



Logarithmic thickening of a dense TiO₂-dominated composite passive film on Ti₃SiC₂ coating for enhanced corrosion resistance in chloride environment

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ABSTRACT

Ti₃SiC₂, as a typical MAX phase material, exhibits a unique combination of metallic and ceramic properties, rendering it an ideal candidate for protective coatings in harsh environments. In this study, systematic electrochemical characterization coupled with microstructural analysis was employed to investigate the passive behavior and passive film growth mechanism of Ti₃SiC₂ coating in a 3.5 wt% NaCl solution. The results demonstrate that Ti₃SiC₂ coating exhibit higher impedance and lower corrosion current density. This superior performance stems from the formation of a continuous, compact amorphous passive film approximately 4.8 nm thick, predominantly composed of TiO₂ along with minor SiO₂. The growth of the passive film follows logarithmic kinetics, governed primarily by high-field ionic migration. Although Si atoms exhibit high initial mobility due to their lower vacancy formation energy, the vacancy concentration effect subsequently restricts the continuous growth of a monolithic SiO₂ layer. In contrast, Ti sites manifest higher oxygen adsorption activity, and the lower Gibbs free energy of TiO₂ formation ensures its competitive advantage during the nucleation stage. Concurrently, the lower ionic transport resistance within the TiO₂ lattice under the high-field drive facilitates its sustained thickening and dominance. Ultimately, the resulting dense composite passive film effectively inhibits the infiltration of corrosive species and suppresses the continuous leaching of Si, thereby preserving the compositional and structural stability of the Ti₃SiC₂ coating.

1. Introduction

Critical metallic components in marine engineering infrastructure operate persistently in highly corrosive environments characterized by elevated chloride ion concentrations. The efficacy of their corrosion protection directly governs structural safety, reliability, and service lifetime. Conventional anti-corrosion technologies often suffer from singular protective functionality or carry risks of inducing hydrogen embrittlement [1,2]. Consequently, developing dense coatings that simultaneously deliver high hardness and fracture toughness, or

exploring novel protective coatings tailored for extreme marine conditions, holds significant engineering and scientific value. MAX phases represent a class of ternary carbides/nitrides with a hexagonal layered structure. Since their discovery in the 1960s, these materials have garnered sustained interest due to their exceptional property synergy. Their general formula is M_{n+1}AX_n (typically n = 1–3), where M denotes a transition metal, A primarily comprises A-group elements mainly from IIIA or IVA, and X is C, N, or B [3,4]. Crystallizing in the P6₃/mmc space group, MAX phases feature alternating layers of M₆X octahedra and A-element planes stacked along the c-axis [5]. Within this structure, M-X

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bonds exhibit strong covalent/ionic character, whereas M-A are connected through relatively weak metallic bonds [6,7]. This unique bonding nature and layered arrangement endow MAX phases with exceptional properties inherent to both metals and ceramics: high strength and elastic modulus, machinability, exceptional high-temperature oxidation resistance, outstanding corrosion resilience, and radiation tolerance [8–12]. These characteristics establish MAX phases as ideal candidates for protective coatings on mechanical components operating under harsh conditions, where simultaneous wear and corrosion resistance are paramount.

Among MAX phases, Ti_3SiC_2 stands out as a most promising candidate given its superior combination of properties. Compared with Ti_3AlC_2 and lower-order 211 MAX phases, Ti_3SiC_2 demonstrates superior thermal stability and mechanical properties. It possesses a remarkably high phase stability temperature of 1700–1800 °C, along with enhanced hardness, shear modulus, and Young's modulus [13,14], while simultaneously exhibiting high fracture toughness, excellent damage tolerance, and favorable self-lubricating behavior [15–18]. Additionally, when exposed to harsh service conditions involving high temperatures and corrosive environments, Ti_3SiC_2 exhibits remarkable oxidation and corrosion resistance [19–21]. The corrosion behavior of alloys is intrinsically governed by passive film characteristics. Studies have demonstrated that Ti_3SiC_2 exhibits superior corrosion resistance to pure Ti in acidic solutions, with corrosion proceeding via selective Ti dissolution while Si oxidizes and enriches at the surface to form a protective passive film that impedes further substrate degradation [22]. In chloride-containing environments, Ti_3SiC_2 maintains robust passive capability and high breakdown potential. However, its passive efficiency is compromised by facile Si diffusion pathways inherent to its lamellar structure, resulting in overall inferior passive behavior compared to dense pure Ti [23,24]. Zhang et al. elucidated this phenomenon through comparative electrochemical analysis of Ti_3SiC_2 and Ti_3AlC_2 in NaCl solution, revealing that weak bonding at the A layer and M_6X interfaces drives preferential dissolution at these sites. This generates corrosion pits with minimal secondary deposits, while non-uniform diffusion of Si and Al impedes efficient passive film formation. Conversely, Ti in pure titanium diffuses homogeneously into the barrier layer, providing superior baseline film protection [25,26]. Meanwhile, for Ti_3SiC_2 in strong acids, long-term protection relies on the dissolution of Ti and in situ oxidation of Si, forming a micrometer-thick SiO_2 surface layer that governs its excellent acid corrosion resistance [27].

Nevertheless, most existing studies predominantly focus on the electrochemical behavior of bulk Ti_3SiC_2 [21,27,28]. Owing to phase composition alterations, microstructural defects, and non-equilibrium interfacial features introduced during coating deposition, the charge transfer kinetics and anodic passivation behavior of coatings differ substantially from those of their bulk counterparts. To date, the corrosion mechanisms of Ti_3SiC_2 coatings under polarization conditions remain inadequately elucidated, particularly regarding the compositional evolution, defect-mediated ionic transport mechanisms, and film-formation kinetics of the surface passive layer. Elucidating the electrochemical corrosion mechanisms and performance of Ti_3SiC_2 coatings is thus of fundamental and practical significance for advancing their deployment as corrosion resistant coating in extreme environments. In this work, the Ti_3SiC_2 MAX phase coating was fabricated on Ti-6Al-4V substrates via a two-step process combining high-power impulse magnetron sputtering (HiPIMS) and vacuum annealing. Integrating experimental characterization with first-principles calculations, we systematically interrogated the corrosion behavior and passive mechanisms of these coatings in 3.5 wt% NaCl solution. Our analysis encompasses microstructural evolution, electrochemical performance testing, elemental distribution analysis, and the structure and formation kinetics of the passive film. Special emphasis is placed on investigating the passive characteristics under anodic polarization conditions, aiming to uncover the evolution law of the surface passive film and its underlying mechanism governing the corrosion resistance.

2. Experimental details

2.1. Coating preparation

Ti-Si-C coatings were deposited on Ti-6Al-4V substrates via HiPIMS, followed by subsequent vacuum annealing to obtain Ti_3SiC_2 MAX phase coatings. Substrates were polished to a mirror finish using silicon carbide metallographic abrasive papers, sequentially ultrasonicated in acetone and ethanol, and mounted on holders using conductive adhesive. Deposition occurred in a home-made sputtering system: the chamber was heated to 200 °C and evacuated to a base pressure of 2×10^{-3} Pa. High-purity argon was introduced, and a –200 V DC bias was applied to the substrate to enable argon plasma glow etching, removing surface contaminants and enhancing adhesion. A Ti-Si interlayer was first deposited as a diffusion barrier to improve interfacial bonding and suppress elemental interdiffusion. The Ti-Si-C layer was sputtered from a 99.99% pure TiSi (Ti:Si=1:1 at%) composite target, with substrate rotation ensuring uniform thickness. HiPIMS parameters were: 2000 W peak power, 5% duty cycle, in an Ar (200 sccm)/ CH_4 (10 sccm) reactive atmosphere. The substrate DC bias is –50 V during the deposition process. Deposition duration was 120 min. After deposition, the samples were annealed at 850 °C in a vacuum environment for 90 min to promote the formation of the Ti_3SiC_2 MAX phase. Comprehensive process details are provided in our prior work [29].

2.2. Electrochemical measurements

Electrochemical corrosion testing was conducted in 3.5 wt% NaCl solution using a standard three-electrode system (Gamry Reference 600 + electrochemical workstation). The working electrode comprised a coated sample with an exposed area of 0.2 cm²; platinum mesh served as the counter electrode, and an Ag/AgCl reference electrode was employed. Prior to testing, samples underwent open circuit potential (OCP) monitoring for 5 min, followed by cathodic polarization at –0.8 V (vs. OCP) for 5 min to remove native oxides and establish a consistent initial surface state. A stabilized OCP was then acquired over 120 min to define the reference potential for subsequent measurements. Electrochemical impedance spectroscopy (EIS) measurements were performed at the stabilized E_{OCP} , with a frequency range of 10^5 – 10^{-2} Hz and a perturbing AC amplitude of 10 mV. The EIS data were analyzed via equivalent circuit fitting using ZSimpWin software. Potentiodynamic polarization scans (1 mV/s) spanned –0.5 to +1.5 V vs. E_{OCP} . Based on anodic polarization characteristics, potentiostatic holds at +0.2, +0.5, and +0.8 V (vs. E_{OCP}) for 10 h each were applied to induce stable passive film growth. Mott-Schottky analysis followed, employing downward potential stepping (100 mV steps, 100 Hz frequency) from positive to negative potentials. To further investigate the dynamic evolution of the passive film, successive EIS (SEIS) measurements were conducted: the samples were polarized at an anodic potential of 0.5 V for 10 h, during which impedance spectra were recorded every 30 min.

2.3. Microstructure characterization

Microstructural, compositional, and surface characteristics of the synthesized coatings were systematically interrogated using multimodal characterization. Phase identification and crystallographic structure were determined by X-ray diffraction (XRD; D8 Advance, Bruker). Surface morphology and elemental distribution were observed via field-emission scanning electron microscopy (SEM, Sigma 300, Zeiss) coupled with energy-dispersive X-ray spectroscopy (EDS; Oxford Instruments). The chemical states in the surface passive regions were characterized by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos) with a monochromatic Al K α source. For nanoscale structural validation, cross-sectional transmission electron microscopy (TEM) samples were prepared using a focused ion beam system (FIB, Auriga, Carl Zeiss). Subsequent observation and compositional analysis were

conducted using a high-resolution transmission electron microscope (TEM, Talos F200x, Thermo Fisher).

2.4. Atomic-scale calculations

All DFT calculations in this study were performed using the Vienna Ab initio Simulation Package (VASP). The ion-electron interactions were described by the projector augmented-wave (PAW) method, while the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) functional form was employed to treat exchange-correlation effects. A plane-wave cutoff energy of 500 eV was adopted, and the Brillouin zone was sampled using a $5 \times 5 \times 1$ Monkhorst-Pack k-point grid [30,31]. To investigate structural evolution and defect formation, a $2 \times 2 \times 1$ Ti_3SiC_2 supercell (containing 32 atoms) was constructed. Vacancy defect models were subsequently generated by removing specific atoms from the pristine supercell. The vacancy formation energy (ΔE_V) was determined using the following expression:

$$\Delta E_V = E_{\text{def}} - E_{\text{per}} + \mu_i \quad (1)$$

where E_{def} and E_{per} represent the total energies of the supercell with and without a single vacancy, respectively, and μ_i denotes the chemical potential of element i . Since chemical potentials are highly sensitive to the growth environment, the average energy per atom in its respective ground-state bulk phase was used as the reference value [32]. For surface adsorption studies, a $2 \times 2 \times 1$ Ti_3SiC_2 (0001) model was utilized. The convergence criterion for the self-consistent field (SCF) cycles was set to 10^{-6} eV, and atomic positions were fully relaxed until the residual forces on each atom were less than 0.02 eV/Å. Following structural optimization, the adsorption energy (E_{ads}) was calculated as follows:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{Ti}_3\text{SiC}_2(0001)} - E_{\text{ions}} \quad (2)$$

where E_{total} is the total energy of the Ti_3SiC_2 (0001) surface with the adsorbed ion, $E_{\text{Ti}_3\text{SiC}_2(0001)}$ is the energy of the clean surface, and E_{ions} is

the energy of the isolated ion in the solution phase [33,34].

3. Results and discussion

3.1. Microstructure of the Ti_3SiC_2 coating

Surface morphology (Fig. 1a) reveals a dense, defect-free architecture characteristic of magnetron-sputtered nanogranular aggregates. EDS spot analysis (boxed region) yields a Ti:Si:C atomic ratio of 49.2:14.5:36.3, which is essentially consistent with the theoretical stoichiometry of Ti_3SiC_2 . Fig. 1b presents the XRD pattern of the as-prepared coating. Except for the substrate diffraction peaks detected due to the thin coating thickness, all major diffraction peaks align with Ti_3SiC_2 reference data (ICDD PDF#89-1356). Sharp (101) and (104) reflections at $2\theta \approx 34.1^\circ$ and 39.6° , exhibiting narrow full-width half-maximum values, confirm long-range crystalline order and high phase purity. Minor TiSi_x peaks originate from crystallization of the Ti-Si interlayer during annealing, without compromising Ti_3SiC_2 structural dominance. Cross-sectional TEM (Fig. 1c) reveals a dense and fully crystalline cross-section without visible defects such as pores or cracks. Fig. 1d is a high-resolution TEM (HRTEM) image of the framed region in Fig. 1c, clearly illustrating the intrinsic nano-layered structure of Ti_3SiC_2 , which arises from the alternating stacking of Ti_6C octahedral layers and Si atomic layers. In Area I, three Ti(C) layers alternating with one Si layer are observed, and the measured c -axis lattice parameter is approximately 1.756 nm, consistent with the standard value of Ti_3SiC_2 [35]. Fast Fourier transform (FFT) of Area II shows an interplanar spacing of 0.2081 nm, matching the theoretical value of the (105) crystal plane of the Ti_3SiC_2 MAX phase. HAADF-STEM elemental mapping (Fig. 1e) demonstrates homogeneous, co-localized distribution of Ti, Si, and C, excluding compositional segregation. Overall, these characterization results confirm that a Ti_3SiC_2 MAX phase coating with high crystalline quality, uniform composition, and intact layered structural features has been successfully fabricated.

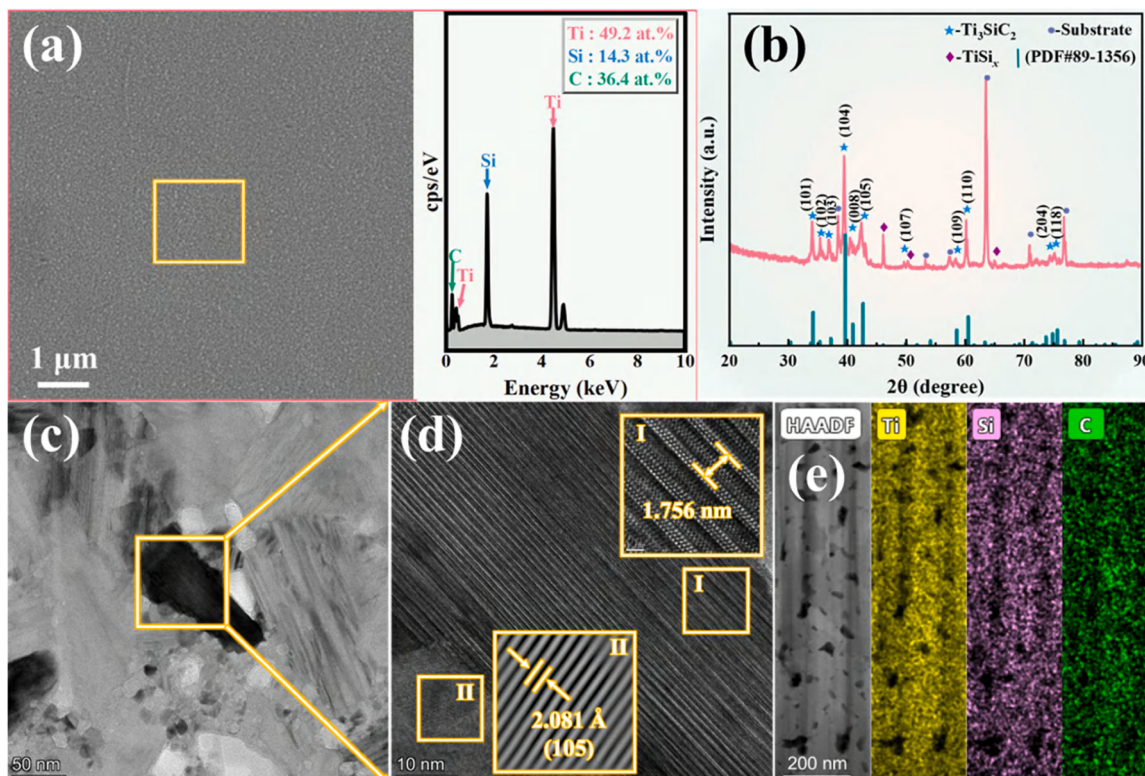


Fig. 1. Microstructure of Ti_3SiC_2 coating. (a) Surface morphology of the coating and the corresponding EDS results, (b) XRD pattern of the prepared coating, (c)-(d) TEM and HRTEM images, (e) EDS element mapping of Ti, Si and C.

3.2. Electrochemical corrosion behaviors

Fig. 2a displays open circuit potential (OCP) transients for Ti_3SiC_2 coating and Ti-6Al-4V substrate in 3.5 wt% NaCl solution. The OCP reflects the mixed potential established between the anodic dissolution and cathodic reduction reactions, serving as a critical indicator to track the dynamic evolution of the coating/electrolyte interfacial electrochemical state [36]. At the initial stage of testing, the Ti_3SiC_2 coating exhibited a significantly more positive OCP than the substrate, indicating a more noble mixed potential response. With prolonged immersion time, both systems displayed characteristic relaxation behavior: an initial rapid positive shift followed by gradual stabilization. This evolution was quantitatively described by a dual-exponential decay function:

$$E_{\text{OCP}} = a \times e^{-t/t_1} + b \times e^{-t/t_2} + c \quad (3)$$

where a and b are constants, c represents the extrapolated long-time steady state potential, and t_1 and t_2 represent the apparent fast and slow OCP relaxation time constants, respectively. The fitting results (Fig. 2a) revealed that t_1 is much smaller than t_2 , indicating that the approach of the system toward a quasi-steady state involves two relaxation processes with distinct characteristic time scales. Specifically, the fast relaxation process dominates the initial interfacial electrochemical response, whereas the slow relaxation process governs the subsequent gradual stabilization of the interface. In the stable stage, the Ti_3SiC_2 coating maintained a higher potential with reduced fluctuations versus the substrate, demonstrating the Ti_3SiC_2 coating possesses a more stable interfacial electrochemical response in NaCl solution.

Fig. 2b-c shows electrochemical impedance spectroscopy (EIS) data for Ti_3SiC_2 coating and Ti-6Al-4V substrate after 2 h immersion in 3.5 wt % NaCl at steady state OCP. Nyquist plots (Fig. 2b) exhibit single capacitive loops without full semicircles, indicating non-ideal interfacial capacitance. Typically, a larger capacitive loops radius corresponds to higher charge transfer resistance and superior corrosion resistance [37]. The significantly larger capacitive loop radius of the Ti_3SiC_2 coating compared to the substrate evidences its superior corrosion resistance. The Bode plots (Fig. 2c) further reveal the dynamic response characteristics of the system: in the high-frequency region, the impedance modulus ($|Z|$) tends to stabilize with a phase angle close to 0° , corresponding to the solution resistance response. In the medium-frequency region, the slope of $\lg|Z|$ versus $\lg f$ approaches -1 , and the phase angle maintains a high plateau near 90° , which indicates that a near-ideal capacitive behavior associated with interfacial polarization and relaxation processes dominates within this frequency range [11]. Notably, the high phase angle plateau of the Ti_3SiC_2 coating exhibits a wider frequency range and higher values ($>80^\circ$) compared to the substrate, suggesting a more ideal capacitive response and a more stable interfacial polarization process over an extended frequency range. This behavior indicates the formation of a more stable and effective protective interfacial layer on the Ti_3SiC_2 coating. The impedance modulus in the low-frequency region directly reflects the corrosion resistance of the material. The impedance value of the Ti_3SiC_2 coating at 0.01 Hz is approximately $1.27 \times 10^6 \Omega \cdot \text{cm}^2$, which is 0.5–1 order of magnitude higher than that of the substrate. This enhancement indicates the higher interfacial charge transfer resistance and better corrosion protection of the coating.

To quantitatively analyze the interfacial processes, the EIS data were

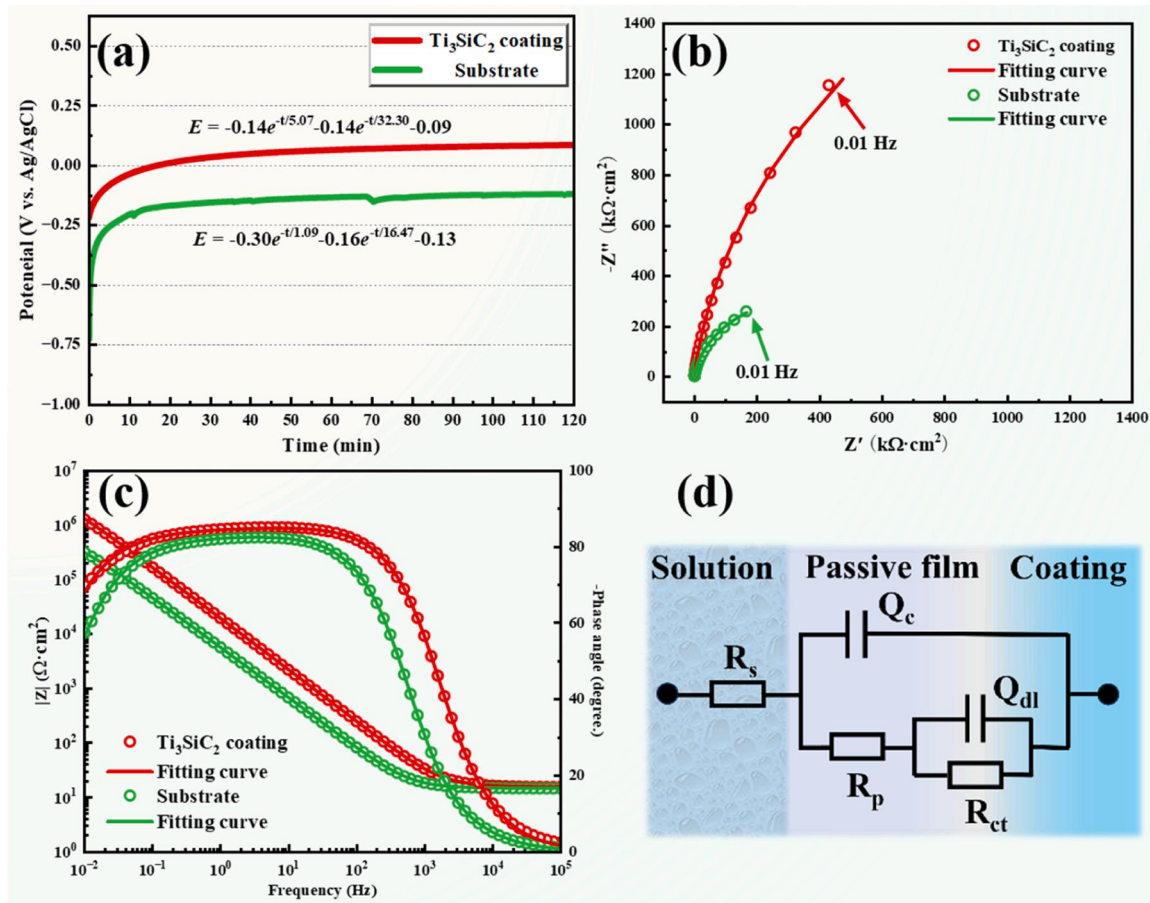


Fig. 2. (a) Changes in open circuit potential with immersion time, (b) Nyquist plots, (c) Bode plots of the Ti_3SiC_2 coating and Substrate after 2 h of immersion at respective open circuit potentials in the 3.5 wt% NaCl solution, and (d) Equivalent electrical circuit (EEC) used to fit the EIS experimental data.

fitted using an equivalent circuit model $R_s(Q_c(R_p(Q_{dl}R_{ct})))$ (Fig. 2d), which is suitable for metal systems covered with a passive film and corresponds to the "electrolyte / surface passive film / Ti_3SiC_2 coating". In this model, R_s represents the solution resistance. The (Q_c, R_p) branch corresponds to the passive film formed on the Ti_3SiC_2 surface, where the constant phase element Q_c denotes the non-ideal capacitive response of the film, and R_p represents passive film resistance. Additionally, the (Q_{dl}, R_{ct}) branch describes the electrochemical reactions at the Ti_3SiC_2 /electrolyte interface beneath the passive film; specifically, Q_{dl} represents the non-ideal double-layer capacitive response, while R_{ct} denotes the charge transfer resistance. Furthermore, the exponential indices n_c and n_{dl} are associated with CPE_c and CPE_{dl} . The parameter n indicates the degree of deviation from ideal capacitance, with a value of 1 representing a perfect capacitor. As shown in Fig. 2b-c, the fitted curves are in good agreement with the experimental data, and all chi-square (χ^2) values are on the order of 10^{-4} , validating the applicability of the model and the reliability of the data. The fitted electrochemical parameters are listed in Table 1. Generally, a larger R_p indicates a denser pore structure within the passive film, providing a stronger physical barrier against aggressive ions [38]. A larger R_{ct} implies a higher kinetic resistance for the corrosion electrochemical reactions at the coating/electrolyte interface, effectively inhibiting the reaction rate [39]. The fitting results show that both the R_p and R_{ct} of the Ti_3SiC_2 coating are significantly higher than those of the substrate. These findings confirm that the passive film formed on the Ti_3SiC_2 coating surface exhibits superior corrosion resistance relative to the underlying substrate. Nevertheless, the relatively low R_p value of the Ti_3SiC_2 indicates that the surface passive film remains in its early stage of formation, likely characterized by a limited continuity, and a high defect density.

Fig. 3 displays the potentiodynamic polarization curves of the Ti_3SiC_2 coating and Ti-6Al-4V substrate in 3.5 wt% NaCl solution. This curve is used to evaluate the corrosion behavior of materials, where the corrosion current density (i_{corr}) characterizes the corrosion rate. As observed from the polarization curves, the cathodic current gradually decreases as the potential approaches the corrosion potential (E_{corr}). At E_{corr} where the anodic and cathodic currents are equal, the corresponding i_{corr} of the Ti_3SiC_2 coating is markedly lower than that of the substrate, demonstrating a lower corrosion rate in the corrosive medium. In the anodic polarization region, the current density of the Ti_3SiC_2 coating increases only slightly with increasing potential, and the rising rate is much slower than that of the substrate, exhibiting typical passive characteristics. This indicates that the anodic dissolution reaction is effectively suppressed on the coating surface during anodic polarization. Collectively, the results of the potentiodynamic polarization tests are consistent with the previous analyses of OCP and EIS, jointly confirming that the Ti_3SiC_2 MAX phase coating can significantly reduce the corrosion tendency and reaction rate of the Ti-6Al-4V substrate under the investigated conditions, thereby providing effective corrosion protection.

3.3. Passive film investigations

3.3.1. Steady-state passive film properties

To gain insight into the formation mechanism of the passive film, potentiostatic tests were performed on the Ti_3SiC_2 coating for 10 h in 3.5 wt% NaCl at +0.2 V, +0.5 V, and +0.8 V (vs. the stable OCP). As shown in the overall trend of the curves (Fig. 4a), the current density of

the Ti_3SiC_2 coating rapidly decreases in the initial stage (0–0.5 h), which indicates that the passive film has already started to form, leading to a rapid decay of the corrosion reaction rate (corresponding to current density). After approximately 1 h, the coating current density tends to stabilize, indicating that a protective passive film has formed on the surface and entered a steady state. When extending the time to 6–10 h (inset local magnification), the steady-state current densities at different potentials follow the order: 0.2 V > 0.8 V > 0.5 V, demonstrating that significant changes in the formation and properties of the passive film occur with increasing potential. Fig. 4b presents the $\lg i$ - $\lg t$ curves of the tested samples at different potentials. It can be observed that in the initial film formation stage, the current density at all potentials decreases linearly with time, which is consistent with the passive film growth behavior described by the high-field model [40], indicating that the film growth rate is much higher than its dissolution rate. Subsequently, the current density gradually stabilizes, reflecting the film entering a steady state. According to the Macdonald model, the relationship between current density and time can be described by the following equation [41,42]:

$$\lg i = A - n \lg t \quad (4)$$

Where i is the current density, A is a constant, n is the passive index, and t is the time. The passive index can indirectly reflect the compactness and protective performance of the passive film: a value of n closer to 1 indicates a denser passive film with stronger protective ability, while a value close to 0.5 implies a porous film structure. Fitting the linear regions in Fig. 4b yields passive indices n of 0.55, 0.86, and 0.66 at 0.2 V, 0.5 V, and 0.8 V, respectively. Notably, the n value at 0.5 V is closest to 1, demonstrating that the passive film formed under this potential possesses the optimal corrosion protection capability. This result is consistent with the order of steady state current densities, further revealing the critical influence of polarization potential on the structure and performance of the passive film.

Fig. 4c-d present the EIS results of the Ti_3SiC_2 coating after 10 h of potentiostatic polarization at various potentials. In the Nyquist plots (Fig. 4c), all curves display a single capacitive loop. The diameter of the loop follows the sequence: 0.5 V > 0.8 V > 0.2 V, indicating that the passive film formed under 0.5 V polarization possesses the highest interfacial impedance and thus the best corrosion resistance. The Bode plots (Fig. 4d) provide further insight into the frequency-dependent behavior. In the high-frequency region ($>10^3$ Hz), the $|Z|$ reaches a plateau corresponding to the solution resistance, which shows little variation among the different potentials, confirming a consistent ohmic drop in the system. Within the medium-frequency range (10^{-1} – 10^3 Hz), the phase-angle peak for the 0.5 V condition is the highest ($>80^\circ$) and exhibits the broadest distribution, reflecting capacitive behavior closest to an ideal dielectric. At the low-frequency limit (0.01 Hz), the $|Z|$ values for both 0.5 V and 0.8 V exceed $10^6 \Omega \cdot \text{cm}^2$, whereas the value for 0.2 V is comparatively lower, further supporting the superior passive achieved at 0.5 V. The EIS data were fitted using the equivalent circuit model $R_s(Q_c(R_p(Q_{dl}R_{ct})))$, consistent with the previously described approach. The fitted curves show excellent agreement with the experimental data (Fig. 4c-d), and detailed fitting parameters are summarized in Table 2. The results reveal that the R_{ct} remains high after potentiostatic polarization, while the R_p increases by approximately 2–3 orders of magnitude compared to that under OCP conditions, demonstrating that the passive film formed during anodic polarization exhibits a more

Table 1

EEC parameters for the EIS data of the Ti_3SiC_2 coating and substrate at their respective open circuit potentials.

Sample	R_s (Ω)	CPE _c		R_p ($\Omega \text{ cm}^2$)	CPE _{dl}		R_{ct} ($\Omega \text{ cm}^2$)	χ^2 (10^{-4})
		Q_c ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	n_c		Q_{dl} ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	n_{dl}		
Ti_3SiC_2 coating	74.35	5.12×10^{-6}	0.99	25.26	4.52×10^{-6}	0.87	5.83×10^6	1.04
Substrate	69.70	1.44×10^{-5}	0.98	5.60	1.99×10^{-5}	0.86	7.11×10^5	0.16

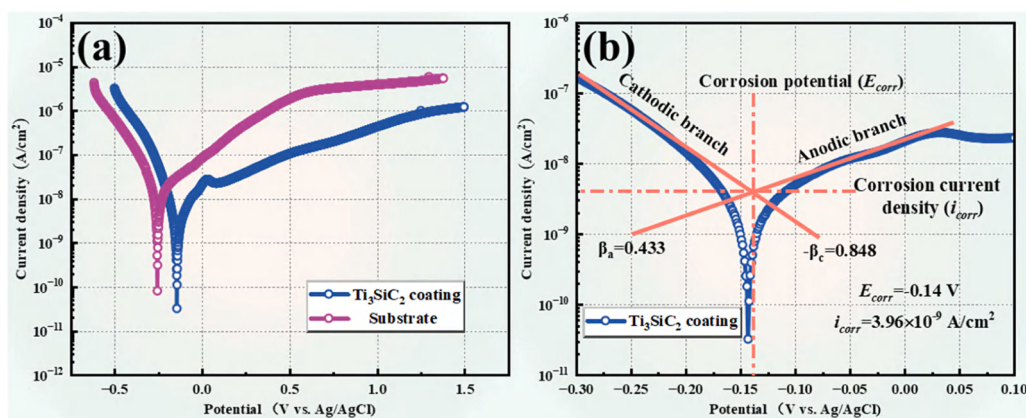


Fig. 3. (a) Potentiodynamic polarization curves of Ti_3SiC_2 coating and Substrate in 3.5 wt% NaCl solution, (b) Enlarged fitting plot of Ti_3SiC_2 coating.

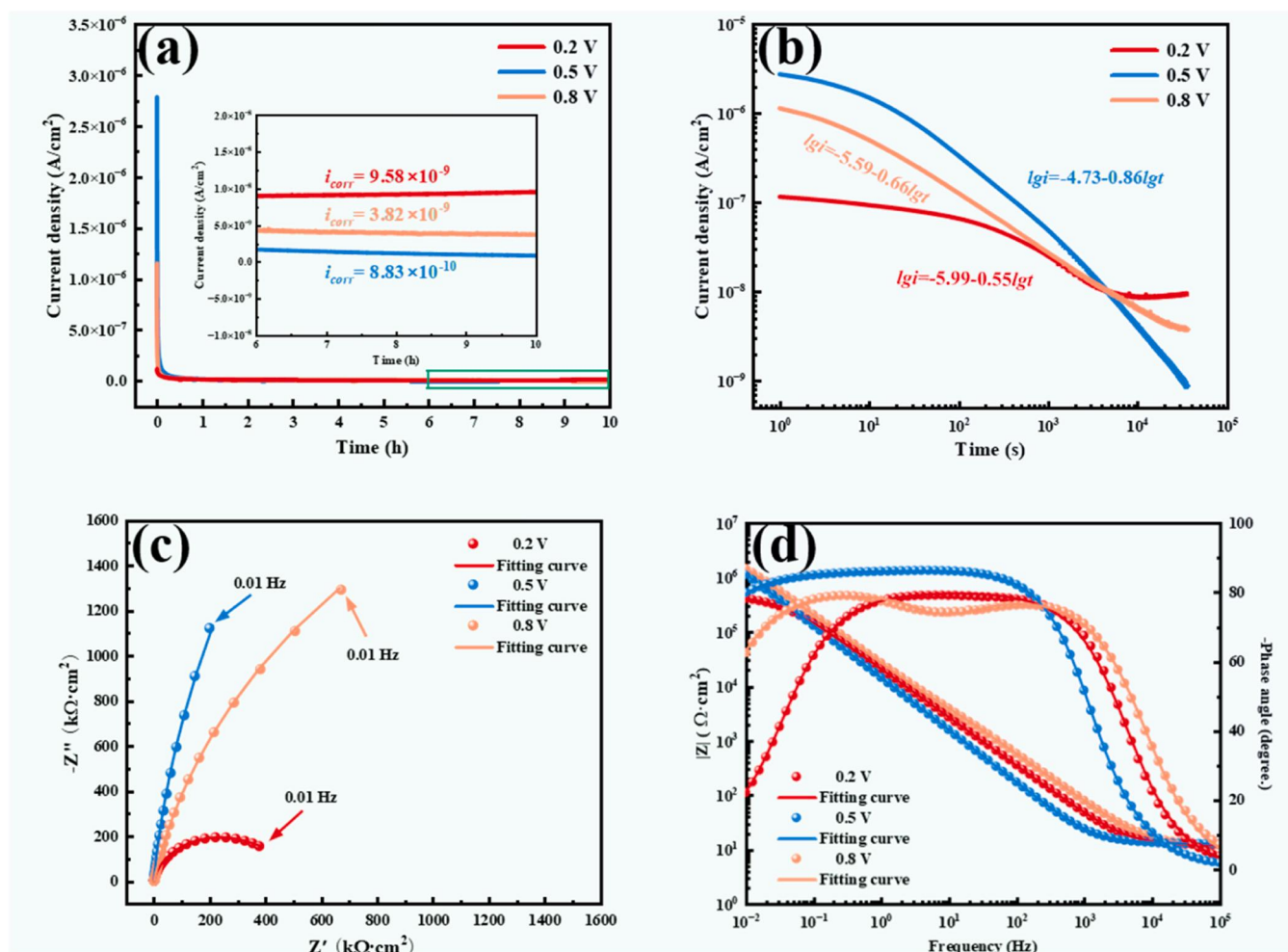


Fig. 4. (a) The current density versus time curves, (b) The logi-logT curves, (c) Nyquist plots and (d) Bode plots of Ti_3SiC_2 coating after potentiostatic polarization at + 0.2 V, + 0.5 V and + 0.8 V (vs. the stable OCP) for 10 h in 3.5 wt% NaCl solution.

Table 2

EEC parameters for the EIS data of the Ti_3SiC_2 coating after potentiostatic polarization at 0.2 V, 0.5 V and 0.8 V (vs. the stable OCP) for 10 h in 3.5 wt% NaCl solution.

Coating		R _s (Ω)	CPE _c		R _p (Ω cm ²)	CPE _{dl}		R _{ct} (Ω cm ²)	χ ² (10 ⁻⁴)
			Q _c (Ω ⁻¹ cm ⁻² s ⁿ)	n _c		Q _{dl} (Ω ⁻¹ cm ⁻² s ⁿ)	n _{dl}		
Ti ₃ SiC ₂	0.2 V	60.60	7.24 × 10 ⁻⁶	0.92	3.22 × 10 ³	2.22 × 10 ⁻⁶	0.77	4.69 × 10 ⁵	0.51
	0.5 V	65.45	1.18 × 10 ⁻⁵	0.96	1.21 × 10 ³	1.89 × 10 ⁻⁷	0.99	9.05 × 10 ⁶	3.82
	0.8 V	59.15	6.01 × 10 ⁻⁶	0.88	2.33 × 10 ⁴	1.25 × 10 ⁻⁶	0.94	4.88 × 10 ⁶	1.41

compact and protective structure. Notably, $R_{ct} > R_p$ under all three potentials, implying that corrosion inhibition is predominantly governed by the charge transfer resistance. In summary, the polarization potential exerts a pronounced influence on the structure and performance of the passive film. At 0.2 V, the relatively low driving force leads to insufficient film formation and lower interfacial impedance. The optimal potential is 0.5 V, which induces the growth of a dense, stable passive film and maximizes corrosion resistance. At 0.8 V, the excessively high potential may induce local transpassive or mild film dissolution, compromising film integrity and consequently reducing the overall impedance. Therefore, potentiostatic polarization at 0.5 V yields the best corrosion resistant performance for the Ti_3SiC_2 coating.

3.4. Chemical composition of formed passive film

To clarify the chemical composition and atomic bonding state of the passive film, high-resolution XPS analysis was performed on the passivated surface of the Ti_3SiC_2 coating after potentiostatic polarization at +0.5 V (vs. the stable OCP), with the results presented in Fig. 5. The XPS spectra of each element before and after Ar sputtering reveal distinct differences in their chemical states. Before sputtering, the Ti 2p spectrum (Fig. 5a) can be deconvoluted into four peaks: the peaks at binding energies of 454.6 eV and 460.7 eV are assigned to the $2p_{3/2}$ and $2p_{1/2}$ states of Ti in Ti_3SiC_2 [43], respectively, while those at 458.4 eV

and 464.5 eV correspond to Ti-O bonds in TiO_2 [23,37]. The Si 2p spectrum (Fig. 5b) exhibits a characteristic peak of Si in Ti_3SiC_2 at 98.8 eV [44], with an additional signal of Si-O bonds detected at 102.5 eV [45]. The C 1s spectrum (Fig. 5c) is deconvoluted into four components: the peak at 281.0 eV originates from C in the Ti_3SiC_2 [25], while the peaks near 284.8 eV, 285.9 eV, and 288.6 eV correspond to sp^2 and sp^3 hybridized carbon formed during oxidation, and adsorbed organic contaminants ($C=O$) on the sample surface [46], respectively. The O 1s spectrum (Fig. 5d) shows two distinct peaks: O-Ti bonds from TiO_2 at 531.8 eV [47] and O-Si bonds from SiO_2 at 533.1 eV [48], with a peak area ratio of approximately 82:18. After sputtering, the Ti 2p spectrum (Fig. 5e) still contains characteristic peaks corresponding to the Ti_3SiC_2 and TiO_2 , indicating no significant change in the chemical state of Ti. For the Si 2p spectrum (Fig. 5f), only the signal of Si in Ti_3SiC_2 is detected, with the disappearance of the Si-O bond peak. In the C 1s spectrum (Fig. 5g), aside from the sp^2 hybridized carbon peak at 284.8 eV, C-Ti and C-Si bonds in the Ti_3SiC_2 phase are identified at 282.0 eV and 282.7 eV [49], respectively. The O 1s spectrum (Fig. 5h) exhibits a single peak at 532.3 eV, corresponding to O-Ti bonds in TiO_2 . Collectively, these results demonstrate that the passive film formed on the Ti_3SiC_2 coating surface is primarily composed of a mixture of TiO_2 and a small amount of SiO_2 .

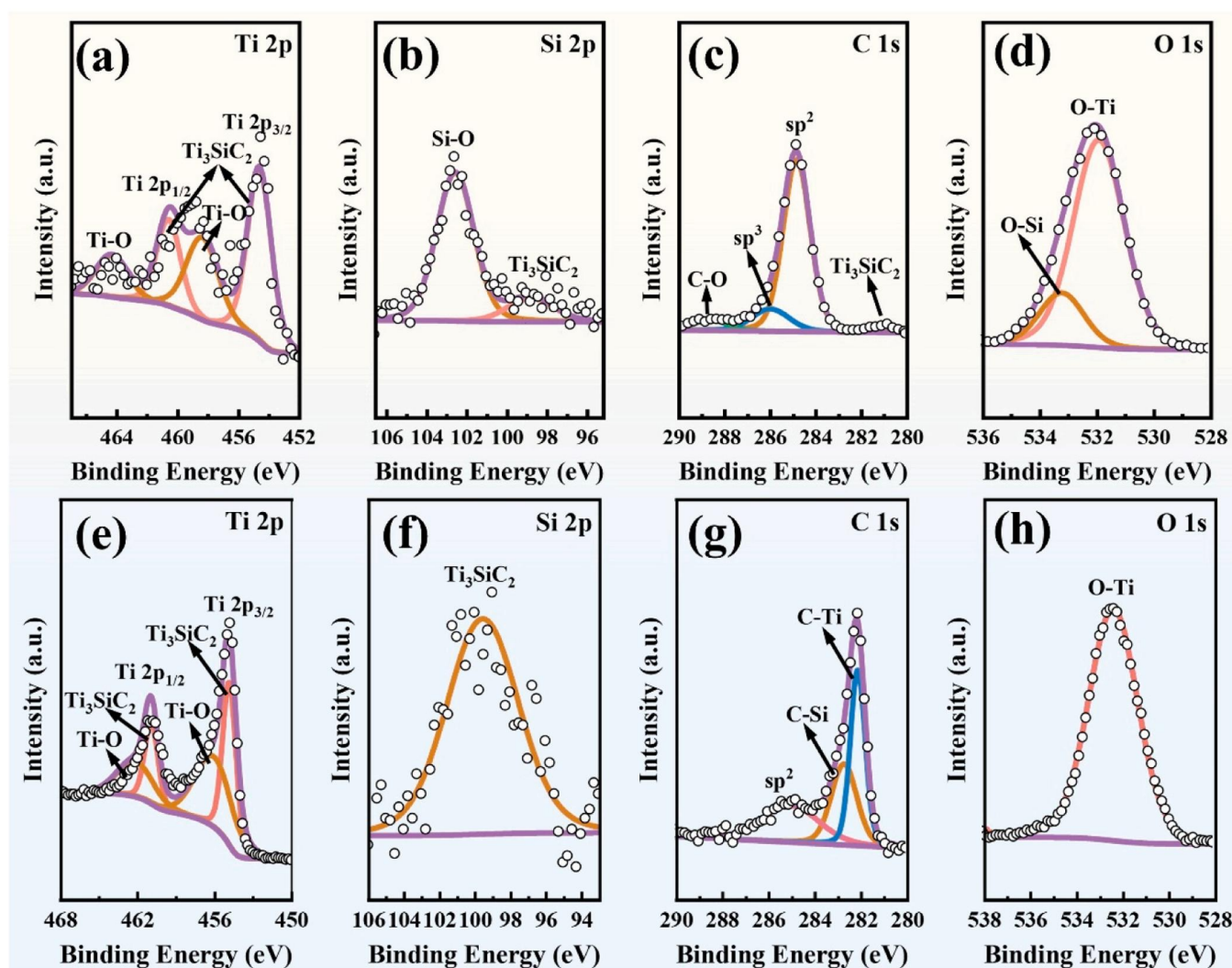


Fig. 5. High resolution XPS spectra of the passive film formed on the Ti_3SiC_2 coating after potentiostatic polarization at 0.5 V (vs. the stable OCP) for 10 h: (a)-(d) and (e)-(h) correspond to the Ti 2p, Si 2p, C 1s and O 1s before and after ions sputtering for 3 min, respectively.

3.4.1. Mott-Schottky analysis

Passive films on metallic/coated surfaces exhibit semiconductor behavior, where long-term corrosion resistance depends critically on electronic structure rather than thickness alone. Mott-Schottky analysis quantifies this relationship by measuring space-charge layer capacitance (C_{CS}) versus applied potential (E) to determine semiconductor type and calculate the donor density (N_D) using the slope of the curve [50]. The relevant expressions are as follows:

$$\frac{1}{C_{CS}^2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left(E - E_{fb} - \frac{e}{kT} \right) \quad (5)$$

$$N_D = \frac{2}{\epsilon\epsilon_0 e} \left[\frac{d(C_{CS}^{-2})}{dE} \right]^{-1} \quad (6)$$

Where ϵ_0 is the permittivity of free space ($8.85 \times 10^{-14} \text{ F}\cdot\text{cm}^{-1}$), e is the elementary charge ($1.602 \times 10^{-19} \text{ C}$), N_D is the donor density in the semiconductor passive film (n-type semiconductors), E_{fb} is the flat-band potential, k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$), T is the temperature, and ϵ is the dielectric constant of the passive film (typically 60 for TiO_2 [11] and 4 for SiO_2 [51], the effective dielectric constant in this work is 45 for $\text{TiO}_2/\text{SiO}_2$ composite films calculated via Bruggeman model [52]). Fig. 6a displays the Mott-Schottky curves of the passive films formed on the Ti_3SiC_2 coating after 10 h of passive at different polarization potentials in 3.5 wt% NaCl solution. All curves show that C_{CS}^{-2} increases linearly with the positive shift of potential, with a positive slope, which is a typical characteristic of n-type semiconductors. This indicates that the passive films formed on the coating surface are n-type semiconductors. Notably, there are significant differences in the slopes of the curves at different polarization potentials: as the polarization potential increases, the slope first increases and then decreases. Generally, a lower donor density indicates fewer defects and better structural integrity of the passive film, leading to stronger corrosion protection capability. The slopes were extracted by fitting the linear regions of the Mott-Schottky curves, and the N_D of the oxide films was calculated based on Eq. 6. The results are shown in Fig. 6b. When the potential is 0.2 V, the N_D is relatively high, indicating a higher number of structural defects in the passive film. As the potential increases to 0.5 V, the N_D decreases significantly to the lowest value among the three potentials, demonstrating that a passive film with fewer defects and a denser structure can be formed under this condition. However, when the potential is further increased to 0.8 V, the N_D rebounds slightly, suggesting that an excessively high polarization potential may lead to an increase in local defects in the passive film, resulting in reduced structural integrity.

3.4.2. Passive film growth behavior

To investigate the growth behavior of the Ti_3SiC_2 coating during electrochemical corrosion, successive electrochemical impedance spectroscopy (SEIS) measurements were performed [53]: a 10 h potentiostatic polarization experiment was conducted at an anodic potential of +0.5 V (vs. the stable OCP), with impedance spectra recorded every 30 min. Nyquist plots (Fig. 7a) show progressive expansion of capacitive loop diameters, indicating interfacial impedance enhancement from incomplete initial passive (low resistance at $t = 0$) to a highly protective state. As shown in Fig. 7b, the $|Z|$ in the low-frequency region (0.01 Hz) of the Bode plots maintains a high impedance level of approximately $10^6 \Omega\cdot\text{cm}^2$ and exhibits an increasing trend with polarization time. This directly confirms that a passive film with high impedance and excellent barrier properties is gradually formed on the Ti_3SiC_2 coating surface, which can effectively resist the long-term penetration and erosion of chloride ions. Although the phase angle curve (Fig. 7c) exhibits a high peak value ($>80^\circ$) in the initial stage, the peak plateau is narrow, similarly indicating the limited protective capability of the passive film formed at this time. As potentiostatic polarization proceeds, the medium-frequency region maintains a high phase angle peak while the frequency range of the peak gradually broadens, reflecting the gradual improvement in the structural uniformity and compactness of the passive film with a reduction in defect density.

Furthermore, the capacitance (C_p) of the passive film can be calculated using the Hsu-Mansfeld (H-M) equation [54] with the parameters Q_c and n_c obtained from CPE fitting. Based on this effective capacitance (C_p), the thickness (δ) of the passive film can be roughly estimated [55], with the relevant equation as follows:

$$C_p = Q_c \frac{1}{R_p} \frac{1-n}{n} \quad (7)$$

$$\delta = \frac{\epsilon_0 \epsilon A}{C_p} \quad (8)$$

Where ϵ_0 is the permittivity of free space ($8.854 \times 10^{-14} \text{ F}/\text{cm}$), ϵ is the dielectric constant of the passivation film (taken as 45), and A is the exposed area of the electrode (0.2 cm^2). The calculated passive film thicknesses are presented in Fig. 7d. The thickness at $t = 0$ (approximately 2.4 nm) is derived from EIS data under OCP conditions, where the coating is in a natural corrosion state and only an initial passive film formed by spontaneous oxidation exists on the surface. Data for $t > 0$ are obtained from SEIS measurements: the applied anodic potential provides an electrochemical driving force for anodic oxidation, promoting the growth and evolution of the passive film. The thickness evolution trend shows that the passive film thickness exhibits a "rapid initial growth followed by stabilization" characteristic: in the initial stage ($t < 2 \text{ h}$), intense oxidation reactions occur under the drive of the anodic

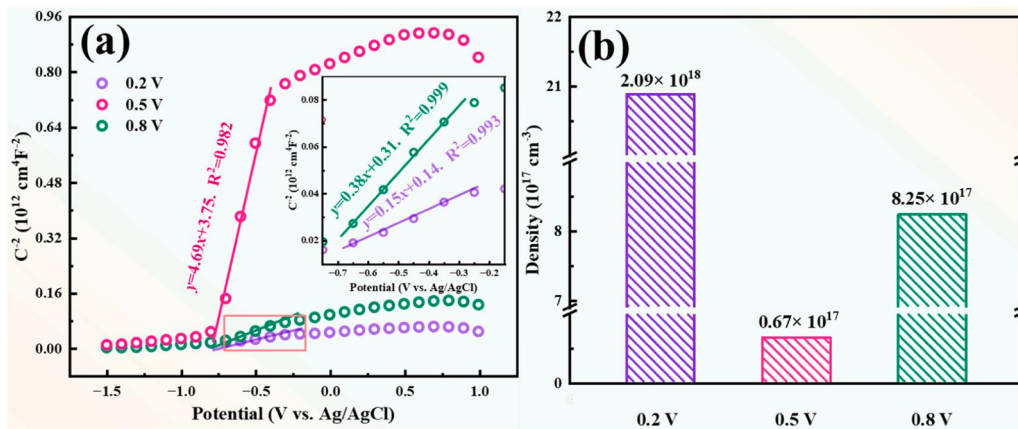


Fig. 6. (a) Mott-Schottky plots and (b) the corresponding donor densities of the passive films formed on the Ti_3SiC_2 coating after 10 h of potentiostatic polarization at various potentials in 3.5 wt% NaCl solution.

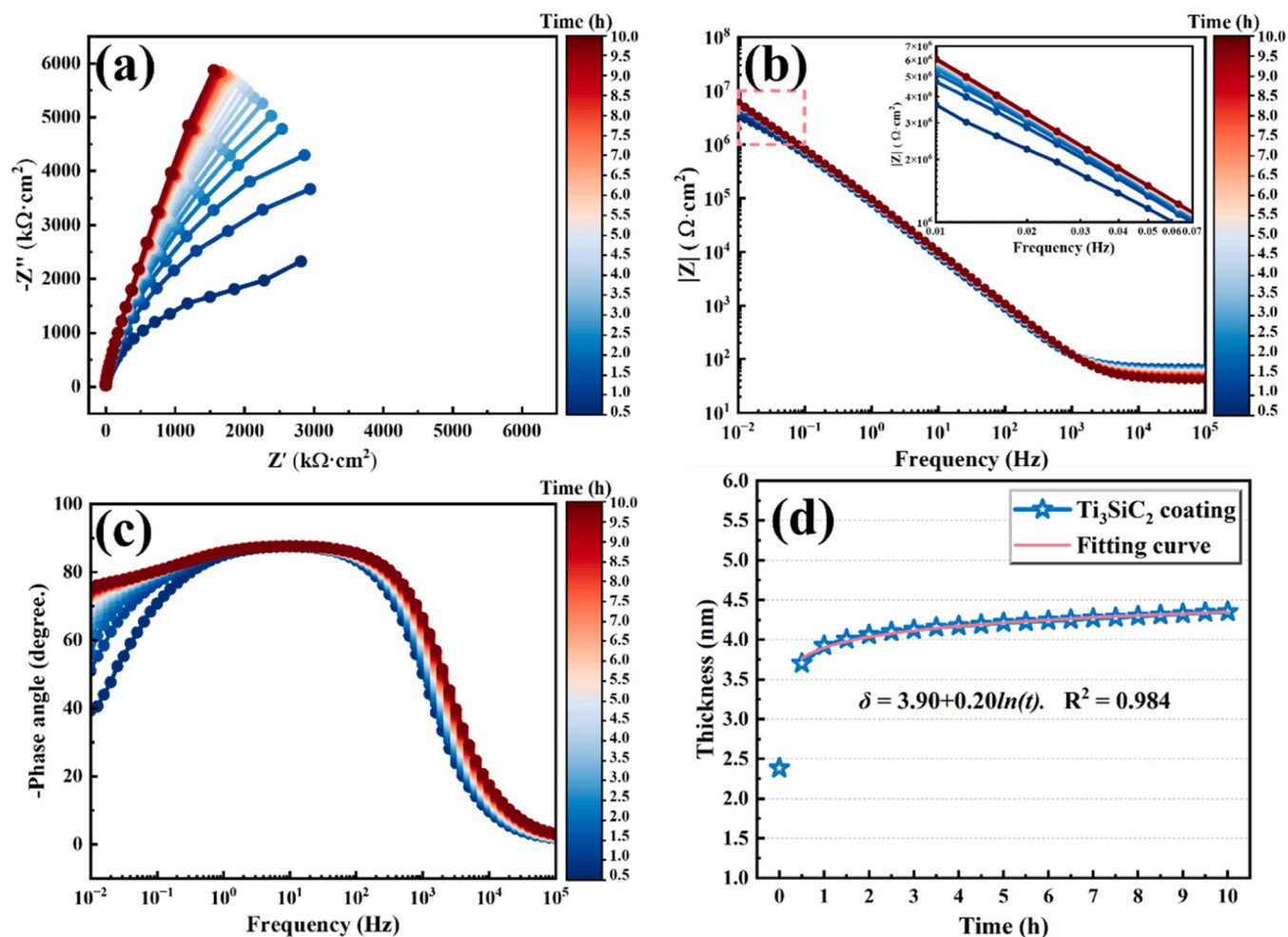


Fig. 7. Evolution of EIS spectra and physical parameters versus time of the passive film form on the Ti_3SiC_2 coating in 3.5 wt% NaCl solution. (a) Nyquist plots, (b) (c) Bode plots and (d) The passive film thickness.

potential, with metal cations and oxygen anions rapidly combining to form an oxide layer. The film thickness growth rate is high, and the thickness quickly increases to approximately 4.0 nm. With prolonged time ($t > 2$ h), the passive film has reached a certain thickness, and the transport resistance of ions within the film increases significantly with thickness. During anodic polarization, the growth behavior of the passive film thickness (δ) with time (t) can be explained by the following model [56]:

$$\delta = A + B \ln(t) \quad (9)$$

where A and B are constants. As shown in Fig. 7d, the fitted curve is in excellent agreement with the experimental data, demonstrating that the growth of the Ti_3SiC_2 coating passive film follows a logarithmic growth law. This indicates that the growth of the passive film on the Ti_3SiC_2 coating surface during electrochemical corrosion is controlled by the ion migration process, and the migration resistance increases with the passive film thickness. According to the high-field migration and point defect diffusion models [56,57], the passive film is thin and the internal electric field strength is high in the initial stage of the electrochemical reaction. The strong electric field drives metal cations or oxygen anions to rapidly cross the film, promoting passive film growth. As the film thickness increases, the electric field strength decays inversely with thickness, leading to a significant reduction in ion migration rate and a gradual slowdown in film thickness growth. In addition, the growth of the passive film relies on the diffusion of point defects such as oxygen vacancies and metal interstitial atoms. However, with increasing film

thickness, the transport path length of defects within the film increases, and their accumulation rate decreases, ultimately resulting in the stabilization of the passive film thickness.

TEM characterization was performed on the passive film formed on the Ti_3SiC_2 coating surface after electrochemical corrosion to reveal its structural mechanism of corrosion protection at the microscale. Fig. 8a clearly shows a uniform and continuous passive film formed between the physically protective C layer and the Ti_3SiC_2 coating. Based on the HAADF image and elemental mapping analysis of Ti, Si, C, and O (Fig. 8b), the passive film region exhibits homogeneous co-distribution of Ti and O within the film, while the distribution of Si is not obvious. Quantitative EDS of Area I (Fig. 8e) yields the atomic ratio of Ti to O is close to 1:2. (29.01 at% Ti, 59.04 at% O, 4.68 at% Si), confirming the passive film formed during Ti_3SiC_2 corrosion is a mixed phase of TiO_2 and minor SiO_2 , which is consistent with the XPS results. Fig. 8c is the HRTEM image of the red highlight frame region in Fig. 8a, showing that the passive film grows directly epitaxially along the Ti_3SiC_2 grains. The distinct and defect-free interface, combined with the in-situ growth nature of the passive film on the coating surface, confirms the excellent interfacial bonding and strong adhesion between the passive film and the coating. Additionally, the passive film is structurally dense, with the lack of lattice fringes confirming its amorphous nature. The measured thickness of the passive film is approximately 4.8 nm, which is basically consistent with the thickness estimated from SEIS data. Selected-area electron diffraction (SAED) analysis was performed on the inner coating region adjacent to the passive film (Fig. 8d), and the diffraction spots perfectly match the hexagonal crystal structure of Ti_3SiC_2 . The EDS

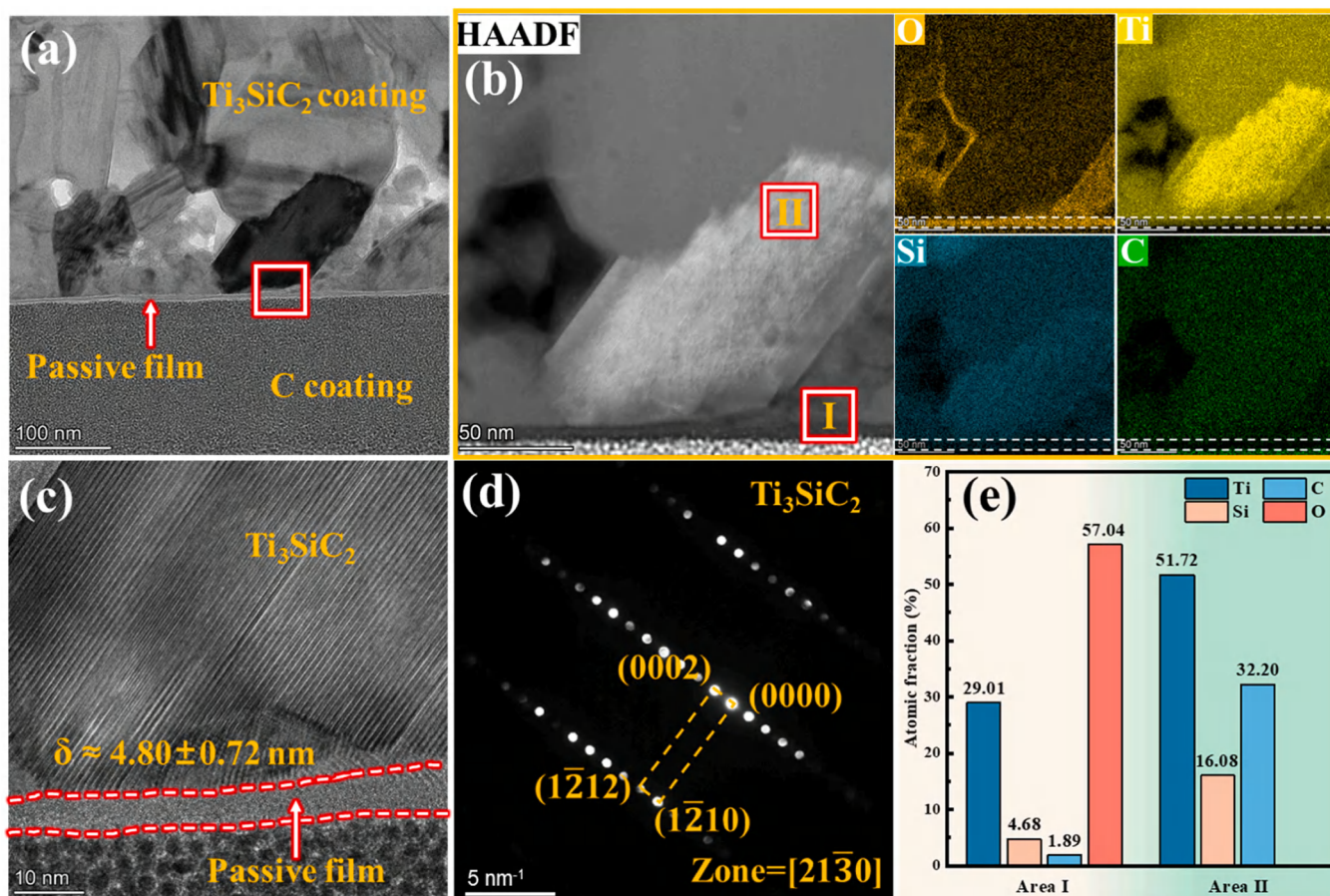


Fig. 8. TEM images of the passive film after SEIS test. (a) TEM bright image, (b) STEM-HAADF image and elemental maps, (c) HRTEM image at the interface between the passive film and Ti_3SiC_2 coating, (d) corresponding SAED pattern, (e) Elemental fraction of area I and II.

results of Area II show that the atomic ratio of Ti:Si:C is approximately 3:1:2, which is consistent with the standard stoichiometry of the Ti_3SiC_2 MAX phase. This indicates that during the corrosion process, the Ti_3SiC_2 coating substrate retains its original crystal structure without phase decomposition. Even though a passive film is formed by surface oxidation, the main phase maintains structural integrity, thereby avoiding the degradation of protective performance caused by coating degradation.

3.4.3. Formation mechanism of passive film

The electrochemical corrosion behavior of Ti_3SiC_2 coating is intrinsically governed by their unique nanolaminated crystal structure and anisotropic bonding characteristics. Within the Ti_3SiC_2 lattice, Ti-C bonds exhibit strong covalent character, whereas Ti and the A-site Si atoms are linked by relatively weak metallic bonds. This asymmetry in bond strength dictates that, under anodic polarization, the weakly bound Si atoms are more susceptible to dissociation from their lattice sites. From a kinetic perspective, the integrity of the passive film is primarily determined by the outward diffusion flux of elemental species. As vacancies serve as the fundamental vehicles for atomic transport, their formation energies directly dictate the diffusion barriers [11]. DFT calculations (Fig. 9) reveal that the vacancy formation energy for A-site Si in Ti_3SiC_2 is 3.05 eV, significantly lower than those of Ti atoms at two distinct crystallographic sites (Ti_I = 5.46 eV and Ti_II = 7.39 eV). This substantial energy gradient implies that Si atoms can more easily overcome lattice constraints, exhibiting higher intrinsic mobility and preferentially diffusing toward the surface via lattice defects to participate in oxidation. However, a positive correlation exists between the Si vacancy formation energy and its concentration. As Si vacancies accumulate, the energy barrier for generating additional defects increases

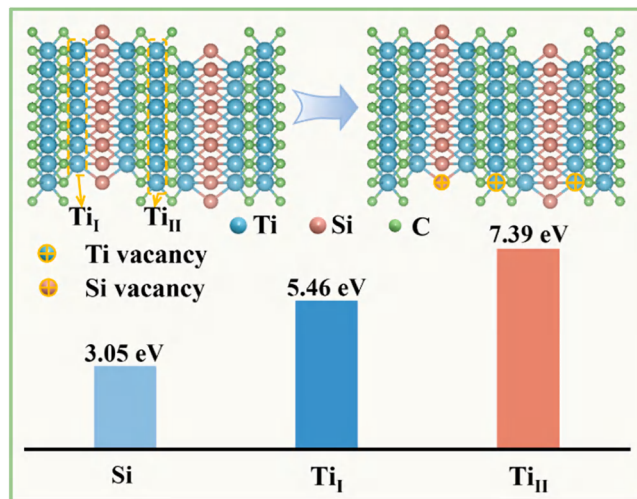


Fig. 9. Vacancy formation energies of Ti/Si atoms and models of supercell in Ti_3SiC_2 coating.

sharply [58]. This thermodynamic "self-limitation" restricts the continuous outward flux of Si, hindering the formation of a continuous, dense SiO_2 passive layer and thus diminishing the barrier effect against corrosive media.

Furthermore, the adsorption energy, a critical thermodynamic parameter describing interfacial interactions, determines the nucleation pathway of the passive film during the nascent stages of corrosion [34,

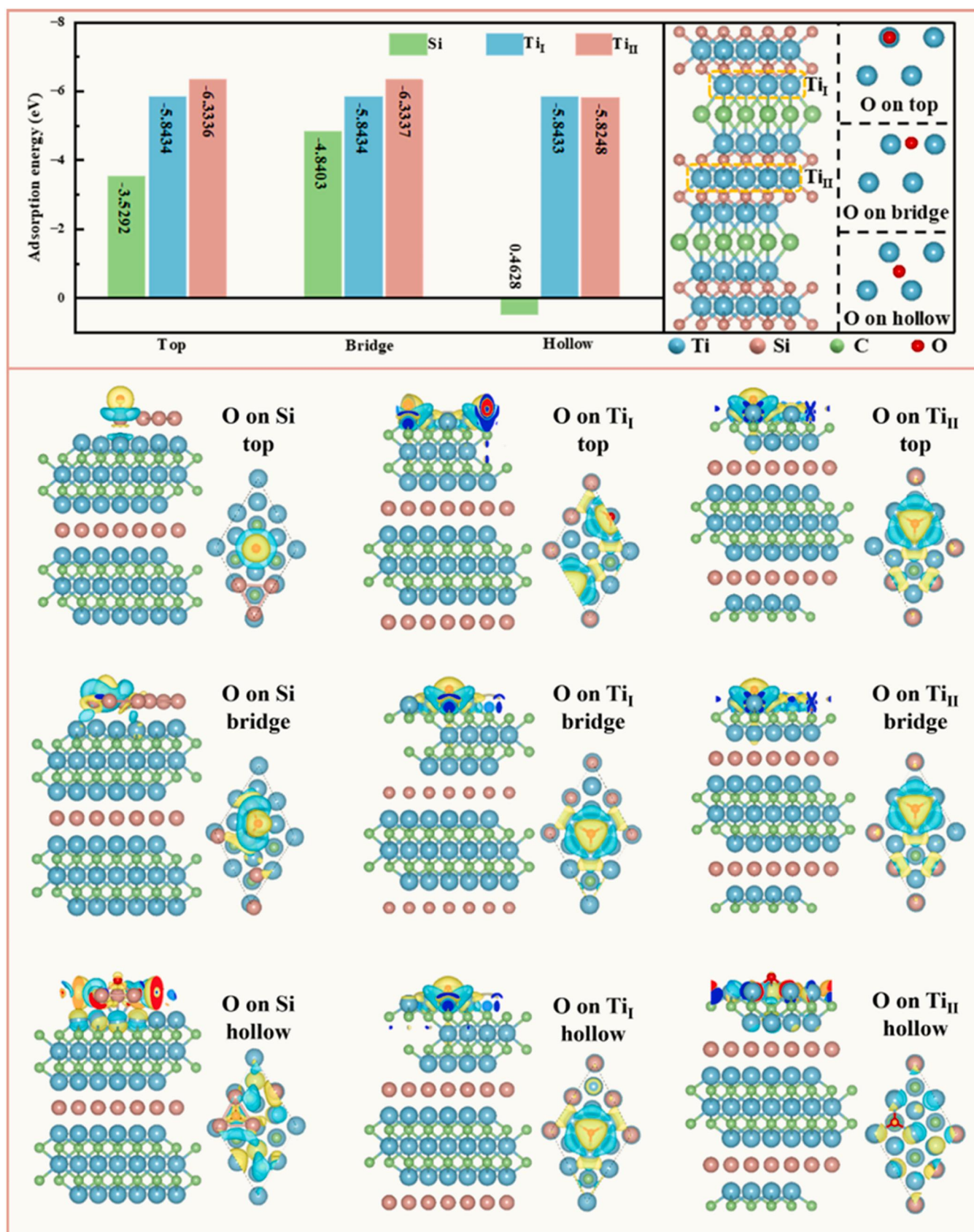


Fig. 10. Adsorption energy of O at different sites on the (0001) surface of Ti_3SiC_2 .

59]. Fig. 10 illustrates the binding characteristics of oxygen (O) atoms at various sites (Top, Bridge, and Hollow) on the Ti_3SiC_2 (0001) surface. The results indicate that the absolute values of adsorption energies for O at Ti sites are markedly higher than those at Si sites. Since negative adsorption energies signify spontaneous exothermic processes, the larger absolute values at Ti sites indicate a more stable adsorbed state and a stronger thermodynamic driving force. Consequently, Ti atoms act as primary active centers, preferentially capturing oxygen species during exposure. Thermodynamic considerations further support this, as the standard Gibbs free energy of formation for TiO_2 (-889.4 kJ/mol) is more negative than that of SiO_2 (-856.4 kJ/mol) [60,61]. This suggests that TiO_2 formation is energetically more favorable when inward-diffusing O ions encounter both Ti and Si under anodic potential. The corresponding anodic and cathodic reactions are as follows:



As the initial passive film consolidates, the growth mechanism shifts from substrate-limited diffusion to ion transport control within the oxide layer. The transport mechanisms in TiO_2 and SiO_2 differ fundamentally: TiO_2 growth is primarily driven by the inward diffusion of anions (O^{2-}) and the migration of Ti interstitials [62], whereas SiO_2 growth is strictly limited by oxygen ion diffusion through oxygen vacancies [63]. Under the influence of the anodic electric field, the migration rate of Ti^{4+} within the passive layer exceeds that of Si^{4+} . This facilitates the continuous migration of Ti to the film/electrolyte interface to react with O, leading to the sustained thickening and eventual dominance of the TiO_2 layer. In summary, the electrochemical passivation of Ti_3SiC_2 evolves through two distinct stages. In the initial stage, the disparity in bond strength triggers the preferential selective leaching and oxidation of Si. However, as oxygen ingresses, the superior adsorption activity and thermodynamic stability of Ti drive a competitive nucleation process, rapidly establishing a continuous TiO_2 -based skeletal oxide layer. In the growth stage, as the film thickens, ion transport becomes the rate-controlling step. Due to the lower ion migration resistance in the TiO_2 lattice, the synergistic effect of outward Ti migration and inward O diffusion promotes the densification of the TiO_2 layer. Conversely, the depletion of Si is inhibited by the concentration-dependent vacancy formation energy and its lower mobility within the oxide film, which helps maintain the structural integrity of the Ti_3SiC_2 phase. Ultimately, a dual-layered composite passive film is formed, consisting of a tightly adherent, amorphous TiO_2 matrix with a localized distribution of SiO_2 . The proposed corrosion and passivation mechanism of the Ti_3SiC_2 MAX phase coating in 3.5 wt% NaCl solution is schematically summarized in Fig. 11.

4. Conclusions

In summary, we systematically investigated the electrochemical behavior of Ti_3SiC_2 coating in 3.5 wt% NaCl through integrated electrochemical and microstructural analyses. The coating exhibits significantly enhanced corrosion resistance compared to the bare substrate, manifested by a higher impedance modulus and lower corrosion current density. This performance originates from a 4.8 nm thick, amorphous, and adherent passive film composed predominantly of TiO_2 with minor SiO_2 . The amorphous structure endows passive film with exceptional barrier properties against chloride penetration, while its growth follows logarithmic kinetics governed by high-field ion migration. From the perspective of passivation evolution, the initial stage of Ti_3SiC_2 coating corrosion is characterized by the preferential outward diffusion of A-site Si atoms to participate in the formation of the passive film, a process driven by their relatively low vacancy formation energy. As corrosion progresses, the outward diffusion of Si is significantly retarded due to

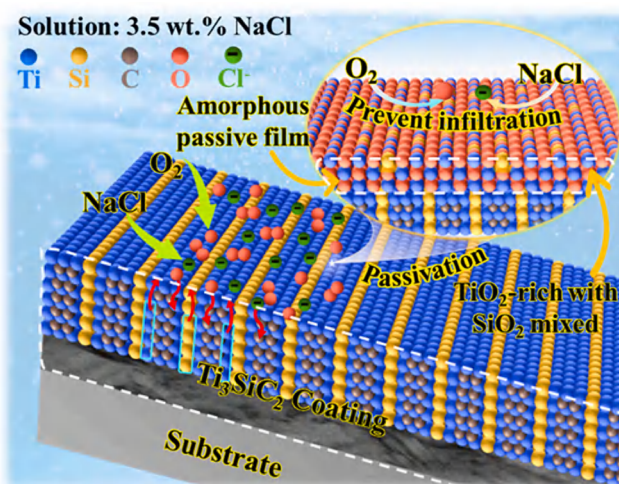


Fig. 11. Schematic diagram showing the passivation mechanism of Ti_3SiC_2 coating in 3.5 wt% NaCl solution.

the positive correlation between the Si vacancy formation energy and the vacancy concentration. In contrast, the Ti sites within the Ti_3SiC_2 lattice exhibit superior oxygen adsorption activity. This, coupled with the lower Gibbs free energy of TiO_2 formation, ensures the competitive advantage of Ti during the nucleation stage of the passive film. As the film thickens, growth becomes ion migration controlled; the lower migration barrier for $\text{Ti}^{4+}/\text{O}^{2-}$ in TiO_2 under high electric fields enables sustained outward growth, whereas Si diffusion is suppressed, restricting Si oxidation to the film/electrolyte interface. Consequently, this TiO_2 -dominated passive architecture not only provides a highly effective barrier against corrosive medium but also minimizes Si leaching, thereby preserving the structural integrity of the underlying MAX phase coating and ensuring long term stability. These findings elucidate the fundamental passive mechanism of Ti_3SiC_2 in chloride environments and offer critical insights for the rational design of high-performance MAX phase corrosion-resistant coating.

CRediT authorship contribution statement

Yuxi Xu: Writing – original draft, Investigation, Data curation. **Qizhen He:** Software, Data curation. **Kaihang Wang:** Methodology, Formal analysis. **Zhenyu Wang:** Supervision, Funding acquisition. **Yue Pan:** Funding acquisition. **Guanshui Ma:** Writing – review & editing, Funding acquisition. **Aiying Wang:** Writing – review & editing, Supervision, Investigation, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The authors do not have permission to share data.

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