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Effect of substrate nature on the electrochemical deposition of calcium-deficient hydroxyapatites

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Abstract. Calcium phosphates were obtained by reducing nitrate ions to produce hydroxide ions on TiO₂/stainless steel and TiO₂/titanium electrodes. TiO₂ coatings on metallic substrates were prepared by sol-gel dip-coating method. The morphology of deposits was observed by FESEM. Chemical nature of calcium phosphate deposits was identified by Raman micro-spectroscopy and FESEM/EDS microanalysis. Electrochemical behavior of nitrate and nitrite reduction on stainless steel and titanium electrodes was studied by linear sweep voltammetry. In addition, voltammetric study of the calcium phosphate electrodeposition on both electrodes was performed. From these measurements was selected the potential to form a calcium phosphate. A catalytic current associated to nitrate reduction reaction was obtained for stainless steel electrode, leading to significant deposition of calcium phosphate. Ca/P ratio for both substrates was less than 1.67. The formation of calcium deficient hydroxyapatite was confirmed by Raman spectroscopy.

1. Introduction

Calcium phosphates (CP) are ceramics used as coatings to improve the biocompatibility between an implant and the damaged tissue during the surgery recovering, because its composition is similar to osseous tissues, besides has been demonstrated that CP promote the tissue growth [1]. Depending on pH, temperature of synthesis and mainly Ca/P ratio, different CP phases can be obtained, such as dicalcium phosphate dehydrate (DCPD), octacalcium phosphate (OCP), hydroxyapatite (HAp) and calcium-deficient hydroxiapatite (CDHAp), being this latter one the most studied in biomedicine. Although HAPs are widely known by their high bioactivity in reparation or substitution of bond [2], other CP exhibits a more extended applicability. Thus, CP as DCPD and CDHAp have a high commercial interest since they have been used as bioinorganic material in tooth calcification [3], and as drugs nanocarriers for periodontitis treatment [4].

The CP are usually obtained as coatings on metallic substrates for biomedical applications, employing conventional techniques as plasma spraying [5], chemical vapor deposition [6] and sputtering [7], which requires simultaneously high vacuum and control of temperature, high power laser or an electron beam to perform the process. In addition, CP powders are used as starting material, thereby elevating the cost of synthesis. Electrochemical deposition of CP has been considered as an attractive alternative to obtain coatings on diverse sizes or shapes of metallic substrates. Modification either of the applied current or potential, or the chemical composition of the deposition bath, can lead to morphological change. Besides depending on time and temperature, different coating thicknesses



are achieved [1]. Different electrolytes have been used to prepare CP coatings on titanium [2] and stainless steel [3] substrates. Nitrates are preferred over other electrolytes because they can be electrochemically reduced generating hydroxide ions (OH^-), which increases the interfacial pH, and causes the precipitation of CP [2,3].

Recently, stainless steel surfaces have been coated with a TiO_2 sol-gel film to improve their corrosion resistance and the adhesion of CP during its deposition [8], but as far as it knows, there is no reports on the influence of substrate nature on the CP electrodeposition.

2. Experimental

2.1. Preparation of electrodes

Commercial AISI 304 stainless steel (SS) and titanium (Ti, 99.5% of purity) plates were polished with SiC emery papers of different grades. Samples were degreased with ethanol, acetone, and rinsed with deionized water for 5min in each solvent. TiO_2 films were prepared by sol-gel method and deposited on SS and Ti substrates by dip-coating technique, details of the method can be found elsewhere [9]. Coatings were dried at 100°C and annealed at 400°C during 2h at a heating rate of 3°C min^{-1} .

2.2. Physicochemical and electrochemical characterization

Electrochemical measurements were performed in a three-electrode cell with a jacket for temperature control. SS or Ti disk electrodes (diameter: 6.0mm) or TiO_2/SS or TiO_2/Ti plates were used as working electrode. A graphite rod (AGKSP grade) was employed as counter electrode while an Ag/AgCl (3M KCl) was used as reference electrode. The composition of electrolyte solution to deposit electrochemically CP was 0.1M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.06M $\text{NH}_4\text{H}_2\text{PO}_4$ at pH 5.0, adjusted with 1M NaOH. In order to determine the condition to perform the CP electrodeposition, voltammetry measurements for SS and Ti electrodes without TiO_2 coating were carried out in negative direction from open circuit potential at 298K, 313K and 323K. The aforementioned electrodes were also characterized in a) 0.1M NaNO_2 , b) 0.1M NaNO_3 and c) 1M NaNO_3 with and without stirring. The deposition of CP on TiO_2/SS and TiO_2/Ti electrodes was performed applying a bias potential of -1.41V at 323K during 30min. All measurements were performed using an Autolab PGSTAT 302N potentiostat and Nova software. The surface of TiO_2/SS and TiO_2/Ti electrodes coated with CP was observed with a FESEM (Quanta FEG 650), and their chemical composition was analyzed with an EDAX Apollo X. Raman spectra were obtained using a confocal high-resolution Raman spectrometer with a 473nm blue laser, integration time of 2s and an average of 100 scans.

3. Results and discussion

3.1. Electrochemical characterization

Cracking of TiO_2 films has frequently been reported in the literature [9,10]. When a sol-gel film is immersed in a solution, inter-crack spacing causes exposure of the substrate to solution. For this reason, initial electrochemical study was performed on metallic substrates. Figure 1 shows the electrochemical behavior of nitrate and nitrite ions on stainless steel in the potential range from $\sim -0.3\text{V}$ to -1.2V . In both cases, a reduction peak appears at -0.61V and -0.65V under quiet condition. These peaks can be associated either to nitrate or nitrite reduction [11], or to iron oxides reduction from passive layer of SS [12]. In order to know more about the reduction process, solution was stirred (Figures 1(a'), (b')). An increase of the current was registered for nitrate and nitrite solutions in disturbed condition, indicating that process depends on ion concentration at interface. However, increasing the nitrate concentration 10 times and maintaining the solution stirred, the magnitude of the current stayed the same (Figures 1(b'), (c)); hence, the reduction peak at $\sim -0.6\text{V}$ corresponds to Fe(III) reduction from passive layer of SS [12].

Figure 2 shows the electrochemical behavior of nitrate and nitrite ions on titanium, a significant increase of current around -1.1V is observed, which is also registered for SS. In addition, current of C2

and C3 peaks increases as the temperature of system increases. According to literature [11], these processes are associated to nitrate and nitrite reduction, Equations (1) and (2).

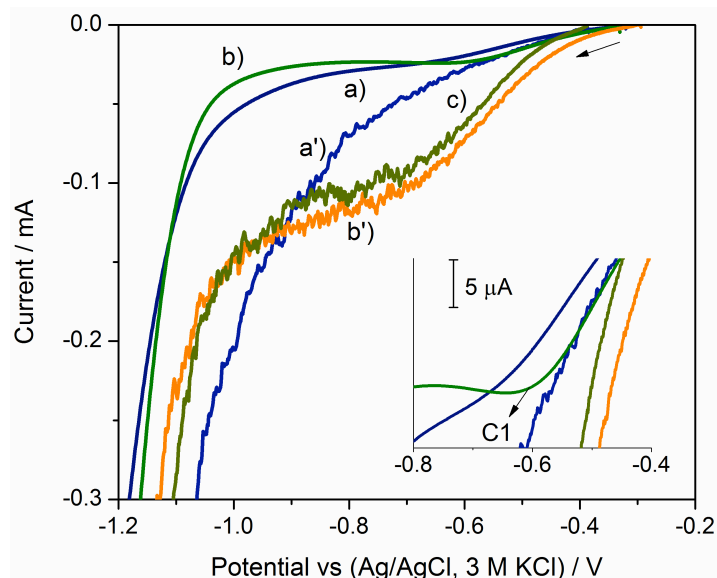
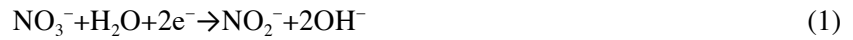


Figure 1. Voltammetric responses of (a) 0.1M NaNO₂, (b) 0.1M NaNO₃ and (c) 1.0M NaNO₃ under quiet (a), (b) and disturbed (a'), (b'), (c) conditions.

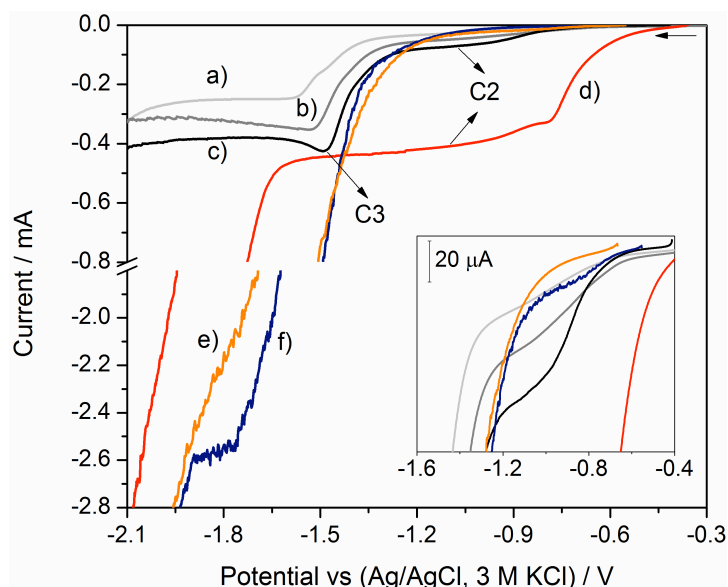


Figure 2. Nitrate reduction on (a)-(c) titanium and (d) stainless steel in a phosphate containing electrolyte at (a) 298K, (b) 313K and (c) 323K. Reduction of (e) nitrite and (f) nitrate ions on stainless steel at 298 K under disturbed condition.

The nitrate and nitrite reduction processes occurs at C2 and C3 peaks, respectively. On the other hand, the current generated by SS at 323K was higher than that of Ti. It has been reported that Cu or Ni has a catalytic activity on nitrate reduction [13]; hence, nickel present in the passive layer of SS could catalyze the reduction of nitrate. According to Equations (1) and (2), the potential selected for carrying out the electrochemical deposition of CP was -1.41V (Figure 3). In order to prevent the depletion of electroactive species at interface, a temperature of 323K was chosen to compact the thickness of the diffusion layer, and thereby increase the flux of electroactive species diffusing to the interface.

During the nitrate and nitrite reduction, hydroxide ions are formed and react with the monobasic phosphate to produce dibasic phosphate and then produce phosphate ions (Equations (3) and (4)), which lead to the formation of CP [1].



The high current generated by TiO₂/SS in comparison with TiO₂/Ti electrode indicates indirectly the formation of a high amount of phosphate ions (Figures 3 and 4), as result of a high production of hydroxide ions at interface.

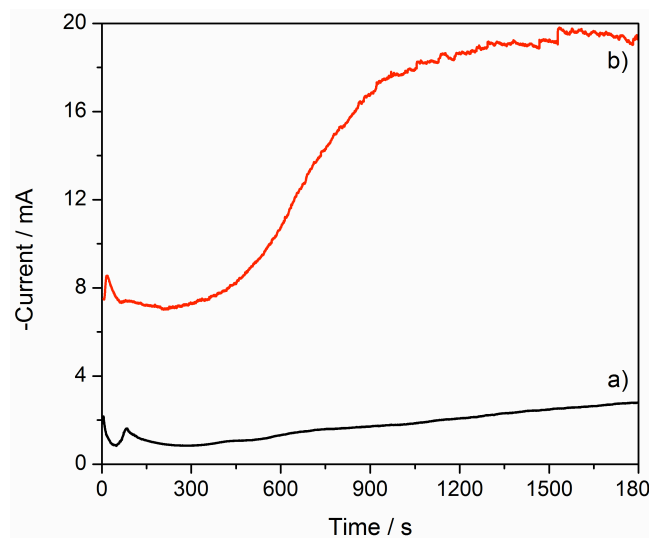


Figure 3. Transient current generated upon the CP deposition on (a) titanium and (b) stainless steel by holding the potential at -1.41V vs Ag/AgCl. Temperature: 323K.

3.2. Characterization of calcium phosphate deposits

Figure 4 shows FESEM images of electrodeposited CP coatings on TiO₂/SS and TiO₂/Ti. The CP deposit is coat more evenly on SS substrate (Figure 4(a), (a')) than that on Ti substrate (Figure 4(b), (b')). In order to determine the chemical nature of electrodeposited CP, Ca/P ratio was estimated from EDS analysis. A Ca/P ratio of 1.51 and 1.57 was determined for TiO₂/SS and TiO₂/Ti, respectively. This suggests the formation of CDHAp because Ca/P < 1.67 [4]. Indeed, Ca/P values determined from EDS corresponds to an average of chemical composition, and more than one CP species could be present. Hence, other technique is required to confirm the presence of CDHAp. Figure 4(c) shows the Raman spectrum of CP deposited on TiO₂/SS. Typical peaks of anatase phase from TiO₂ film appears at 140.3cm⁻¹, 191.4cm⁻¹, 393.3cm⁻¹, 512.9cm⁻¹ and 635.7cm⁻¹. Peak centered at 958.4cm⁻¹ is

representative of CP deposit on TiO₂/SS and TiO₂/Ti, and it has been commonly attributed to HAp [14]. Take into account EDS results and the structural similarity between HAp and CDHAp [4], CP deposit corresponds to CDHAp.

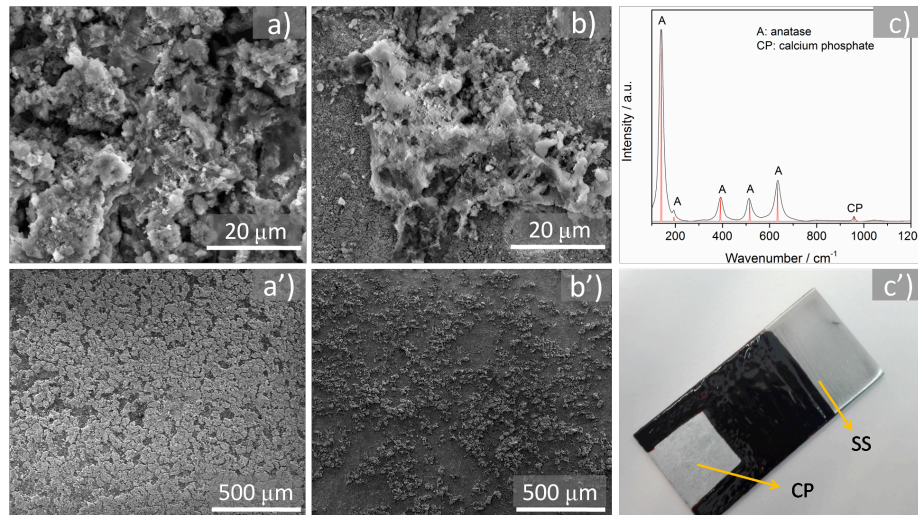


Figure 4. FESEM images of CP electrodeposited on TiO₂/SS (a), (a') and TiO₂/Ti substrates (b), (b'). Typical Raman spectrum and photo of CP deposited on SS (c), (c').

4. Conclusions

It has been found an electrochemical condition to deposit calcium-deficient hydroxyapatites on stainless steel and titanium substrates coated with a TiO₂ sol-gel film. Nickel from stainless steel catalyze the production of hydroxide ions on TiO₂/SS electrode, which increases the production of calcium-deficient hydroxyapatite and thus enabling a homogeneous coating. The condition chosen in this study can further be modified to obtain others CP.

Acknowledgements

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