



Article Adsorption Characteristics between Ti Atoms of TiO₂(100) and Corrosive Species of CO₂-H₂S-Cl⁻ System in Oil and Gas Fields

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Abstract: The service environment of OCTG (Oil Country Tubular Goods) in oil and gas fields is becoming more and more severe due to the strong affinity between ions or atoms of corrosive species coming from solutions and metal ions or atoms on metals. While it is difficult for traditional technologies to accurately analyze the corrosion characteristics of OCTG in CO2-H2S-Cl- systems, it is necessary to study the corrosion-resistant behavior of TC4 (Ti-6Al-4V) alloys based on an atomic or molecular scale. In this paper, the thermodynamic characteristics of the $TiO_2(100)$ surface of TC4 alloys in the CO₂-H₂S-Cl⁻ system were simulated and analyzed by first principles, and the corrosion electrochemical technologies were used to verify the simulation results. The results indicated that all of the best adsorption positions of corrosive ions (Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO₃²⁻) on TiO₂(100) surfaces were bridge sites. A forceful charge interaction existed between Cl, S, and O atoms in Cl⁻, HS^- , S^{2-} , HCO_3^- , CO_3^{2-} , and Ti atoms in TiO₂(100) surfaces after adsorption in a stable state. The charge was transferred from near Ti atoms in TiO₂ to near Cl, S, and O atoms in Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO₃²⁻. Electronic orbital hybridization occurred between 3p⁵ of Cl, 3p⁴ of S, 2p⁴ of O, and 3d² of Ti, which was chemical adsorption. The effect strength of five corrosive ions on the stability of TiO₂ passivation film was $S^{2-} > CO_3^{2-} > CI^- > HS^- > HCO_3^-$. In addition, the corrosion current density of TC4 alloy in different solutions containing saturated CO2 was as follows: NaCl + Na2S + $Na_2CO_3 > NaCl + Na_2S > NaCl + Na_2CO_3 > NaCl$. At the same time, the trends of R_s (solution transfer resistance), $R_{\rm ct}$ (charge transfer resistance), and $R_{\rm c}$ (ion adsorption double layer resistance) were opposite to the corrosion current density. The corrosion resistance of TiO₂ passivation film to corrosive species was weakened owing to the synergistic effect of corrosive species. Severe corrosion resulted, especially pitting corrosion, which further proved the simulation results mentioned above. Thus, this outcome provides the theoretical support to reveal the corrosion resistance mechanism of OCTG and to develop novel corrosion inhibitors in CO₂-H₂S-Cl⁻ environments.

Keywords: TiO₂(100); first principles; thermodynamic stability; adsorption characteristics; corrosive species

1. Introduction

Corrosion has been considered as one of the major social problems in pipelines and industries using such materials since the early industrial revolution. A large number of accidents occur frequently, which leads to a greater threat to the safe production of oil and gas [1]. The annual cost of corrosion in China is about CNY 2.3 trillion, accounting for 3.3% of GDP [2].

In recent years, with the development of deep and ultra-deep wells to meet the social demand for energy, the working environment of tubing and casing is becoming more and more complex. In addition to the stringent service conditions, metal OCTG are inevitably subjected to different degrees of corrosion, and the working properties of OCTG have



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). decreased. For example, the presence of H_2S leads to severe localized corrosion, as well as cracks caused by stress and hydrogen [3]. In some special working conditions, CO_2 and H_2S exist at the same time [4], which greatly deteriorates the service environment of OCTG [5]. The high temperature, pressure, acid gas content, and Cl^- concentration of oil and gas wells increase the requirements for corrosion-resistant OCTG.

The TC4 titanium alloy (Ti-6Al-4V) is now considered to be the ideal material applied in oil and gas fields, accounting for about half of the market share of titanium alloys currently used in the world [6]. A dense TiO₂ oxide film with a thickness of 4~6 nm of TC4 will be spontaneously formed at room temperature [7], which can effectively prevent the matrix in a solution from being corroded by corrosive ions (such as H⁺, Cl⁻, etc.) [8]. However, the film is not always able to maintain its integrity; it is very likely to be destroyed in some medium containing some corrosive species, resulting in serious corrosion of the titanium alloy matrix [9]. It is difficult for traditional technologies to accurately analyze the corrosion characteristics of OCTG in CO₂-H₂S-Cl⁻ systems.

Therefore, the first-principles calculation software (Materials Studio) on account of DFT (Density Functional Theory) was selected to research the interface characteristics between the corrosive species and TiO₂ passivation film on the surface of TC4 alloys in CO₂-H₂S-Cl⁻ systems containing Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO₃²⁻ based on an atomic or molecular scale. Additionally, the corrosion characteristics of the TC4 alloy in NaCl, NaCl + Na₂CO₃, NaCl + Na₂S, and NaCl + Na₂S + Na₂CO₃ solutions containing saturated CO₂ were carried out by the electrochemical technologies to verify the simulation results above.

2. Research Methods

2.1. First Principles

2.1.1. Modeling

TiO₂ passivation film on titanium alloy surfaces has three crystal structures: rutile, anatase, and brookite [10]. Figure 1 shows the Raman spectra of TiO₂ film on TC4 alloy, and Table 1 shows the frequency shift positions of Raman spectral characteristics of three crystalline TiO₂. The four peaks, 145.53 cm⁻¹, 241.76 cm⁻¹, 612.53 cm⁻¹, and 824.16 cm⁻¹ in Figure 1, are consistent with the corresponding peak value of the rutile TiO₂ in Table 1. Some scholars found that the composition of titanium alloy passivation film was rutile TiO₂ [11]. Therefore, rutile TiO₂ was selected as the research object in this paper.



Figure 1. Raman spectra of TiO₂ passivation film on TC4 titanium alloy surface.

Crystal Structure of TiO ₂	Raman Frequency Shift (cm ⁻¹)		
Brookite	127, 150, 193, 212, 247, 286, 318, 366, 412, 462,		
	502, 544, 582, 645		
Anatase	143, 196, 326, 395, 512, 645		
Rutile	143, 244, 440, 610, 825		

Table 1. Raman spectra characteristic frequency shift position of three crystalline TiO₂.

There are (110), (100), and (001) low index surfaces in Rutile phase TiO₂. The characteristics of the various ions on TiO₂(110) surfaces have been studied, including our previous research [2], but few reports were focused on the adsorption of TiO₂(100) and TiO₂(001) surfaces. Furthermore, compared with TiO₂(001) surfaces, TiO₂(100) surfaces present a higher possibility of stable existence at high temperatures [12]. Therefore, the adsorption properties of various corrosive ions (Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO₃²⁻) on rutile TiO₂(100) surfaces were studied.

The CASTEP in Material Studio, the first-principles computing software, was used to conduct geometric optimization for all adsorption configurations [13]. According to the setting requirements of the CASTEP module, a $2 \times 3 \times 1$ three-dimensional supercell structure with periodic boundary conditions was established for the rutile TiO₂(100) surface. In addition, a vacuum area with a thickness of 20 Å was added between the two plates to prevent interaction between them [14]. Figure 2 reveals the boundary surface models of various corrosive ions (Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO₃²⁻) at different adsorption sites (top, bridge, and hole) on a TiO₂(100) surface.



Figure 2. Cont.



Figure 2. Interface model of TiO₂100) including corrosive ions. (a) TiO₂(100)-Cl⁻(top); (b) TiO₂(100)-Cl⁻(bridge); (c) TiO₂(100)-Cl⁻(hole); (d) TiO₂(100)-HS⁻(top); (e) TiO₂(100)-HS⁻(bridge); (f) TiO₂(100)-HS⁻(hole); (g) TiO₂(100)-S²⁻(top); (h) TiO₂(100)-S²⁻(bridge); (i) TiO₂(100)-HCO₃⁻(hole); (j) TiO₂(100)-HCO₃⁻(top); (k) TiO₂(100)-HCO₃⁻(bridge); (l) TiO₂(100)-HCO₃⁻(hole); (m) TiO₂(100)-CO₃²⁻(top); (n) TiO₂(100)-CO₃²⁻(bridge); (o) TiO₂(100)-CO₃²⁻(hole).

2.1.2. Computing Method

Using the PBE functional of GGA, the pseudopotentials were constructed using the plane wave ultrasoft pseudopotential SCF [1,12,15], where the truncation energy of the plane wave was set as 400 eV, the convergence accuracy in the iteration process was 2×10^{-6} eV/atom, the self-consistent iteration was 300 times, the force converge was 0.03 eV/atom, the tolerance deviation was not higher than 0.005, the stress deviation was under 0.08 GPa, and the k-points value was $2 \times 3 \times 1$ in the Brillouin zone.

2.2. Electrochemical Test

2.2.1. Preparation of Experimental Materials

The electrochemical test sample was TC4 titanium alloy, which was $ø10 \text{ mm} \times 3 \text{ mm}$. A wire was welded to one end of the sample and tested for conductivity with a multimeter to verify whether the wire was welded correctly. The surface at the other end of the sample was the electrochemical test surface. The surface other than the electrochemical test surface was glued and stamped with epoxy resin AB glue and then polished with sandpaper with mesh sizes of 400[#], 800[#], 1200[#], 1500[#], and 2000[#]. For the purpose of reaching the test requirements for sample roughness, the sample surface was polished to 2000[#], cleaned with distilled water, degreased with acetone, dehydrated and desiccated with alcohol, and dried with cold air for later use.

2.2.2. Experimental Methods and Equipment

The electrochemical test was carried out by Princeton P4000 electrochemical workstation, in which the working electrode was TC4 alloy, the reference electrode was polytetrafluoro silver chloride, and the auxiliary electrode was a platinum electrode. Before the electrochemical test, high-purity nitrogen was used to deoxygenate the required corrosive medium for 1 h., and the temperature was heated up to the preset temperature (80 °C). The electrochemical test was performed when the entire test system reached stability, and each experiment was performed three times.

The working electrode was pre-polarized at a voltage set value of -1200 mV for 3 min in advance of the electrochemical test. After the oxide film spontaneously took shape on the surface of the sample in the air and was eliminated, the working electrode was put in the prepared medium and stood for 30 min to form new film. The test frequency was set to $10^{-2} \text{ HZ} \sim 10^5 \text{ HZ}$, the measured signal amplitude was 10 mV sine wave, and the number of points was 50. The scanning rat was set as 0.3333 mV/s, and the potential was $-1000 \text{ mV} \sim +1600 \text{ mV}$.

The corrosive medium was 35 g/L NaCl, 35 g/L NaCl + 1 g/L Na₂CO₃, 35 g/L NaCl + 1 g/L Na₂S, and 35 g/L NaCl + 1 g/L Na₂CO₃ + 1 g/L Na₂S, respectively, which were all chemically pure agents.

3. Results and Discussion

3.1. Thermodynamic Stability of Passivation Film

3.1.1. Stable Adsorption Model

To simulate the species in the CO₂-H₂S-Cl⁻ environment (CO₂+H₂O \rightarrow H₂CO₃, H₂CO₃ \rightarrow H⁺+HCO₃⁻, HCO₃⁻ \rightarrow H⁺+CO₃²⁻, H₂S \rightarrow H⁺+HS⁻, HS⁻ \rightarrow H⁺+S²⁻), the final energy of five corrosive ions (Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO₃²⁻) at different adsorption sites on TiO₂(100) surface after geometric optimization is shown in Table 2. By comparison, it was found that the energy of each corrosive ion was the lowest at the bridge site of the TiO₂(100) surface. If the energy of the adsorption system were more negative, its structure would be more stable [16]. Therefore, it can be determined that all of the best adsorption sites of Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO₃²⁻ on the TiO₂(100) surface were bridge sites. The final energy of each corrosive ion at the bridge site of the TiO₂(100) surface was in the following order: S²⁻ > HS⁻ > Cl⁻ > CO₃²⁻ > HCO₃⁻.

3.1.2. Charge Density

Figure 3 reveals the charge density distribution of each corrosive ion (Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO₃²⁻) at the bridge site of the TiO₂(100) surface. It could be seen that a forceful charge interaction exists between the Cl, S, O, and Ti atoms which was in the Cl⁻, HS⁻ and S²⁻, HCO₃⁻, CO₃²⁻, and TiO₂(100) surface, respectively.

Table 3 reveals the charge numbers of Cl, S, and O atoms in various corrosive ions. It could be seen that the absolute values are as follows: $S^{2-}(S) > CO_3^{2-}(O) > Cl^-(Cl) > HS^-(S) > HCO_3^-(O)$, which are in accordance with our previous research [2]. The metal surface with a higher charge density value is more likely to be corroded by the corrosive

ions, leading to the TiO₂ passivation film suffering from stronger corrosion. It could be seen that the stability of the TiO₂ in the environment containing corrosive species was the following: $S^{2-} < CO_3^{2-} < CI^- < HS^- < HCO_3^-$. That is, TiO₂ film on the surface of TC4 alloy is more easily damaged in the mediums containing S^{2-} than in CO_3^{2-} , CI^- , HS^- , and HCO_3^- .

Table 2. Final energy of five corrosive ions on the $TiO_2(100)$ surface at different sites.

Models	Final Energy/eV	
TiO ₂ (top)-Cl ⁻	-69,578.2607299930	-
TiO ₂ (bridge)-Cl ⁻	-69,578.6903762455	
TiO ₂ (hole)-Cl ⁻	-69,578.6028239061	
TiO ₂ (top)-HS ⁻	-69,462.8589004437	
TiO ₂ (bridge)-HS ⁻	-69,463.9047289728	
$TiO_2(hole)-HS^-$	-69,463.8965710229	
$TiO_2(top)-S^{2-}$	-69,443.5255285524	
$TiO_2(bridge)-S^{2-}$	-69,445.7491433063	
$TiO_2(hole)-S^{2-}$	-69,445.3972256848	
TiO ₂ (top)-HCO ₃ ⁻	-70,647.8573602164	
TiO ₂ (bridge)-HCO ₃ ⁻	-70,651.6819378591	
TiO ₂ (hole)-HCO ₃ ⁻	-70,649.4503215808	
$TiO_2(top)-CO_3^{2-}$	-70,633.5143850651	
TiO_2 (bridge)- CO_3^{2-}	-70,633.5232150766	
$TiO_2(hole)-CO_3^{2-}$	-70,633.5217354935	



Figure 3. Charge density distribution of five ions on the $TiO_2(100)$ surface. (a) Cl^- ; (b) HS^- ; (c) S^{2-} ; (d) HCO_3^- ; (e) CO_3^{2-} .

Atom	Cl ⁻ (Cl)	HCO ₃ ⁻ (O)	CO ₃ ^{2–} (O)	HS-(S)	S ^{2–} (S)
Charge/e	-0.15	-0.12	-0.22	-0.14	-0.34

Table 3. Charge numbers of Cl, O, and S atoms in corrosive ions.

3.1.3. Charge Density Difference

Figure 4 shows the charge density of the corrosive ions (Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO₃²⁻) at the bridge site of the TiO₂(100) under the stable state adsorption. It could be seen that a very distinct charge transfer appearance was presented between Cl, S, O, and Ti atoms which was in the Cl⁻, HS⁻ and S²⁻, HCO₃⁻ and CO₃²⁻, and TiO₂(100) surfaces, respectively. Charge segregation and electronegativity decreased near Cl, S, and O atoms, while charge dissipation and electronegativity increased near the Ti atom in TiO₂ [17]. Therefore, the interface binding energy between Cl, S, O, and Ti atoms was in the Cl⁻, HS⁻ and S²⁻, HCO₃⁻ and CO₃²⁻, and TiO₂(100) surfaces, respectively. Finally, the specific charge transfer process moved from the Ti atom on the TiO₂(100) surface to Cl, S, and O atoms.



Figure 4. Differential charge density distribution of five ions on the $TiO_2(100)$ surface at the bridge site. (a) Cl⁻; (b) HS⁻; (c) S²⁻; (d) HCO₃⁻; (e) CO₃²⁻.

3.1.4. Density of States

Figure 5 shows PDOS (Projected Density of States) diagrams of five corrosive ions at the bridge site of the $TiO_2(100)$ surface, which can be calculated to investigate the characteristics of various ions on the $TiO_2(100)$ surface deeply [18]. It could be seen that a certain extent of the charge interaction existed between Cl, S, O, and Ti atoms, indicating that the adsorption process was chemical adsorption [19]. The charge interaction and interfacial bonding were primarily made of hybrid orbitals between $3d^2$ of the Ti atoms and $3p^5$ of Cl, $3p^4$ of S, and $2p^4$ of O.



Figure 5. PDOS curves of (**a**) Cl^- , (**b**) HS^- , (**c**) S^{2-} , (**d**) HCO_3^- , and (**e**) CO_3^{2-} adsorbing on the $TiO_2(100)$ surface at the bridge site.

3.1.5. Binding Energy

The corrosiveness of each corrosive ion to the matrix can be ensured through the interface binding energy, which was calculated as follows [20]:

$$E = E_t - (E_1 + E_2)$$
(1)

 E_t is the total energy of whole model after geometry optimization; E_1 is the energy after geometric optimization of TiO₂(100); E_2 is the energy after geometric optimization of each corrosive ion.

Table 4 displays the final energy between Cl⁻, HS⁻, S²⁻, HCO₃⁻, CO₃²⁻, and TiO₂(100) after geometric optimization. According to Tables 2 and 4, combined with Formula (1), the interface binding energies of various corrosive ions (Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO₃²⁻) at the bridge site of the TiO₂(100) surface were obtained, as shown in Table 5. It could be seen that when HCO₃⁻ was adsorbed on the TiO₂(100) surface, the entire adsorption system had low energy. Compared with Cl⁻, HS⁻, HCO₃⁻, and CO₃²⁻, the interface between S²⁻ and TiO₂(100) was easier to bond and react, indicating that S²⁻ had a stronger adsorption capacity on TiO₂. Therefore, TiO₂ has poor stability in the environment containing S²⁻. The steadier the interface model is, the smaller interface binding energy

is [20], so the film stability of TiO₂ in the solutions containing Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO₃²⁻ was S²⁻ < CO₃²⁻ < Cl⁻ < HS⁻ < HCO₃⁻, which is consistent with the charge density results mentioned above.

Model	Final Energy/eV
Cl ⁻	-411.7437852366
HCO ₃ ⁻	-1483.4813928615
CO ₃ ^{2–}	-1467.9443448936
HS ⁻	-296.3156703881
S ^{2–}	-280.4987150773
TiO ₂	-4961.8922752454
TiO ₂ (100)	-69171.5619281723

Table 4. The final energy of five ions, TiO_2 , and $TiO_2(100)$.

Table 5. Interface binding energies of five ions on $TiO_2(100)$ surface at bridge sites.

Model	Interface Binding Energy/eV
$TiO_2(bridge)-Cl^-$	4.6153371666
TiO ₂ (bridge)-HS ⁻	3.9728695881
TiO ₂ (bridge)-S ²⁻	6.3114999473
$TiO_2(bridge)-HCO_3^-$	3.3613831813
TiO_2 (bridge)- CO_3^{2-}	5.9830579936

3.2. Corrosion Behavior

3.2.1. Alternating-Current Impedance

The alternating-current impedances of TC4 alloy in NaCl, NaCl + Na₂CO₃, NaCl + Na₂S and NaCl + Na₂S + Na₂CO₃ solutions containing saturated CO₂ are shown in Figure 6. It could be seen that the radius of the capacitive arc of TC4 alloy in four corrosive solution was NaCl > NaCl + Na₂CO₃ > NaCl + Na₂S > NaCl + Na₂S + Na₂CO₃. The radius of electrochemical Nyquist impedance spectroscopy can determine the corrosion resistance of materials; the larger the radius of the electrochemical Nyquist impedance spectrum is, the stronger the corrosion resistance of materials to local corrosion is [21]. Therefore, the corrosiveness of four corrosive solutions to TC4 alloy was NaCl + Na₂S + Na₂CO₃ > NaCl + Na₂S > NaCl + Na₂S + Na₂CO₃ > NaCl + Na₂S > NaCl + Na₂S + Na₂CO₃ > NaCl + Na₂S > NaCl + Na₂S + Na₂CO₃ > NaCl + Na₂S > NaCl + Na₂S + Na₂CO₃ > NaCl + Na₂S > NaCl + Na₂S + Na₂CO₃ > NaCl + Na₂S > NaCl + Na₂S + Na₂CO₃ > NaCl + Na₂S > NaCl + Na₂S > NaCl + Na₂S > NaCl + Na₂S + Na₂CO₃ > NaCl + Na₂S > NaCl + Na₂CO₃ > NaCl + Na₂S > NaCl + Na₂



Figure 6. Alternating-current impedance diagram of TC4 titanium alloy under different corrosion environments.

The equivalent circuit was shown in Figure 7. It can be seen that C_{dl} (double layer capacitance) and C_c (ion adsorption double layer capacitance on the electrode surface) increased, and that both R_{ct} (charge transfer resistance) and R_c (ion adsorption double layer resistance) decreased, concluding that the TC4 alloy has poor corrosion resistance [22].



Figure 7. Equivalent circuit diagram.

As seen in Table 6, when there was only NaCl in the electrolyte, the C_c value of ion adsorption double layer capacitance on the electrode surface was 3.617×10^{-7} , the C_{dl} value of double layer capacitance was 4.925×10^{-6} , the R_c value was $1565 \ \Omega \cdot \text{cm}^2$, and the R_{ct} value was $3.135 \times 10^4 \ \Omega \cdot \text{cm}^2$. With the addition of CO_3^{2-} and S^{2-} , the values of C_c and C_{dl} increased to varying degrees, while the values of R_c and R_{ct} decreased. When CO_3^{2-} and S^{2-} exited together, the corresponding electrochemical parameters increased. The corrosion resistance of the TC4 alloy to four solutions is NaCl > NaCl + Na₂CO₃ > NaCl + Na₂S > NaCl + Na₂S + Na₂CO₃, which is consistent with the above numerical simulation results.

Table 6. Alternating-current fitting results of TC4 titanium alloy in various corrosion environments.

Corrosion Environments	$R_{\rm s}$ / $\Omega \cdot {\rm cm}^2$	$C_{ m c} imes 10^{-7}$ /F·cm ⁻²	$R_{\rm c}$ / $\Omega \cdot {\rm cm}^2$	$C_{ m dl} imes 10^{-6}$ /F·cm ⁻²	$R_{ m ct} imes 10^4 \ /\Omega\!\cdot\! m cm^2$
NaCl	68.12 ± 0.72	3.617 ± 0.035	1565 ± 33	4.925 ± 0.062	3.135 ± 0.039
$NaCl + Na_2CO_3$	54.38 ± 0.55	3.826 ± 0.029	1324 ± 15	5.236 ± 0.051	2.754 ± 0.058
$NaCl + Na_2S$	33.05 ± 0.61	4.182 ± 0.042	1069 ± 24	56.480 ± 0.038	2.376 ± 0.066
$NaCl + Na_2S + Na_2CO_3$	9.923 ± 0.58	8.793 ± 0.053	948 ± 16	56.641 ± 0.042	0.633 ± 0.045

3.2.2. Polarization Curve

Figure 8 displays the polarization curves of the TC4 titanium alloy in four corrosive media (NaCl, NaCl + Na₂CO₃, NaCl + Na₂S, NaCl + Na₂S + Na₂CO₃). Table 7 shows the fitting results. The i_{corr} (self-corrosion current density) was $1.689 \times 10^{-4} \text{ mA/cm}^2$, and the E_{corr} (self-corrosion potential) of TC4 alloy in NaCl solution containing saturated CO₂ was -578 mV. With the addition of CO₃²⁻ or/and S²⁻, the E_{corr} of the electrode decreased, and i_{corr} increased. The E_{corr} can reflect the tendency of corrosion [23], and the i_{corr} represents the speed of corrosion rate. The value of the i_{corr} is larger, indicating that the corrosion rate is more rapid [24]. It could be seen that the TC4 titanium alloy showed excellent corrosion resistance in a corrosive solution containing only NaCl. In a NaCl + Na₂CO₃ solution, the resistance of the TC4 alloy decreased. While in the NaCl + Na₂S + Na₂CO₃ solution, the TC4 alloy suffered from the most severe corrosion. This finding is consistent with the above alternating-current impedance results and numerical simulation results.

The results of the electrochemical experiments mentioned above also are in good accordance with the previous research in a 35% NaCl + 0.4% Na₂S solution at 80 °C [25], as shown in Table 8.



Figure 8. Polarization curves of TC4 titanium alloy under four corrosion environments.

Table 7. Electrochemical	parameters of TC4 titanium all	oy in vari	ous corrosion	environments.
		/		

Corrosion Media	E _{corr} /mV	b _c /mV	b _a /mV	$i_{ m corr} imes 10^{-4}$ /mA \cdot cm $^{-2}$
NaCl	-578 ± 3.56	35.704 ± 0.086	29.744 ± 0.066	1.689 ± 0.034
$NaCl + Na_2CO_3$	-595 ± 2.35	33.951 ± 0.092	41.011 ± 0.085	9.399 ± 0.042
$NaCl + Na_2S$	-667 ± 4.62	27.320 ± 0.075	27.218 ± 0.073	19.173 ± 0.071
$NaCl + Na_2S + Na_2CO_3$	-1014 ± 4.85	22.659 ± 0.088	32.778 ± 0.069	252.519 ± 0.099

Table 8. Electrochemical parameters of titanium alloy in 35% NaCl + 0.4% Na₂S [25].

Temperature/°C	Materials	$R_{\rm s}/\Omega \cdot {\rm cm}^2$	$R_{\rm ct}/\Omega \cdot {\rm cm}^2$	E _{corr/} V	$i_{ m corr} imes 10^{-4}$ /mA·cm $^{-2}$
25	TC4	62.49	947,740	-0.596	1.751
	TC4ELI	9.15 15.52	290,050	-0.553 -0.546	2.408 5.651
80	TC4ELI	6.15	93,617	-0.402	4.105

4. Conclusions

- (1) All of the most suitable adsorption sites of corrosive ions (Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO_3^{2-}) on the TiO₂(100) surface were bridge sites, then hole sites and top sites.
- (2) A forceful charge interaction occurred between Cl, S, O, and Ti atoms. The charge was transferred from near the Ti atoms in the TiO₂(100) surface to near Cl, Ss, and O atoms in Cl⁻, HS⁻, S²⁻, HCO₃⁻, and CO₃²⁻, respectively. Interface binding energy was primarily formed by electronic orbital hybridization between 3p⁵ of Cl, 3p⁴ of S, 2p⁴ of O, and 3d² of Ti, and they were chemical adsorption.
- (3) Interface binding energy between five corrosive species and the TiO₂(100) was as follows: $S^{2-} > CO_3^{2-} > Cl^- > HS^- > HCO_3^-$.
- (4) With the addition of CO₃²⁻ and S²⁻, local corrosion of the TC4 alloy in an NaCl solution containing saturated CO₂ increased, especially the synergistic effect between Cl⁻, CO₃²⁻, and/or S²⁻, which made the corrosion electrochemical parameters of TC4 alloy change by two orders of magnitude.

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