The effect of pulsed current electrodeposition parameters of calcium phosphates coating on Ti6Al4V ELI

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Abstract. Pulse current electrodeposition is a technique of special interest, due to the advantages it has, like easy operation, high control in the amount, homogeneity and purity of the deposited material, and low cost. This work studies the influence of the pulsed electrodeposition parameters variation on the characteristics of calcium phosphates coatings, including the composition, crystallinity and morphology. The influence of the current density and pulse on and off time on the physicochemical properties of the obtained coatings were evaluated. The coatings were electrodeposited on Ti₆Al₄V using Ca(NO₃)₂·H₂O and NH₄H₂PO₄ with a Ca/P molar ratio of 1.67. The coatings were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). The analysis of DRX confirmed the formation of HAP. The results revealed that the variation of the current density modified the morphology of the coating. Also, the amount of material deposited increases as the off-time pulse increases, allowing the diffusion of the ions in the solution towards the working electrode.

1. Introduction
Titanium and its alloys are materials widely used in orthopedic implants due to its excellent corrosion resistance and biocompatibility, however, these materials show low chemical bonding with osseous structures [1]. Bioactive materials, such as calcium phosphates, can improve the osteoconductive and osseointegration of orthopedic prosthesis, and have good adaptation with the human body, high crystallinity and biocompatibility [2]. The calcium phosphates have been widely used as coating on bio-inert materials such as the Ti₆Al₄V alloy. Since this one is present in the mineral bone phase, it encourages the regeneration of the surrounding osseous tissue in the implant. In order to obtain calcium phosphates coatings on metallic surfaces, studies have been carried out applying techniques such as Electrophoretic deposition [3], Sol-Gel [4], plasma spraying [5,6], pulsed laser deposition [7], and electrochemical deposition [8-10]. Several authors have a great interest in electrochemical deposition due to the advantages of this technique, since it is easy to apply on pieces with irregular shapes and the pieces can be coated at low temperature and low cost of operation. The amount of material deposited in the coatings can be modified by controlling the process variables such as time, temperature, current density and number of pulses applied. In the present text we studied the influence of current density and pulse on/off ratio on the morphology and structure of coatings on Ti₆Al₄V obtained by means of pulsed current electrodeposition.
2. Materials and methods

Ti₆Al₄V cylindrical discs with 14 mm diameter and 3 mm thick were used as the substrate for the pulsed electrodeposition. The specimens were polished with sandpaper with different grades from 400 to 1200 grit, after polishing, the substrate was pre-etched in an acidic mixture (HF:HNO₃:H₂O=1:3:10) for 30s, washed with distilled water and cleaned by sonication in ethanol for 15 minutes.

The electrolyte for deposition was prepared by mixing 0.042mol/L of Ca(NO₃)₂·H₂O and 0.025mol/L of NH₄H₂PO₄ with a Ca/P molar ratio of 1.67. The pH of the electrolyte was adjusted to 4.5 using NH₄OH and the temperature was maintained at 65°C, the magnetic stirring was of 450rpm to keep the uniform concentration of the electrolyte. The electrodeposition was performed in a three-electrode cell using a Gamry reference 600 potentiostat; Ti₆Al₄V was used as a working electrode, a platinum mesh as a counter (anode) electrode and the reference electrode was a standard silver-silver chloride (Ag/AgCl in saturated KCl). The deposition process was carried out in a galvanostatic mode and the deposition time was 30min. The current density values were i_on=10mAcm⁻², i_off=0mA.cm⁻² and i_on=20mA.cm⁻², i_off=0 mAcm⁻², the on time (t_on) pulsed was 1s and the off time (t_off) pulsed were varied as 4s and 8s. After deposition, the specimens were removed from the electrolyte solution, washed with distilled water and dried at 70°C for 5h and annealed at 550°C for 2h.

The samples of pulsed electrodeposition of calcium phosphates on Ti₆Al₄V with 1s constant pulse on time will refer: P1—10mA.cm⁻², 4s pulse off time, P2—10mA.cm⁻², 8s pulse off time, P3—20mA.cm⁻², 4s pulse off time and P4—20mA.cm⁻², 8s pulse off time.

The surface characterization of the coatings was carried out by (Quanta FEG-650 field emission scanning electron microscope (FESEM)). It was used to observe the morphology of the calcium phosphates coating deposited by electrochemical deposition method, and the Bruker D8 advance X-ray diffractometer (XDR) with Cu Kα radiation generated at 40kV and 40mA was used for studying the crystallinity and the present phases on the coating. The chemical composition of the coating was analyzed for Fourier transform infrared spectroscopy (FT-IR) using Nicolet iS50 Spectrometer with ATR technique. The spectrum range was from 1600cm⁻¹ to 400cm⁻¹ with a number of 32 scans at the 4cm⁻¹ resolution.

![Figure 1](image_url)  
Figure 1. Pulsed current scheme.

3. Results

Figure 2 shows SEM images of the calcium phosphates coating on Ti₆Al₄V by pulsed electrodeposition for 30min at constant pulse on time of 1s, varying the current density and off time pulse. The surface morphology obtained from the coating changes a little with increasing current density, mostly needle-like and plate-like structures were formed. This structure difference could be attributed to a small amount of Brushite (CaHPO₄·H₂O) and calcium pyrophosphate (Ca₃P₂O₇) contained in the as-deposited coating. A needle-like structure may be beneficial for bone growth, as reported Seyedraoufi et al and Liou et al [11,12].

The needle-like coating deposited crystal sizes were uniform. Nevertheless, there is a decrease in the size of the crystals with the increasing current density Figure 2(a1, b1 and c1). In the same way, it is observed that when the pulse off time is at 8s, the crystal sizes are bigger than the registers for off time pulse at 4s as show Figure 2(b1, c1 and d1). This can be related to a change in the transport mechanisms...
that could affect the nucleation and growth mechanisms of the deposited crystals [13]. On the other hand, Figure 2(d1). Shows a coating with more porosity, the reason for this may be that, when current density increases at 20mAcm\(^{-2}\), the cathodic hydrogen evolution reaction increases too, and the escaping \(\text{H}_2\) gas leads to a porous structure in the layer. Cracking is not observed on the coating obtained by pulsed electrodeposition.

**Figure 2.** SEM morphologies and cross-sectional image and EDS elemental mappings of coating on Ti6Al4V by pulsed electrodeposition with 1 s constant pulse on time and (a) P1 (b) P2 (c) P3 (d) P4.

The cross sections of the coating along with substrates material have been presented in Figure 2(a2, b2, c2 and d2) in order to assess the coating thickness at various current densities and off time pulsed. The thickness of the calcium phosphates coating on Ti6Al4V at different conditions ranged from 4 to 31\(\mu\)m. The thickness measurement for coated sample at pulsed time of 4s with low current density 10mAcm\(^{-2}\) resulted in 4.75\(\mu\)m (Figure 2(a2)). When the current density increased to 20mAcm\(^{-2}\), the thickness was 31.39\(\mu\)m (Figure 2(c2)), in the same way, the sample at pulsed time of 8s with 10mAcm\(^{-2}\) presented a thickness of 13.465\(\mu\)m (Figure 2(b2)) and for 20mAcm\(^{-2}\) it was 14.83\(\mu\)m (Figure 2(d2)). Hence, the coating obtained by the pulsed electrodeposition method with increases in the current density...
produces a thicker coating than the one that can be obtained from a low current density and it’s further supported by the results from Chakraborty et al. and Gopi, et al. [14,15].

The mapping was carried out to evaluate the distribution of calcium and phosphorus on \textit{Ti}_{6}A_{1}V. EDS elemental mappings of the coating are shown in Figure 2 and it can be inferred that the Ca, P and O are uniformly distributed on the substrate.

The XRD patterns of the layer deposited on the \textit{Ti}_{6}A_{1}V substrates after annealing obtained at constant 1s pulse on are presented in Figure 3(a-d). The results indicate that Calcium phosphates crystals were successfully fabricated by pulsed electrodeposition. The patterns indicated that during the electrodeposition process a mixture in the coating whose contents were hydroxyapatite, brushite and calcium pyrophosphate was obtained. The diffraction peaks are observed at 2θ values for HA at 25.8°, 32.2° and 40.5°, for calcium pyrophosphate at 26.7°, 38.5, 47.05° and brushite 29.2° and 35.4°. Similar results were observed in other research by Gopi \textit{et al} and Sameri \textit{et al.} [15,16].

Figure 4(a-d) represents the FTIR spectra of the calcium phosphates coating. The bands characteristics for HA, CaHPO$_{4}$·H$_{2}$O and Ca$_{3}$P$_{2}$O$_{7}$ have been reported in the literature [17–19]. The bands characteristics for PO$_{4}^{3-}$ appear at 497-557, 1032-1188cm$^{-1}$ and for P$_{2}$O$_{7}$ appear at 719 and 923cm$^{-1}$ respectively. The trace at 497cm$^{-1}$ is attributed to the band PO$_{4}^{3-}$ bending O─P─O (υ1), the bending mode for the phosphate group O─P─O (υ4) is reflected at 533, 557cm$^{-1}$ and stretching mode P─O (υ3) of the PO$_{4}^{3-}$ 1032, 1075, 1135, 1168 and 1188cm$^{-1}$. On the other hand, the bands assigned to pyrophosphate groups P$_{2}$O$_{7}$ are attributed to the conversion of CaHPO$_{4}$ into Ca$_{3}$P$_{2}$O$_{7}$ during annealing, as reported by Raynaud [17]. In fact, the results of FTIR spectra corroborate the results of XRD regarding the obtainment of calcium phosphates coating by the pulsed electrodeposition.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{The XRD patterns of coating obtained pulsed electrodeposition with 1s constant pulse on time and (a) P1 (b) P2 (c) P3 (d) P4.} 
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{FT-IR spectra of coating obtained pulsed electrodeposition with 1s constant pulse on time and (a) P1 (b) P2 (c) P3 (d) P4.} 
\end{figure}

4. Conclusion
In this study, calcium phosphate coatings were produced by pulsed electrodeposition at different current densities and pulse off time. Calcium phosphates coating with mostly needle-like partially and plate-like structures morphology were formed by the pulse electrodeposition method. The patterns of XDR and FTIR show that the as-deposited coating contained calcium phosphates such as HA, CaHPO$_{4}$·H$_{2}$O and Ca$_{3}$P$_{2}$O$_{7}$. Results showed that pulse electrodeposition parameters have an effect on the morphology and crystal size of the coatings. The SEM results revealed that the size of the crystals varies with the increase of the current density. In the same way, the coating presents a higher porosity when it is electrodeposited with a current density of 20mAcm$^{-2}$. The increment of pulse off time effectively influenced the coating. The thickness of the deposited coating increases as the off-time pulse increases; the range of the thickness was about 4 to 31μm. Furthermore, it is believed that the off time pulsed in
the electrodeposition affects the nucleation and growth mechanisms of the deposited crystals maintaining more favorable conditions for deposition.

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