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The Role of Fluoride Ions on the Corrosion of Ti36 in Normal Saline Solution as applied to Dental Implants

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The corrosion behavior of a newer beta titanium alloy, Ti36, in normal saline has been compared to that in normal saline containing 2% NaF using open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy measurements to ascertain its suitability for dental implant applications involving the Knutson fluoridation prophylactic therapy. Fluoride ions affect the corrosion behavior of Ti36 alloy by making the passive oxide film thin and defective. The polarization resistance of Ti36 in normal saline containing fluoride decreases by one order of magnitude as compared to that of pure normal saline just on immersion whereas the difference increases to three orders of magnitude after 240 hours of immersion. This is because at longer immersion times, the fluoride ion is able to interfere in the anodic dissolution process, resulting in a significant increase in anodic current density. Exposure of a dental implant to fluoride is usually for brief time during the application of prophylactic techniques and the area of the implant that comes in contact with fluoride ions is typically limited to its neck. Ti36 alloy can thus be an acceptable dental implant material for a short term fluoride use.

Keywords: Corrosion, fluoride, EIS, titanium implants, normal saline

1. INTRODUCTION

Titanium and its alloys are routinely used in dental vocation as a prosthetic and implant material because of their high corrosion resistance and biocompatibility. These properties are due to the formation of a passive titanium oxide film that is rapidly formed on exposure to the oral environment [1-4].

Dental caries is a chronic, infectious bacterial disease caused by the growing bacterial plaque/bio-film onto the hard (tooth) and soft tissues (mucosa and sub-mucosa along the gingiva, tongue, cheeks and tooth pockets) in the oral cavity[5-7]. Anti-bacterial agents in addition to several other preventive measures can prevent plaque accumulation and dental caries.

Fluoride containing toothpastes, mouth-rinses and prophylactic agents are commonly used as a part of in-home and in-office therapy to get rid of dental bacterial decay[6-8].

After extensive research, Knutson, Bibby and his co-workers[8-13] suggested the application of sodium fluoride (NaF) onto the tooth surface to prevent dental decay. Knutson used 2% solution of freshly prepared NaF (dissolving 20 gm of ACS grade NaF in 1L of the solvent), applied 4 times at weekly intervals for 4 minutes, at the age group of 3, 7 11 and 13 years respectively depending upon the eruption patterns for the deciduous and permanent dentitions. When NaF is applied topically, it reacts with the hydroxy-apatite crystals in the enamel matrix to form calcium fluoride (CaF_2), which forms a thick layer over the enamel surface and causes the choking off effect.

$$Ca_{10}(PO_4)_6(OH)_2 + 20F^- \text{ (from NaF)} \rightarrow 10CaF_2 + 6PO_4^{3-} + 2OH^-$$

$$CaF_2 + 2Ca_5(PO_4)_3OH \rightarrow 2Ca_5(PO_4)_3F + Ca(OH)_2$$

This high concentration of CaF_2 reacts with hydroxy apatite to form fluoridated hydroxy apatite, thus increasing the overall fluoride content at the surface and leading to tooth structure that is more stable, resistant to acid dissolution, has high enzymatic activity, inhibits plaque metabolism and further causes re-mineralization of the decalcified areas over the tooth surface[14- 19].

However, on the other hand, decreasing corrosion resistance of titanium alloys in fluoride containing solutions has been reported in literature[20-26]. The corrosion behavior of an implant is related to the concentration of fluoride and the localized environment surrounding the implant. Thus, it is of prime importance to understand the surface chemistry of an implant and the changes occurring on its surface[27-32] in the presence of fluoride treatment in order to evaluate its corrosion behavior and tarnish properties in the oral environment.

The aim of this work is to evaluate the effect of Knutson fluoridation in-office technique on the corrosion behavior of a newer beta Ti36 alloy[33].

2. **EXPERIMENTAL**

2.1. Materials Preparation

Titanium alloy grade Ti36 (UNS R58450, AMS 4982)[33] (composition as mentioned in Table 1) of exposed area 0.81 cm^2 was used for the present investigation. The exposed surface of the specimens was finished with different grades of silicon carbide grit papers (up to 2400 grit) and polished using the diamond abrasive wheel to a quarter micron finish, washed with double distilled water and acetone.

Normal Saline solution [0.9% Sodium chloride Inj., USP, (Hospira, Inc., IL, USA) (containing 154 meq./1000mL solution of sodium and chloride)] of pH 5.6 (4.5-7.0) was used to carry out the electrochemical testing for the titanium alloy. 2% w/v solution of NaF was prepared in normal saline to study the effect of fluoride ion on the corrosion behavior of Ti36 alloy.

Table 1. Composition of Ti36 (UNS R58450, AMS 4982) [33]

Components (wt. pct.)						
C	H	N	O	Nb	Fe	Ti
0.04 max	0.0035 max	0.03 max	0.16 max	42.0- 47.0	0.03 max	bal

2.2. Measurements

For the electrochemical measurements, Ti36 titanium alloy was used as the working electrode, platinum wire as the auxiliary electrode and a saturated calomel electrode as the reference electrode, as shown in a schematic representation in Figure 1. The DC electrochemical measurements were conducted using a Princeton Applied Research (PAR) Potentiostat 273A and for AC measurements, the same potentiostat was used together with a PAR 1255 frequency response analyser (FRA).

The following scheme of experiments was performed on the Ti36 alloy in normal saline in the absence and presence of 2% NaF solution at the ambient temperature, 298 K.

2.2.1. Open circuit potential (OCP)

OCP values of the alloy were monitored for various time intervals up to 240 hours.

2.2.2. Potentiodynamic polarization

Polarization measurements were performed on immersion and at 240 hours of immersion by polarizing each electrode from an initial potential -500 mV versus the OCP up to the vertex potential of 2 V versus the reference electrode, after which the scan was reversed and the final potential was same as the initial potential. The ASTM standard scan rate of 1 mV/s was used for the polarization sweep[34].

2.2.3. Electrochemical impedance spectroscopy (EIS)

Impedance measurements were performed on the system at the open circuit potential for various time intervals from immersion up to 240 hours. The frequency sweep was applied from 10^5 to 10^{-2} Hz with the AC amplitude of 10 mV.

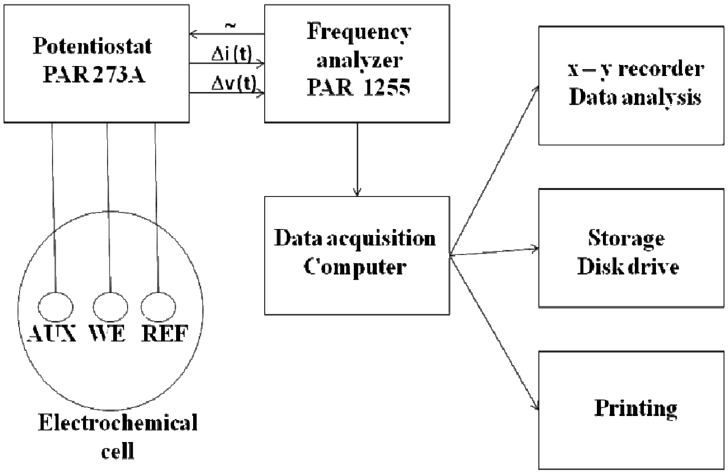


Figure 1. Schematic representation of the three electrode system in electrochemical testing.

3. RESULTS AND DISCUSSION

The progression of the mixed potential (OCP) with time for Ti36 in normal saline and normal saline containing 2% NaF is shown in Figure 2. The increase in OCP with time is observed in pure normal saline solution. This indicates the stability of the air-formed native oxide on the alloy under the conditions used. This increase in OCP for titanium alloys in simulated body fluid solutions has been related to the thickening of the passive oxide film with time[3]. On the other hand, in the presence of 2% NaF, there is a large initial decrease in OCP at 24 hours after immersion, following which the OCP remains more or less constant with time. The initial decrease suggests the instability of the oxide film due to the action of fluoride, thereby causing dissolution of the air-formed oxide. The OCP values for normal saline are more positive as compared to the 2% NaF solution suggesting greater stability of the oxide film on the Ti36 alloy in normal saline compared to 2% NaF solution.

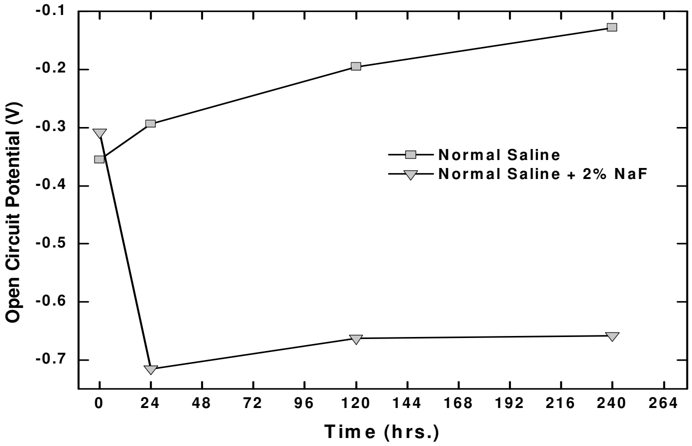


Figure 2. Open circuit potential as a function of time for Ti36 in normal saline and in the presence of 2% NaF

The EIS data for Ti36 in pure normal saline solution at all immersion hours followed the equivalent circuit shown in Figure 3a. The EIS data for Ti36 in the presence of 2% NaF at immersion also followed the same equivalent circuit, however at other immersion hours, it followed the equivalent circuit shown in Figure 3b. In the circuits described, R_s is the solution resistance, R_{ct} is the charge transfer resistance, W is the Warburg coefficient used to represent diffusional impedance, Z_D [35-37] and CPE is the constant phase element, which has been used in place of a pure capacitor. Generally, the appearance of CPE is due to a distribution of the relaxation times as a result of the inhomogeneities present at the microscopic level of the oxide and at the oxide/electrolyte interface [38-40]. The impedance of CPE is given by,

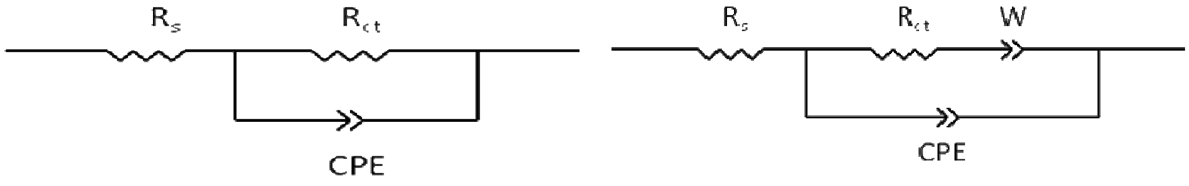
$$Z_{CPE} = Y_0^{-1}(j\omega)^{-\alpha} \quad (1)$$

where ω is the angular frequency in radians/sec, Y_0 is the admittance magnitude of the CPE and α is the exponential term which can vary between 1 for pure capacitance and 0 for a pure resistor[41]. α is a measure of surface inhomogeneity, the lower is its value, the higher is the surface roughening of the metal/alloy[42]. These one-time constant equivalent circuits shown are generally used to fit EIS data in case of a single passive film present on the surface of the metal[43-44].

Diffusional impedance is characterized by three parameters, W(R), W(T) and W(P) [35-37]. W(R) shows the length of Z_D, W(T) is the diffusion time constant and W(P) is the phase factor, $0 < W(P) < 1$. To assess the corrosion resistance of an alloy, polarization resistance values (R_p) need to be determined, which can be obtained using equations 2 and 3.

$$R_p = R_{ct} \text{ (no diffusion).} \quad (2)$$

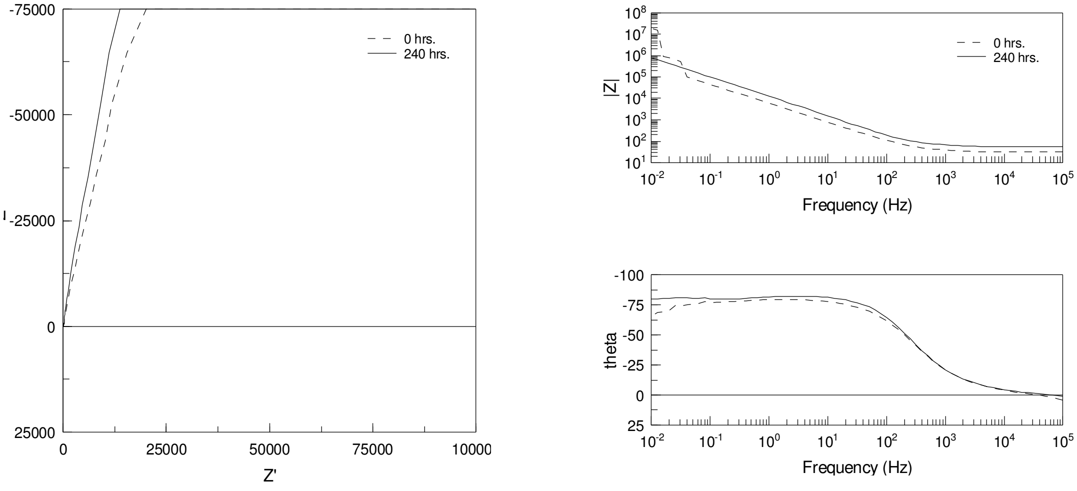
$$R_p = R_{ct} + Z_D \text{ (diffusion).} \quad (3)$$



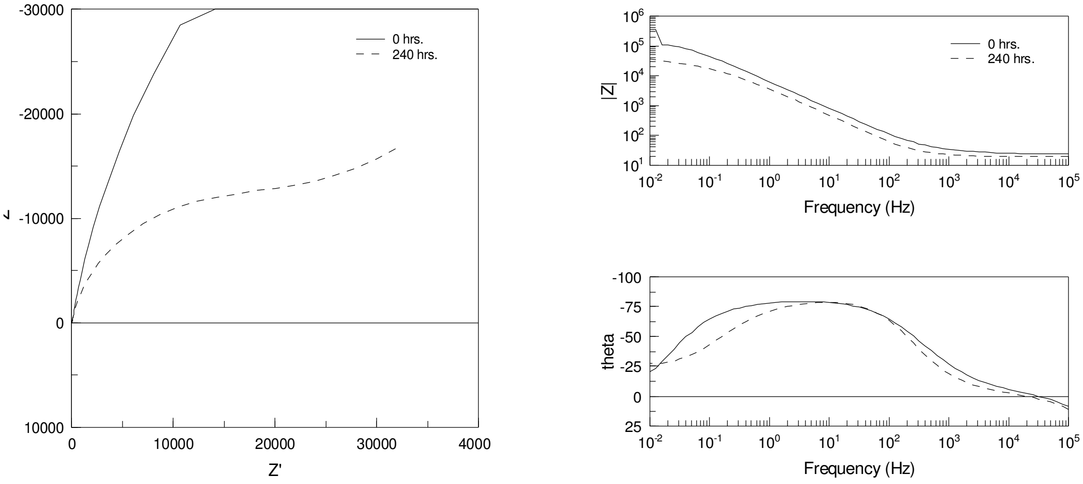
(a) (b)

Figure 3. Circuit models used to fit EIS data

Figure 4 shows the impedance plots for Ti36 alloy in pure normal saline and in the presence of 2% NaF at immersion and after 240 hours of immersion. The impedance parameters derived from circuit modeling at all immersion hours have been listed in Table 2.



(a) Normal saline



(b) 2% NaF in normal saline

Figure 4.(a-b) Impedance plots (Nyquist & Bode) for normal saline and in the presence of 2% NaF at immersion and after 240 hours

In Figures 4a and 4b, it can be clearly seen that the size of the Nyquist plot (diameter of the semi-circle) increases with immersion time for Ti36 in pure normal saline, whereas in the presence of 2% NaF, it decreases with immersion time. This is due to the attack of fluoride ions on the passive oxide formed on Ti36. In addition, at higher immersion hours, a diffusional impedance component is also observed at low frequencies. This observation is suggestive of the fact that due to the attack by fluoride ions, the oxide layer develops porosity and gives rise to the mass transport of ions which is revealed as a diffusion tail in the Nyquist plots. From the phase angle Bode plot for 2% NaF in Figure 4b, it can also be noticed that at low frequencies, the phase angle drops with increasing immersion time. These observations suggest that the polarization resistance value for Ti36 in pure normal saline increases with immersion time, while it decreases in the presence of 2% NaF.

Table 2. Impedance parameters for Ti36 in normal saline and in the presence of 2% NaF

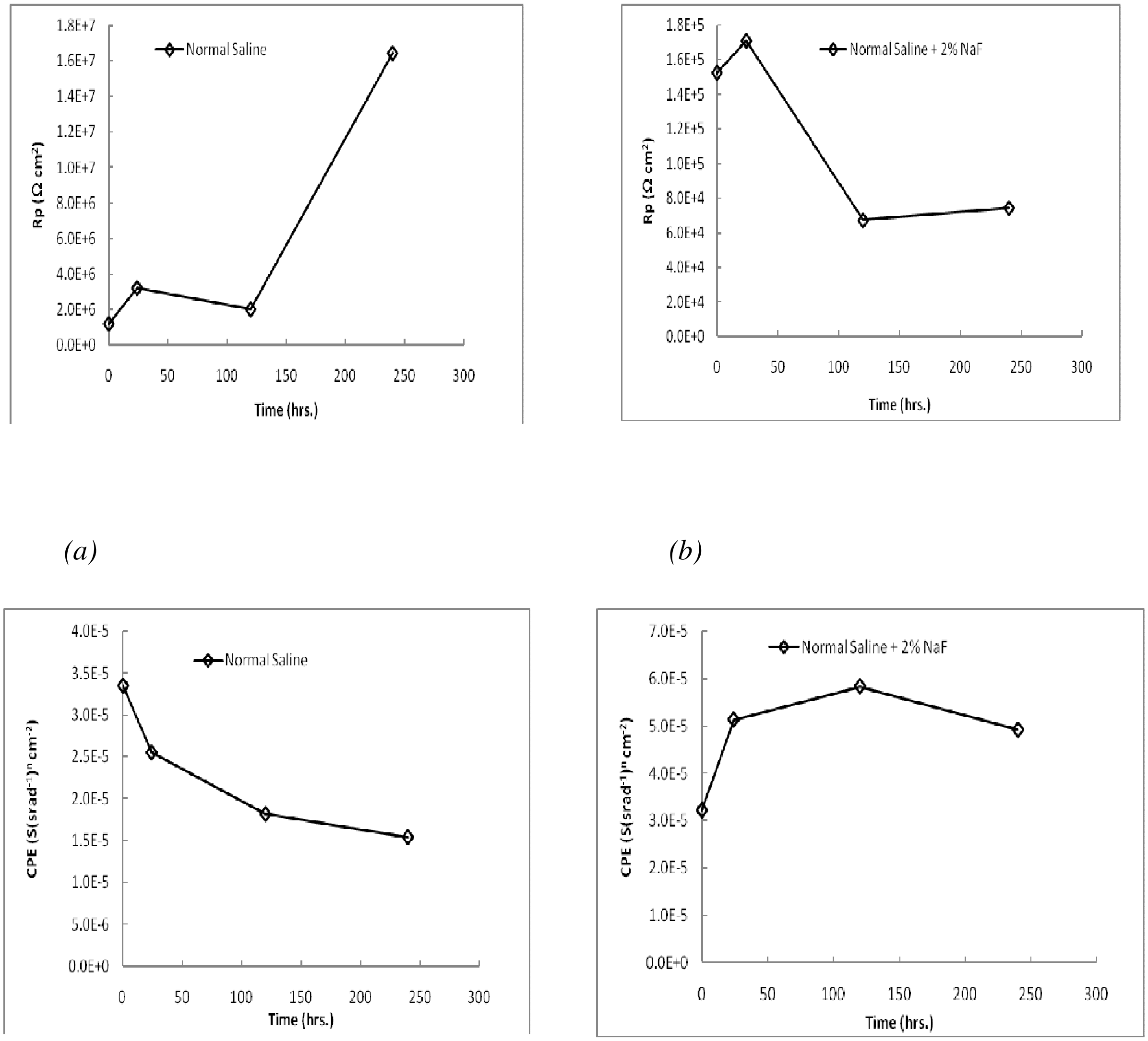
Normal Saline

Ti 36	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	CPE ($S(srad^{-1})^n$/ cm^2)	α	Chi-Square	Weighted sum of squares
0 hrs.	32.30	1.20×10^6	3.35×10^{-5}	0.88	2.98×10^{-3}	0.37
24 hrs.	39.10	3.22×10^6	2.55×10^{-5}	0.89	3.01×10^{-3}	0.37
120 hrs.	38.92	2.01×10^6	1.81×10^{-5}	0.91	3.31×10^{-3}	0.39
240 hrs.	56.19	1.64×10^7	1.53×10^{-5}	0.91	5.14×10^{-3}	0.70

Normal Saline + 2% NaF

Ti 36	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	W (R) (Ω cm^2)	W (T) (s)	W (P)	CPE ($S(srad^{-1})^n$/ cm^2)	α	Chi-Square	Weighted sum of squares
0 hrs.	25.52	1.52×10^5	-	-	-	3.21×10^{-5}	0.88	7.41×10^{-3}	0.99
24 hrs.	27.81	3.19×10^4	1.39×10^5	189	0.49	5.13×10^{-5}	0.87	1.3×10^{-3}	0.16
120 hrs.	28.85	2.53×10^4	4.20×10^4	138	0.53	5.83×10^{-5}	0.87	1.2×10^{-3}	0.15
240 hrs.	19.97	1.59×10^4	5.85×10^4	189.3	0.36	4.91×10^{-5}	0.86	7.2×10^{-4}	0.08

The evolution of polarization resistance and capacitance of the passive oxide film with immersion time for both the cases has been shown in Figure 5. Figure 5a shows an increase in R_p with immersion time in case of normal saline whereas a decrease in the presence of NaF. From Figure 5b, it can be observed that the capacitance of the oxide film on Ti36 in pure normal saline, decreases with immersion time, which indicates the thickening of the oxide film with time. On the other hand, the capacitance of the oxide formed in the presence of NaF increases with immersion time, suggesting the thinning of the oxide due to an increase in its porosity due to the attack by fluoride ions. A decrease in the value of parameter α as observed in the presence of NaF in Table 2, further supplements this proposition. A rough surface with localized corrosion has been reported elsewhere from SEM analyses of titanium upon fluoride addition to NaCl; on the other hand, a smooth Ti surface was found for pure NaCl[45].

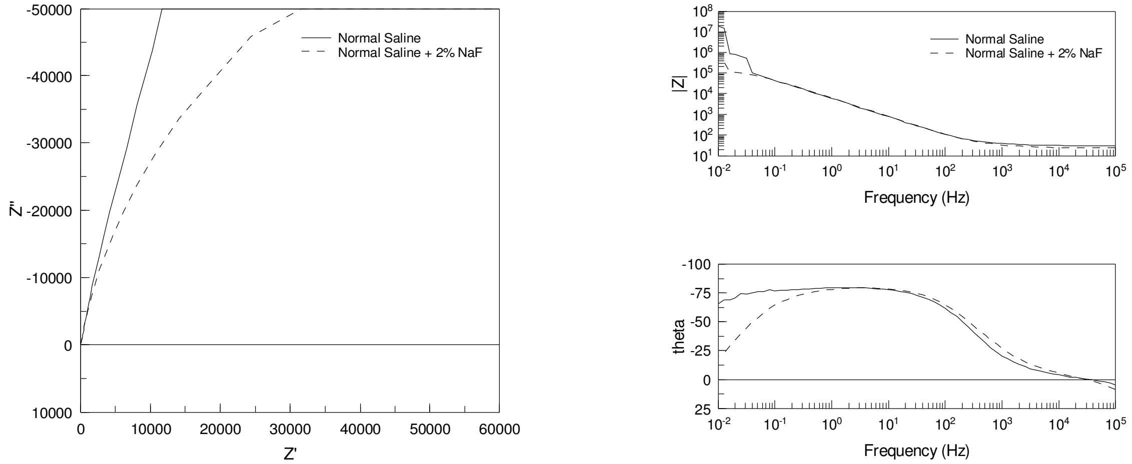


(a) *(b)*

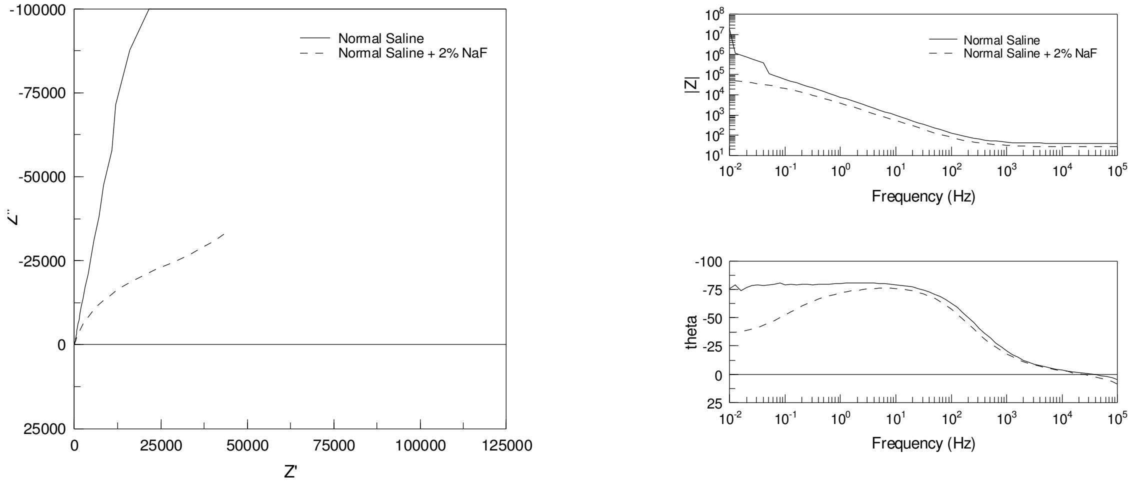
(c) *(d)*

Figure 5.(a-d) Variation of R_p and CPE as a function of time for Ti36 in normal saline and in the presence of 2% NaF

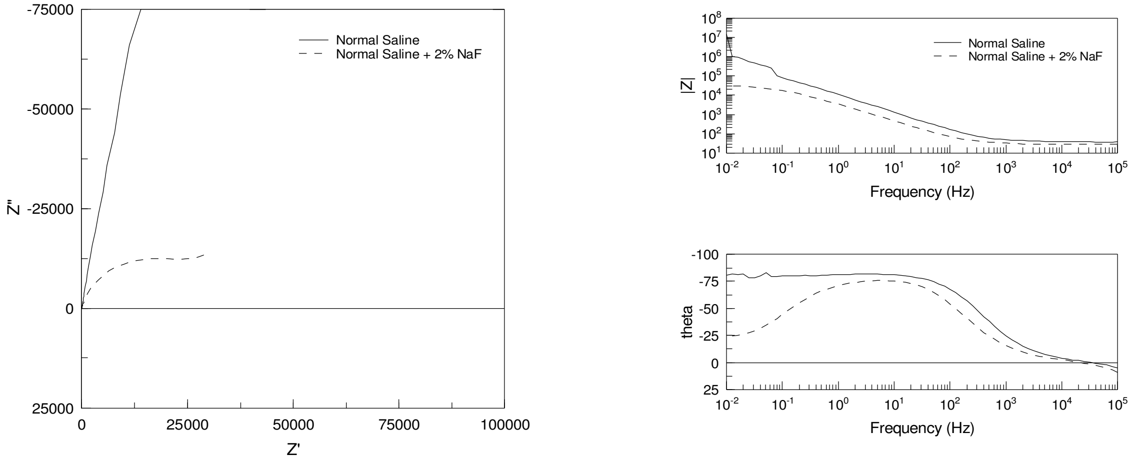
Figure 6 compares the impedance plots for Ti36 in pure normal saline with those in the presence of 2% NaF at various immersion hours.



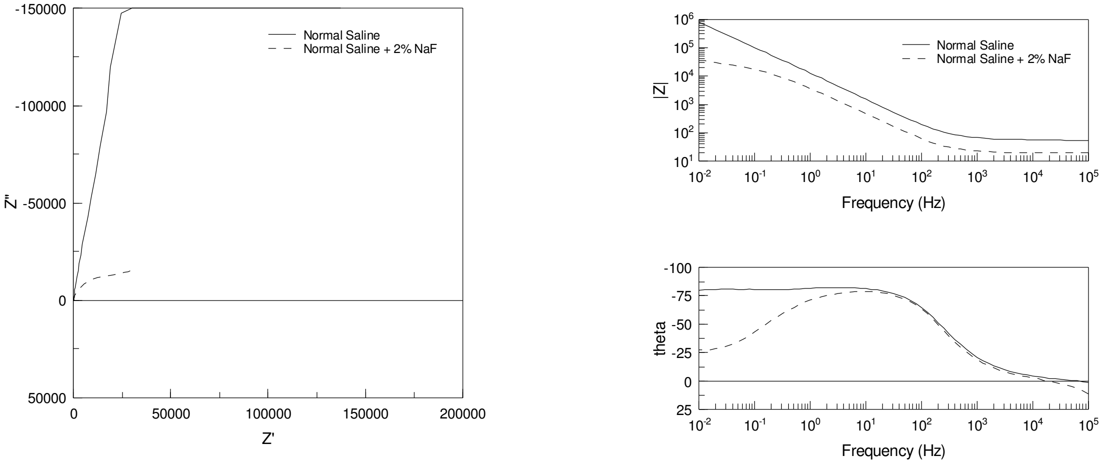
(a) on immersion (0 hrs)



(b) 24 hrs of immersion



(c) 120 hrs of immersion



(d) 240 hrs of immersion

Figure 6. (a-d) Impedance plots (Nyquist & Bode) for normal saline and in the presence of 2% NaF at various time intervals

In the plots shown in Figure 6, it is observed from the phase angle Bode curves for normal saline that the Ti36 alloy exhibits a near capacitive response with phase angles approaching -90º in the intermediate and low frequency regions for all the immersion hours. This indicates a high stability of the oxide film, also marked by high impedance values in the low frequency region, which are related to the polarization resistance of the alloy. However, the phase angles for Ti36 alloy in the presence of 2% NaF at all immersion hours decrease at low frequencies, thus deviating from the near capacitive behavior. At the low frequency end of the spectrum, on comparing the phase angles for pure normal saline with those in the presence of NaF, it is clearly visible that the phase angle difference increases as the time of immersion increases. This suggests that the passive film in the presence of NaF is not stable and starts to dissolve due to the adverse effect of fluoride ions. The size of the Nyquist plots in the presence of NaF is also smaller as compared to pure normal saline, which shows a large difference in the polarization resistance values of the alloy in the two cases. The difference in the order of polarization resistance values for the two cases, as seen in Table 2 increases with immersion time from an order of magnitude at immersion to three orders of magnitude at 240 hours of immersion.

There are several reports on the effect of fluoride ions on the passive film characteristics of titanium alloys[46-50]. Fluoride ions are known to interfere in titania formation which causes changes in the protective passive properties of the oxide layer over the metal[47-48]. The role played by fluoride towards the thinning of the metal oxide layer is dependent on the concentration[47-49] and pH of the solution[49] which causes a substantial decrease in corrosion resistance and increase in the oxide layer capacitance. Fluoride ions in the 2% concentration studied play a significant role in making the oxide film defective as seen by the decrease in polarization resistance and increase in capacitance as compared to pure normal saline from our results.

Kaneko et al.[50] have proposed a mechanism for the destructive decay of the oxide layer over the metal surface in fluoride environment. On addition of NaF to the normal saline solution, it dissociates into Na^+ and F^- ions. The F^- ion becomes hydrofluoric acid partially, depending upon the pH of the solution and attacks the passive film over the metal surface. An increase in pH value after immersion of titanium in solution containing fluoride suggests that the hydrofluoric acid decomposes to form titanium fluoride compounds on the metal surface by one or more ways as below:

$$Ti_2O_3 + 6HF \rightarrow 2TiF_3 + 3H_2O$$

$$TiO_2 + 4HF \rightarrow TiF_4 + 2H_2O$$

$$TiO_2 + 2HF \rightarrow TiOF_4 + H_2O$$

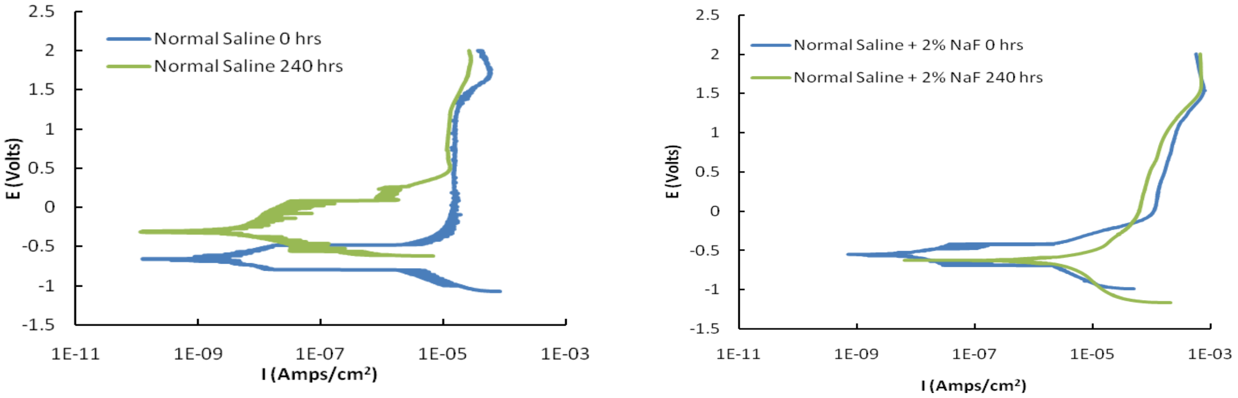
Titanium fluoride compounds are formed because the fluoride ions bound to titanium or titanium oxide surface degrade in the solution.

Fovet et al.[51] described a similar mechanism for the dissolution of surface film under the influence of fluoride, following hydrolysis of sodium fluoride and depletion of surface film under an attack of the hydrated halide complex. A critical pH (neutral range for high fluoride concentrations and acidic range for low fluoride concentrations) was proposed for the dissolution of TiO_2 film and conversion to $TiHF_6^-$. The following mechanism was proposed:

$$TiO_2 + 6HF \rightarrow TiHF_6^- + 2H_2O + H^+$$

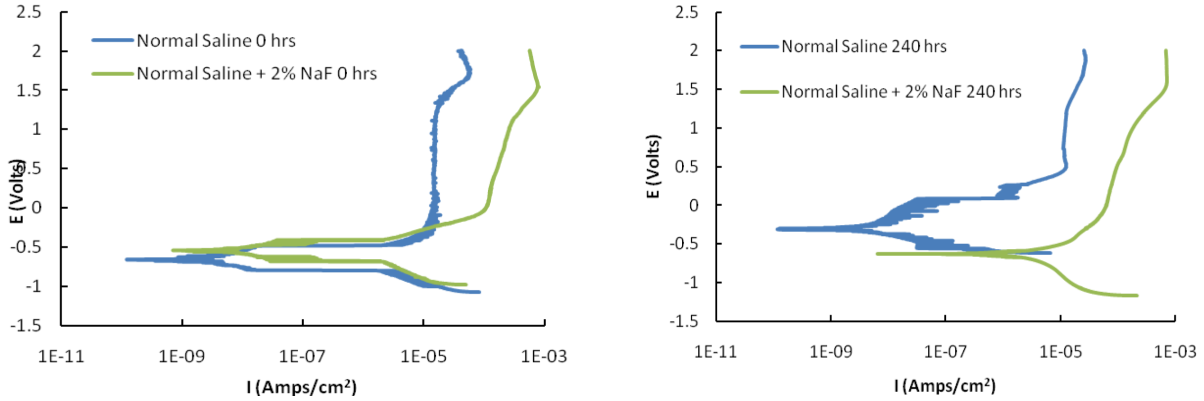
$$TiO_2 + 3HF_2^- + 2H^+ \rightarrow TiHF_6^- + 2H_2O$$

Figure 7 shows the potentiodynamic polarization curves for Ti36 in normal saline and in the presence of 2% NaF at immersion and after 240 hours.



(a) Normal saline
(0 & 240 hrs)

(b) Normal saline + 2% NaF
(0 & 240 hrs)



(c) Pure normal saline & in the presence of 2% NaF (0 hrs.)

(d) Pure normal saline & in the presence of 2% NaF (240 hrs.)

Figure 7.(a-d) Potentiodynamic polarization curves for normal saline and in the presence of 2% NaF at immersion and after 240 hours

The polarization curves for Ti36 in normal saline exhibit similar features to those for the fluoride containing solution.

For pure normal saline, it is observed from Figure 7a that the anodic branch of the Tafel curve shifts towards lower current densities at 240 hours as compared to immersion, whereas in case of a fluoride containing solution, the anodic current density in Figure 7b, appears to have shifted to higher current densities at 240 hours compared to immersion. This trend supports the results obtained from impedance analyses. Because of the decrease in corrosion rate in pure normal saline with increasing immersion time, its OCP increases and because of the increase in corrosion in case of fluoride containing solution with increasing immersion time, its OCP decreases, as was seen in Figure 2. There are also reports on the increase in the anodic current density both in the active and passive regions with increasing fluoride concentration [52].

In Figures 7c and 7d, the behavior of Ti36 in pure normal saline is compared to normal saline containing fluoride at immersion and after 240 hours. It is observed that at immersion, in the presence of fluoride, the anodic current density in the passivation range shifts towards higher current densities as compared to pure normal saline. However, at 240 hours, the anodic current density has increased in both the active and passive regions in the presence of NaF compared to pure normal saline. This suggests that at longer immersion times, the fluoride is able to interfere in the anodic dissolution process, resulting in significant corrosion as compared to immersion. This is also seen in the impedance results where the difference in polarization resistance values for the two systems (pure normal saline and normal saline containing fluoride) on immersion is less than at 240 hours.

Use of fluoride in the oral cavity for short-term in-office prophylactic applications such as Knutson, Muller and Brudevold,[8-13] with the aim of preventing caries in the dental tissues offers a less change in the protective properties of the passive oxide film on a dental implant and hence could be acceptable for a short-term use. In addition, exposure of a dental implant to fluoride is usually for brief time duration during the application of oral techniques clinically and the area that comes in contact with fluoride is typically limited to the neckline of an implant, enabling the use of fluoride as safe for a short-term use.

On the other hand, the use of fluoride for long-term in-home applications could lead to an adverse effect on the passive nature of an implant due to a significant increase in the corrosion rate. Thus adequate care must be taken to prevent titanium tarnish and corrosion during long treatments with exposure to fluoride containing compounds by choosing an appropriate pH and concentration of fluoride containing prophylactic solution.

4. CONCLUSIONS

Fluoride ions affect the corrosion behavior of Ti36 alloy by making the passive oxide film less protective. This happens to a higher degree at longer immersion times as compared to a brief immersion period. The polarization resistance of Ti36 in normal saline containing fluoride decreases by one order of magnitude as compared to that of pure normal saline at immersion, on the other hand, the difference increases to three orders of magnitude at 240 hours of immersion as confirmed from EIS results. Polarization measurements show that at longer immersion hours in the fluoride environment, there is a significant increase in the anodic current density in both active and passive regions, as compared to the environment without fluoride.

High levels of fluoride ions can be supplied in the oral cavity by mouth rinses, tooth pastes, fluoride containing restorative materials (composites and glass-ionomers) and certain prophylactic techniques. Thus adequate care must be taken to prevent titanium tarnish and corrosion during long treatments with exposure to fluoride containing compounds. A cautious examination and selection of titanium dental materials should be made in such an environment.

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