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Effects of Peracetic Acid on the Corrosion Resistance of Commercially Pure Titanium (grade 4)

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The aim of this study was to evaluate the corrosion resistance of pure titanium grade 4 (cp-Ti-4), subjected to disinfection with 0.2% and 2% peracetic acid during different immersion periods using anodic potentiodynamic polarization test in acid and neutral artificial saliva. Cylindrical samples of cp-Ti-4 (5 mm x 5 mm) were used to fabricate 24 working electrodes, which were mechanically polished and divided into eight groups (n=3) for disinfection in 2% and 0.2% peracetic acid for 30 and 120 min. After disinfection, anodic polarization was performed in artificial saliva with pH 4.8 and 6.8 to assess the electrochemical behavior of the electrodes. A conventional electrochemical cell, constituting a reference electrode, a platinum counter electrode, and the working electrode (cp-Ti specimens) were used with a scanning rate of 1 mV/s. Three curves were obtained for each working electrode, and corrosion was characterized by using scanning electron microscopy (SEM) and energy dispersive x-ray spectrometry (EDS). Data of corrosion potential (E_{corr}) and passive current (I_{pass}) obtained by the polarization curves were analyzed statistically by Student's t-test (α=0.05). The statistical analysis showed no significant differences ($p>0.05$) between artificial saliva types at different concentrations and periods of disinfection, as well as between control and experimental groups. No surface changes were observed in all groups evaluated. In conclusion, disinfection with 0.2% and 2% peracetic acid concentrations did not cause corrosion in samples manufactured with cp-Ti-4.

Key Words: corrosion, commercially pure titanium, peracetic acid, disinfection, dental implants.

Introduction

Concerns about the dissemination and transmission of contagious diseases in dental offices have led to professionals taking safety measures, with the aim of preventing cross-infection among professionals, assistants and patients (1).

Metallic structures in dentures have been submitted to several clinical trials and are considered potential sources of infection because they are capable of disseminating pathogenic microorganisms when they are incorrectly disinfected. As they cannot be heat sterilized, denture metals must be disinfected with solutions not affecting the metal alloys, specifically by using non-corrosive substances. Protocols for disinfection of implant's prosthetic components must also be established, mainly, for immediate load cases.

The substances to disinfect prosthetic items are chlorine-based and peracetic acid. Chlorine compounds can cause discoloration and formation of corrosive oxides on alloy surfaces, leaving irregular surfaces and favoring additional corrosion (2). Peracetic acid-based solutions have been used as chemical disinfection in medical (3) and dental professions (4). Peracetic acid is considered a feasible alternative because it is composed of acetic acid and hydrogen peroxide, and its byproducts are biocompatible substances (5). It is also considered as a bactericidal, virucidal, sporicidal, and fungicidal agent (6). It has the advantage of remaining active even in the presence of organic matter, particularly blood, body fluids and fats (7).

The oral cavity can simulate an electrochemical cell wherein the saliva would act as the electrolyte (8). Hydrogen peroxide present in peracetic acid (5,7) as well as that produced by bacteria and leukocytes during inflammatory reactions in surgical processes, can affect titanium's resistance to corrosion (9,10).

Although several studies (10-13) have investigated the electrochemical behavior of titanium in artificial saliva, it does not exist information about the action of chemical disinfectants in commercially pure titanium alloy, used in the fabrication of dental implants and prosthetic components.

The aim of this study was to evaluate the *in vitro* action of 0.2% and 2% peracetic acid on the resistance to corrosion of commercially pure titanium (cp-Ti) grade 4, using different immersion periods in acid and neutral artificial saliva, using potentiodynamic polarization test, scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) analyses.

Material and Methods

Screws of commercially pure titanium (Cp-Ti) grade

4, (Synthes; Rio Claro, SP, Brazil), with 5 mm in diameter, were cut into a mechanical cutter (Isomet 2000; Buehler Ltd., Lake Bluff, IL, USA) with diamond disc, being used only the cylindrical central portions with 5 mm in diameter and 5 mm in length. Titanium screws were used because they have the same composition as the prosthetic components, thus facilitating the execution of the test due the difficulty for titanium castings.

The screws stripping were performed to removal of superficial covering (gold) resulting from anodizing process (14). Next, specimens were immersed in an acidic solution composed of 20% v/v of nitric acid at 70% (300 g/L) and 2% v/v of hydrofluoric acid at 60% (24 g/L) and then placed in ultrasound (Q335D; Quimis, Diadema, SP, Brazil) for 2 min. Subsequently, the specimens were washed with distilled water and dried hot air.

A total of 24 working electrodes (specimens) were fabricated, according the protocol ASTM F-2129 (15). The electrodes were subjected to surface finishing in a horizontal polishing machine (DPU-10-Struers, Panambra, São Paulo, SP, Brasil) with aluminum oxide sandpaper (#100, 220, 400 and 600 grits), silicon carbide (#1200 and 1500 grits) (Norton-ABZ, Guarulhos, SP, Brazil) and distilled water. After the use of each sandpaper, the electrodes were washed with distilled water and polished with felts (Fortel Ind. e Com. Ltda, São Paulo, SP, Brazil) and alumina suspension (AP-A Suspension aluminum agglomerated, Struers, Danmark). Subsequently, the electrodes were washed with isopropyl alcohol (Labsynth Produtos para Laboratórios Ltda, Diadema, SP, Brazil) and dried with hot air. The working electrodes (n=24) were divided into two groups according to saliva type. After this, they were subdivided in four subgroups (n=3), according to the peracetic acid concentration and immersion time.

The peracetic acid solution (Sekusept aktiv; Henkel Ecolab GmbH, Düsseldorf, Germany) was prepared in accordance with the manufacturer's instructions at concentrations of 0.2% and 2%. Each group of working electrodes (n=3) was immersed in 150 mL of disinfectant solution. After the immersion periods (30 and 120 min), the working electrodes were removed from the peracetic acid, were washed in distilled water and dried with hot air.

After disinfection, an anodic potentiodynamic polarization assay was performed based on the ASTM F-2129 Standard (15). The anodic polarization test is a method for evaluating the corrosion properties of metallic materials by the relation between the current density per surface area. The current density indicates the dissolution of metal ions in the electrolyte material (16).

A galvanic cell constituted of a saturated calomelane electrode, a platinum counter electrode and the working electrode were used in the anodic potentiodynamic polarization test. CorrWare software (Scribner, Southern Pines, NC, USA) was used for data acquisition, and CorrView (Scribner) for data visualization and treatment. Every measurement was scheduled to be taken one hour after stabilization on the open circuit potential, or when no variation of 3 mV was detected within 60 s. This measurement of initial potential was defined as the corrosion potential (E_{corr}).

The test was performed in an artificial saliva (Table 1) solution neutral (pH 6.8) and acidic (pH 4.8), 300mL, pH adjusted by the addition of lactic acid added in 1 mL increments (8), naturally aerated, temperature was maintained 37 °C and the scan rate was 1 mV/s, starting from a corrosion potential (E_{corr}) until 800 mV_{ECS}. After chemical disinfection, the anodic potentiodynamic polarization test generated three anodic polarization curves for each sample, selecting as representative the curve closer to the average value obtained from the three measures for each group. The control group was kept in distilled water.

The polarization curves were analyzed and the values of E_{corr} and I_{pass} were used for statistical analysis (Student's-*t* test). A microstructural characterization of the surfaces was performed using scanning electron microscopy (Philips FEG XI30; Amsterdam, Netherlands) and energy dispersive x-ray spectrometry (Philips FEG XI30), choosing one representative sample of each group.

Results

The titanium samples of control group polarized in both electrolytes (acid and neutral saliva) showed similar corrosion potentials (Table 2). The curves exhibited low passive current density I_{pass} throughout the potential scanning until the 800mV_{ECS} (Fig. 1). The corrosion parameters (E_{corr} and I_{pass}) are illustrated in Table 3.

The polarization curves (Fig. 2) exhibited that titanium samples polarized in both types of saliva showed similar

Table 1. Artificial saliva composition

Substances	Concentration (1L)
Potassium diacid phosphate	0.326 g
Potassium dibasic phosphate	0.803 g
Potassium chloride	0.62 g
Sodium chloride	0.865 g
Magnesium chloride($6H_2O$)	0.125 g
Calcium chloride (H_2O)	0.072 g
Sodium fluoride	4.25 mg
Preservatives (Nipagin/Nipasol)	5.0 g
Distilled water up to	1.0 L

corrosion potential, being similar to that observed with 2% peracetic acid (Table 3, Fig. 3).

Statistics showed that no difference ($p>0.05$) was observed between artificial saliva types at different concentrations and periods of peracetic disinfection, as well as between control and experimental groups.

Analysis of the photomicrographs of the titanium polarized in acidic (Fig. 4) and neutral (Fig. 5) saliva, after immersion in 0.2% and 2% peracetic acid for 30 min and 120 min and in distilled water, showed no passive defects of generalized corrosion or pits. The graphs obtained by the energy dispersive X-ray spectrometry showed only the composition of commercially pure titanium, without any corrosion product.

Discussion

Peracetic acid is considered a feasible alternative because it is composed of acetic acid and hydrogen peroxide, and its byproducts are biocompatible substances (5). It is also considered as a bactericidal, virucidal, sporicidal, and fungicidal agent (6). It has the advantage of remaining active even in the presence of organic matter, particularly blood, body fluids, and fats (7).

The oral cavity can simulate an electrochemical cell wherein the saliva would act as the electrolyte (8). Hydrogen peroxide present in peracetic acid (5,7), as well as that produced by bacteria and leukocytes during inflammatory reactions in surgical processes, can affect titanium's resistance to corrosion (9,10,17).

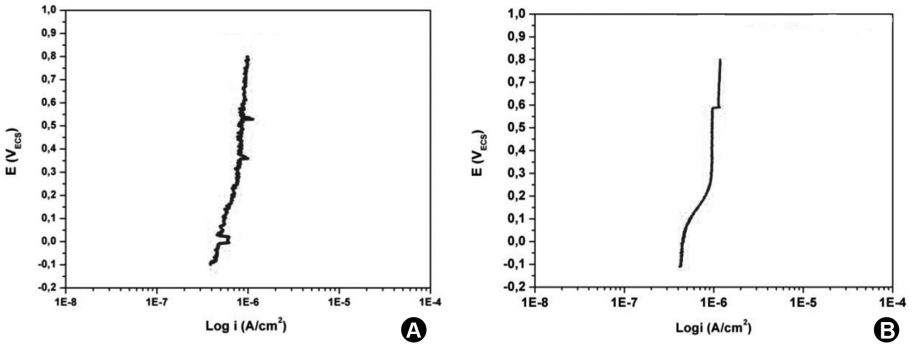


Figure 1. Potentiodynamic anodic polarization curve representative of CP titanium grade 4 after immersion in distilled water as control. A: acidic saliva; B: distilled water.

The specimens immersed in distilled water (control) and both saliva types showed lower values of passive current density (I_{pass}), thus demonstrating the high corrosion resistance of titanium. The curves in both electrolytes showed passive current densities (I_{pass}) being reduced in the order of -10^{-6} A/cm throughout the test, not characterizing the break of passive oxide layer, thus indicating a high corrosion resistance after disinfection with 0.2% and 2% peracetic acid in all evaluated periods of immersion. The behavior characterized by a partial stabilization of the current density suggested that a passive protective layer was formed in these potential variations (18).

The increase in the period of disinfection with

Table 2. Mean values (standard deviation) of corrosion potentials (E_{corr}) and densities of passive current (i_{pass}) obtained from the anodic polarization curves (distilled water as control)

Distilled water (control)			
Acidic saliva		Neutral saliva	
E_{corr}(mV)	i_{pass}(A/cm^2)	E_{corr}(mV)	i_{pass}(A/cm^2)
4 (±1.04)	1.02×10^{-6} (±0.19)	-160 (±0.50)	0.98×10^{-6} (±0.02)

Table 3. Mean values (standard deviation) of corrosion potentials (E_{corr}) and densities of passive current (i_{pass}) obtained from the anodic polarization curves in acidic and neutral artificial saliva

Peracetic acid	Disinfection period							
	30 min				120 min			
	Acidic saliva		Neutral saliva		Acidic saliva		Neutral saliva	
	E_{corr}(mV)	i_{pass}(A/cm^2)	E_{corr}(mV)	i_{pass}(A/cm^2)	E_{corr}(mV)	i_{pass}(A/cm^2)	E_{corr}(mV)	i_{pass}(A/cm^2)
0.2%	-10 (±0.6)	1.08×10^{-6} (±0.05)	-103 (±0.40)	1.38×10^{-6} (±0.63)	18 ±0.24	1.20×10^{-6} (±0.35)	-121 ±1.05	1.04×10^{-6} (±0.23)
2%	-14 (±0.63)	1.37×10^{-6} (±0.34)	-72 (±0.37)	1.38×10^{-6} (±0.38)	-61 (±0.71)	1.18×10^{-6} (±0.28)	-39 ±0.5	1.77×10^{-6} (±0.56)

0.2% peracetic acid in both saliva showed a tendency to stabilization of passive layer. The increase of E_{corr} and reduction of I_{pass} values indicate a less corrosive activity.

The average value of corrosion potential (E_{corr}) in neutral saliva and disinfection with 2% peracetic acid for 120 min was smaller than in distilled water, suggesting that the pH and the presence of H_2O_2 in the peracetic acid solution might have influenced in the E_{corr} decrease, as observed in the researches of Abey et al. (8) and Fonseca and Barbosa (9), respectively, thereby leading to a reduction in the corrosion resistance of titanium.

Abey et al. (8) showed that oxide film (TiO_2) formed on the surface of the specimens was thinner in those immersed in neutral artificial saliva with pH 7.5, leading therefore to an increase of the corrosion potential, because this thin passive layer is easier to be broken.

Studies on the effect of hydrogen peroxide (H_2O_2) in passivity of titanium in phosphate-buffered saline solution (19,20) showed that, after addition of H_2O_2, it was increased the titanium corrosion potential, being this increase proportional to the potential concentration. The thickness of the passive layer formed over titanium surface in contact with aqueous solution was reduced, suggesting an increase of its dissolution (19). The thickness of the protective oxide layer (TiO_2) in phosphate-buffered saline solution was very thin, but after addition of H_2O_2 this film became thicker and porous, which may be attacked by H_2O_2, and the ions released in the initial phase of exposure (20).

Hattori and Oda (21) observed that polished titanium immersed in saline showed no changes in color or dissolution, but in acidic solution with hydrogen peroxide there was identified a slight reduction in the electrode frequency indicating mass gain by oxidation. However in alkaline solution it was increased frequency and mass loss by dissolution indicating that the alkaline solution caused corrosion in titanium surface.

Signs of pitting have been reported when titanium samples were immersed in artificial saliva with 0.1%

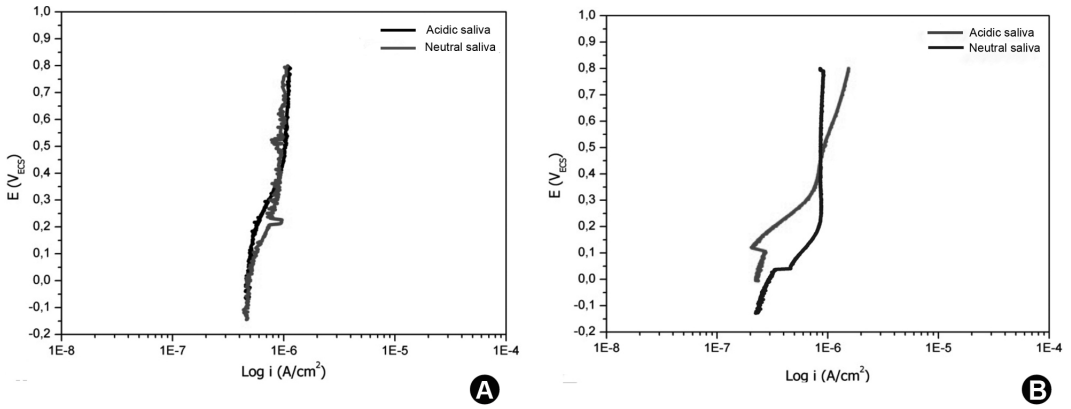


Fig. 2. Potentiodynamic anodic polarization curve representative of CP titanium grade 4 after disinfection in 0.2% peracetic acid. A: acidic and neutral saliva for 30 min; B: acidic and neutral saliva for 120 min (Electrolyte: mimetizing saliva solution pH 4.8 and 6.8, v=1 mV/s).

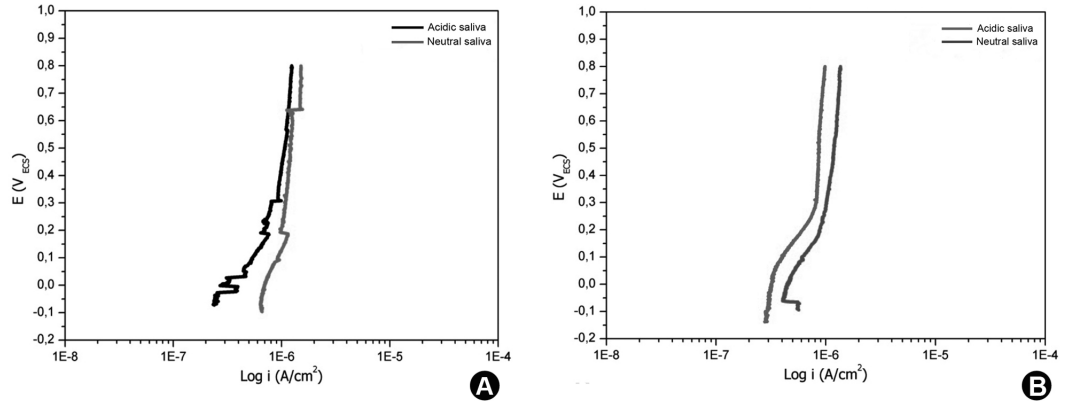


Fig. 3. Potentiodynamic anodic polarization curve representative of CP titanium grade 4 after disinfection in 2% peracetic acid. A: acidic and neutral saliva for 30 min; B: acidic and neutral saliva for 120 min (Electrolyte: mimetizing saliva solution pH 4.8 and 6.8, v=1 mV/s).

and 10% H_2O_2. However, surface roughness values demonstrated that titanium corrosion was not related to H_2O_2 concentration, suggesting a mechanism dose-dependent (17).

The results of another study (22) showed that a decrease in the dissolved oxygen concentration does not cause corrosion of titanium; but decreases its corrosion resistance. The corrosion of titanium alloys in the oral environment may result from the presence of corrosive elements such as H^+, S^{-2}, O_2 and Cl^- (23).

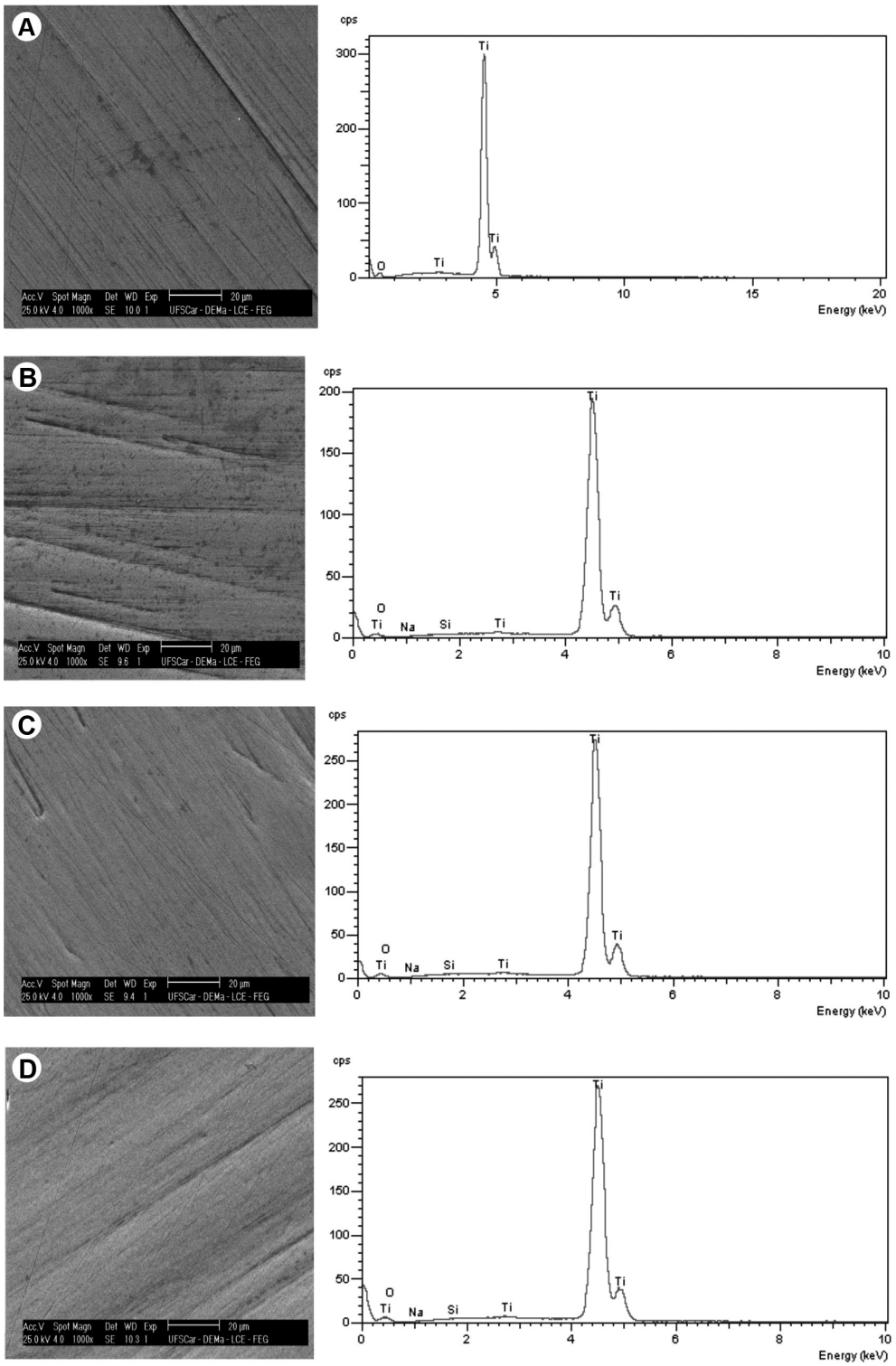


Fig. 4. SEM images of CP titanium grade 4 polarized in a saliva solution (pH 4.8) and immersion in: A: 0.2% peracetic acid for 30 min; B: 0.2% peracetic acid for 120 min; C: 2% peracetic acid for 30 min; and D: 2% peracetic acid for 120 min.

The results of this current study showed passivation of the titanium samples in artificial saliva, which are in agreement with the observations from the study by Canay et al. (11). This fact occurred independently of the concentration levels and immersion periods.

No significant differences in anodic behavior were observed between neutral and acidic saliva, indicating that the pH of the saliva did not influence the corrosive behavior of the samples after disinfection. Mareci et al. (24) demonstrated a passive behavior of titanium alloys

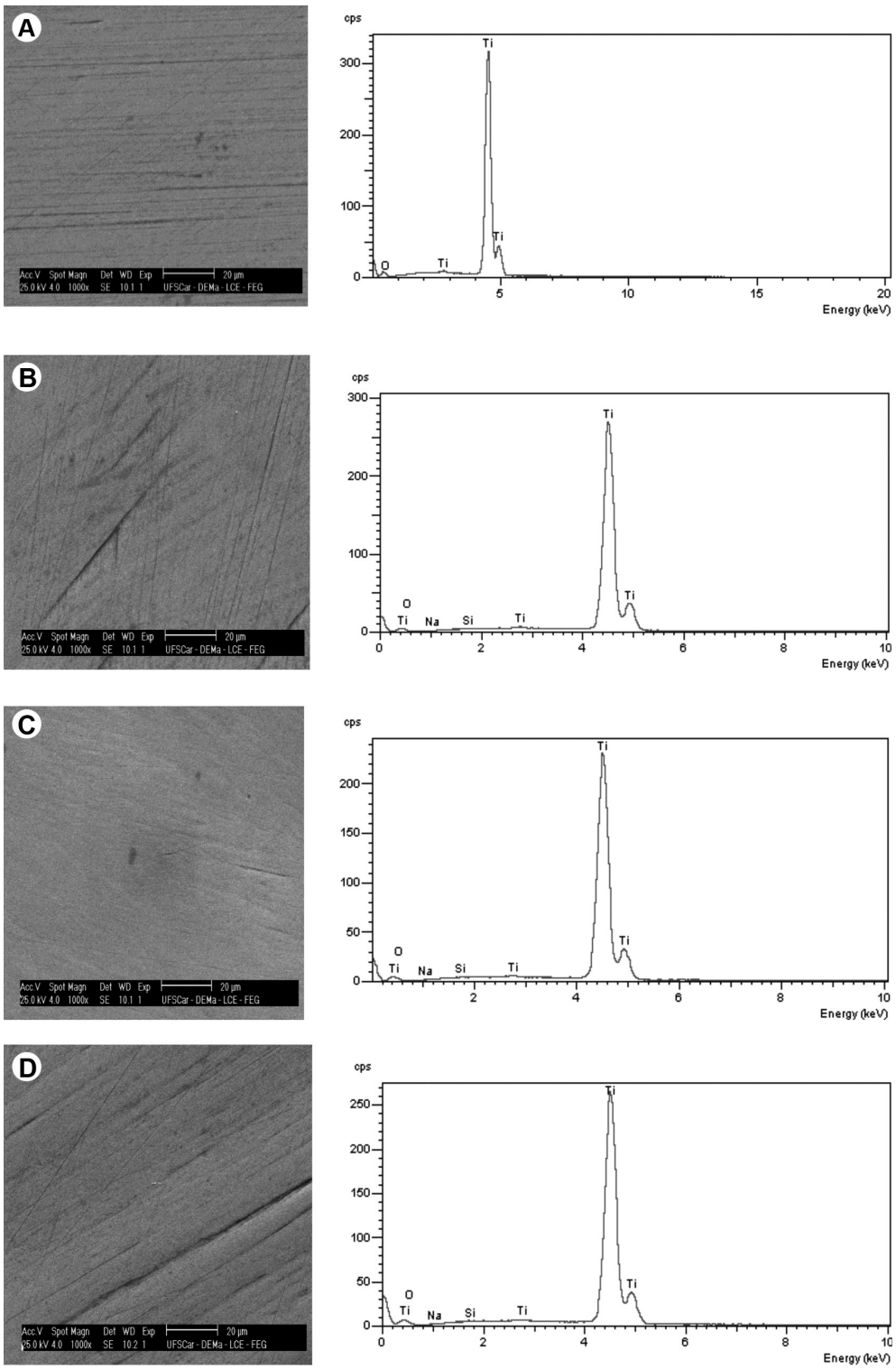


Fig. 5. SEM images of CP titanium grade 4 polarized in a saliva solution (pH 6.8) and immersion in: A: 0.2% peracetic acid for 30 min; B: 0.2% peracetic acid for 120 min; C: 2% peracetic acid for 30 min; and D: 2% peracetic acid for 120 min.

in artificial, acidified (pH 2.5) and fluoride (pH 8.0) saliva.

In the anodic polarization curves, no repassivation was observed even with the increase in the corrosion potential. This observation is supported by the increase in current density, which showed the passivity of titanium in acidic saliva after immersion in 0.2% and 2% of peracetic acid for different periods. It was not associated with the H_2O_2 present in the peracetic acid and its action on the surface of titanium. Also, the microphotographs showed no corrosion points by pits.

The scanning electron microscopy images confirmed no point of localized corrosion or "pit" in any sample. Similarly, graphs from EDS revealed no evidence that composition of the disinfectant solutions affected titanium or the stable oxide film of TiO_2. Titanium exhibits a higher corrosion resistance, in saline solution or artificial saliva due the presence of a dense and stable titanium oxide layer, which spontaneously cover the metal surface (21).

Peracetic acid can be used for disinfection of prosthetic components by professionals, in both laboratory and clinical fields during the making process of implant-supported prosthesis.

In conclusion, disinfection with 0.2% and 2% peracetic acid did not cause corrosion of samples manufactured with cp-Ti-4.

Resumo

O objetivo deste estudo foi avaliar a resistência à corrosão de titânio puro grau 4 (cp-Ti-4) submetido à desinfecção com ácido peracético a 0,2% e 2% durante diferentes períodos de imersão por meio do teste de polarização potenciodinâmica anódica em saliva artificial ácida e neutra. Amostras cilíndricas de cp-Ti-4 (5 mm x 5 mm) foram usadas para confeccionar 24 eletrodos de trabalho, os quais foram polidos mecanicamente e divididos em oito grupos (n=3) para desinfecção com ácido peracético a 2% e 0,2% por 30 e 120 minutos. Após a desinfecção, foi realizado o teste de a polarização anódica em saliva artificial com pH 4,8 e 6,8 para avaliar o comportamento eletroquímico dos eletrodos. Uma célula electroquímica convencional, composta por eletrodo de referência, contra-eletrodo de platina, e eletrodo de trabalho (amostras de cp-Ti) foi usada com taxa de varredura de 1 mV/s. Foram obtidas três curvas para cada eletrodo de trabalho e a corrosão foi analisada por microscopia eletrônica de varredura (MEV) e espectrometria de energia dispersiva de raios-X (EEDX). Os dados de potencial de corrosão (Ecorr) e corrente passiva (Ipass) obtidos com as curvas de polarização foram analisados estatisticamente pelo teste t de Student (α=0,05). A análise estatística não mostrou diferenças significantes (p>0,05) entre os tipos de saliva artificial nas diferentes concentrações e períodos de desinfecção, bem como entre os grupos controle e experimental. Não foram observadas alterações nas superfícies das amostras de todos os grupos avaliados. Conclui-se que a desinfecção com ácido peracético nas concentrações de 0,2% e 2% não provocou corrosão nas amostras confeccionadas com cp-Ti-4

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