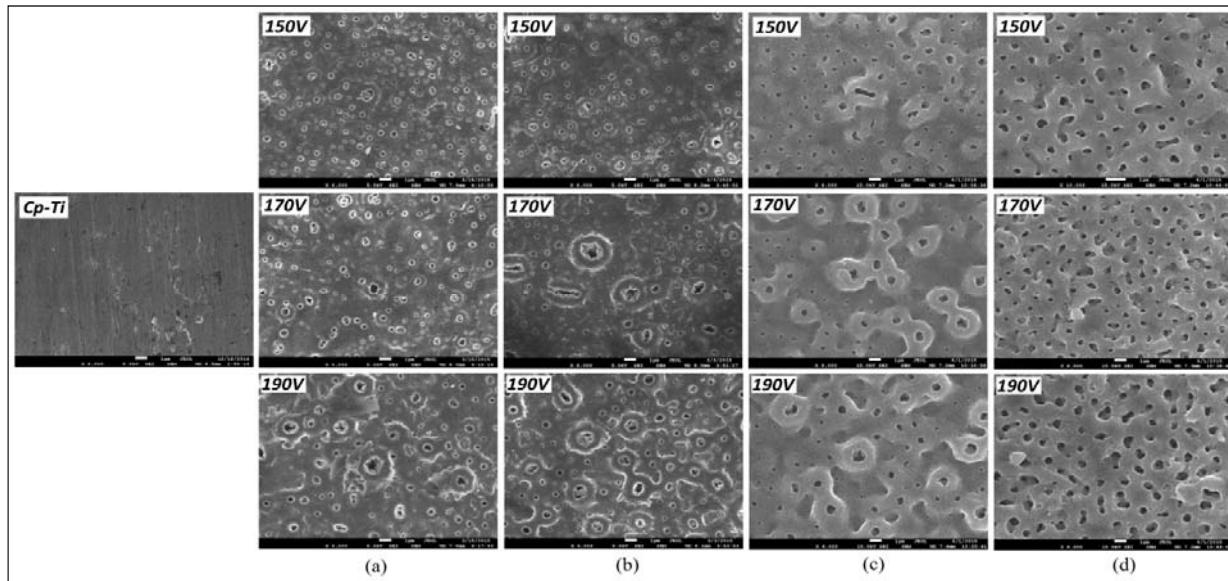
Table-2 observe similar studies used same experimental essentially the same condition, where (Diamanti et al., 2011) used GAXRD, while (Abdullah, 2010) used Raman microspectroscopy to analyze and observe the anatase crystallinity formation.

#### FESEM-images

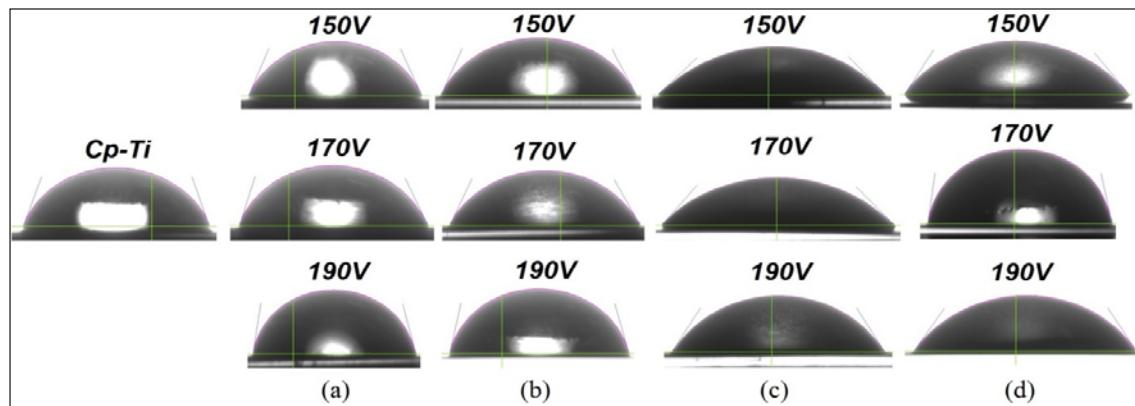
FESEM images show two types of surface morphologies as obtain in Table-4 and Figure-3, (1) a non-porous structure on natural Cp-Tiand, (2) a porous structure in which pore size increases with applied voltage (150-190 V) at current density of 60  $mA/cm^2$ . It is clearfrom the figure that surface morphology dependents on the electrolyte composition. Surface morphology have porous surface which resulted from local film breakdown. Films produced at 0.5 M  $H_2SO_4/0.1 M H_3PO_4$ , 0.5 M  $H_2SO_4/0.3 M H_3PO_4$  and 1 M  $H_2SO_4/0.1 M H_3PO_4$  at(Figure-5 (a), (b) and (c)) respectively observe donut shape porous structure with pore size can reach up to 1 $\mu m$  in diameter. When  $H_3PO_4$ concentration increased from 0.1 M (Figure-5 (a)) to 0.3 M (Figure-5 (a)) the donut shape pore size increased. While  $H_2SO_4$ concentration increase the donut shape pores flatten and transfer to flake pores as it is observed clearly at films produced at 2 M  $H_2SO_4/0.1 M H_3PO_4$  (Figure-5 (d)). The surface morphology at lower  $H_2SO_4$ concentration is more affected with  $H_3PO_4$ acid (Saleh and Abdullah, 2015a) as shown in films produced at Figure-5 (a).  $H_2SO_4$  have great effect on surface morphology as its concentration increase and this clear in Figure-5 (d) (Saleh and Abdullah, 2015b).

**Table-3.** Anatase phase obtained at different parameters in  $H_2SO_4/H_3PO_4$ mixture electrolyte.

<b>Molarity (M) <math>H_2SO_4/H_3PO_4</math></b>	<b>Current density (<math>mA.cm^2</math>)</b>	<b>Voltage (V)</b>		
		150	170	190
0.5/0.1	40			
	60			
0.5/0.3	40	150	170	190
	60	150	170	190
1/0.1	40	150	170	190
	60	150	170	190
2/0.1	40	150	170	190
	60	150	170	190



**Figure-5.** FESEM images of film surfaces (magnification X 6,000) is obtained as follows: (1) non-porous structure of Cp-Ti, (2) porous structure as a function of applied voltage at molar concentrations, (a) 0.5 M H<sub>2</sub>SO<sub>4</sub>/0.3 M H<sub>3</sub>PO<sub>4</sub>, (b) 0.5 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub>, (c) 1 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub>and (d) 2 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub>and current density 60 mA/cm<sup>2</sup>



**Figure-6.** Images of WCA of film is obtained as follows: (1) Cp-Ti, (2) as a function of applied voltage at molar concentrations, (a) 0.5 M H<sub>2</sub>SO<sub>4</sub>/0.3 M H<sub>3</sub>PO<sub>4</sub>, (b) 0.5 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub>, (c) 1 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub>and (d) 2 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub>and current density 60 mA/cm<sup>2</sup>.

### Surface hydrophilicity

The WCA was measured for (1) Cp-Ti and (2) anodized samples at 0.5 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub> (Figure-6 (a)), 0.5 M H<sub>2</sub>SO<sub>4</sub>/0.3 M H<sub>3</sub>PO<sub>4</sub> (Figure-6 (b)), 1 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub> (Figure-6 (c)) and 2 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub> (Figure-6 (d)) at 60 mA/cm<sup>2</sup> as obtained in Table-5 using a 4 µm droplet of distilled water on the sample surface for 1 min after autoclaving. In general, the coated samples have shown to be more hydrophobic at higher voltages while observed to be more hydrophilic at higher molarity. An increase in H<sub>3</sub>PO<sub>4</sub> concentration from 0.1 M (Figure-6 (a)) to 0.3 M (Figure-6 (b)) results in more hydrophilic surface, also hydrophilicity is more likely to increase at higher H<sub>2</sub>SO<sub>4</sub> concentration with sample anodized at 1 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub> (150 V (c)) in Figure-6 have the lowest contact angle, thus the highest surface energy.

While samples anodized at 0.5 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub> (190 V (a)) in Figure-6 have shown more hydrophobic thus, lower wettability. The increase of anatase crystalline with increasing molarity could be related to the more wettability, an exception for the less wettability for sample surfaces produced at 2 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub> could be due to the rutile presence according to GAXRD results. Previous work on surface samples anodized in H<sub>2</sub>SO<sub>4</sub> electrolyte observed hydrophobic surface as the voltage and molar increased (Saleh and Abdullah, 2015a), while films produced in H<sub>3</sub>PO<sub>4</sub> electrolyte have observed hydrophilic with increasing voltage and molar concentration. A study by (Yamamoto *et al.*, 2012) concluded that anatase containing coatings show higher hydrophilic surface than rutile containing oxides, and this phenomena could relate to the presence



and/or absence of OH groups and hydrocarbons on the surface.

**Table-4.** Anodized samples based on surface structure at 60 mA/cm<sup>2</sup>.

Molarity (M)	Non-porous structure	Porous structure		
		Voltage (V)		
0.5/0.1	Cp-Ti	150	170	190
0.5/0.3		150	170	190
1/0.1		150	170	190
2/0.1		150	170	190

**Table-5.** Contact angles and surface energies for samples anodized mixed at 60 mA/cm<sup>2</sup>.

Sample	Contact angle	Surface energy (mJ/m <sup>2</sup> )
CP-Ti	71.70 ± 0.02°	40.66 ± 0.01
		0.5 M H <sub>2</sub> SO <sub>4</sub> /0.1 M H <sub>3</sub> PO <sub>4</sub>
150 V	67.89 ± 0.04°	43.02 ± 0.02
170 V	70.02 ± 0.02°	41.70 ± 0.01
190 V	79.07 ± 0.02°	36.06 ± 0.01
		0.5 M H <sub>2</sub> SO <sub>4</sub> /0.3 M H <sub>3</sub> PO <sub>4</sub>
150 V	64.23 ± 1.43°	45.26 ± 0.88
170 V	64.47 ± 0.03°	45.12 ± 0.02
190 V	76.82 ± 0.01°	37.47 ± 0.01
		1 M H <sub>2</sub> SO <sub>4</sub> /0.1 M H <sub>3</sub> PO <sub>4</sub>
150 V	47.04 ± 0.03°	55.46 ± 0.02
170 V	49.09 ± 0.02°	54.29 ± 0.01
190 V	59.46 ± 0.03°	48.16 ± 0.02
		2 M H <sub>2</sub> SO <sub>4</sub> /0.1 M H <sub>3</sub> PO <sub>4</sub>
150 V	55.95 ± 0.02°	50.27 ± 0.01
170 V	80.66 ± 0.02°	35.07 ± 0.01
190 V	57.69 ± 0.02°	49.23 ± 0.01

## CONCLUSIONS

Anodic oxidation used to form thick oxide layer on Cp-Ti foils in phosphoric acid electrolyte to evaluate the effects of pure titanium in order to maximize and characterize the TiO<sub>2</sub>anatase crystalline phase under potentials 200 V-350 V for 10 min. According to GAXRD results the intensity of the major peak increased with increasing applied voltage and current density. Molar concentration of H<sub>3</sub>PO<sub>4</sub> has inverse impact on the crystallinity, thus the peak intensity. Anatase peaks decreased at all voltages when H<sub>3</sub>PO<sub>4</sub> increased from 0.1 M to 0.3 M. An increase in H<sub>2</sub>SO<sub>4</sub> molarity results in higher amount of crystallinity, where anatase peaks grows higher at higher voltages. Rutile is formed alongside anatase at solution mixture with very high H<sub>2</sub>SO<sub>4</sub> concentration (2 M) at higher voltages (170, 190 V) at 40 and 60 mA/cm<sup>2</sup>. A predominance of anatase is noticed at all cases. This means that the amount and/or crystallinity of anatase are/is influenced with these parameters. FESEM images observed porous structure in which pore size increases with applied voltage (150-190 V) at current density of 60 mA/cm<sup>2</sup>. Surface morphology depends

on the electrolyte composition. Surface morphology have porous surface which resulted from local film breakdown. Films produced at 0.5 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub>, 0.5 M H<sub>2</sub>SO<sub>4</sub>/0.3 M H<sub>3</sub>PO<sub>4</sub> and 1 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub> at 60 mA/cm<sup>2</sup>observed donut shape porous structure with pore size can reach up to 1μm in diameter. When H<sub>3</sub>PO<sub>4</sub> concentration increased from 0.1 M to 0.3 M the donut shape pore size increased. While H<sub>2</sub>SO<sub>4</sub>concentration increase the donut shape pores flatten and transfer to flake pores as it is observed clearly at films produced at 2 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub>at 60 mA/cm<sup>2</sup>.WCA results of the coated samples have shown to be more hydrophobic at higher voltages while observed to be more hydrophilic at higher molarity. An increase in H<sub>3</sub>PO<sub>4</sub> concentration from 0.1 M to 0.3 M results in more hydrophilic surface, also hydrophilicity is more likely to increase at higher H<sub>2</sub>SO<sub>4</sub> concentration with sample anodized at 1 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub>at 150 V at 60 mA/cm<sup>2</sup> have the lowest contact angle, thus the highest surface energy. While samples anodized at 0.5 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub> at 190 V 60 mA/cm<sup>2</sup>have shown more hydrophobic thus, lower wettability. The increase of anatase crystalline with increasing molarity could be related to the more wettability, an exception for the less wettability for sample surfaces produced at 2 M H<sub>2</sub>SO<sub>4</sub>/0.1 M H<sub>3</sub>PO<sub>4</sub>at 60 mA/cm<sup>2</sup>could be due to the rutile presence according to GAXRD results.

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