



Electrochemical Behavior of Titanium in Artificial Saliva: Influence of pH

Savithri Abey, DDS¹
 Mathew T. Mathew, PhD²
 Damian J. Lee, DDS, MS³
 Kent L. Knoernschild, DMD, MS³
 Markus A. Wimmer, PhD²
 Cortino Sukotjo, DDS, PhD^{3*}

Titanium is the most common material chosen for dental implants because it is highly corrosion resistant because it constantly reforms a protective passive film layer. The formation and composition of the passive film layer is dependent on the environmental conditions. If the stable oxide layer is damaged, the titanium surface underneath can corrode. The purpose of this study was to determine if basic corrosion of commercially pure titanium (CpTi) alloy in artificial saliva was affected by pH and to understand the corrosion kinetics/mechanisms of CpTi as a function of pH. In this study, titanium alloy discs were subjected to corrosion tests. Before the tests, all samples were cleaned and polished using standard metallographic preparation methods. Artificial saliva was used as the testing medium. The following pH values were tested: 3.0, 4.5, 6.0, 6.5, 7.5, and 9.0. Different pH values were achieved by adding lactic acid (acidic) or NaOH (basic) in appropriate amounts. Potentiodynamic curves indicated behavior change at each pH. In addition, the corrosion current density value determined from the potentiodynamic curve exhibited the poorest corrosion resistance for pH 7.5. The Nyquist plot (from the electrochemical impedance spectroscopy results) indicated that pH 7.5 had the poorest resistance. Scanning electron microscopy images indicated that pH levels of 6.5, 7.5, and 9.0 had considerable surface corrosion. The results showed that the media's pH significantly influenced the corrosion behavior of CpTi. The poor corrosion behavior at the neutral pHs invites some concerns and highlights the need for further study.

Key Words: titanium, corrosion, biocompatibility, artificial saliva, electrochemical impedance spectroscopy

INTRODUCTION

Titanium (Ti) is the most widespread material used for dental implants because of its mechanical properties, exceptional corrosion resistance, and biocompatibility.¹⁻³ Although Ti alloys are highly corrosion resistant because of the stability of the TiO₂ oxide layer, they are not inert to corrosive attack. When the stable oxide layer is broken down

¹ Department of Restorative Dentistry, School of Dentistry, Indiana University, Indianapolis, Ind.

² Department of Orthopedics, Rush University Medical Center, Chicago, Ill.

³ Department of Restorative Dentistry, Comprehensive Dental Implant Center, University of Illinois at Chicago, College of Dentistry, Chicago, Ill.

* Corresponding author, e-mail: csukotjo@uic.edu
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or cannot reform on parts of the surface, Ti can be as corrosive as other base metal alloys.⁴⁻⁸ In addition, the oral cavity can simulate an electrochemical cell because saliva acts as a weak electrolyte. Electrochemical corrosion of Ti alloys may lead to surface corrosion of dental implants, and ultimately may release the corrosion products into the system over time.^{9,10} It is not known whether corrosive products are beneficial or harmful to osseointegration.

The corrosion resistance of Ti results from the formation of an extremely stable, continuous, highly adherent, and protective oxide film on the metal's surface.³ The nature, composition, and thickness of the protective surface oxides that form on Ti alloys depend on the environmental conditions.^{3,7,8} Recent studies have shown that the corrosion resistance of Ti (commercially pure Ti [CpTi] and Yt alloys) becomes weaker with exposure to varying fluoride concentrations and NaF solution with a concentration of 0.5%. In addition, pH has been known to have a strong influence on the corrosion resistance of CpTi and Ti alloys.^{1-3,11,12} Understanding the corrosion behavior of Ti in dental implants is very important because it can negatively affect biocompatibility and mechanical integration, thus leading to failure of dental implants over time.^{9,13-15}

In the oral environment, Ti implants are constantly exposed to saliva. Upon placement, the entire surface of the implant can be contaminated with saliva. Once placed, the implant interface is continuously washed with saliva via the gingival sulcus. The presence of electrolytes in saliva can create damage by inducing crevice corrosion, which has been found in many dental implants.^{16,17}

In addition to the constant contamination, the pH of saliva can vary around dental implants. Many factors can change the pH of saliva. For example, infection can acidify the pH of saliva.¹¹ Food, oral hygiene products, age, periodontitis, oral habits such as smoking, systemic disease, and salivary gland radiation can also contribute to the pH changes in saliva.¹⁷⁻²² The normal saliva pH for a healthy adult ranges from 6.3 to 7.²³ However, the resting pH of saliva can temporarily decrease to an average of 3.5 if acidic food and beverages are ingested and chronic/systemic disease is present,²⁴⁻²⁶ or can increase to 8.3 if certain alkaline foods are taken in, such as milk, vegetables, and grains.²⁴ The

Component	Quantity (g/L)
KCl	0.4
NaCl	0.4
CaCl ₂ ·2H ₂ O	0.906
NaH ₂ PO ₄ ·2H ₂ O	0.690
Na ₂ S·9H ₂ O	0.005
Urea	1

*To achieve lower pH (acidic), lactic acid was added; to achieve high pH (basic), NaOH was added.

pH of saliva may contribute to the corrosion of dental implants.^{22,27-32}

Many studies have investigated the influence of pH in artificial saliva on the corrosion behavior of Ti.^{1,3,11,12,18,22,31} However, most of the studies were performed using pH 5, which does not replicate the normal clinical situation. In addition, the interaction between Ti and the oral environment gives rise to electrochemical reactions.^{22,28} Within the corrosion studies of dental alloys, knowledge of the electrochemical environment of the oral cavity is limited.²⁸ It is hypothesized that a lower saliva pH level induces greater corrosive damage on Ti, and as the pH level increases from 3 to 9, the amount of corrosive damage will decrease. Hence, the aim of this study was to investigate the corrosive behavior of CpTi in artificial saliva at 37°C, as a function of pH values (3-9) and to characterize the Ti surfaces as a result of the corrosion process.

MATERIALS AND METHODS

Materials and solutions

In the current study, 25 CpTi alloy discs (American Elements, Los Angeles, Calif) 12 mm and 7 mm thickness were used. The tests were conducted in artificial saliva with different pH levels: 3, 4.5, 6, 6.5, 7.5, and 9. The artificial saliva and the electrolytes were formed based on studies by Fusayama et al and Meyer.^{32,33} The composition of this solution, as seen in Table 1, closely resembles that of natural human saliva. To obtain a more acidic artificial saliva solution, lactic acid was added in 1 mL increments, and to obtain a more basic artificial saliva solution, NaOH was added in 1 mL increments.

Before the test, all the samples were polished and cleaned using standard metallographic methods. The samples were first mounted in mounting

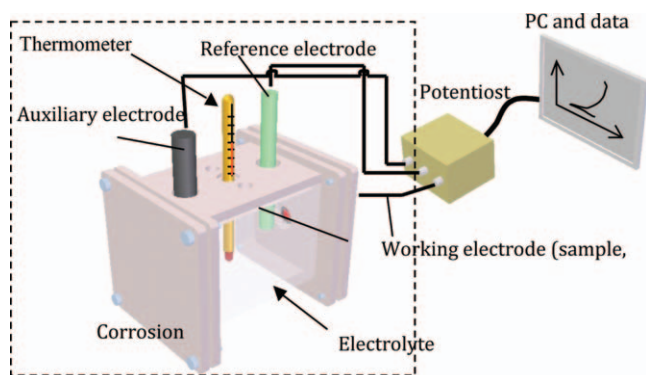


FIGURE 1. Electrochemical experimental set-up.

cups (Buehler, Lake Bluff, Ill) with clear orthodontic resin (Dentsply, Milford, Del). The samples were cured under 20 psi. Samples were removed and rough polished using 8" 320 grit SiC paper to ensure that the sample was flat. The intermediate polishing step was accomplished using a TexMet polishing cloth and 9- μm diamond polishing paste suspended in Meta-Di fluid (Buehler). Once all deep scratches were removed from the surface, the final polishing step was accomplished using a Chemomet polishing cloth and colloidal silica (Buehler). Both the intermediate and final polishing steps were conducted for 10 minutes. Samples were cleaned using 70% Isopropyl alcohol for 15 minutes, then dionized water for 15 minutes in an ultrasonic bath before testing. Samples were dried using a hot air gun.

Electrochemical test methods

Tests were conducted in an electrochemical cell (Figure 1) and performed in triplicate for each group. The corrosion cell held 150 mL of artificial saliva solution. All measurements were made in a standard 3-electrode cell system. A saturated calomel electrode was used as the reference electrode and a graphite rod as a counter electrode. A Gamry potentiostat (Gamry Instruments, Warminster, Pa) was used to carry out the corrosion measurements. After mounting the samples, a period of 30 minutes was allotted for initial stabilization and heating of the solution to 37°C, to mimic the normal body temperature. Initially, the evolution of open circuit potential (OCP) was monitored for 3 600 seconds.

The 2-hour electrochemical impedance spectroscopy (EIS) test was conducted after OCP monitoring. The EIS measurements were performed in the

frequency range from 100 KHz to 0.01 Hz, with AC sine wave amplitude of 10 mV applied to the electrode at its corrosion potential. These values were used to determine the real (Z') and imaginary (Z'') components of the impedance, which were plotted with the Nyquist plot. The total impedance ($|Z|$) and phase angle were seen in a Bode plot as a function of the frequency. Impedance data are frequently interpreted in terms of an "equivalent circuit" based on a plausible physical model where the circuit elements represent electrochemical properties of the metal and its oxide film.²⁷ The EIS data were modulated into equivalent electrical circuits using the Zview2 corrosion software (Scribner Association Inc, Southern Pines, NC) to better understand the pH effect on CpTi. Finally, the samples were anodically polarized from -0.8 V to 1.8 V at a scan rate of 5 mV/sec. Potentiodynamic measurements were carried out to determine the initiation and propagation of local corrosion, which is associated with the breakdown of passive (protective) film. The electrochemical corrosion properties of CpTi at each pH were measured in terms of corrosion potential (E_{corr}), corrosion current density (I_{corr}), and passivation current density (I_{pass}).

Surface characterization

Surface characterization was conducted using scanning electron microscopy (SEM) (Joel JSM-6490 LV, Oxford Instruments, Oxford, UK).

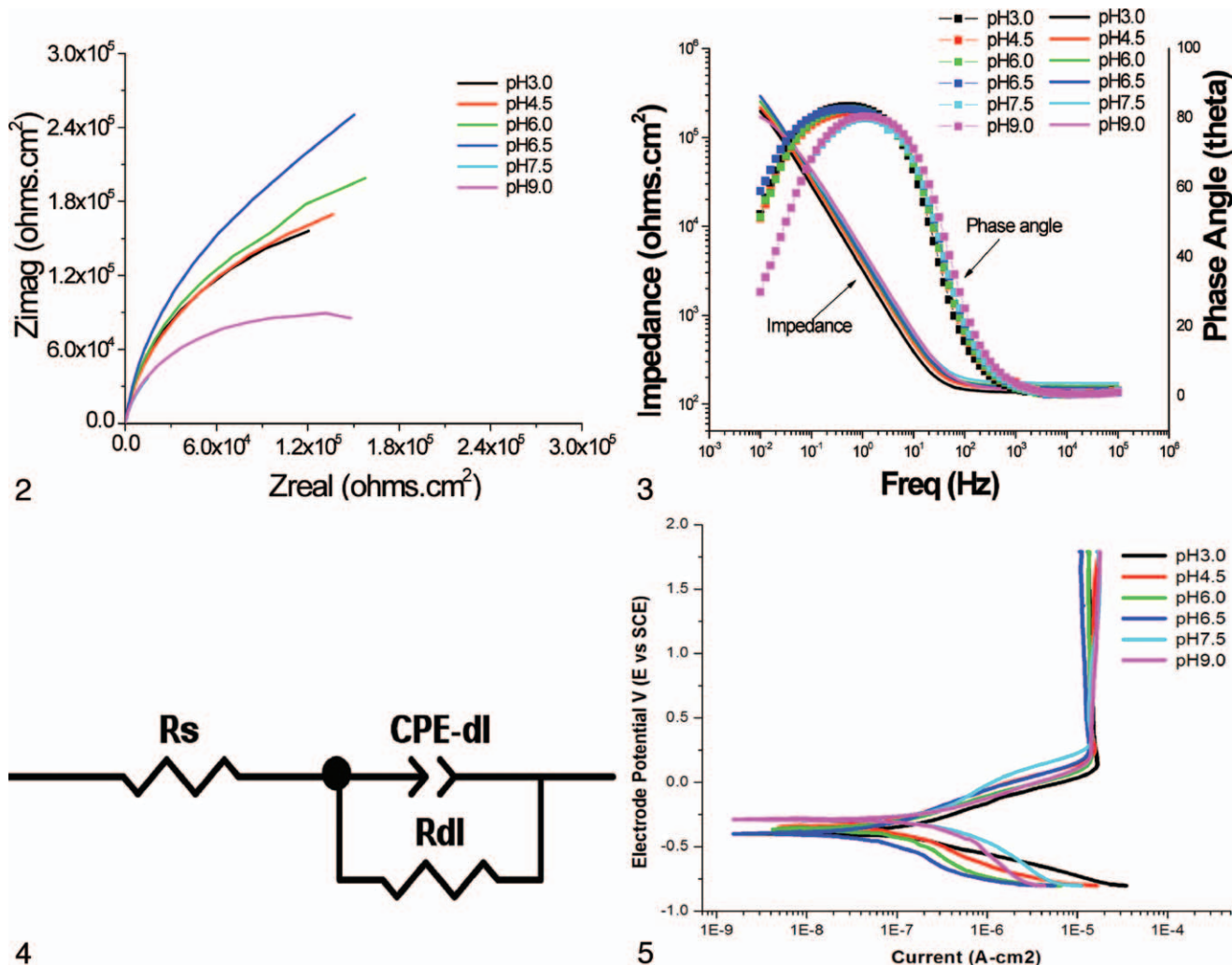
Statistical analysis

The corrosion parameters, including E_{corr} , I_{corr} , double-layer capacitance (C_{dl}), solution resistance (R_{sol}), and polarization resistance (R_{p}) were statistically analyzed using one-way analysis of variance (ANOVA) for analyzing how pH affects the corrosion parameters. Tukey's honestly significant difference test ($\alpha = 0.05$) was chosen as the multiple-comparison technique when necessary (Statistical Package for the Social Sciences, version 17.0, SPSS Inc, Chicago, Ill).

RESULTS

EIS data

The Nyquist (Figure 2) and Bode plots (Figure 3) provide the corrosion kinetics (impedance and



FIGURES 2–5. **FIGURE 2.** Representative Nyquist plot from electrochemical impedance spectroscopy (EIS) results for commercially pure titanium (CpTi) in artificial saliva as a function of pH. **FIGURE 3.** Representative Bode plot from EIS results for CpTi in artificial saliva as a function of pH. **FIGURE 4.** Equivalent circuit used for fitting the experimental data. **FIGURE 5.** Representative polarization curves at each pH for CpTi in artificial saliva.

frequency information). The Nyquist plot shows the electrochemical resistance of the Ti surface.

From the Nyquist plot, it can be noted that pH 7.5 had the poorest electrochemical resistance, followed by pH 9.0. For both pH 7.5 and 9.0, there was an increase in the semicircular diameter of the capacitance loop (as indicated by the Nyquist plot). An increase in capacitance leads to a decrease in the overall corrosion resistance. Corrosion resistance appeared to be highest at pH 3.0. Unlike the Bode plot, the Nyquist plot did not account for frequency. The Bode plot also suggested that the resistance of pH 7.5 is the poorest because of the lower R_p value (resistance of the passive film). Only one time constant was observed at each pH,

indicating the formation of a homogenous passive film.³⁴

Figure 4 represents the Randles equivalent circuit used to model the corrosion behavior based on the EIS results. The components of the equivalent circuit are R_s , R_p , and C_{dl} . Mean values at each pH are compared in Table 2.

Potentiodynamic curves

Results of the cyclic potentiodynamic polarization curves for the Ti alloy are presented in Figure 5. All samples revealed an active to passive behavior for each pH. However, the varying potentiodynamic curves indicated a behavior change dependent on pH. This was exhibited by the unique curves

TABLE 2

Corrosion parameters obtained from potentiodynamic polarization curves and from electrochemical impedance spectroscopy modeling of commercially pure titanium in artificial saliva as a function of pH*

pH	pH 3.0	pH 4.5	pH 6.0	pH 6.5	pH 7.5	pH 9.0	ANOVA P Values
E_{corr} (V)	-0.40 ± 0.16	-0.39 ± 0.11	-0.35 ± 0.014	-0.37 ± 0.13	-0.38 ± 0.18	-0.40 ± 0.18	$P = .006$
I_{corr} (A/cm ²)	8.33E-08 ± 6.81E-09	9.47E-08 ± 1.46E-09	1.27E-07 ± 5.60E-08	1.31E-07 ± 6.89E-08	1.65E-07 ± 6.81E-08	1.17E-07 ± 5.98E-08	$P < .0001$
I_{pass} (A/cm ²)	1.33E-05 ± 6.67E-06	3.5E-05 ± 4.58E-06	1.33E-05 ± 1.53E-06	1.57E-05 ± 6.03E-06	4.1E-05 ± 9.54E-05	3.7E-05 ± 5.51E-06	$P = .007$
C_{dl} (F)	2.66E-05 ± 6.72E-06	1.74E-05 ± 1.63E-06	1.69E-05 ± 3.54E-07	1.61E-05 ± 7.07E-07	2.06E-05 ± 7.07E-08	1.68E-05 ± 2.55E-06	$P < .0001$
R_{sol} (Ωcm ²)	359.65 ± 14.64	391.40 ± 14.42	390.55 ± 26.52	402.70 ± 11.31	451.70 ± 9.05	364.90 ± 7.92	$P < .0001$

* C_{dl} indicates double-layer capacitance; E_{corr} , corrosion potential; I_{corr} , corrosion current potential; I_{pass} , passivation current density; R_{sol} , solution resistance.

represented in Figure 5. A summary of the corrosion data obtained from the cyclic potentiodynamic polarization curves and EIS modeling is provided in Table 2. From the cyclic potentiodynamic polarization curves, the following values were determined: E_{corr} , I_{corr} , and I_{pass} . Mean values for each pH are compared in Table 2.

Results of one-way ANOVA showed that pH had a significant influence on the E_{corr} , I_{corr} , C_{dl} , and R_{sol} values ($P < .05$). The change in C_{dl} was significant when comparing pH 3.0 to all other pH values ($P < .05$). The E_{corr} was significant when comparing pH 3.0 to all other pH ($P < .05$). The I_{corr} was significant for pH 6.0 and 7.5 when compared to pH 9.0 ($P < .05$). The R_p showed no significance when comparing pH between tests ($P > .05$). The I_{pass} values, although not statistically significant, indicated greater current was required for development of the passive film layer at neutral pH.

Surface examination of corroded surfaces

The SEM images taken after the electrochemical tests suggest surface corrosion at pH 6.5, 7.5, and 9.0 (Figure 6e through g, respectively, arrows). Considerable evidence of surface corrosion represented by surface damage can be seen, particularly at pH 7.5. Negligible surface corrosion existed at pH 3.0, 4.5, and 6.0 with respect to the control sample (Figure 6a through d). The control sample was not subjected to the electrochemical tests.

DISCUSSION

This study showed that the hypothesis was partially accepted. The pH does affect the corrosion behavior of CpTi in artificial saliva; however, E_{corr} , I_{corr} , and I_{pass} values suggested that artificial saliva at neutral pH (6.0, 6.5, and 7.5) led to greater corrosion of the CpTi discs compared with more acidic saliva. This was indicated by the decreasing E_{corr} values, increasing I_{corr} values, and increasing I_{pass} values for all three pH values.

Pure Ti and Ti alloys are highly reactive; therefore, when they are exposed to fluid media or air, they quickly develop a layer of titanium dioxide (TiO₂). This layer of TiO₂, also known as a passive film, acts as a protective interface between the metal structure and biological medium, that is, saliva.^{4,9} The thickness and composition of the passive film layer is dependent on the environ-

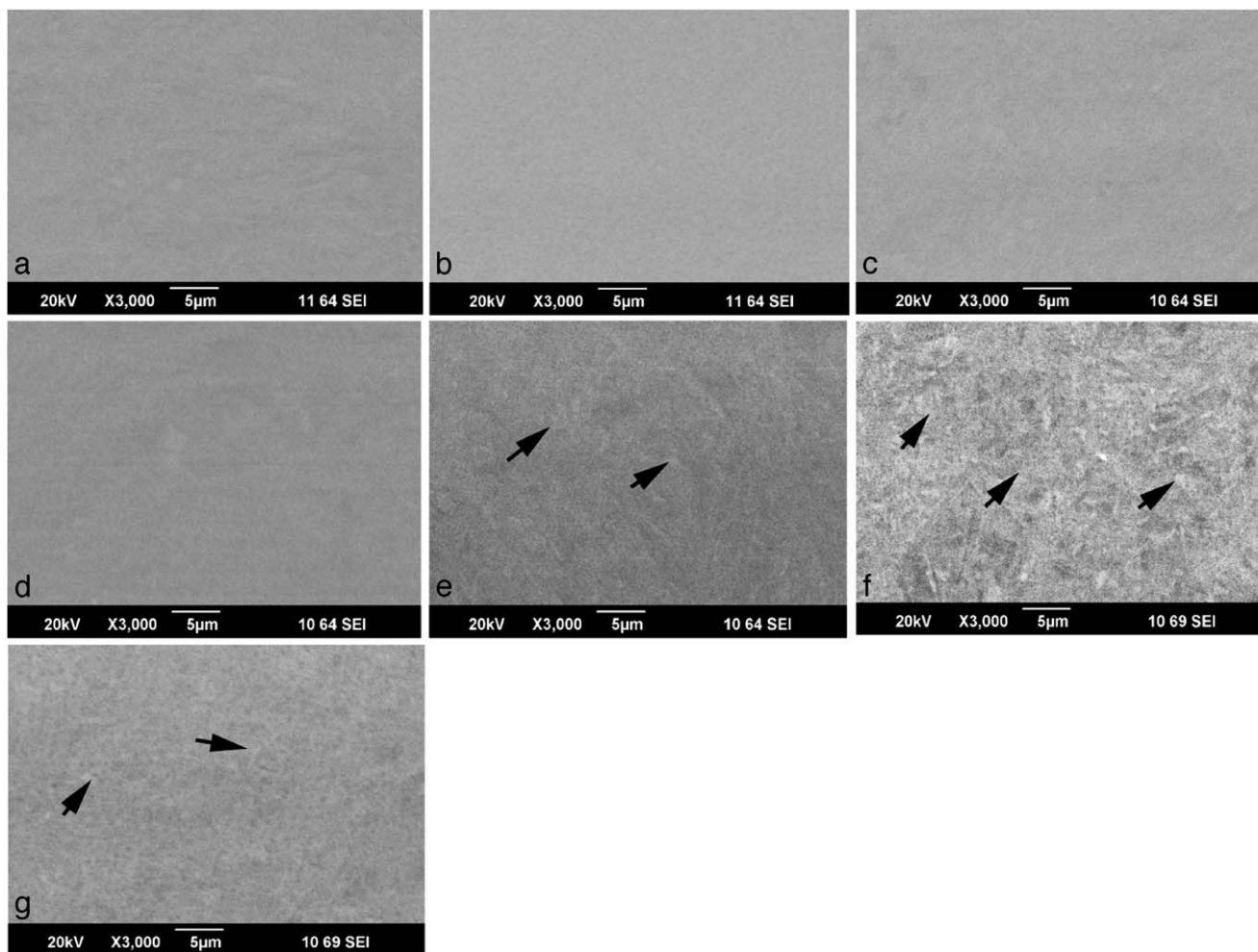


FIGURE 6. Scanning electron microscopy images of commercially pure titanium samples after electrochemical tests were performed taken at $\times 3000$. (a) Control; (b) pH = 3.0; (c) pH = 4.5; (d) pH = 6; (e) pH = 6.5; (f) pH = 7.5; (g) pH = 9.

ment the Ti is subjected to. Once formed, the passive film layer is constantly broken down and reformed in the oral cavity due to the existence of electrochemical reactions present in the saliva and mechanical actions caused by mastication and micromovements. The combination of chemical reactions and mechanical actions can lead to a complex degradation process of the passive film layer, which can ultimately lead to surface corrosion.

All 3 testing values (E_{corr} , I_{corr} , and I_{pass}) suggested that an increase in current is required for the development of the passive film layer. This behavior can indicate that although a passive layer is forming, defects in the oxide film may form as well, that is, there is a tendency toward formation of a more irregular or porous oxide layer.^{2,8,35} The defects can eventually lead to dissolution and subsequent release of metal ions into the system.

The results from the Nyquist and Bode plots

indicated that the oxide film formed on the surface of CpTi is thinner at the neutral pH 7.5 (higher corrosion kinetics). If the passive film is thinner, it is easier to penetrate, also leading to an increase in potential pitting. Although the Nyquist and Bode plots agree with potentiodynamic results for pH 7.5, they do not support the results of potentiodynamic tests for pH 6.0 and 6.5. In addition, only the C_{dl} value for pH 7.5 (capacitance was higher for 7.5) is in agreement with potentiodynamic and SEM results. An increase in capacitance is associated with an decrease in the thickness of the passive layer over time.^{27,34,36,37} A possible explanation is that the EIS tests performed in this study were conducted over a short time, only 2 hours. Over a prolonged period of time (days, weeks, years) the passive film layer at pH 6.0 and 6.5 may increase in thickness, improving the overall corrosion resistance. However, as noted by the SEM images,

during the short time of the potentiodynamic test performed in this study, breakdown of the passive film layer was possible. Earlier studies also reported such particular behavior of heavy surface damage, even pitting, on Ti under the influence of surrounding media, particularly pH level and amount of dissolved oxygen.^{8,13}

A previous study by Souza et al²² suggested that the protective passive film on Ti alloys is less protective at lower pH. The study evaluated the effect of pH on the electrochemical behavior of Ti alloys in Ringer solution and found that, in contrast to the current study, Ti alloys tend to be more corrosive at a lower pH. In their study, 2 Ti alloys were compared (Ti-13Nb-13Zr and Ti-6Al-4 V), not CpTi, at only 2 pH values, 5.5 and 7.0. In addition, Ringer solution differs greatly in electrolytic composition from artificial saliva.^{8,13,15,16,34,35}

This study had several limitations. It was limited by the small number of samples tested and the large range of pH values. In addition, acidic or basic components within the artificial saliva solution may have contributed to the corrosion at more neutral pH. Future work will look at close pH intervals of artificial saliva in order to identify the pH value with the greatest electrochemical corrosion. Galvanic studies should be incorporated; in addition, the chemical and mechanical components of corrosion should be combined via tribocorrosion studies of the implant system.^{37,38}

This study provided a novel and systematic approach to studying corrosion of Ti in the oral environment by using different electrochemical techniques, particularly impedance measurements.³⁵ Understanding the corrosion process of Ti alloys is crucial in predicting the long-term effects of current implant therapy. Corrosion products may have a beneficial or potentially detrimental effect on osseointegration of dental implants.¹⁰ Further studies via electrochemical studies and tribocorrosion^{37,38} will continue the corrosion investigation and ultimately lead to the most effective treatment for patients.

CONCLUSIONS

The results from this study showed that the pH of the media had a significant influence on the corrosion behavior of CpTi. The following conclusions were drawn:

1. The I_{corr} values indicated that neutral pH 7.5 had inferior corrosion resistance. This finding was supported by the impedance results of the Nyquist plot and R_p value determined via the Bode plot.
2. The E_{corr} , I_{corr} , and I_{pass} values suggested a greater corrosion potential at more neutral pH values of 6.0, 6.5, and 7.5. The EIS results did not support greater corrosion kinetics at pH values of 6.0 and 6.5; however, it did support greater corrosion kinetics at pH 7.5.
3. The SEM images showed considerable surface damage under pH values of 6.5, 7.5, and 9.0.
4. The weak corrosion behavior at neutral pH invites some concerns and highlights the need for further study.

ABBREVIATIONS

- C_{dl} : double-layer capacitance
 CpTi: commercially pure titanium
 E_{corr} : corrosion potential (Tafel method)
 EIS: electrochemical impedance spectroscopy
 I_{corr} : corrosion current potential (Tafel method)
 I_{pass} : passivation current density
 OCP: open circuit potential
 R_p : polarization resistance
 R_{sol} : solution resistance
 SEM: scanning electron microscopy
 Ti: titanium

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