

Article

Electrochemical Stability of Passive Films on β -TiZrNbTa Alloys in Seawater-Based Electrolytes: Influence of Fluoride, pH, and Scan Rate

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Abstract

The corrosion behavior and passive-film stability of a β -TiZrNbTa (β -TZNT) alloy were investigated in artificial seawater (ASW), focusing on the effects of pH, temperature, immersion time, fluoride ion concentration, and potential scan rate. In addition to electrochemical methods such as open-circuit potential (OCP), potentiodynamic polarization (PDP), and electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and X-ray diffraction (XRD) were employed for surface characterization. The establishment of a stable and efficient passive layer enriched in Zr-, Nb-, and Ta-oxides was responsible for the β -TZNT alloy's superior corrosion resistance in fluoride-free ASW when compared to commercially pure titanium. Reduced passive-film resistance resulted from corrosion kinetics being greatly accelerated by decreasing the pH and increasing the temperature. The presence of fluoride ions strongly affected the passivity of the alloy due to the chemical dissolution of TiO_2 through the formation of soluble fluoride complexes, resulting in an increase in the corrosion current densities by more than one order of magnitude. A bilayer passive structure with a compact inner barrier layer and a porous outer layer was identified by EIS analysis. The stability of this structure gradually decreased with increasing fluoride concentration and acidity. Over time, passive-film degradation was dominant in fluoride-free seawater, whereas prolonged exposure in fluoride-containing media promoted partial re-passivation. Overall, these results highlight the potential and limitations of the β -TZNT alloy for marine and offshore applications by offering new mechanistic insights into the synergistic effects of fluoride ions and environmental factors on corrosion performance.

Keywords: passive film; Ti alloys; electrochemical impedance spectroscopy; fluoride ions; electrode; polarization



Academic Editor: Yong-Joon Park

Received: 1 January 2026

Revised: 11 February 2026

Accepted: 12 February 2026

Published: 15 February 2026

Correction Statement: This article has been republished with a minor change. The change does not affect the scientific content of the article and further details are available within the backmatter of the website version of this article.

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1. Introduction

Corrosion of marine metals remains one of the most significant challenges in maritime environments, where harsh conditions such as high salinity, fluctuating pH levels, and low dissolved oxygen accelerate material degradation [1]. Owing to their exceptional strength, low density, superior corrosion resistance, and biocompatibility, titanium and its alloys are considered promising materials for various engineering applications, particularly in shipbuilding, automotive, aerospace, and biomedical industries [2–7]. Their superior performance is primarily attributed to the spontaneous formation of a thin, stable, and

highly protective TiO_2 passive film, which exhibits excellent durability in a wide range of aqueous environments [8–11]. When mechanically or chemically disrupted, this film rapidly re-forms through the reaction of dissolved Ti ions with oxygen, demonstrating a pronounced self-healing capability [7,12]. Consequently, Ti alloys typically tolerate wide pH ranges and remain resistant in solutions containing chlorides, sulfates, nitrates, silicates, phosphates, and carbonates [8–11,13]. However, the protective passive film can be severely damaged in the presence of fluoride ions (F^-) in saltwater, even at relatively low concentrations [13–15], leading to accelerated corrosion of the Ti substrate [16,17].

Among the principal anions in seawater is fluoride, with an average concentration of approximately 1.3 mg/kg, although this value can vary significantly with water depth and environmental conditions.

In recent decades, wastewater discharge into the sea has increased due to increased sand extraction activities. Paper mills and coastal mining operations also play a major role in this trend. Fluoride levels in marine environments have increased due to these combined sources. For example, one bay area near a mine had a dissolved fluorine value of roughly 16.68 mg/kg [18]. In addition, localized seawater acidification near metal/biofilm interfaces or within crevices may further accelerate the degradation of passive films by fluoride ions [19–21]. These conditions raise serious concerns for Ti-based components used in seawater systems, including ship structures, desalination units, offshore platforms, and heat exchanger tubing [22–24].

Although several studies have investigated the corrosion behavior of titanium alloys in fluoride-containing environments, most have focused on biomedical conditions, such as artificial saliva. In contrast, studies on marine or saline environments, where the chemistry and corrosion mechanisms are very different, are far less common. For example, Sun et al. [25] examined the effects of low temperature, high pressure, and low oxygen content on the electrochemical corrosion and stress corrosion cracking of Ti-6Al-3Nb-2Zr-1Mo alloy welded joints in simulated seawater. Nevertheless, despite these efforts, the combined influence of pH and F^- concentration on the passive-film stability and corrosion mechanisms of titanium alloys in seawater is still not well understood. Furthermore, the corrosion behavior of the promising β -TiZrNbTa (β -TZNT) alloy in saline environments containing fluoride ions has not yet been systematically evaluated.

Because Zr, Nb, and Ta are highly biocompatible and corrosion-resistant β -stabilizers that significantly enhance both the mechanical strength and passive-film stability of titanium, the β -TZNT alloy is particularly interesting [26].

The incorporation of Nb and Zr promotes the formation of homogeneous composite hydroxyl oxides, which can effectively suppress oxide-film dissolution [27]. These characteristics suggest that β -TZNT is a strong candidate for demanding marine applications; however, little is known about how it responds to corrosion in saline environments that contain fluoride.

Therefore, the present study aims to elucidate the corrosion behavior and underlying mechanisms of β -TZNT alloy in artificial seawater, with particular emphasis on the effects of fluoride ions and pH. Potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), and open-circuit potential (OCP) are employed to characterize the electrochemical response, while post-corrosion surface morphologies are examined to clarify degradation processes.

In addition, mixed-potential theory is applied to examine the dominant anodic and cathodic reactions governing film passivation and re-passivation. The findings of this work provide a deeper understanding of passive-film stability in complex saline–fluoride environments and offer valuable guidance for the design of Ti-based materials with enhanced corrosion resistance for marine applications.

2. Materials and Methods

The β -TZNT's corrosion behavior in an artificial seawater (ASW) was investigated using electrochemical techniques. The chemical constituents (wt. %) of the β -TZNT alloy are 52.19 Ti, 25.43 Zr, 10.45 Nb, 7.09 Ta, 0.39 Al, 0.32 V, 2.55 C, and 1.58 N, while commercially pure Ti contains 98.9 Ti, 0.3 Al, 0.68 C, and 0.12 Si. The electrodes were prepared by employing epoxy cold glue to attach the alloy, leaving 1.0 cm² of the electrode surface exposed to ASW. Fine sandpaper of different grades, from 500 to 800 and 1200, was used to polish them. Distilled water and acetone are used to clean the electrodes. After a minute of activation in 1.0 M HF, the electrodes are rinsed with double-distilled water to thoroughly clean. In all experiments, freshly prepared ASW at pH 6.5 was used, following ASTM D1141-98 [28]. The chemical composition of the ASW was (g/L): 5.20 MgCl₂, 24.53 NaCl, 1.16 CaCl₂, 4.09 Na₂SO₄, 0.201 NaHCO₃, 0.695 KCl, and 0.101 KBr. When necessary, HCl was used to change the pH of the ASW to 2.0, 3.0, 4.0, and 6.5. Furthermore, by varying the amount of NaF, various F[−] concentrations (0, 0.005, 0.0075, and 0.01 M) were obtained in the ASW [15,29]. For potential measurement, a Pt wire was used as the counter electrode and Ag/AgCl as the reference electrode. The electrode specimens used as the working electrode in the electrochemical study were Ti and TZNT electrodes (provided by the Japan Coating Center Co., Tokyo, Ltd., Tokyo, Japan). All electrochemical measurements were carried out using Gamry a 1000 Potentiostat/Galvanostat/ZRA. Each electrochemical parameter was determined using the Echem Analyst (Version 6.11) software from Gamry Instruments. After 30 min of submersion in ASW, the EIS diagrams were produced over a frequency range of 100,000 Hz to 10.0 mHz and an amplitude of 5 mV peak-to-peak. The PDP curves were made with a scan rate of 5 mV s^{−1} within a potential range of −0.8 to +1.0 V. Since the corresponding iR drop was insignificant and had no effect on comparative corrosion analysis, OCP and PDP tests were carried out without iR adjustment.

To evaluate corrosion resistance, electrochemical investigations were performed using standard and validated procedures. Each experiment was repeated three times to ensure reproducibility. The sample surface morphology under test was examined using a JEOL JEM-1200EX II Electron Microscope manufactured by JEOL Ltd., Tokyo, Japan, a form of scanning electron microscopy (SEM). CuK α radiation ($\lambda = 1.54045 \text{ \AA}$) was used in an X-ray diffraction examination (Pana-lytical Empyrean, The Netherlands), with an accelerating voltage of 40 kV and a current of 35 mA. XRD patterns were collected with a calibrated diffractometer using standard reference materials to ensure accurate peak positions. Phase identification was performed by comparing the results with the PDF database, and measurements were repeated to confirm reproducibility.

3. Results and Discussion

3.1. Potentiodynamic Polarization (PDP) Curves

The PDP curves of the β -TZNT alloy and Ti specimens, used for comparison, in artificial seawater (ASW) under identical circumstances at 25 °C, are displayed in Figure 1. The potentials were measured from −0.80 V, where hydrogen evolution is dominant, to 1.0 V at a scan rate of 5 mVs^{−1}. Each sample exhibits active–passive behaviour. Both Ti and the β -TZNT alloy show a wide passive region extending up to +1.0 V, suggesting the formation of a stable passive oxide film and the absence of pitting corrosion. The lack of any detectable pitting over the entire potential range examined confirms that these materials maintain a stable passive film and high resistance to localized corrosion in seawater. The corrosion behavior was evaluated using the passivation potential, E_{pass} , and passivation current density, i_{pass} , for the β -TZNT alloy and Ti, respectively (Table 1). The electrochemical

corrosion parameters listed in Table 1 were used to determine the polarization resistance (R_p) of the β -TZNT alloy and Ti corrosion using Equation (1) [30].

$$R_p = 1/I_{corr} [\beta_c \times \beta_a / 2.303 (\beta_c + \beta_a)] \quad (1)$$

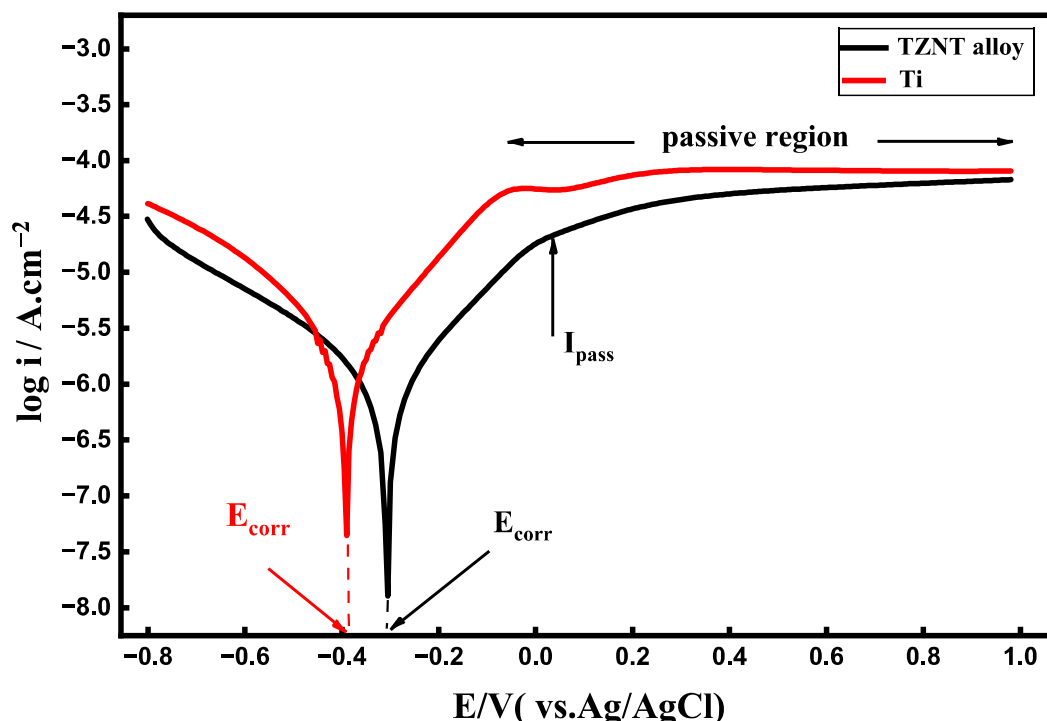


Figure 1. Potentiodynamic polarization (PDP) curves of the β -TZNT alloy and Ti electrode in artificial seawater (ASW) recorded with a scan rate of 5 mVs^{-1} at pH 6.5 and 25°C .

Table 1. Tafel kinetic parameters obtained for a Ti and TZNT alloy in artificial seawater.

Materials	I_{Corr} A cm^{-2}	$-E_{Corr}$ /V	Ba (V dec $^{-1}$)	β_c (V dec $^{-1}$)	$-E_{pass}$ /V	i_{pass} mA cm^{-2}	Corr Rate Mpy	R_p ($\text{k } \Omega \text{ cm}^2$)
Ti	6.26×10^{-6}	0.399	0.687	0.408	0.470	0.080	0.408	17.75
TZNT alloy	1.30×10^{-6}	0.306	0.274	0.368	0.235	0.041	0.168	52.47

The electrochemical parameters summarized in Table 1 demonstrate that the β -TZNT alloy has the lowest E_{pass} and i_{pass} , while Ti exhibits the highest E_{pass} and i_{pass} . The results reveal that in an ASW solution, Ti shows a higher corrosion current, I_{corr} , and lower polarization resistance, R_p , whereas β -TZNT alloy has a higher R_p and lower I_{corr} . This indicates that at 25°C , the TZNT alloy has the highest corrosion resistance in ASW. The TZNT alloy's β -type microstructure, which promotes passive-film formation and moves the corrosion potential toward more noble (positive) values, is responsible for its corrosion resistance. The alloy's enhanced overall corrosion performance is probably a result of this β -phase stability [11]. It is evident from the earlier data that the presence of Ta, Nb, and Zr significantly enhances the corrosion resistance of the TZNT alloy, in contrast to titanium in ASW [31].

3.2. Electrochemical Impedance Spectroscopy (EIS)

Bode graphs are shown in Figure 2a. The impedance modulus value, Z_{mod} , at the lower frequency of the TZNT alloy ($39.81 \text{ k}\Omega \text{ cm}^2$) is higher than that of the Ti ($17.37 \text{ k}\Omega \text{ cm}^2$), indicating enhanced corrosion resistance of the protecting oxide film of the β -TZNT alloy in ASW. Additionally, the fact that the β -TZNT alloy exhibits a higher phase angle

value (-77.46°) than titanium (-70.09°) suggests that the β -TZNT alloy possesses a more protective passive film in ASW. Figure 2b illustrates the Nyquist plots of the titanium electrode and TZNT alloy after 30 min of immersion in an ASW at 25°C . Due to frequency dispersion, all of the curves in Figure 2b are shown as depressed semicircles [32]. This observation implies that the corrosion mechanisms in both samples are mainly governed by charge-transfer reactions rather than diffusion-controlled processes.

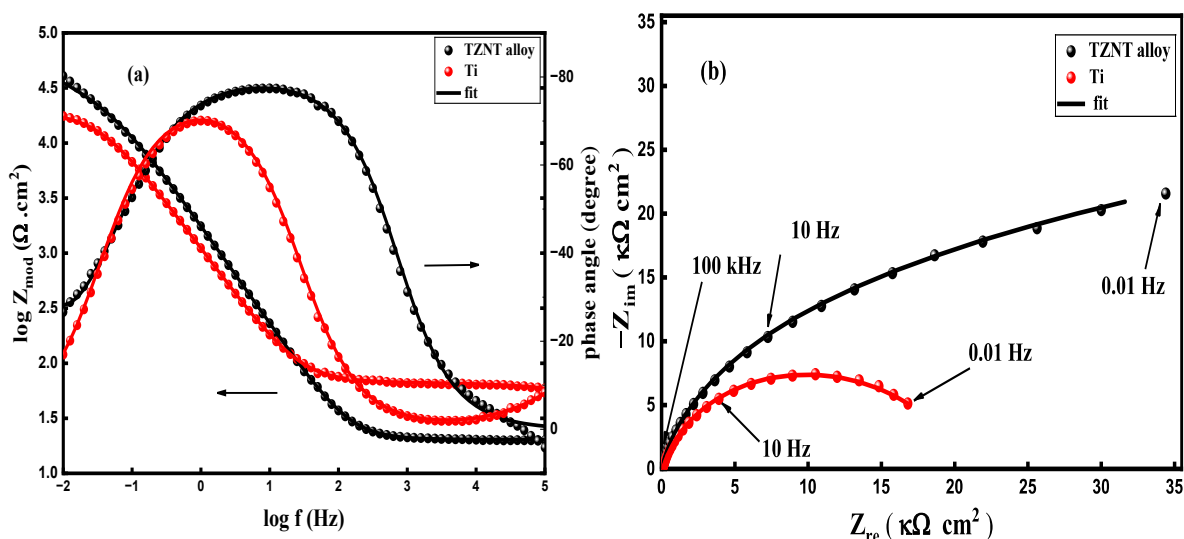


Figure 2. (a) Bode plots and (b) Nyquist plots of electrochemical impedance spectroscopy (EIS) data of the β -TZNT alloy and Ti in artificial seawater (ASW) at 25°C .

The equivalent circuit (EC) depicted in Figure 3 was used to satisfactorily fit the experimental data for all specimens (Ti and β -TZNT alloy). The impedance spectra were analyzed using several electrical circuit models. A bilayer model with an outer porous layer and an inner compact barrier layer was used to describe the passive film on the β -TZNT alloy. The consistent variation of the model parameters with environmental conditions confirms its physical validity.

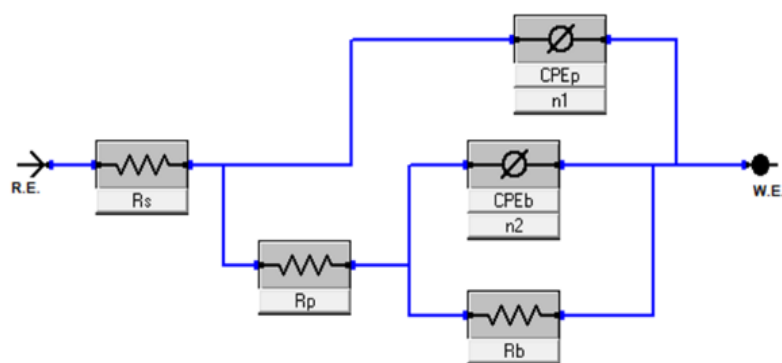


Figure 3. The equivalent circuit (EC) model used to fit the electrochemical impedance spectroscopy data.

The electrolyte resistance (R_s), oxide film–electrolyte interface resistance and constant phase elements, respectively, (R_p and CPE_p), and bulk titanium alloy resistance and constant phase elements (R_b and CPE_b) comprise this EC. To achieve good agreement between the simulated and experimental data, the CPE (constant phase element) was utilized in the fitting procedure instead of pure capacitors. The CPE impedance was estimated using [33]:

$$Z_{\text{CPE}} = [C(j\omega)^n]^{-1} \quad (2)$$

where n is related to non-uniform current distribution arising from surface roughness or inhomogeneity, C represents the capacitance, and ω is the angular frequency. The exponent values n_1 and n_2 were close to 1.0. Table 2 reports the basic EC parameters (R_s , R_b , CPE_b , R_p , and CPE_p) for all specimens examined. For every specimen in ASW, the polarization resistance R_p was calculated as the sum of $R_p + R_b$ on each impedance diagram in the Nyquist form [34]. Nyquist draws (Figure 2b) revealed that the R_p for the TZNT alloy soaked in ASW ($50.81 \text{ k}\Omega \text{ cm}^2$) is higher than that for the Ti ($19.17 \text{ k}\Omega \text{ cm}^2$), indicating an enhanced corrosion resistance of the protective oxide of the TZNT alloy in ASW.

Table 2. EIS fitting parameters that were acquired for a Ti and β -TZNT alloy in ASW at pH 6.5 and 25°C .

Materials	R_s ($\Omega \text{ cm}^2$)	R_b ($\text{k}\Omega \text{ cm}^2$)	CPE_b ($\text{F cm}^2 \text{ Hz}^{1-n_1}$)	n_1	R_p ($\Omega \text{ cm}^2$)	CPE_p ($\text{F cm}^2 \text{ Hz}^{1-n_2}$)	n_2	R_p ($\text{k}\Omega \text{ cm}^2$)
Ti	2.52	19.11	237.4×10^{-6}	0.803	66.48	18.85×10^{-6}	0.798	19.17
TZNT alloy	20.13	50.80	106.7×10^{-6}	0.889	14.25	251.3×10^{-6}	0.766	50.81

3.3. OCP Measurements

Figure 4 illustrates the changes in the OCP of the β -TZNT alloy and Ti electrode in ASW at pH 6.5 and 25°C . Materials can be evaluated for electrochemical nobility by comparing their OCP values [35,36] where higher corrosion resistance is typically indicated by a higher (more noble) open-circuit potential. The OCP rise in the positive direction at a particular time indicates that each sample is vulnerable to the formation of passive oxide layers. The β -TZNT alloy showed a more positive OCP (-0.070 V) than the Ti sample (-0.288 V), demonstrating its superior corrosion resistance and higher passive state stability. The PDP results are in good agreement with the OCP steady-state potential, highlighting the order in which the samples' long-term corrosion resistance declines. In this respect, the TZNT alloy exhibits better performance than Ti.

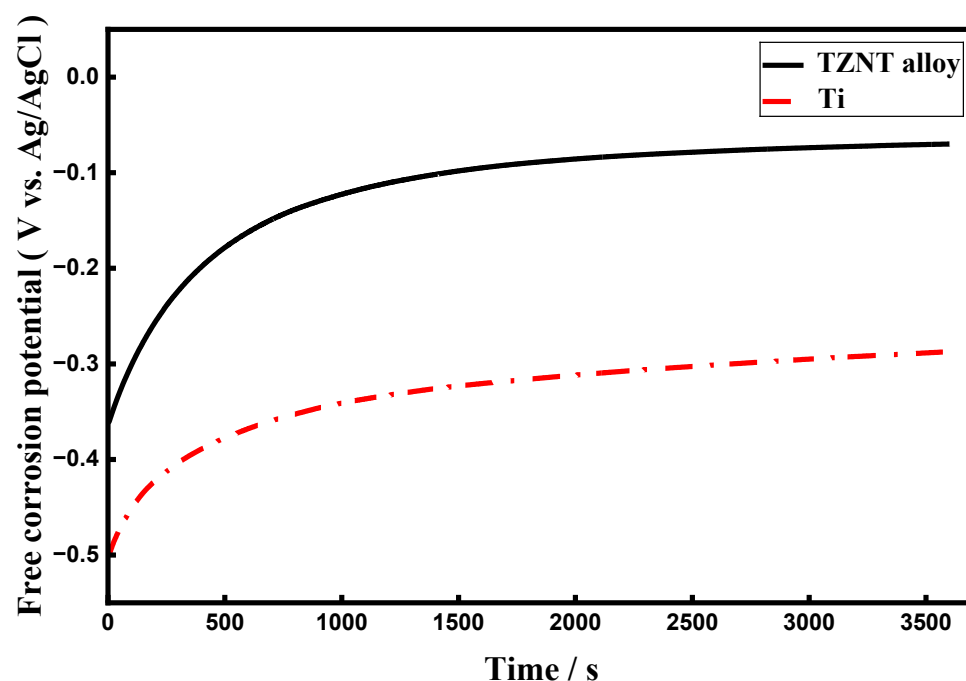


Figure 4. Behavior of open-circuit potential (OCP) as a function of time for Ti and TZNT alloy in artificial seawater at pH 6.5 and 25°C .

3.4. Effect of pH

3.4.1. PDP Curves

Figure 5 displays the PDP curves of the β -TZNT alloy at various pH values in ASW. The PDP curves for the various pH values demonstrated a well-known active–passive behavior. A pronounced decrease in the corrosion resistance of the β -TZNT alloy specimen, reflected by an increased corrosion rate, is evidenced by the shift in the i – E curves toward less noble potentials with decreasing pH. According to Table 3, the I_{corr} is $1.30 \mu\text{A cm}^{-2}$ at pH 6.5, but it increases significantly at pH 4.0 ($4.66 \mu\text{A cm}^{-2}$), pH 3.0 ($8.89 \mu\text{A cm}^{-2}$), and pH 2.0 ($41.4 \mu\text{A cm}^{-2}$), indicating a progressively faster corrosion rate (~ 31 times higher) under increasingly acidic conditions.

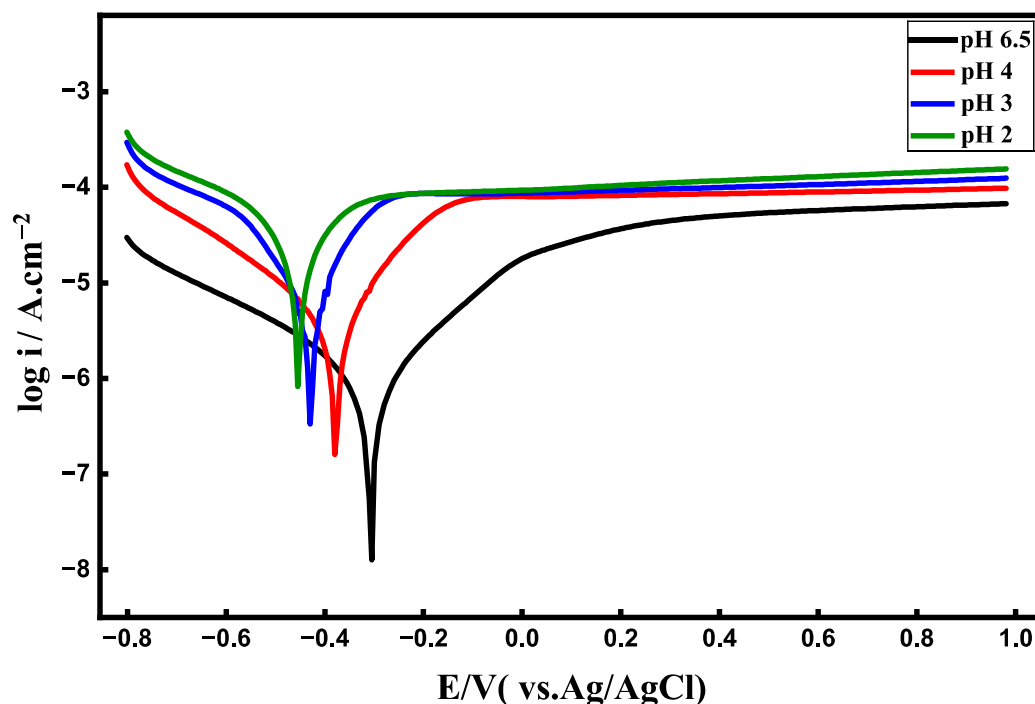


Figure 5. Potentiodynamic polarization (PDP) curves of TZNT alloy electrodes in artificial seawater recorded with a scan rate of 5 mVs^{-1} at various pH values.

Table 3. Tafel kinetic parameters obtained for a TZNT alloy in ASW with various pH values.

pH	I_{Corr} A cm^{-2}	$-E_{Corr}$ /V	β_a (V dec $^{-1}$)	β_c (V dec $^{-1}$)	$-E_{pass}$ /V	i_{pass} mA cm^{-2}	Corr Rate Mpy
6.5	1.30×10^{-6}	0.306	0.274	0.368	0.235	0.041	0.168
4.0	4.66×10^{-6}	0.378	0.175	0.296	0.034	0.080	0.600
3.0	8.89×10^{-6}	0.429	0.143	0.204	−0.179	0.085	1.145
2.0	4.14×10^{-5}	0.454	0.345	0.312	−0.129	0.089	5.334

Furthermore, the passive current density (i_{pass}) measured at 235 mV at pH 6.5, 4.0, 3.0, and 2.0 is relatively stable, with values of 0.041, 0.080, 0.085, and 0.089 mA cm^{-2} , respectively, suggesting that the alloy retains a passive oxide film even as the environment becomes more acidic. This shows that the passive oxide film dissolves quickly in acidic environments, but its rate of degradation is much slower close to neutral pH (6.5), indicating the strong dependence of oxide stability on the pH of the surrounding solution. Despite the limited passivity domain at pH 6.5, the oxide film is highly stable and effectively protects the alloy surface from seawater. The passivity domain is longer at lower pH values, but it has a penetrable, non-protective thin oxide layer that is unable to shield the alloy. This

behavior can be attributed to the detrimental interaction of chloride ions present in ASW with the passive layers.

3.4.2. Electrochemical Impedance Spectroscopy (EIS)

EIS measurements at E_{corr} were performed in ASW at different pH values (Figure 6a,b). According to the Bode phase plot (Figure 6a), the phase angle in seawater at pH 6.5 was approximately -77.43° between 0.5 and 2.5 Hz, covering a broad frequency domain. This behavior indicates the formation of a stable passive oxide layer on the metal surface. As we go closer to the lower pH levels, or pH 4.0, 3.0, and 2.0, the phase angle's height and width diminish, signifying a drop in the resistance of the surface layer and its impact on the impedance. The equivalent circuit shown in Figure 3 was applied to fit the experimental EIS data. R_s represents the resistance of the ASW solution, and the resistance and capacitance of the passive barrier layer on the TZNT alloy's surface are denoted by R_b and CPE_b , respectively. The values of R_s , R_b , CPE_b , and n according to the model's fit are shown in Table 4. As the ASW solution gets more acidic (pH 6.5, 4.0, 3.0, and 2.0), the EIS results for the TZNT alloy show a progressive decrease in oxide-layer resistance. These results are consistent with those derived from the PDP data. The increase in R_s observed at lower pH could be assigned to the fact that the fluoride ion is protonated into neutral HF, which reduces ionic conductivity and consequently increases solution resistance. This trend suggests that bulk electrolyte transport processes, rather than proton concentration alone, govern the observed behavior.

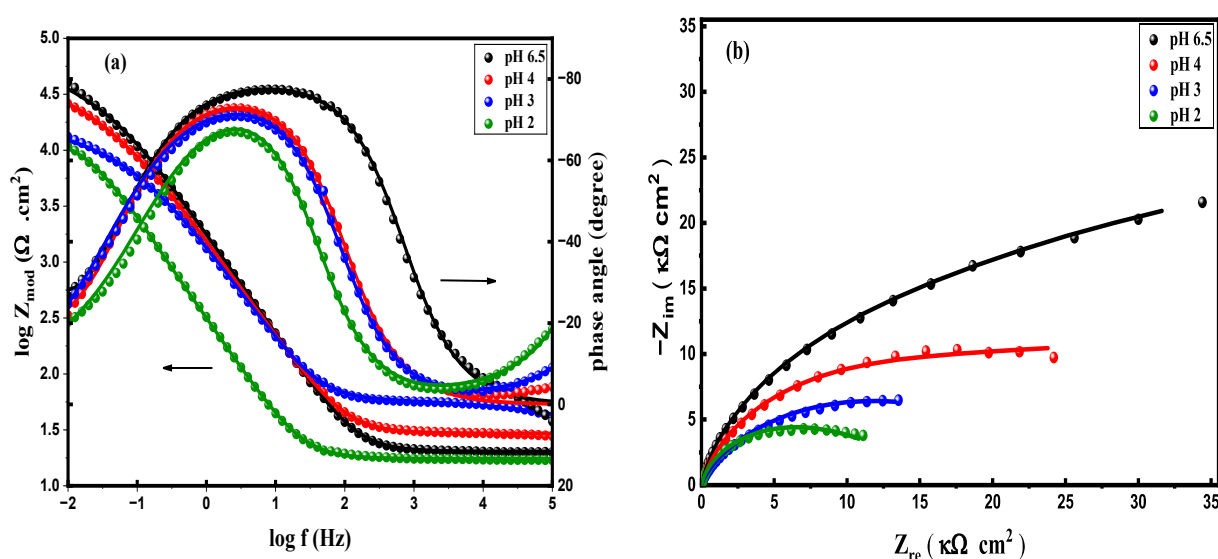


Figure 6. (a) Bode plots and (b) Nyquist plots of the electrochemical impedance spectroscopy (EIS) data of TZNT alloy in artificial seawater with various pH values.

Table 4. Fitting parameters of EIS obtained for a TZNT alloy in ASW with various pH.

pH	R_s ($\Omega \text{ cm}^2$)	R_b ($\text{k}\Omega \text{ cm}^2$)	CPE_b ($\text{F cm}^2 \text{ Hz}^{1-n_1}$)	n_1	R_p ($\Omega \text{ cm}^2$)	CPE_p ($\text{F cm}^2 \text{ Hz}^{1-n_2}$)	n_2
6.5	20.13	50.80	106.7×10^{-6}	0.889	14.25	251.3×10^{-6}	0.766
4.0	28.95	26.65	146.3×10^{-6}	0.840	62.90	345.8×10^{-6}	0.699
3.0	44.35	19.07	189.4×10^{-6}	0.832	29.07	410.2×10^{-6}	0.915
2.0	24.11	12.63	281.0×10^{-6}	0.820	16.14	476.1×10^{-6}	0.862

3.4.3. OCP Assessments

Figure 7 displays the OCP of the TZNT alloy as a function of time at various pH levels in ASW. Compared with pH 4.0, 3.0, and 2.0, the OCP measured at pH 6.5 exhibits a more positive potential. The trends require some time to reach a steady condition. This might result from the development of a novel passivation film that slows down the rate of OCP change in ASW. A quasi-steady state is reached when the potential stabilizes, and the protective (passive) layer reaches a dynamic equilibrium between formation and dissolution [37]. At pH 6.5, the OCP rapidly shifted to a higher positive potential, suggesting that it might quickly re-passivate. The steady-state potential of the passive layer created at pH 6.5 and those formed at lower pH differ significantly, according to the acquired results. For instance, the steady-state potential is -0.070 V at pH 6.5, compared with -0.076 V, -0.085 V, and -0.104 V at pH 4.0, 3.0, and 2.0, respectively. The progressive negative shift observed at lower pH values is likely caused by the thinning of the passive film that followed the early dissolution of the local passivation layer on the TZNT alloy surface.

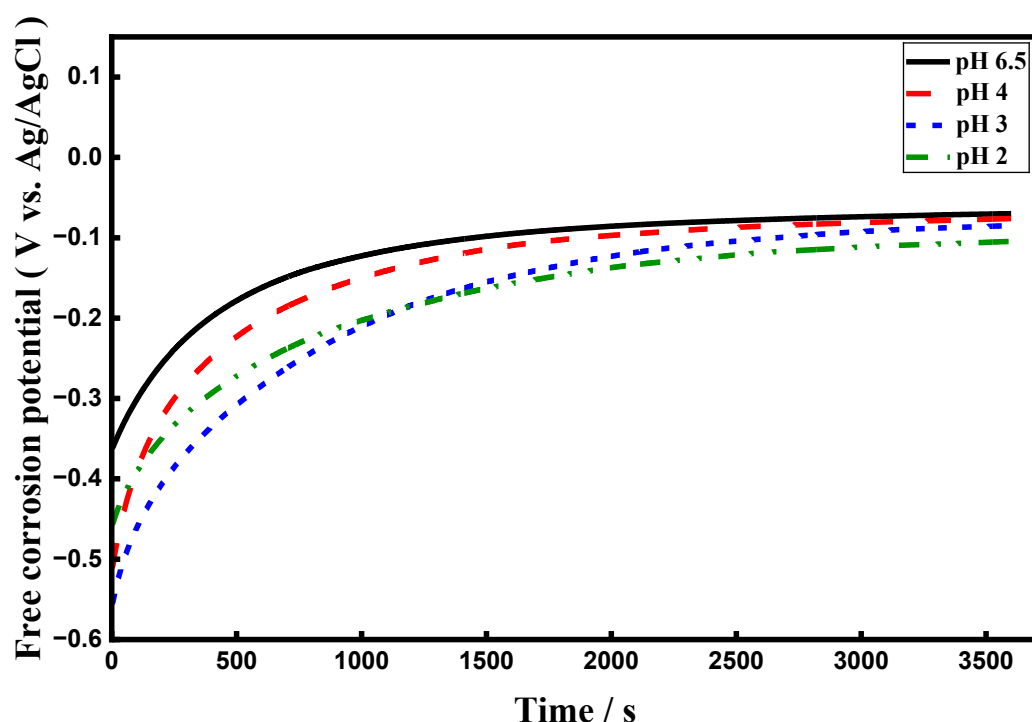


Figure 7. Time-dependent open-circuit potential (OCP) of the β -TZNT alloy in artificial seawater (ASW) at different pH values.

3.5. F^- Ion Concentration's Effect

3.5.1. PDP Curves

Due to its low polarizability and high electronegativity, the F^- ion possesses a great chemical affinity. The F^- , which is easier to adsorb on the titanium alloy and has a smaller radius than Cl^- , occupies the oxygen vacancies in the passive film as opposed to other halide ions. Because TiF_6^{2-} and TiF_6^{3-} complexes form at low pH, it particularly speeds up the cathodic and dissolving rates of β -TZNT alloys under the combined influence of F^- and H^+ [38]. This behavior is mainly attributed to the aggressive dissolution induced by fluoride ions. Figure 8 displays the PDP curves of β -TZNT alloy at various F^- ion concentrations in ASW at pH 6.5. As fluoride ion concentration increases, both the corrosion current density (I_{corr}) and the corrosion potential (E_{corr}) increase, which is obtained when the cathodic and anodic reaction rates are equal, advancing toward a more negative potential. The electrochemical parameters that were found are shown in Table 5. A propensity to create

a passive film is indicated by the values of i_{pass} , E_{pass} , I_{corr} , and E_{corr} ; the lowest values imply straightforward and efficient passivation. The TZNT alloy specimen submerged in ASW with 0.01 M F^- ions exhibits corrosion rates that are 36 times higher than those without F^- ions, indicating severe degradation of the protective oxide film in solutions with high fluoride concentration and acidity [36,39]. According to numerous reports in the literature [17,21], the loss of passivity in fluoride-containing ASW is primarily caused by the chemically assisted dissolution of TiO_2 via fluoride complexation with Ti^{4+} ions, leading to the formation of soluble fluorotitanate complexes. The observed electrochemical and surface reactions are entirely compatible with this dissolution process, even though these species were not directly discovered in our investigation. When F^- ions are present, the chemical dissolution mechanisms of the protective compact passive film mainly match the chemical dissolution of TiO_2 .

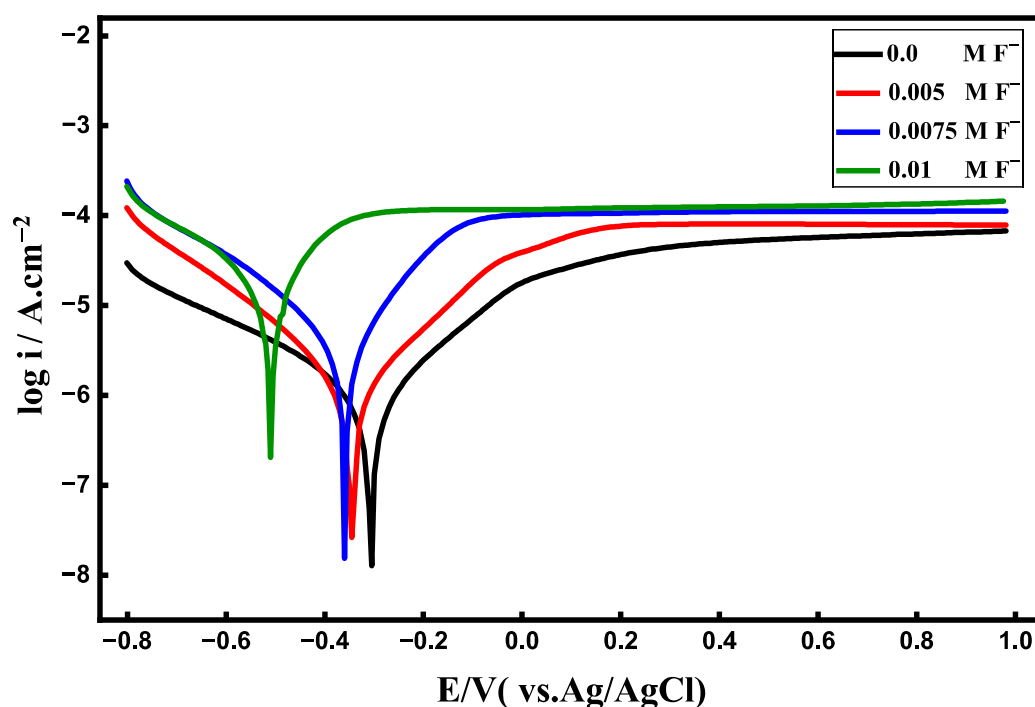


Figure 8. Potentiodynamic polarization (PDP) curves of the β -TZNT alloy electrodes in artificial seawater (ASW) recorded with a scan rate of 5 mVs^{-1} under varying fluoride ion concentrations.

Table 5. Tafel kinetic parameters obtained for a TZNT alloy in ASW with various concentrations of fluoride ions at pH 6.5.

F^-/M	I_{Corr} $A \text{ cm}^{-2}$	$-E_{Corr}$ /V	β_a (V dec $^{-1}$)	β_c (V dec $^{-1}$)	E_{pass} /V	i_{pass} $mA \text{ cm}^{-2}$	Corr Rate Mpy
0.0	1.30×10^{-6}	0.306	0.274	0.368	0.235	0.041	0.168
0.005	2.59×10^{-6}	0.341	0.220	0.267	0.130	0.076	0.336
0.0075	3.59×10^{-6}	0.360	0.159	0.219	0.040	0.103	0.463
0.01	4.76×10^{-5}	0.557	0.279	0.582	−0.239	0.142	6.129

3.5.2. Electrochemical Impedance Spectroscopy (EIS)

The TZNT alloy was submerged in ASW at pH 6.5 and with different fluoride ion concentrations for 30 min after undergoing EIS studies at open circuit potentials. In the absence of fluoride ions, bode plots exhibit significant capacitive behavior with phase angles of approximately 77.43° , and a linear slope of -1 in $\log |Z|$ as a function of $\log (f)$

in the low and middle-frequency range, indicating the presence of a relatively stable and compact passive film on the TZNT surface [39]. The maximum phase angles in Bode plots (Figure 9a) decrease from approximately -77.43° to -73.4° as they move somewhat to the higher frequency area, and the Zmod sharply drops from 39.81 to 10 $k\Omega\text{ cm}^2$ when the fluoride ion concentration increases from 0 to 0.01M, reflecting a pronounced deterioration in the corrosion resistance of the passive film. According to L. V. Taveira et al. [40], the film in 1 M $(\text{NH}_4)_2\text{SO}_4$ electrolytes containing 0.5 weight percent NH_4F consists of an inner layer of TiO_2 and an exterior layer of $\text{Ti}(\text{OH})_4$. They also clarified the formation of a porous structure. The presence of fluoride ions causes the oxide film to randomly disintegrate and decompose. Owing to the proof of the oxide film's bi-layered structure on titanium surfaces, several researchers [41–45] adopted this framework to explain titanium's film characteristics in corrosive liquids. These findings attribute the bi-layered structure of the oxide film formed on the TZNT surface to the overall passive-film behavior and the corresponding EIS responses. Throughout the various ASW conditions examined, the suggested model verifies the existence of an outer porous layer and an inner compact barrier layer. Nyquist plots (Figure 9b) show that the width of the capacitive semicircles decreases markedly as the F^- concentration increases, indicating a decline in corrosion resistance. Compared to pH 6.5/0.005 M, pH 6.5/0.0075 M, and pH 6.5/0.01 M, the impedances of pH 6.5/0 M fluoride ions are substantially higher. These results demonstrate that the alloy's resistance to corrosion decreases as fluoride ion concentrations rise. The enhanced effect of F^- on the β -TZNT alloy corrosion in ASW solutions is therefore quantitatively supported by the EIS results. These observations correlate well with the potentiodynamic polarization data. This bilayer configuration shows excellent agreement with the measured spectra, successfully reproducing the experimental impedance behavior in both the active and passive regions (Figure 9a,b). The values of R_s , R_b , CPE_b , R_p , and CPE_p that resulted from fitting the experimental impedance data of the TZNT alloy in ASW with different fluoride ion concentrations are listed in Table 6 (Figure 9). When TZNT alloy exhibits remarkable corrosion resistance (high impedance values), such as at pH 6.5 and 0 M fluoride ions, it displays compact inner film resistance (R_b) and porous outer film resistance (R_p). This implies that R_b is significant, demonstrating that the passive film can remain compact and undamaged, serving as a corrosion barrier layer in ASW without fluoride ions. When fluoride ion concentrations are high (pH 6.5/0.01 M), the small film's relatively low resistance demonstrates that the TZNT alloy has no corrosion resistance. The porous outer (CPE_p) and compact inner (CPE_b) films' capacitances rise as F^- ion concentration rises, indicating that the dissolution is the reason for the two oxide films' diminishing thickness. CPE_b is higher than CPE_p in the pH and fluoride ion concentration parameters under investigation, indicating a compact and dense layer rather than a porous outer coating. It was further shown that the dissolution of the TZNT alloy in acidic fluoride environments is driven by the presence of other alloying metals [46] and HF/HF_2^- species, rather than fluoride ions alone [47].



$$K1 = [\text{H}^+][\text{F}^-]/[\text{HF}] = 1.30 \times 10^{-3} \text{ mol L}^{-1} \quad (5)$$

$$K2 = [\text{HF}][\text{F}^-]/[\text{HF}^{-2}] = 0.104 \text{ mol L}^{-1} \quad (6)$$

$$[\text{Total F}] = [\text{F}^-] + [\text{HF}] + 2[\text{HF}^{-2}] \quad (7)$$

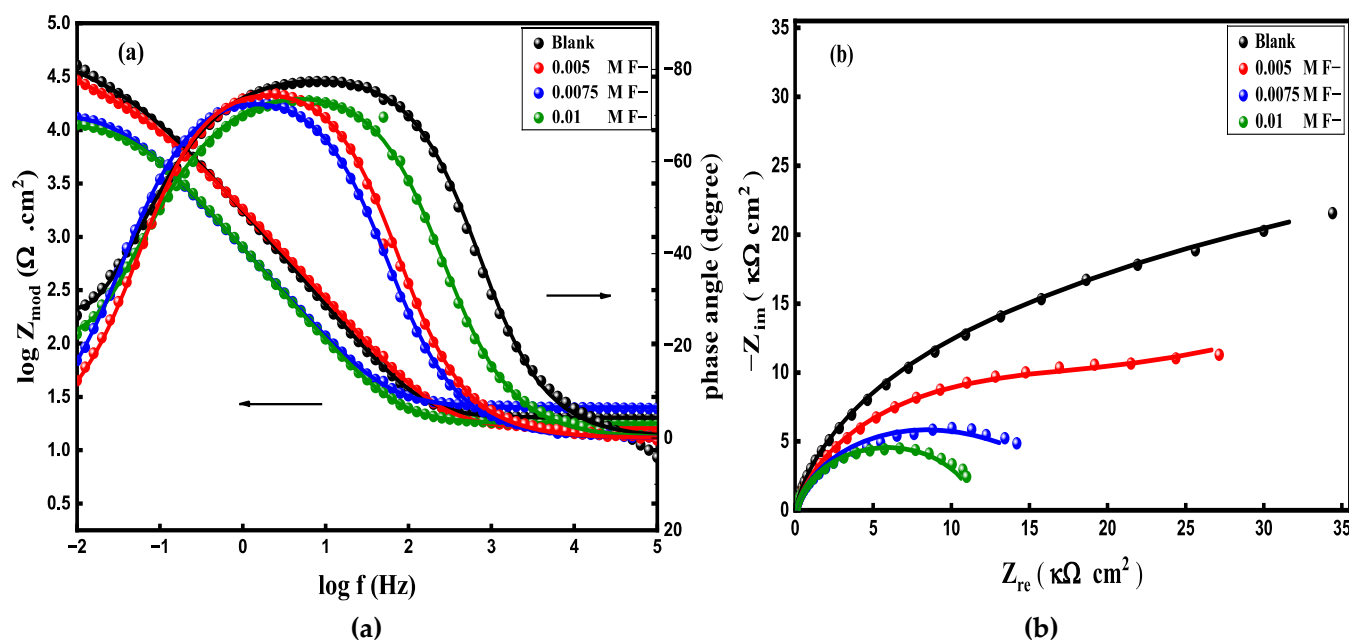


Figure 9. (a) Bode plots and (b) Nyquist plots of electrochemical impedance spectroscopy (EIS) data of β -TZNT alloy in ASW with various concentrations of fluoride ions at pH 6.5. Note that the Nyquist loop diameter reflects charge transfer resistance, whereas the Bode phase angle is governed by capacitive behavior and time-constant distribution.

Table 6. Fitting parameters of EIS obtained for a TZNT alloy in ASW with various concentrations of fluoride ions at pH 6.5.

F^-/M	R_s ($\Omega \text{ cm}^2$)	R_b ($\text{k}\Omega \text{ cm}^2$)	CPE_b ($\text{F cm}^2 \text{ Hz}^{1-n_1}$)	n_1	R_p ($\Omega \text{ cm}^2$)	CPE_p ($\text{F cm}^2 \text{ Hz}^{1-n_2}$)	n_2
0.0	20.13	50.80	106.7×10^{-6}	0.889	14.25	251.3×10^{-6}	0.766
0.005	15.76	27.50	178.3×10^{-6}	0.768	59.12	389.1×10^{-6}	0.836
0.0075	31.25	14.41	193.5×10^{-6}	0.840	64.12	364.2×10^{-6}	0.993
0.01	17.82	9.701	221.3×10^{-6}	0.885	32.15	423.1×10^{-6}	0.957

3.5.3. OCP Measurements

Figure 10 shows the results of an analysis of the presence of different fluoride ion concentrations (0–0.01 M) at pH 6.5 and the change in the OCP evaluation of the β -TZNT electrode with immersion time in ASW. The results show that the environment with and without F^- ions exhibits significantly different OCP values. Over time, the corrosion potential increased to higher potential values due to film formation on the TZNT alloy surface before achieving steady-state potential values (after 1.0 h) at nearly -0.070 , -0.197 , -0.255 , and -0.316 V, which correspond to 0, 0.005, 0.0075, and 0.01 M of F^- ions, respectively. Each sample exhibits an initial increase in OCP toward more positive potentials, which indicates that all samples undergo oxide-film formation (passivation) on their surfaces.

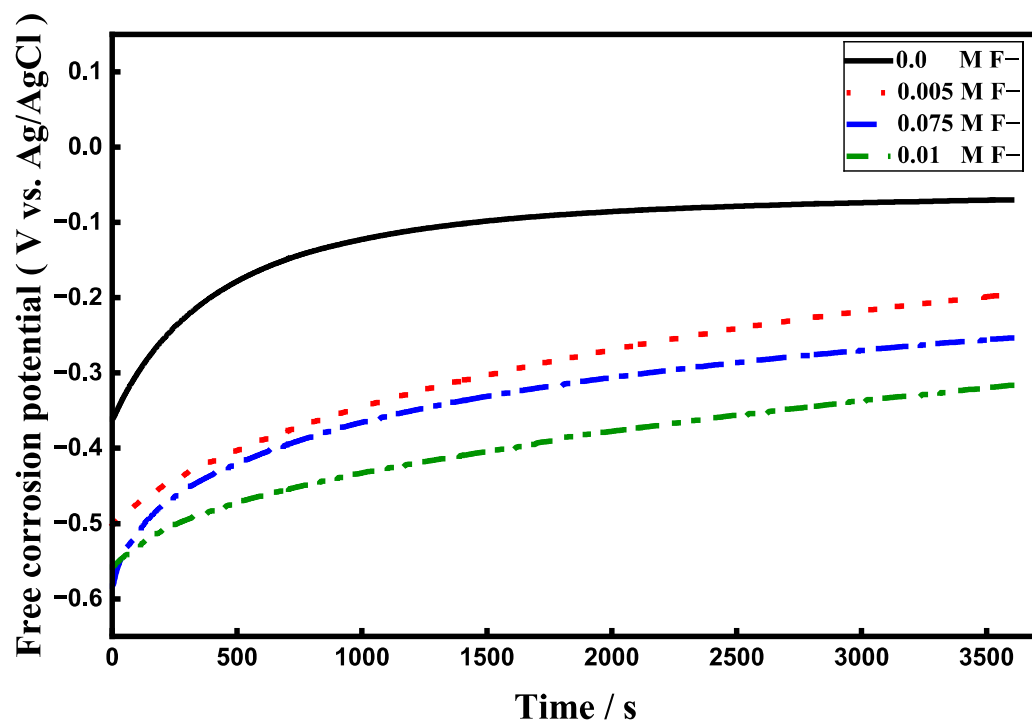


Figure 10. Time-dependent open-circuit potential (OCP) of β -TZNT alloy in artificial seawater (ASW) under varying fluoride ion concentrations.

3.6. Effect of Temperature

Oxygen diffusion accelerates as the experimental medium's temperature rises because the concentration of dissolved oxygen decreases while the diffusion coefficient and total mass-transfer coefficient increase simultaneously. Consequently, the passive film forms more rapidly as the temperature rises. However, as temperatures rise, other corrosive ions also migrate faster. Conversely, at lower temperatures, due to the lower solubility and slower diffusion of oxygen and other species, passive-film growth is slower, but the film exhibits better corrosion resistance. The PDP curves of β -TZNT alloy in ASW at various solution temperatures (298–338 K) are shown in Figure 11. The results indicate that the polarization curves shift toward more negative potentials, and I_{corr} increases significantly as the temperature rises from 298 K to 338 K, suggesting that the β -TZNT alloy dissolves more rapidly at higher temperatures. The increase in Cl^- ion adsorption on the passive layer may also contribute to this behavior [48], along with faster diffusion and migration of reactants and products into and out of pits. Additionally, data in Table 7 show a shift in E_{corr} to more negative values and a substantial increase in I_{corr} , indicating that increasing the solution temperature strongly affects the corrosion rate, i_{pass} , and I_{corr} . For example, as Table 7 illustrates, raising the temperature from 298 to 338 K increases the TZNT alloy's corrosion rate by more than 27 times. The apparent activation energy, or E_a , was calculated using Equation (8) based on the Arrhenius plot's slope (Figure 11 inset).

$$\text{Log } I_{corr} = \frac{-E_a}{2.303 RT} + \log A \quad (8)$$

The data shows that $\log I_{corr}$ is dependent on T^{-1} . The slope $d \log I_{corr} / d(T^{-1})$ is used to get an activation energy of 31.75 kJ mol $^{-1}$. The enhanced solubility of oxides at higher temperatures may explain the temperature-induced increase in oxide formation, and temperature also accelerates the diffusion rate of reactive species [49].

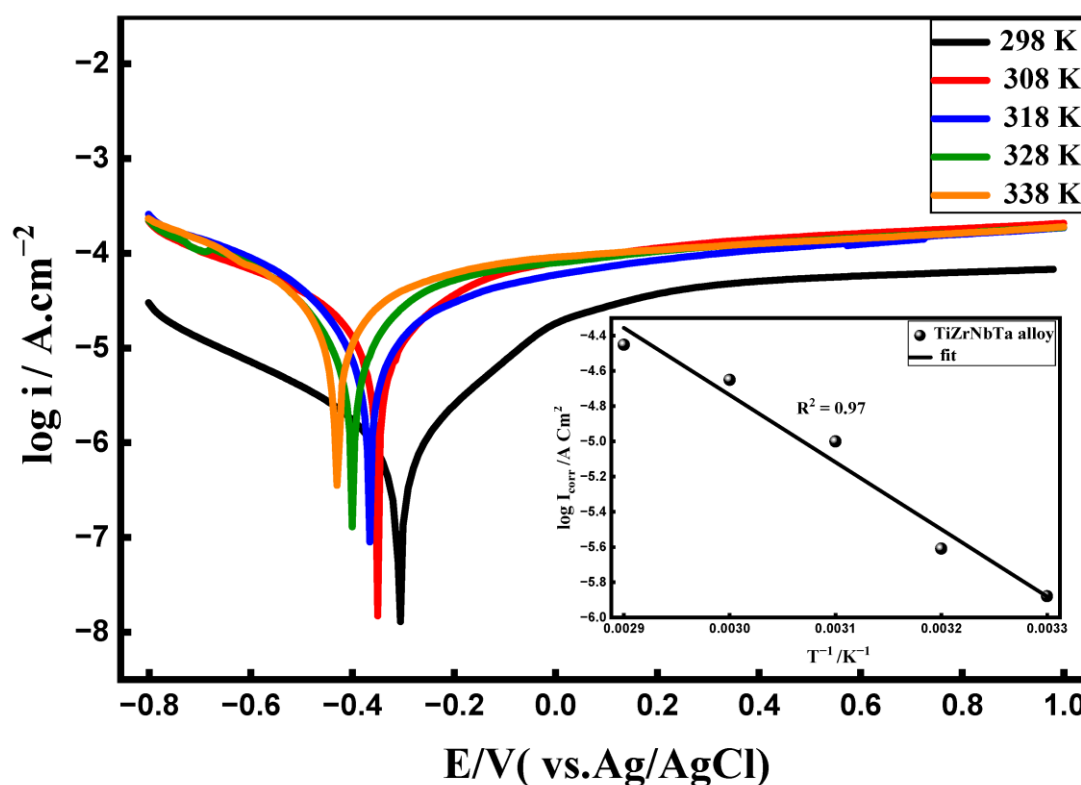


Figure 11. Potentiodynamic polarization (PDP) curves of β -TZNT alloy electrodes in artificial seawater (ASW) recorded at a scan rate of 5 mVs^{-1} at different temperatures. Inset: Arrhenius plot showing the dependence of $\log I_{\text{corr}}$ on T^{-1} (K^{-1}).

Table 7. Tafel kinetic parameters obtained for a TZNT alloy in artificial seawater at different solution temperatures.

Temperature/ K	I_{Corr} A cm^{-2}	$-E_{\text{Corr}}$ /V	β_a (V dec $^{-1}$)	β_c (V dec $^{-1}$)	E_{pass} /V	i_{pass} mA cm^{-2}	Corr Rate mpy
298	1.30×10^{-6}	0.306	0.274	0.368	0.235	0.041	0.168
308	2.43×10^{-6}	0.350	0.050	0.049	0.090	0.085	0.313
318	9.79×10^{-6}	0.365	0.266	0.194	0.100	0.072	1.261
328	2.23×10^{-5}	0.399	0.449	0.372	0.120	0.098	2.873
338	3.54×10^{-5}	0.430	0.703	0.340	0.130	0.094	4.559

3.7. Potential Scan Rate's Impact

Figure 12 illustrates the influence of potential scan rate ν ($5.0\text{--}40 \text{ mVs}^{-1}$) on PDP curves for a TZNT electrode in ASW at 25°C . Table 8 lists the electrochemical parameters i_{corr} , E_{corr} , β_c , β_a , i_{pass} , and CR. The plot of i_{pass} vs. $\nu^{1/2}$ is a regular line (Figure 12 inset), indicating that the i_{pass} grows significantly as ν increases. The equation for diffusion [50,51] goes as follows:

$$i_{\text{pass}} = abn^{1/2}CD^{1/2}\nu^{1/2} \quad (9)$$

where D is the diffusion coefficient of the diffusing species, C is the concentration, n is the electron transmitted, and a and b are constants. This finding implies that the creation of Ti oxide passive layers is a diffusion-controlled process. Because of this, the rate of oxide layer dissolving may compete with the risk of oxide film development at higher sweep rates (dissolution-passivation process) [52]. The chemical breakdown of Ti oxide is expected as the time needed to form the Ti oxide layer reduces as ν increases. Additionally, it was recently demonstrated that the porosities of films made at different scan rates differ

considerably [53]. The data also showed that while the values of i_{corr} , CR , and i_{pass} grow significantly as ν rises, the values of E_{corr} move somewhat to more negative values.

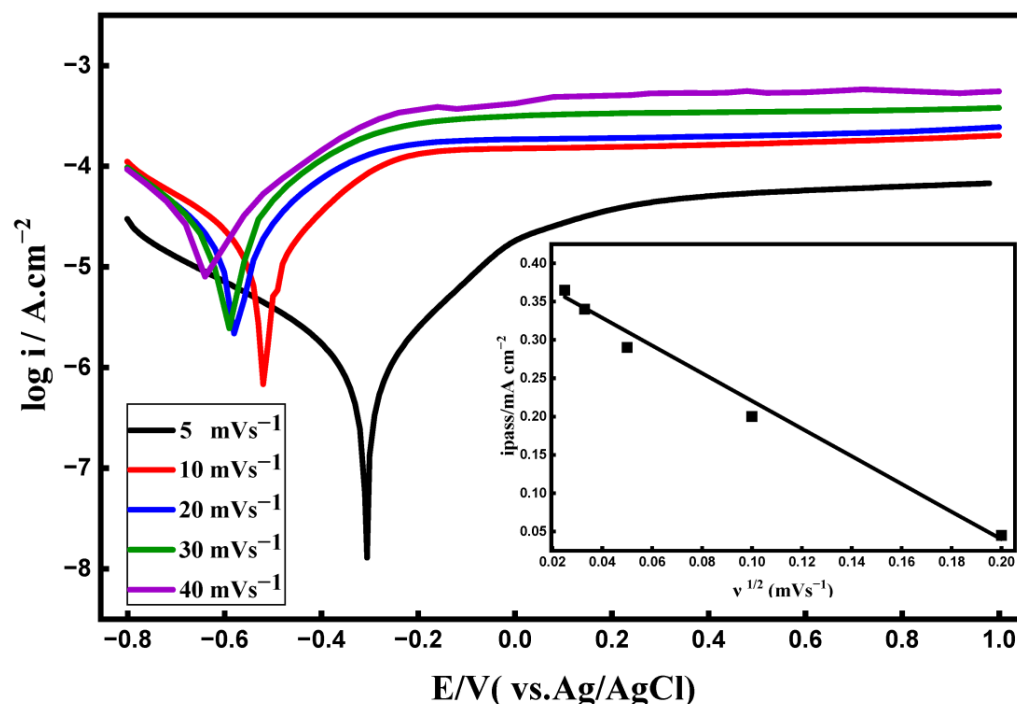


Figure 12. Potentiodynamic polarization (PDP) curves of TZNT alloy in artificial seawater (ASW) at different scan rates (5.0–40 mVs^{-1}) at 25 °C. Inset: dependence of the passive current density (i_{pass}) on the square root of the scan rate ($\nu^{1/2}$).

Table 8. Tafel kinetic parameters obtained for a TZNT alloy in ASW at different scan rates.

Scan Rate mVs^{-1}	I_{Corr} A cm^{-2}	$-E_{Corr}$ /V	β_a (V dec $^{-1}$)	β_c (V dec $^{-1}$)	E_{pass} /V	i_{pass} mA cm^{-2}	Corr Rate mpy
5	1.30×10^{-6}	0.306	0.274	0.368	0.235	0.045	0.168
10	1.85×10^{-5}	0.517	0.314	0.343	0.130	0.200	2.379
20	3.28×10^{-5}	0.574	0.391	0.532	0.140	0.290	4.231
30	5.41×10^{-5}	0.596	0.759	0.594	0.130	0.340	6.969
40	7.76×10^{-5}	0.623	0.636	0.915	0.130	0.365	10.00

3.8. Effect of Immersion Time

3.8.1. Potentiodynamic Polarization (PDP) Curves

The PDP of TZNT alloy in ASW at various immersion periods with and without 0.01 M fluoride ions at pH 6.5 with a 5 mVs^{-1} scan rate at 298 K are shown in Figure 13a,b. The TZNT alloy's polarization curves for test immersion periods in ASW with and without 0.01 M fluoride ion concentrations showed both active and passive behavior. With fluoride ions, polarization curves are pushed toward more noble potential from 0.0 to 15 days (Figure 13a), suggesting an enhancement in β -TZNT alloy corrosion resistance. The polarization curves in Figure 13b change toward less noble potential from 0.0 days to 15 days without fluoride ions, suggesting that the β -TZNT alloy's corrosion resistance declines. Table 9 lists the electrochemical parameters (i_{pass} and E_{pass}) of the β -TZNT alloy exposed to the ASW both with and without 0.01 M fluoride. The statistics indicate a tendency to create passive film (easy and good passivation is indicated by minimum values). The values of E_{pass} and i_{pass} in ASW with 0.01 M fluoride at immersion times of 15 days are lower

than those at immersion times of 0.0 days, as shown in Table 9. This suggests that the passive oxide layer on the TZNT alloy surface is more protective at immersion times of 15 days, while it dissolves quickly at these immersion times of 0.0 days. Additionally, it was observed that the TZNT alloy showed the highest i_{pass} and E_{pass} during the test period in ASW without 0.01 M fluoride when compared to their values in ASW with 0.01 M fluoride. These results demonstrate the exceptional stability and protective ability of the oxide layer formed on the β -TZNT alloy in fluoride-free ASW.

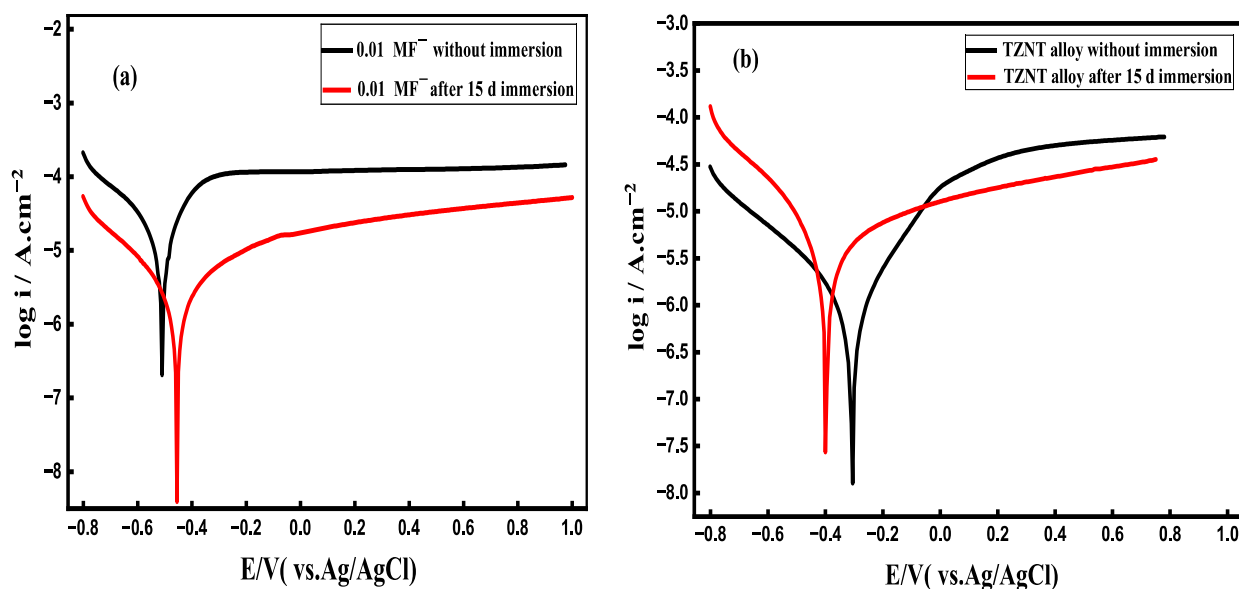


Figure 13. Potentiodynamic polarization (PDP) curves of the β -TZNT alloy electrodes recorded with a scan rate of 5 mVs^{-1} after 15 days immersion in artificial seawater (ASW) with and without fluoride ions at pH 6.5: (a) without and (b) with 0.01 M fluoride ions.

Table 9. Tafel kinetic parameters obtained for a TZNT alloy in ASW at pH 6.5: (a) with and (b) without F^- after different immersion times.

Immersion Time	I_{Corr} A cm^{-2}	$-E_{Corr}$ $/\text{V}$	β_a (V dec^{-1})	β_c (V dec^{-1})	$-E_{pass}$ $/\text{V}$	i_{pass} mA cm^{-2}	Corr Rate mpy
(b) Without F^-							
15 days	3.72×10^{-6}	0.399	0.591	0.199	0.450	0.013	0.478
0.0	1.30×10^{-6}	0.306	0.274	0.368	0.235	0.041	0.168
(a) With F^-							
15 days	5.00×10^{-6}	0.455	0.681	0.409	0.210	0.024	0.643
0.0	4.76×10^{-5}	0.557	0.279	0.582	-0.239	0.142	6.129

3.8.2. Electrochemical Impedance Spectroscopy (EIS)

The findings of impedance measurements in the form of Bode plots for the β -TZNT alloy at longer immersion times in ASW in the presence and absence of 0.01 M fluoride ions are displayed in Figure 14a,b. An electrochemical equivalent circuit depicted in Figure 3 was utilized to analyze the experimental data. According to the Bode plots (Figure 14a), the passive oxide layer is more protective at immersion times of 15 days ($20.89 \text{ k}\Omega \text{ cm}^2$, -73.62°) than it is at immersion times of 0.0 days ($10.71 \text{ k}\Omega \text{ cm}^2$, -74.67°), indicating that the passive oxide layer on the alloy surface dissolves quickly at these immersion times in ASW. The values of Z_{mod} and phase angle in Bode plots (Figure 14b) at immersion times of 0.0 days were ($39.81 \text{ k}\Omega \text{ cm}^2$, -77.41°), suggesting that the passive oxide layer is more protective but less protective in comparison to the 15 days ($14.45 \text{ k}\Omega \text{ cm}^2$, -64.95°), showing that

the passive oxide TZNT layer on the alloy surface dissolves quickly at these immersion times in ASW without 0.01 M fluoride ions. The results of impedance measurements in the form of Nyquist plots for the TZNT alloy at increasing immersion times in the ASW, with and without 0.01 M fluoride ions, are displayed in Figure 14c,d. Figure 3 depicts an electrochemical equivalent circuit used to assess the experimental data. Cyclical changes are depicted in the Nyquist graphs (Figure 14c). In Nyquist plots (Figure 14d), the impedance dramatically rises at 15 days and falls at 0.0 days. These findings show that the corrosive attack of 0.01 M fluoride ions primarily affects the oxide film, which leads to a reduction in the barrier layer impedance. These findings demonstrate that while no immersion in ASW enhances oxide film instability, the oxide layer generated on TZNT alloy by immersion in ASW with 0.01 M fluoride ions is extremely stable and protective. The findings of fitting experimental data to the suggested equivalent electric circuit depicted in Figure 3 are displayed in Table 10. The results demonstrate the exceptional stability and protection of the oxide layer that is created on a TZNT alloy by immersion in ASW with 0.01 M fluoride ions. The potentiodynamic polarization data and the EIS data are in good agreement.

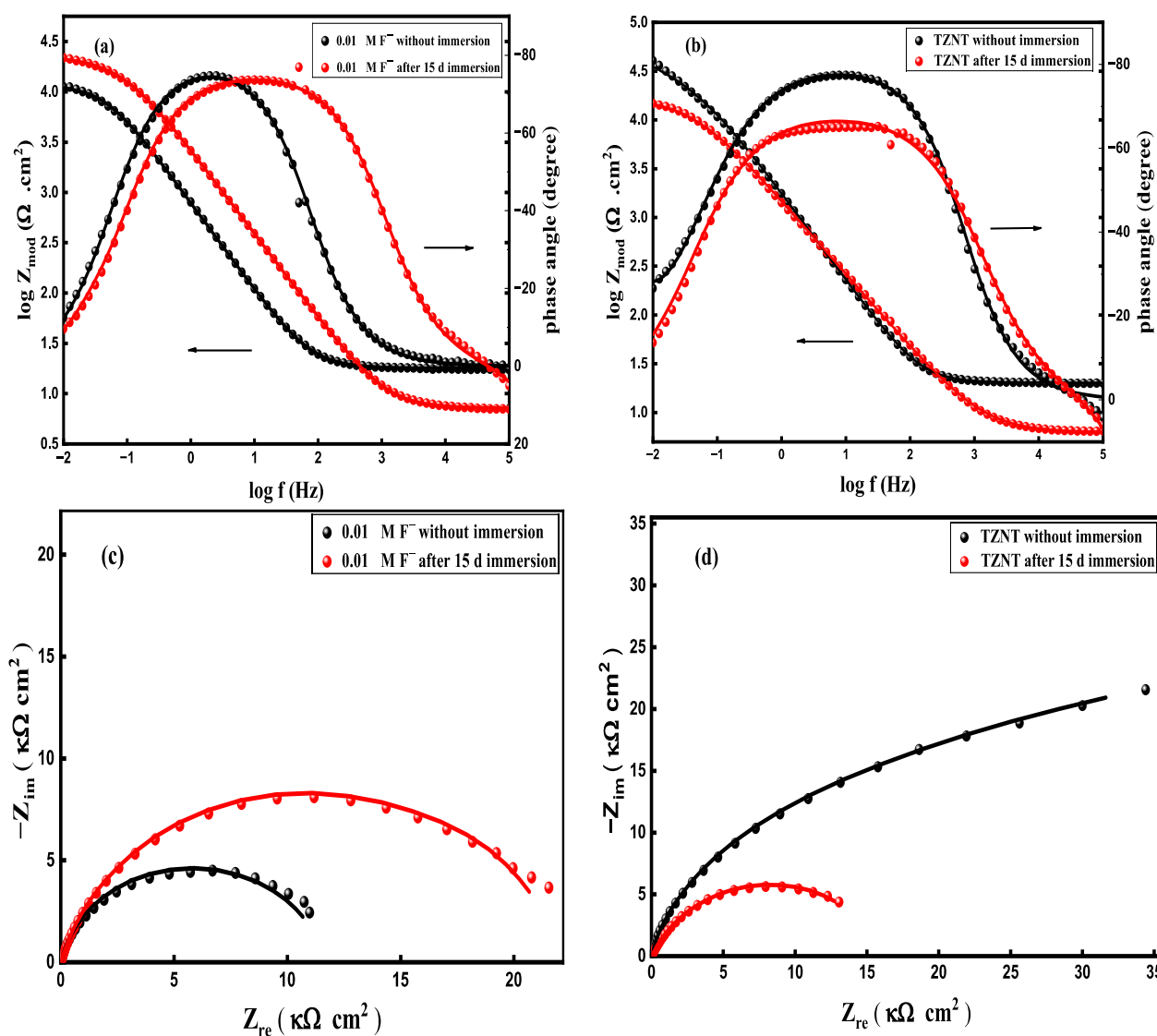


Figure 14. (a,b) Bode plots and (c,d) Nyquist plots of electrochemical impedance spectroscopy (EIS) data of the β -TZNT alloy after 15 days immersion in artificial seawater (ASW) with and without 0.01 M fluoride ions at pH 6.5: (a) without and (b) with 0.01 M fluoride ions.

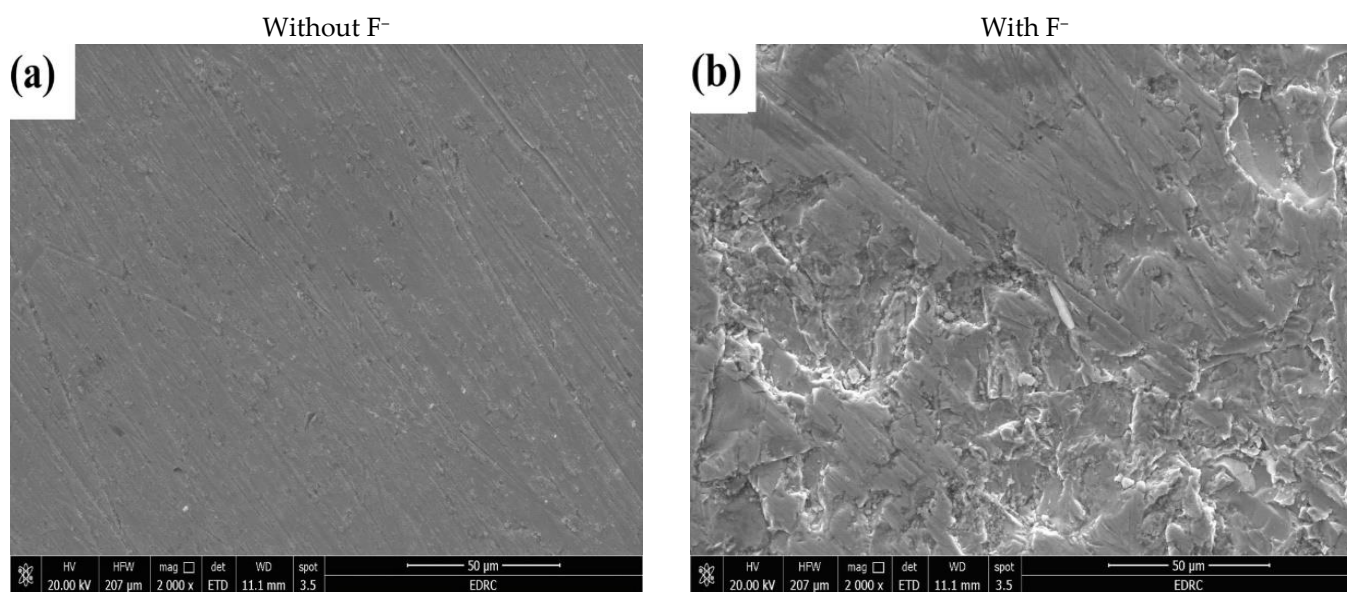
Table 10. Fitting parameters of EIS obtained for a TZNT alloy in ASW at pH 6.5 with and without F[−] after different immersion times.

Immersion Time	R_s ($\Omega \text{ cm}^2$)	R_b ($\text{k}\Omega \text{ cm}^2$)	CPE_b ($\text{F cm}^2 \text{ Hz}^{1-n_1}$)	n_1	R_p ($\Omega \text{ cm}^2$)	CPE_p ($\text{F cm}^2 \text{ Hz}^{1-n_2}$)	n_2
Without F [−]							
15 days	23.16	15.90	135.1×10^{-6}	0.875	6.23	264.5×10^{-6}	0.759
0.0	20.13	50.80	106.7×10^{-6}	0.889	14.25	251.3×10^{-6}	0.766
With F [−]							
15 days	37.22	20.62	83.21×10^{-6}	0.895	35.23	278.4×10^{-6}	0.722
0.0	17.82	9.701	221.3×10^{-6}	0.885	32.15	423.1×10^{-6}	0.957

3.9. Surface Characterization

3.9.1. Surface Morphology

The SEM analysis (Figure 15a,b) showed a clear contrast in the surface state of the TZNT alloy after polarization in ASW with and without fluoride ions. In fluoride-free ASW, the alloy surface remained smooth and intact, showing only polishing marks and no evidence of localized attack, confirming the stability of its passive film. On the other hand, the addition of 0.01 M F[−] caused severe surface degradation, including deep grooves, dissolution patches, and a highly roughened morphology, indicating extensive breakdown of the passive layer. These results demonstrate that while β -TZNT maintains excellent corrosion resistance in normal seawater, fluoride ions significantly destabilize the protective oxide film, leading to severe localized corrosion.

**Figure 15.** SEM images showing the surface morphology of the β -TZNT alloy in artificial seawater (ASW) at pH 6.5 and 25 °C following PDP measurements: (a) without and (b) with 0.01 M fluoride ions.

3.9.2. X-Ray Diffraction

To comprehend the microstructure and phase composition of the β -TZNT sample, an XRD structural analysis was conducted. The X-ray diffractograms for β -TZNT materials as received and following potentiodynamic polarization in ASW with and without F[−] ions are shown in Figure 16. A graph shows the relationship between the relative intensity (counts per second) and the diffraction angle (2θ). The (100), (002), (101), (102), (110), (103), and (104) planes are indexed to the peaks of the as-received β -TZNT alloy at 2θ values of 35.5, 38.75,

40.63, 53.44, 63.59, 71.07, and 77.6°, respectively. The hexagonal α -Ti is represented by these peaks. The (110) and (211) levels of the β -Ti phase are responsible for the two peaks that emerged at $2\theta = 38.75$ and 71.07° , respectively [54]. The most prevalent crystallographic orientation for the hexagonal Ti phase, according to the results, was the (101) plane. The XRD analysis showed no appreciable change in the passive-film composition with or without F-ions (Figure 16). However, following the anodic potentiodynamic polarization in ASW, the primary peak's peak intensity (at $2\theta = 40.63$) of (α 101) increases. On the other hand, following the potentiodynamic polarization in ASW, this peak intensity decreases in the presence of 0.01 M F^- ions. This decrease in peak intensity could be explained by the rapid partial disintegration of the passive layer that takes place during anodic polarization in the presence of F^- ions. The drop in the XRD peak could be explained by the structure becoming more amorphous [55]. A reduction in crystallization, especially at the grain boundaries, might change a material's corrosion resistance [56].

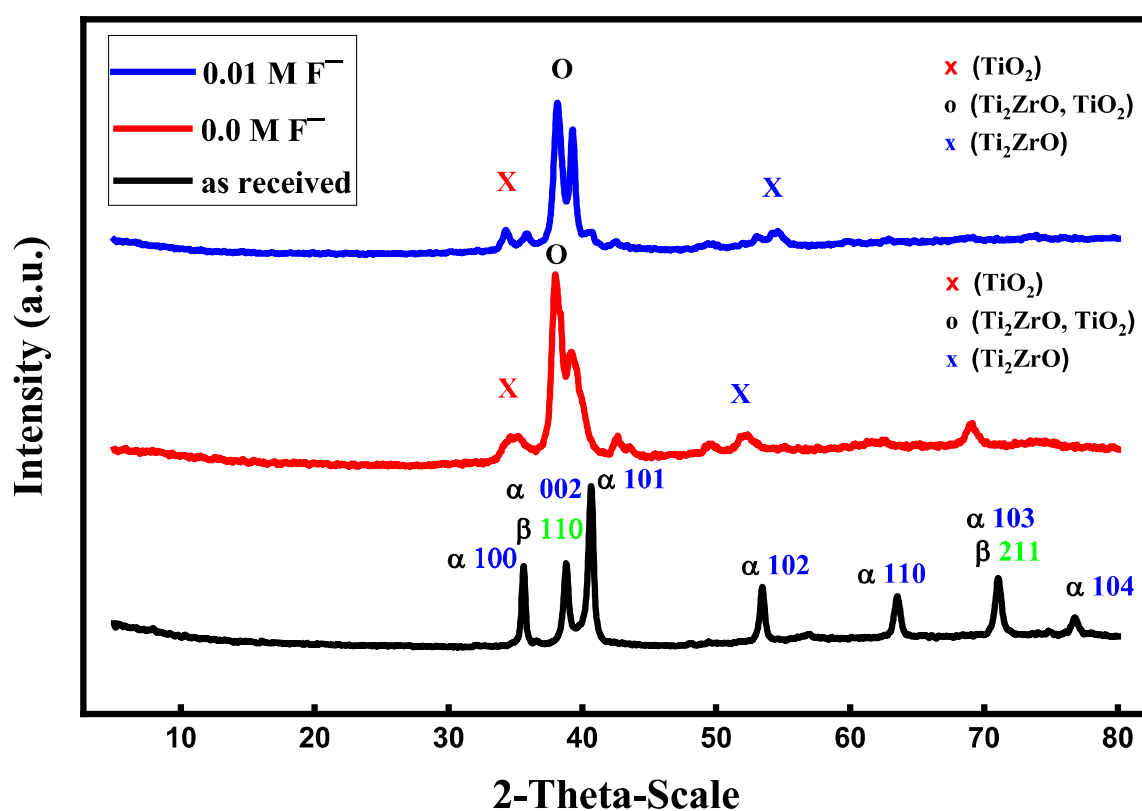


Figure 16. X-ray diffraction (XRD) patterns of the β -TZNT alloy in the as-received state and after potentiodynamic polarization (PDP) in artificial seawater (ASW), without and with fluoride ions. Minor peak shifts after polarization are attributed to lattice strain and surface oxide modifications induced by electrochemical exposure, rather than instrumental artifacts.

It is worthwhile to mention here that XRD revealed no crystalline corrosion products and verified the β -TZNT alloy's bulk phase stability both before and after exposure. Therefore, surface passive coatings, which were evaluated using EIS and supported by SEM observations, govern corrosion behavior.

4. Conclusions

Under a variety of environmental and electrochemical conditions, the β -TZNT alloy's corrosion behavior and passive-film properties in artificial seawater were thoroughly assessed. The following conclusions can be drawn:

1. Superior baseline corrosion resistance: As shown by lower corrosion current densities, higher polarization resistance, and more noble OCP values, the β -TZNT alloy exhibited significantly greater corrosion resistance than commercially pure titanium in fluoride-free artificial seawater at near-neutral pH. This improved performance is attributed to the formation of a stable passive film enriched with an Nb-, Zr-, and Ta-based oxide.
2. pH-dependent passive-film stability: The corrosion rate increased significantly, and passive-film resistance decreased as the seawater environment became more acidic. Even at low pH, passivity was preserved; however, the protective effectiveness of the oxide layer significantly declined due to faster chemical dissolution.
3. Detrimental role of fluoride ions: The integrity of the passive film was seriously jeopardized by fluoride ions, leading to notable decreases in impedance parameters and increases in corrosion current density. The primary mechanism of passive-film breakdown was the formation of soluble titanium–fluoride complexes and HF/HF_2^- species.
4. Bilayer passive-film structure: The passive film on the β -TZNT alloy is made up of an outer porous layer and an inner compact barrier layer, according to EIS analysis. Increasing fluoride concentration, lowering pH, and raising temperature reduced the resistance and thickness of both layers, ultimately leading to film destabilization.
5. Effects of temperature, scan rate, and immersion time: Higher temperatures accelerated corrosion and decreased passive-film stability, with an apparent activation energy of about $31.75 \text{ kJ mol}^{-1}$. The dependence of passive current density on the square root of scan rate indicated diffusion-controlled oxide growth. In fluoride-containing media, prolonged immersion promoted partial film stabilization, whereas in fluoride-free seawater, it caused gradual degradation.
6. Surface and structural confirmation: While XRD analysis revealed partial amorphization of the passive layer after fluoride-induced attack, SEM observations supported electrochemical findings, showing severe surface degradation in fluoride-containing environments.
7. Overall conclusion: The β -TZNT alloy exhibits excellent corrosion resistance in typical seawater conditions, but it is highly susceptible to fluoride-induced deterioration, especially under acidic and high-temperature conditions. These findings guide the safe application of β -TZNT alloys in marine, offshore, and desalination systems exposed to fluoride-contaminated seawater.

Author Contributions: Conceptualization, M.A.E.S., I.H.E. and M.A.M.I.; methodology, M.A.E.S., S.M.A. and I.H.E.; validation, M.A.E.S., I.H.E. and M.A.M.I.; formal analysis, M.A.E.S., I.H.E., S.M.A. and M.A.M.I.; investigation, M.A.E.S., I.H.E., S.M.A. and M.A.M.I.; resources, M.A.E.S. and I.H.E.; writing—original draft preparation, M.A.E.S. and M.A.M.I.; writing—review and editing, M.A.E.S., I.H.E. and M.A.M.I.; visualization, M.A.E.S., supervision, M.A.M.I. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: All data generated or analyzed during this study are included in this published article.

Acknowledgments: The Researchers would like to thank the Deanship of Graduate Studies and Scientific Research at Qassim University for financial support (QU-APC-2026).

Conflicts of Interest: The authors declare no conflicts of interest.

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