



# Electrical characteristics and discharge properties of hybrid plasma electrolytic oxidation on titanium



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## ABSTRACT

In this study double-layered plasma electrolytic oxidation coatings are synthesized by coating in two different electrolytes. The effects of electrical properties of first fabricated layer (in first electrolyte) on morphology and properties of total hybrid coating are investigated. First layers were applied in four different basic electrolytes consisting of sodium phosphate/citrate (PC), sodium phosphate/silicate (PS), sodium phosphate/tungstate (PT), and sodium phosphate/aluminate (PA) solutions and the second layer was synthesized in calcium acetate/sodium dihydrogen phosphate hydrate solution. The top surface and cross sectional morphology, composition and corrosion resistance properties were thoroughly studied by scanning electron microscopy (SEM), X-ray diffraction (XRD), potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and Mott-Schottky analysis (M-S) methods. It was found that the morphology of the second layer depends on the morphology of the first layer, in terms of shape and size of the pores. However, XRD analysis revealed that there was no significant difference between the compositions of the oxide layers. Application of the second layer over PS sample reduced corrosion resistance from 163 to 95 KΩ cm<sup>2</sup> while application of the second layer over PT sample led to increase of corrosion resistance from 31 to 126 KΩ cm<sup>2</sup>. The constructive or destructive role of two layers was correlated to discharge energy of the second layer which is in turn determined by the required energy for electrical charging of the first layer. The energy of electrical charging of PS and PT samples are 0.04 and 1.17 J, respectively. Therefore, plasma discharges over PS sample have higher energy, compared to PT sample, and as a result, corrosion resistance of barrier layer of PS sample drops. Electrical parameters extracted from M-S tests also verified our theory that donor density and capacitance of the first layer affect discharge behavior and intensity of the second layer. M-S results are also in conformance with evaluated corrosion resistances measured by EIS method.

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## 1. Introduction

Titanium and its alloys are widely used in biomedical applications owing to their favorable mechanical properties and low toxicity. However, the natural passive film of un-treated titanium surface is known to be bio-inert which shows low level of bio-activity and biocompatibility [1]. Moreover, the natural passive film might be destroyed when used for implant applications, due to presence of mechanical loads and chemical environment [2]. When titanium implant is used *in vivo*, Ti<sup>4+</sup> ions are released gradually due to corrosion and accumulate in the surrounding tissue which

might adversely affect the biocompatibility [3]. The problem would be more serious when other metallic ions are released from the substrate: such as Al and Zr [4]. Surface treatments such as physical vapor deposition (PVD) [5], chemical vapor deposition (CVD) [6], and sol-gel [7] were commonly used to improve the surface properties. Among the conventional methods, plasma electrolytic oxidation (PEO) is highly interested, due to its high flexibility. This method develops a thick oxide layer, compared to the natural passive layer, which improves the corrosion and wear resistance [8]. Introduction of metallic and non-metallic elements to the oxide layer might be used to improve corrosion and erosion performance of oxide layer [9,10]. Furthermore, PEO coating usually develops a porous morphology, which is favorable for biocompatibility properties such as osseointegration, proliferation and differentiation [11,12] and also it has the advantage of being able to control the stoichiometric chemical composition of the coating [13].

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Hybrid coating, combination of two coating methods, might be used for improvement of coating properties. For instance, combination of PVD, CVD, magnetron sputtering, impregnation and plasma electrolytic oxidation methods might be used. In the current paper, term “hybrid coating” refers to two-step coating by PEO coating but with different electrolytes. Application of post-treatments mechanical pre-treatments such as SMAT and sand blasting [14] and post-treatments such as alkali treatment [15], electrophoretic deposition [16] and impregnation [17] have been widely used for further improvement of properties of PEO coatings. However, hybrid PEO coatings that are successively synthesized in two different electrolytes have been rarely studied. Firstly, the samples are coated in first electrolyte (PS, PA, PT and PC) and subsequently, samples are washed, rinsed, dried and placed in the second electrolyte. After placing in the second electrolyte, voltage is applied up to breakdown voltage and then discharges appear on the surface and second layer develops.

Dual PEO coating might be used to improve corrosion resistance, wear resistance or other desired properties. Kumar et al. [18] studied dual PEO coating on AZ31 Mg alloy in phosphate and silicate electrolytes. They found that hybrid PEO coating modifies surface morphology and as a result corrosion resistance is improved and corrosion current density is reduced. Tsunekawa et al. [19] found that application of two-step PEO coating in aluminate and sulfuric/phosphoric solution enhances wear resistance significantly. It was reported post treatment in acidic solution leads to development of an intermediate layer and oxide layer develops inward. As a result, the weak primary wear resistance was improved due to enhanced adhesion strength.

The aim of this study is to synthesize a double-layered Ca/P PEO coating which has higher corrosion performance than conventional single-layered PEO coatings. Selection of the first layer plays an important role in determination of discharge pattern and characteristics of the second layer and it is suggested that internal complexity and morphology of the first layer have constructive role in determination of the characteristics of the hybrid coating. The aim of this research is to highlight the role of first layer's properties on corrosion resistance and morphology of the second layer. Usually, electrolytes with two or more constituents provide a fine microstructure with enhanced corrosion resistance, compared to single-constituent electrolytes [20]. Therefore, mixture of phosphate-based electrolytes with sodium silicate, sodium tungstate, sodium citrate and sodium aluminate are studied.

## 2. Experimental procedure

### 2.1. Sample preparation

Samples were cut with dimension of  $4 \times 4 \times 0.5$  mm<sup>3</sup> from a sheet of commercially pure titanium. Prior to coating, samples were ultrasonically cleaned in ethanol, rinsed by distilled water, and finally dried by air. A home-made 20KW DC power source with constant current regime was used for PEO treatment. Stainless steel cooling system, which was also used as cathode, was designed to keep the temperature of the electrolyte below 30 °C. The first layer was synthesized in 4 different electrolyte mixtures, according to Table 1. Afterwards, samples were washed with ethanol followed by rinsing and drying. Coating of the second layer was carried out in the electrolyte composed of 0.2 M Ca(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> (calcium acetate) and 0.1 M NaH<sub>2</sub>PO<sub>2</sub>·2H<sub>2</sub>O (Sodium hypophosphite monohydrate).

### 2.2. Voltage-time graphs

Appa 503 multimeter was used to record voltage variations against coating time. Recording was done with 1 Hz of frequency.

### 2.3. Microstructure and morphology

Surface and cross section of the single and hybrid coatings were studied by scanning electron microscope (SEM, Philips XL30) operating at 25 kV. Thickness measurements were carried out on the cross section image to obtain average value of thickness.

### 2.4. X-ray diffraction

Phase constituents of PEO coatings were identified by X-ray diffraction (XRD, Philips X'Pert, Netherlands). XRD patterns were recorded in a 2 $\theta$  range of 10° to 100°.

### 2.5. Corrosion tests

Corrosion behavior of the coatings was studied by potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) tests. Corrosion tests were carried out in Ringer's simulated body fluid [21], composed of 8.6 g dm<sup>-3</sup> NaCl, 0.3 g dm<sup>-3</sup> KCl, and 0.48 g dm<sup>-3</sup> CaCl<sub>2</sub>·6H<sub>2</sub>O and using potentiostat/galvanostat (EG&G model 273A). Samples were immersed the Reinger's solution about 30 min at room temperature to reach the steady-state potential. The samples were polarized from -250mV to +2000 mV vs. OCP with the scan rate of 1 mV/s. Corrosion parameters (corrosion resistance (R<sub>p</sub>), corrosion potential (E), and corrosion current density (i<sub>corr</sub>)) were calculated from Tafel extrapolation of polarization curves using power suite software. EIS measurements were carried out in frequency range of 1 Hz–65535 Hz and amplitude of  $\pm 10$ mV was applied. Zview software was used to fit the electrical equivalent circuits (EEC) to the experimental data and to obtain the appropriate EEC.

### 2.6. Mott-Schottky analysis

The semiconducting properties of coatings were studied by Mott-Schottky (M-S) analysis. Capacitance measurements were performed cathodically between -1000 mV vs. SCE to +1000 mV vs. SCE with intervals of 100 mV at 10<sup>4</sup> Hz of frequency. High frequency was chosen for M-S analysis to ensure that the solid state of the interface is being studied [22]. The capacitance values were calculated by measurement of imaginary impedance at frequency of 10<sup>4</sup> Hz and employing  $C = 1/\omega Z''$ , where Z'' is imaginary impedance at 10<sup>4</sup> Hz frequency and  $\omega$  is angular frequency ( $\omega = 2\pi f$ ) [23].

## 3. Results and discussions

### 3.1. Voltage-time

Schematic view of PEO is presented Fig. 1. Initially when voltage is applied Ti starts to dissolve and Ti<sup>4+</sup> ions are produced. OH<sup>-</sup> and O<sup>2+</sup> ions, produced through electrolyte reactions, react with Ti<sup>4+</sup> ions to form an oxide layer [24]. When the oxide layer develops, resistance of the oxide layer drops and subsequently, more voltage is needed to be applied. Variation of voltage during coating is indicative of coating growth. Studying of voltage variations provide insight into the underlying reasons for morphological changes and developed microstructures.

Fig. 2 shows variation of voltage during coating of single- and double-layered samples. Usually, in the first step of coating voltage increases sharply due to passivation of the substrate [25]. During this step, a passive layer develops due to interaction of electrolyte and substrate, same as conventional anodizing. Development of the passive layer is accompanied by release of gas bubbles from sample surface. Since we are focused on the events which take place during

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