

Article

Electrochemical Corrosion Performance of W-MoS₂ Coatings Fabricated by Electrospray Deposition

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Abstract

The self-lubricating MoS₂ coating is highly susceptible to degradation in marine environments due to oxidative corrosion. To expand its application in high-humidity and high-salt-fog conditions, this study mixed W with MoS₂ and prepared W-MoS₂ self-lubricating coatings on the surface of CrNi3MoVA steel by electrospray deposition technology. The electrochemical corrosion behaviors of these coatings, with varying W/MoS₂ mass ratios, were examined using an electrochemical workstation in a 3.5 wt.% NaCl solution. The findings indicated that as the MoS₂ content increased, the low-frequency impedance modulus (LIMs) of the W-MoS₂ coating initially rose and then declined. At a MoS₂ content of 20 wt.%, the coating exhibited the highest LIM and the greatest corrosion resistance. In comparison to the CrNi3MoVA steel substrate, the corrosion current density was reduced by 67.4%, a result attributed to the coating's dense microstructure and improved charge transfer resistance, thereby demonstrating its optimal protective performance. These results provide a laboratory electrochemical basis for designing corrosion-resistant self-lubricating ESD coatings for steel components exposed to chloride-containing environments; however, long-term immersion, cyclic salt-spray, field-exposure, and quantitative adhesion tests are still required before direct long-term marine-service durability can be confirmed.

Keywords: electrospray deposition; CrNi3MoVA steel; W-MoS₂ coating; corrosion

1. Introduction

Among the traditional lubricating materials, MoS₂ self-lubricating coatings exhibit excellent tribological properties, especially in vacuum or an inert atmosphere. Therefore, they are widely used in the aerospace industry [1–6]. However, when pieces of equipment with MoS₂ self-lubricating coatings are stored and operated on the ground, especially in a simulated marine environment, under the influence of active media such as O₂, H₂O, and chloride ions (Cl[−]) in seawater, such coatings easily corrode and form hard oxides that weaken lubrication performance, resulting in an increased friction coefficient and a reduced lifetime [7–13].

For marine protection, zinc-rich primers, epoxy, polyurethane, polysiloxane, polyurea, and superhydrophobic organic/inorganic hybrid coatings are widely used and may exhibit very low corrosion current densities when applied as thick continuous barrier films. However, these systems are mainly designed for broad-area antifouling or anticorrosion protection, whereas localized load-bearing and high-contact steel components may also



Academic Editor: Renato Altobelli Antunes

Received: 26 May 2026

Revised: 2 July 2026

Accepted: 3 July 2026

Published: 16 July 2026

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require solid-lubricating functionality. Therefore, the present study does not aim to replace mature high-build marine organic coatings, but to improve the initial chloride-corrosion resistance of a thin self-lubricating coating prepared directly on CrNi3MoVA steel by ESD.

Previous studies have shown that metal-doped MoS₂ self-lubricating coatings can exhibit improved protective performance [14]. Metal incorporation may increase coating hardness, suppress MoS₂ grain growth, improve coating compactness, and reduce porosity, thereby inhibiting oxidation of MoS₂ and improving corrosion resistance in humid or saline environments [15]. More recent studies further indicate that the performance of MoS₂-based coatings is strongly dependent on the modifier and processing route: doped MoS₂ coatings can improve wear resistance, mechanical durability, and environmental stability, while MoS₂-containing organic or electrospark-alloyed coatings usually enhance protection through barrier effects, phase control, and coating/substrate diffusion bonding [16–18]. Existing Ni, Ti, and Co-doped MoS₂ coatings have mainly emphasized tribological properties or general corrosion improvement [7,9,15], but the chloride-solution corrosion response of ESD-fabricated W-MoS₂ coatings with different W/MoS₂ ratios remains insufficiently clarified.

It should be noted that self-lubricating performance cannot be demonstrated by the mere presence of MoS₂. In the present work, the term “self-lubricating” refers to the coating design containing solid-lubricating MoS₂/WS₂ phases and to the design rationale supported by our previously published ESD coating studies. For W-WS₂ coatings prepared by SPS and ESD on CrNi3MoVA steel, the coefficient of friction decreased markedly with increasing WS₂ content; the 30 wt.% WS₂ coating showed a stable coefficient of friction of approximately 0.17–0.20, and its wear loss was only 12.5% of that of the CrNi3MoVA steel substrate [19]. Similarly, an electrospark-deposited Ni/C-MoS₂ coating exhibited a low and stable coefficient of friction of about 0.17, approximately 77% lower than that of CrNi3MoVA steel, which was attributed to the synergistic lubrication effect of graphite and MoS₂ and the support of the strengthened matrix [20]. These published tribological results provide the design basis for the self-lubricating concept of transition-metal-dichalcogenide-containing ESD coatings, whereas the present manuscript specifically focuses on electrochemical corrosion behavior.

Compared with other metallic elements, tungsten (W) has a very high melting point and outstanding mechanical properties. Because W and molybdenum (Mo) are in the same group, they show good chemical compatibility. Tungsten-based dichalcogenide systems have also attracted attention for coupling solid-lubricating and corrosion-inhibition functions [21], suggesting that W may simultaneously regulate phase constitution, defect distribution, and corrosion kinetics in MoS₂-based coatings. Under the transient high-temperature conditions of ESD, W may not only act as a metallic strengthening component, but may also promote the formation of W(Mo)-rich regions and in situ WS₂ lubricating phases [22–24]. This W/MoS₂ combination is therefore expected to couple corrosion resistance with MoS₂/WS₂-related solid lubrication.

Accordingly, W was combined with MoS₂ to prepare W-MoS₂ self-lubricating coatings on CrNi3MoVA steel by electrospark deposition. The corrosion resistance of coatings with different MoS₂ contents was evaluated in 3.5 wt.% NaCl solution. The uniqueness of this work lies in correlating the W/MoS₂ ratio with surface and cross-sectional morphology, phase evolution, roughness, impedance response, polarization behavior, and corrosion products, thereby providing a laboratory electrochemical basis for designing thin self-lubricating ESD coatings for chloride-containing service environments.

2. Experimental Procedure

2.1. Coating Preparation

CrNi3MoVA steel (20 mm × 10 mm × 5 mm) was selected as the substrate. The coating materials consisted of W powder and MoS₂ powder with a purity exceeding 99.9% and an average particle size of 2 µm. First, W powder and MoS₂ powder were uniformly mixed in mass ratios of 70:30, 80:20, and 90:10, respectively, and subsequently formed into W-MoS₂ electrodes by spark plasma sintering (SPS). Subsequently, the CrNi3MoVA steel and W-MoS₂ electrodes were polished and cleaned. Finally, using DJ-2000 ESD equipment, (Shanghai Kangbei Mechanical and Electrical Equipment Co., Ltd., Jiading District, Shanghai, China) 10WMoS₂, 20WMoS₂ and 30WMoS₂ were deposited on the CrNi3MoVA steel substrate under argon gas protection, following the optimized deposition parameters obtained from preliminary experiments (Table 1). For the convenience of discussion, the three coatings with different contents were denoted as the 10WMoS₂ coating, 20WMoS₂ coating, and 30WMoS₂ coating, respectively.

Table 1. Technological parameters of ESD.

Voltage/V	Power/W	Electrode Rotation Speed/ r·min ^{−1}	Argon Flow Rate/ L·min ^{−1}	Unit Area Deposition Time/ min·cm ^{−2}
60	1200	2500	15	1

The nominal chemical composition of the CrNi3MoVA steel substrate is described in Table 2.

Table 2. Chemical composition of CrNi3MoVA steel (wt.%).

Fe	C	Mn	Si	Cr	Ni	Mo	V	S	P
Balance	0.40	0.41	0.25	1.28	3.14	0.37	0.20	0.001	0.012

2.2. Characterization

The surface morphology and elemental composition of the substrate and W-MoS₂ coatings were characterized by scanning electron microscopy (SEM, Gemini360, CarlZeissAG, Oberkochen, Germany) equipped with an energy-dispersive spectrometer (EDS). Cross-sectional samples were mechanically ground, polished, and observed to evaluate coating thickness and interfacial continuity. To quantitatively support the SEM observations, surface roughness was measured using a three-dimensional optical profilometer/surface profilometer. At least five randomly selected regions were measured for each sample, and the average roughness (Ra), root-mean-square roughness (Rq), and maximum height roughness (Rz) were expressed as mean ± standard deviation. The phase composition of the coatings was identified by X-ray diffraction (XRD, D8 Advance, Bruker, Germany) using Cu Kα radiation ($\lambda = 1.5406 \text{ \AA}$) over a 2θ range of 10–90°. Additionally, the corroded surfaces of the tested coatings were investigated by X-ray photoelectron spectroscopy (XPS, Shimadzu Model AXIS Supra+, Kratos Analytical Ltd., Manchester, UK) using monochromatic Al Kα radiation. The binding energies were calibrated with reference to the C 1s peak at 284.8 eV, and the spectra were fitted after background subtraction. These characterization details were included to improve experimental reproducibility.

No independent friction and wear tests were conducted in this study, because the present experimental program was designed to evaluate the electrochemical corrosion behavior of W-MoS₂ coatings in chloride solution. In addition, the present dataset combines as-deposited cross-sectional SEM with surface SEM/EDS and XPS after corrosion; cross-

sectional EDS mapping after corrosion was not available and will be included in follow-up work to quantify through-thickness elemental redistribution and corrosion penetration.

2.3. Electrochemical Corrosion Testing

The corrosion resistance of the samples was investigated using a CHI760E electrochemical workstation with a standard three-electrode cell in 3.5 wt.% NaCl solution. For each condition, electrochemical measurements were performed on at least three independently prepared specimens. The samples were first immersed in the electrolyte for 30 min to obtain a stable open-circuit potential (OCP); this stabilization period was used to evaluate the initial electrochemical response rather than long-term marine-exposure behavior. Electrochemical impedance spectroscopy (EIS) was then conducted at the OCP over a frequency range from 0.001 Hz to 105 Hz. Potentiodynamic polarization (PDP) curves were recorded from -250 mV to 250 mV at a scanning rate of 0.5 mV/s. The PDP and EIS data were fitted and analyzed using CView and ZView software (CView 3.6a-April 2025, ZView 4.2b-Feb 2026). The fitted electrochemical parameters are reported as mean $\pm$ standard deviation where applicable, and error bars are used to present data variability.

3. Results and Discussion

3.1. Microstructure of ESD W-MoS₂ Coatings

As shown in Figure 1a, the surface of the CrNi3MoVA steel substrate was smooth and flat, with localized grinding and polishing scratches. The SEM analysis of the three W-MoS₂ coatings revealed a characteristic micro-roughness morphology typical of ESD, featuring localized micron-scale pores and a pronounced light–dark contrast, as illustrated in Figure 1b–d. In comparison, the 10WMoS₂ coating exhibited high-density agglomerated protrusions, while the 30WMoS₂ coating displayed deep pores and grooves. Conversely, the surface of the 20WMoS₂ coating was notably smoother and flatter.

The quantitative roughness results in Table 3 corroborate the SEM observations. The 20WMoS₂ coating exhibited lower Ra, Rq, and Rz values than the 10WMoS₂ and 30WMoS₂ coatings, consistent with its smoother and denser surface. By contrast, the greater roughness of the 10WMoS₂ and 30WMoS₂ coatings was associated with agglomerated protrusions, pores, grooves, and cracks, which increase the effective electrolyte-contact area and favor localized corrosion.

Table 3. Surface roughness values of the substrate and W-MoS₂ coatings (mean $\pm$ standard deviation, $n \geq 5$).

Sample	Ra/ μm	Rq/ μm	Rz/ μm
CrNi3MoVA steel	12.0 ± 0.6	15.4 ± 0.8	66.8 ± 4.7
10WMoS ₂ coating	21.0 ± 1.1	26.8 ± 1.3	118.5 ± 7.9
20WMoS ₂ coating	19.0 ± 0.9	23.9 ± 1.1	104.2 ± 6.8
30WMoS ₂ coating	23.0 ± 1.2	29.0 ± 1.6	132.6 ± 9.1

The EDS results in Table 4 show that increasing the initial MoS₂ content increased the S and Mo contents of the coatings while decreasing the W content, in agreement with the nominal electrode compositions. The bright regions (A, C, and E) contained substantially more W than the corresponding dark regions (B, D, and F). Fe was also detected in the coatings, indicating substrate-to-coating transfer or intermixing during the ESD process. The compositional contrast between the bright and dark regions confirms that the rapidly solidified coatings were microscopically heterogeneous.

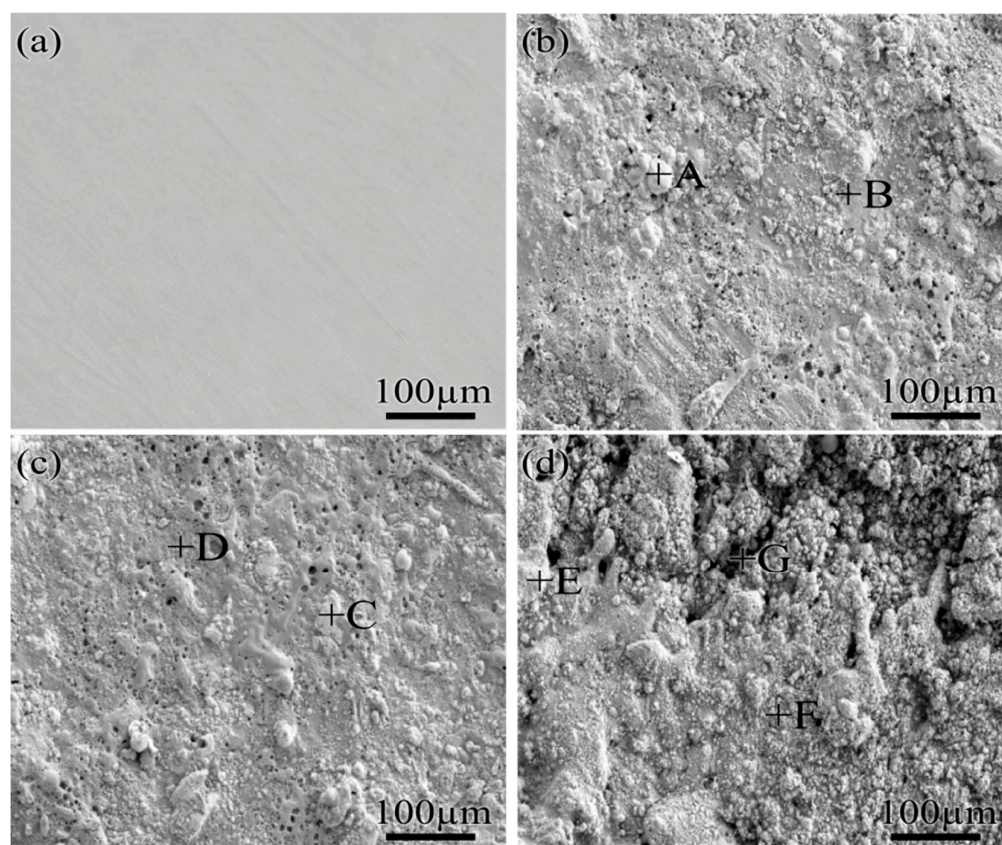


Figure 1. SEM of (a) CrNi3MoVA steel substrate, (b) 10WMoS₂ coating, (c) 20WMoS₂ coating, (d) 30WMoS₂ coating.

Table 4. The EDS results of W-MoS₂ coating.

Coating	Position	Composition (wt.%)			
		W	S	Mo	Fe
10WMoS ₂	Surface scanning	65.0	8.1	8.9	18.0
	A	86.7	3.7	7.4	2.2
	B	61.2	8.5	8.3	22.0
20WMoS ₂	Surface scanning	58.8	10.7	20.4	10.1
	C	79.9	6.6	10.1	3.4
	D	53.4	11.1	15.0	20.5
30WMoS ₂	Surface scanning	50.3	14.5	31.8	3.4
	E	59.0	8.6	27.0	5.4
	F	43.5	18.5	34.5	3.5
	G	48.3	17.6	30.5	3.7

Compared with the other coatings, the 30WMoS₂ coating showed less pronounced W enrichment on the surface and a smaller compositional difference between the bright and dark regions. EDS analysis of the deep concavity (G) also detected W, Mo, and S, confirming that this feature remained part of the deposited coating rather than an exposed substrate area.

The XRD analysis results depicted in Figure 2 revealed that the phase compositions of the W-MoS₂ coatings primarily consisted of W, Mo, MoS₂, and WS₂. The diffraction peaks corresponding to W/Mo and MoS₂/WS₂ exhibited partial overlap, and the intensities near the MoS₂/WS₂ basal reflections increased with increasing initial MoS₂ content, indicating a

(002) preferred orientation. Because these peaks overlap, the phase constitution and lattice relationships cannot be assigned unambiguously from conventional XRD alone.

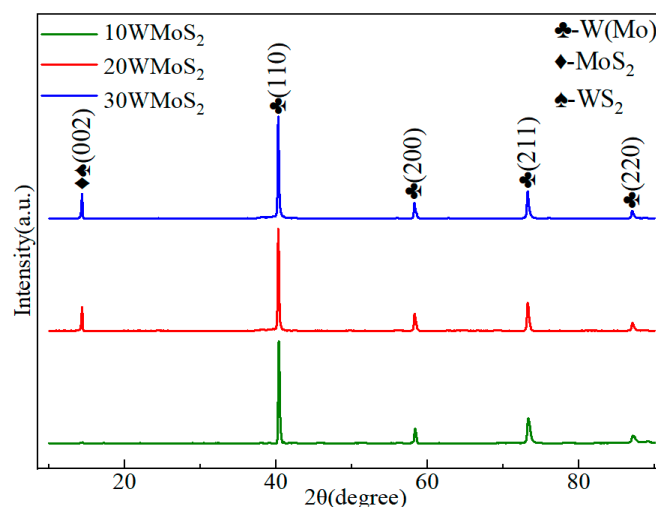


Figure 2. XRD patterns of W-MoS₂ coatings.

During the transient high-temperature cycling of the ESD process, partial decomposition of MoS₂ may occur, and the generated Mo may diffuse into W-rich regions because W and Mo have similar physicochemical characteristics [23,25]. This process may lead to W(Mo)-rich metallic regions or a possible W(Mo) solid-solution tendency. Meanwhile, W may act as a heterogeneous nucleation site and promote preferential orientation of MoS₂/WS₂ along the low-surface-energy (002) plane.

Because the diffraction peaks of W/Mo and MoS₂/WS₂ partially overlap, the exact amount of W-Mo solid solution cannot be determined solely from conventional XRD. Accordingly, the coatings are described as composite structures containing W(Mo)-rich metallic regions and MoS₂/WS₂ lubricating phases, rather than as fully confirmed single W(Mo) solid-solution coatings. More definitive confirmation of lattice relationships and nanoscale phase distribution would require TEM, peak deconvolution, or grazing-incidence XRD, which will be considered in future work.

The decomposition product S can further react with W to generate WS₂ in situ, while residual MoS₂ and formed WS₂ together contribute to the soft lubricating phase. Based on the combined EDS and XRD results, the white bright regions can be cautiously assigned mainly to W(Mo)-rich metallic regions with a small amount of dispersed lubricating phases, whereas the gray dark regions likely contain a more mixed distribution of W(Mo)-rich regions, MoS₂, and WS₂ phases.

This phase constitution differs from previously reported electrospark-alloyed Mo-MoS₂ coatings, in which MoS₂ was detected together with Fe-based solid solutions and the discussion mainly focused on structure and tribological properties [17]. In the present W-MoS₂ system, the coexistence of W(Mo)-rich metallic regions, residual MoS₂, and in situ-formed WS₂ indicates that the corrosion response is regulated jointly by the W/MoS₂ ratio and the distribution of ESD-induced defects.

The (002) preferred orientation can reduce the number of dangling and unsaturated bonds exposed on the basal planes of MoS₂ and WS₂, which is beneficial for reducing the adsorption of O₂ and H₂O. In addition, WS₂ generally exhibits better oxidation resistance than MoS₂, further improving the stability of the coating in humid environments. Therefore, the W-MoS₂ coating formed by ESD is expected to be conducive to improved short-term corrosion resistance. The cross-sectional morphologies (Figure 3a–c) show that

the coating thicknesses are similar, approximately 30 μm , while the internal bright/dark phase distribution differs markedly with the W/MoS₂ ratio.

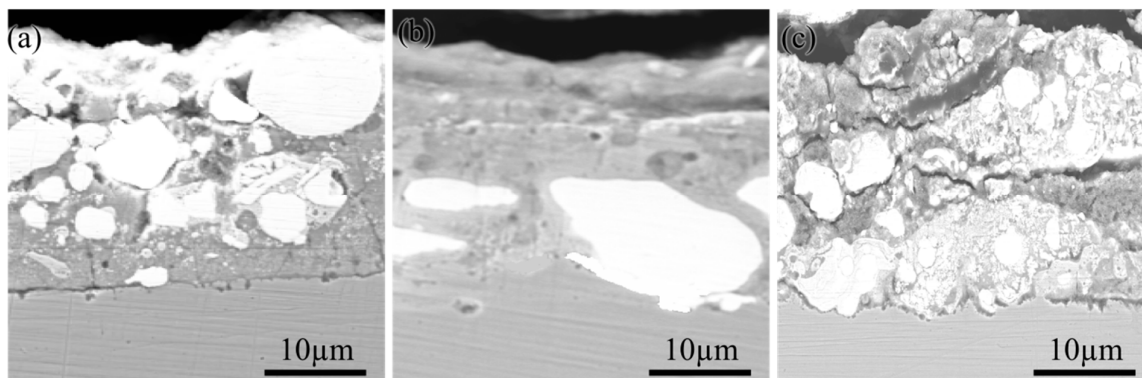


Figure 3. Cross-section morphology: (a) 10W/MoS₂ coating, (b) 20W/MoS₂ coating, (c) 30W/MoS₂ coating.

From the cross-sectional morphology, no catastrophic interfacial delamination was observed for the 20W/MoS₂ coating in the examined area, which qualitatively supports interfacial continuity. However, this observation cannot replace quantitative adhesion testing, such as scratch or pull-off tests, and adhesion performance should be evaluated in future work.

The gray phases in the 10W/MoS₂ coating are sparse and concentrated near the substrate. Consequently, the XRD detection results revealed extremely weak diffraction peak intensities for both MoS₂ and WS₂. The majority of the remaining areas are covered by white phases. During the preparation of the coating, an excessive amount of hard metal W and an insufficient proportion of soft lubricant MoS₂ led to a thermodynamic mismatch between the white W(Mo)-rich metallic region and the gray regions with a high content of lubricant phases, resulting in localized porosity defects. Simultaneously, noticeable microcracks formed within the coating and at the interface between the coating and the substrate.

The upper half of the 20W/MoS₂ coating primarily consisted of a gray phase, accompanied by a small quantity of tiny W(Mo)-rich metallic regions. The lower half, near the substrate, was mainly composed of continuously distributed W(Mo)-rich metallic regions, with a small amount of gray phases interspersed. Moreover, the W(Mo)-rich metallic regions adjacent to the substrate were predominantly metallic phases and exhibited a gradient distribution structure, effectively reducing differences in mechanical properties.

In the cross-section of the 30W/MoS₂ coating, the W(Mo)-rich metallic regions displayed a relatively uniform distribution. However, an excessive content ratio of MoS₂ triggered agglomeration phenomena, leading to the formation of wide cracks at the junction of the gray and white regions. Notably, substantial microcracks were also observed at the interface between the coating and the substrate.

3.2. Testing Curves of PDP

PDP curves were employed to evaluate electrochemical corrosion behavior by analyzing variations in potential or current. A higher self-corrosion potential (E_{corr}) indicated a lower tendency for corrosion, whereas a smaller corrosion current density (I_{corr}) corresponded to a reduced corrosion rate. Figure 4 displays the polarization curves of the samples immersed in a 3.5 wt.% NaCl solution. It could be observed that, compared to those of the CrNi3MoVA steel substrate, the E_{corr} of the W-MoS₂ coatings had generally shifted in the negative direction, and I_{corr} exhibited a significant decrease.

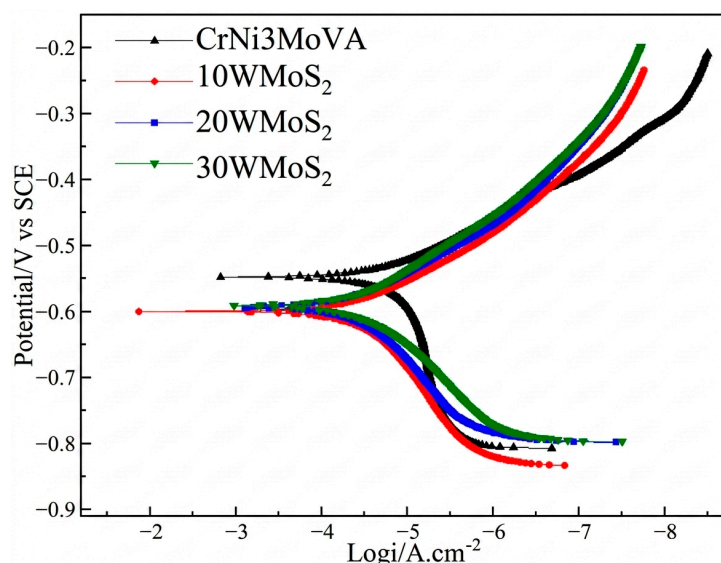


Figure 4. Polarization curves of CrNi3MoVA steel and W-MoS₂ coatings.

The electrochemical corrosion parameters are recorded in Table 5. The results demonstrated that the W-MoS₂ coatings exhibited more negative E_{corr} values and lower I_{corr} values compared to the substrate. Although the coatings displayed slightly more negative E_{corr} values, their significantly lower I_{corr} values indicated suppressed corrosion kinetics. Consequently, once corrosion initiates, the W-MoS₂ coatings can effectively decelerate the corrosion rate. Among them, the 20WMoS₂ coating exhibited the highest E_{corr} and the lowest I_{corr} , reducing I_{corr} by approximately 67.4% compared to the substrate, which indicates that the 20WMoS₂ coating offers the optimal protective performance.

Table 5. PDP fitting results of CrNi3MoVA steel and W-MoS₂ coatings in 3.5 wt.% NaCl solution (mean $\pm$ standard deviation, $n \geq 3$).

Samples	$E_{\text{corr}}/(\text{V vs. SCE})$	$I_{\text{corr}}/(\mu\text{A}\cdot\text{cm}^{-2})$
CrNi3MoVA Steel	-0.550 ± 0.018	8.65 ± 0.45
10WMoS ₂	-0.600 ± 0.021	3.31 ± 0.17
20WMoS ₂	-0.580 ± 0.015	2.82 ± 0.12
30WMoS ₂	-0.590 ± 0.018	3.30 ± 0.16

3.3. EIS Testing

EIS can provide information regarding the electrochemical corrosion process of samples. The test results are presented in Figure 5. The single phase-angle peak (Figure 5c) indicates that one electrochemical process dominated the EIS response within the measured frequency range. However, compared to the substrate, the coatings exhibited a lower peak phase angle and a broader peak shape, suggesting reduced surface uniformity. Meanwhile, the phase angle of the coatings increased significantly at 10^{-2} Hz, demonstrating the presence of a notable phase lag phenomenon. This characteristic implies that the coatings had a longer relaxation time during corrosion compared to the substrate. These findings confirm that the W-MoS₂ coatings can effectively delay the kinetics of interfacial corrosion reactions through their high-resistance physical barrier properties, thereby reducing the corrosion current density and corrosion rate.

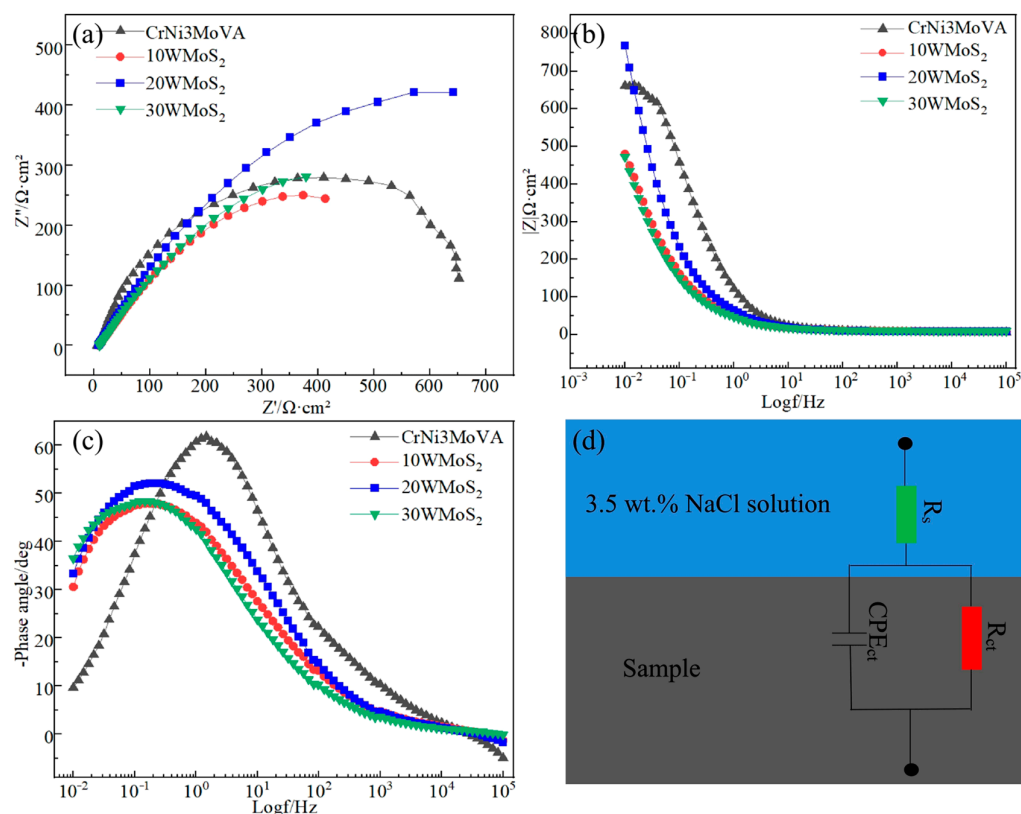


Figure 5. EIS results: (a) Nyquist plots, (b) Bode-modulus plots, (c) Bode-phase angle plots, (d) equivalent circuit diagram.

The Nyquist plot in Figure 5a demonstrates that both the substrate and the coatings exhibit the characteristic of a single capacitive arc, reflecting the parallel nature between double-layer capacitance and charge transfer resistance. Given the significant deviation of the capacitive arc from an ideal semicircle, it is challenging to directly compare the corrosion resistance of the samples quantitatively based on the radius. However, the complete interface electrochemical reaction process can be captured at the low frequency of 10^{-2} Hz. Therefore, this impedance modulus ($|Z|$) serves as a useful comparative parameter for evaluating the corrosion resistance performance of the samples. The higher its value, the stronger the corrosion resistance performance. From the Bode-modulus plot (Figure 5b), it is evident that all samples achieve the maximum $|Z|$ at 10^{-2} Hz. Among them, the $|Z|$ values of the 10WMoS₂ coating and the 30WMoS₂ coating are similar and relatively low, followed by that of the substrate. The 20WMoS₂ coating exhibits the highest $|Z|$, which is approximately 16% higher than that of the substrate. The aforementioned results indicate that the 20WMoS₂ coating possesses the best corrosion resistance and can effectively enhance the protective performance of the substrate, whereas the 10WMoS₂ and 30WMoS₂ coatings demonstrate relatively weaker protective performance.

To further quantify the impedance effect of the coatings, based on the test results depicted in Figure 5a–c and the characteristics of the corrosion system, the R-C parallel equivalent circuit shown in Figure 5d was selected for fitting analysis. Here, R_s represents the resistance of the 3.5 wt.% NaCl solution, R_{ct} denotes the charge transfer resistance, and CPE_{ct} is the constant phase element used to characterize the non-ideal capacitive behavior of the deformed semicircle. Its impedance, Z_{CPE} , can be expressed as shown in Equation (1) [26], where Y_0 is the admittance of the CPE, ω is the angular frequency, and n is the CPE exponent ($0 \leq n \leq 1$). When $n = 1$, the CPE represents a pure capacitor, and when $n = 0$, it represents a pure resistor. A value of $n < 1$ indicates the presence of factors

such as pores, cracks, or inhomogeneity. Furthermore, the corresponding double-layer effective capacitance (C_{ct}) can be calculated using Equation (2) [27]. The fitting results are listed in Table 6.

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (1)$$

$$C_{ct} = Y_0^{\frac{1}{n}} \left(\frac{1}{R_s} + \frac{1}{R_{ct}} \right)^{\frac{n-1}{n}} \quad (2)$$

Table 6. Fitting results of EIS (mean $\pm$ standard deviation, $n \geq 3$; Y_0 in $10^{-3} \Omega^{-1} \cdot S^n \cdot cm^{-2}$ and C_{ct} in $10^{-4} F \cdot cm^{-2}$).

Sample		CrNi3MoVA	10WMoS ₂	20WMoS ₂	30WMoS ₂
Parameters					
	$R_s/(\Omega \cdot cm^2)$	6.744 ± 0.24	8.61 ± 0.31	8.22 ± 0.28	10.08 ± 0.39
	$R_{ct}/(\Omega \cdot cm^2)$	824.8 ± 41.2	1416 ± 73	1968 ± 85	1747 ± 89
CPEct	$Y_0/(10^{-3})$	2.17 ± 0.14	7.71 ± 0.42	5.42 ± 0.30	8.69 ± 0.50
	n	0.73 ± 0.02	0.58 ± 0.04	0.63 ± 0.02	0.59 ± 0.03
	$C_{ct}/(10^{-4})$	4.54 ± 0.27	10.77 ± 0.66	8.70 ± 0.46	15.94 ± 0.89

As shown in Table 6, the solution resistances (R_s) were similar and relatively small, supporting the consistency of the measurements. In general, a higher charge-transfer resistance (R_{ct}) indicates better corrosion resistance [28]. All three coatings had a higher R_{ct} than the substrate, and the 20WMoS₂ coating showed the highest R_{ct} , 1.39 times higher than that of the substrate, consistent with its lowest I_{corr} in the PDP test. The repeated measurements produced the same ranking of corrosion resistance, indicating that the superior electrochemical performance of the 20WMoS₂ coating was reproducible despite the local defects inherent to ESD coatings.

The value of n is associated with the degree of interfacial non-ideality and may qualitatively reflect surface heterogeneity, whereas C_{ct} is related to the interfacial electrochemical response and may increase with a larger effective wetted/active area [29]. In comparison, the substrate exhibited the highest n value and the lowest C_{ct} value. Among the three coatings, the 20WMoS₂ coating demonstrated the highest n value and the smallest C_{ct} value. The results indicated that the surface uniformity of the W-MoS₂ coatings was inferior, leading to an increased electrolyte contact area. Capacitive reactance exhibits an inverse relationship with effective capacitance. Consequently, the W-MoS₂ coatings demonstrated reduced capacitive reactance compared to the substrate. However, among the three coatings, the 20WMoS₂ coating exhibited superior uniformity and density, thereby experiencing the smallest reduction in capacitive reactance.

The results from EIS and Tafel polarization curve tests revealed that the R_{ct} of W-MoS₂ coatings was significantly higher than that of the substrate, thereby substantially reducing I_{corr} and the corrosion rate during the electrochemical corrosion process. However, the 10WMoS₂ and 30WMoS₂ coatings exhibited decreased capacitive reactance due to increased surface roughness and reduced uniformity, which in turn led to a decrease in $|Z|$, indicating an exacerbation of local corrosion. In contrast, the 20WMoS₂ coating demonstrated better uniformity in its coating structure. During electrochemical corrosion, it exhibited higher capacitive reactance, resulting in a significantly enhanced $|Z|$ and superior protective performance compared to both the substrate and the other coatings.

A qualitative comparison was made between the existing W-MoS₂ anti-static coating and the representative ship coating systems reported in the literature, as shown in Table 7. Conventional marine coatings may show lower corrosion currents, but they are usually thick barrier systems rather than thin self-lubricating ESD layers. The significance of the 20WMoS₂ coating is therefore not universal replacement of marine coatings, but a

67.4% reduction in I_{corr} relative to CrNi3MoVA steel while retaining MoS₂/WS₂-related lubricating phases for local wear-corrosion protection.

Table 7. Qualitative comparison between the present W-MoS₂ ESD coating and representative marine coating systems reported in the literature.

Coating Type	Main Function	Typical Advantage	Relation to the Present Work
Zinc-rich/epoxy/PU/polysiloxane [30–32]	High-build marine barrier	Very low I_{corr} possible	Not self-lubricating, thick-film systems
Superhydrophobic hybrids [30–32]	Reduce wetting/fouling	Strong initial water repellence	Surface stability/thickness-dependent
Ni, Ti, or Co-doped MoS ₂ [7,9,15]	Modify MoS ₂ coatings	Improved wear/corrosion behavior	Different dopant chemistry and process
Present W-MoS ₂ ESD coating	Thin self-lubricating layer	I_{corr} reduced by 67.4%, MoS ₂ /WS ₂ retained	Local wear-corrosion protection, not a replacement for all marine coatings

3.4. Corrosion Behavior of CrNi3MoVA Steel

As depicted in Figure 6a, the substrate underwent severe corrosion, resulting in the complete destruction of its originally smooth surface morphology. The surface was now covered with corrosion products that were full of cracks (Zone A). Localized regions displayed significant corrosion pits (Zone C) and extensive flaking phenomena (Zone B). The energy spectra results shown in Figure 6b–d revealed that both Zone A and Zone C exhibited substantial Fe loss along with a relatively high oxygen (O) content, primarily consisting of Fe oxide. In Zone B, the O content was notably reduced, and the Fe content was comparable to that of the original substrate. The findings indicated that Fe underwent oxidation–dissolution reactions, leading to its loss and the formation of the corrosion product Fe oxide (Zone A). Nevertheless, the corrosion layer was riddled with cracks. During the ongoing corrosion process, these cracks gradually propagated and interconnected, causing partial flaking of the products and exposing fresh substrate (Zone B), thereby facilitating further internal corrosion expansion. Particularly in the weaker areas, the detachment of products was more pronounced, resulting in the formation of corrosion pits (Zone C). Under the persistent scouring action of the electrolyte, corrosion products continued to accumulate within these pits, creating regions with a high O content.

The corrosion results mentioned above were as follows: The Fe element in the CrNi3MoVA steel substrate exhibited high reactivity, with an R_{ct} value of merely 824.8 $\Omega \cdot \text{cm}^2$. Under the influence of a 3.5 wt.% NaCl solution, it was highly prone to electron loss, undergoing an oxidation–dissolution reaction and functioning as the anode, thereby generating the corrosion product Fe oxide. Meanwhile, the Cl[−] ions, which were highly concentrated and had a small radius, strongly adsorbed onto the generated Fe²⁺ at the interface, forming the inner layer of the double-layer capacitance. Cations such as Na⁺, which were repelled by electrostatic forces, occupied the outer layer. The potential difference established by this double-layer configuration drove continuous electrochemical reactions.

Despite the substrate exhibiting low C_{ct} and high n during corrosion, along with high capacitive reactance and a relatively uniform interface, the passivating property of Fe oxide further contributed to reducing the severity of corrosion. However, due to the extremely high Fe content (approximately 94%) and low R_{ct} at the interface, the polarization curve indicated a high I_{corr} and a rapid corrosion rate. Furthermore, the formation of Fe oxide corrosion products was accompanied by significant volume expansion, generating substantial internal stress at the interface between the substrate and the product layer,

which induced cracking in the corrosion product layer. Additionally, highly corrosive Cl^- preferentially adsorbed at the weak areas of the product layer, forming soluble complexes with Fe atoms. This further destabilized the passivation layer, thereby accelerating the active dissolution of the substrate and the propagation of cracks.

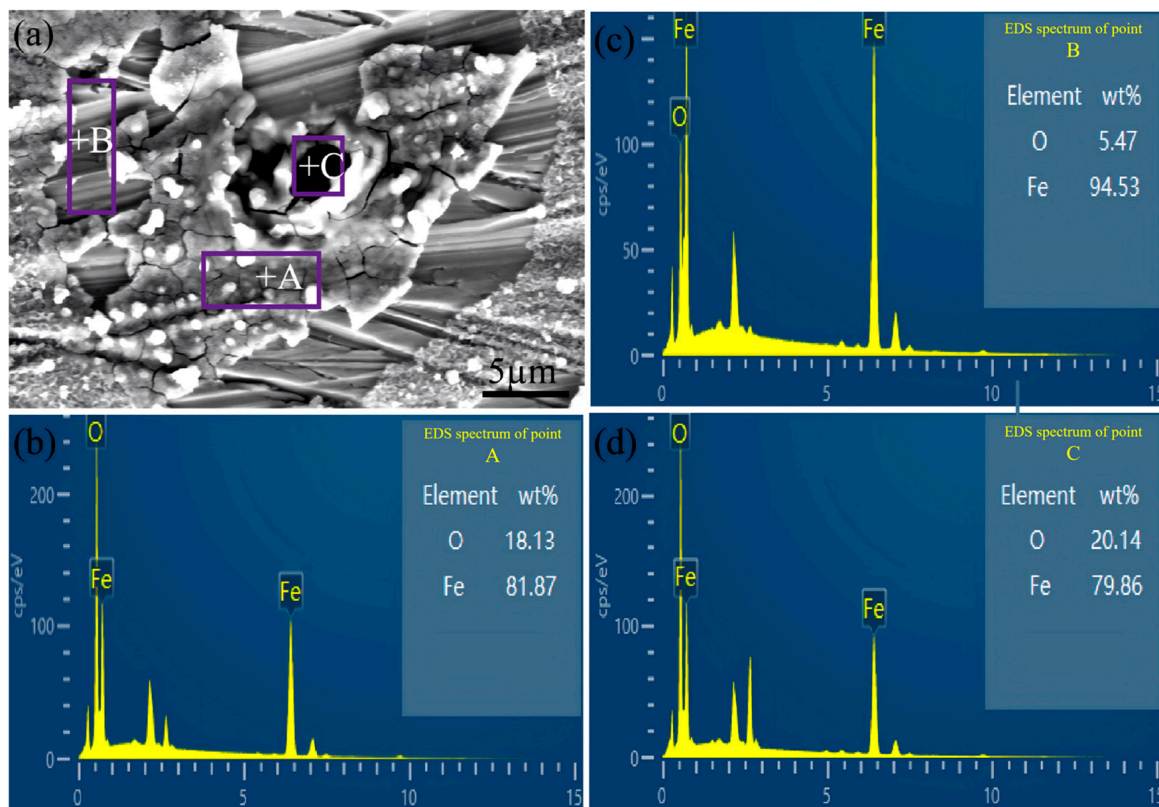


Figure 6. The corrosion morphology (a) and EDS (b–d) results of CrNi3MoVA steel substrate.

As corrosion progressed, cracks continuously extended and interconnected, ultimately leading to extensive peeling of the originally loosely structured corrosion products. The newly exposed surface of the substrate then became the new active anode, facilitating the continuous occurrence of electrochemical reactions and driving the corrosion deeper into the material. Additionally, the standard electrode potential of Fe was lower than that of Ni (the trace element present in relatively higher concentrations) in the substrate, resulting in the formation of micro-couples due to the potential difference. This phenomenon was particularly pronounced at grain boundaries, further accelerating localized anodic dissolution and promoting the initiation and propagation of corrosion pits. Under the synergistic effects of the low R_{ct} of Fe, the strong erosive action of Cl^- , and the micro-galvanic couple, the CrNi3MoVA steel substrate exhibited an extremely high I_{corr} and a rapid corrosion rate, ultimately displaying severe corrosion morphological characteristics.

3.5. Corrosion Behavior of W-MoS₂ Coating

Figure 7 presents the corrosion morphology and EDS results of the W-MoS₂ coatings. As shown in Figure 7a–c, compared to the CrNi3MoVA steel substrate, the W-MoS₂ coatings maintained their original deposition morphology profile, with only significant accumulation of corrosion products observed at the inherent pores. This led to a notable reduction in both the size and quantity of pores on the coated surface after corrosion, indicating a substantially mitigated degree of corrosion.

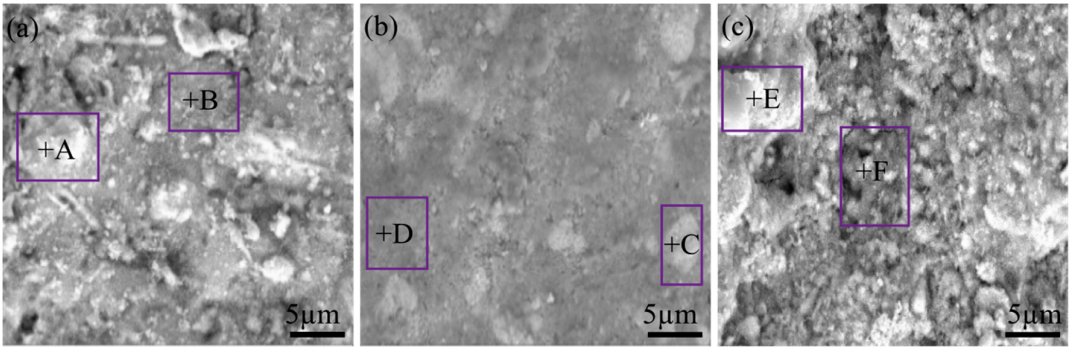


Figure 7. Corrosion morphology: (a) 10W-MoS₂ coating, (b) 20W-MoS₂ coating, (c) 30W-MoS₂ coating.

EDS results for the two typical regions (white and gray) (Table 8) revealed that O was newly detected on the corroded coating surface of the post-corrosion coating, with the O content being significantly higher in the white areas compared to the gray ones. Notably, the O content around the groove in the 30W-MoS₂ coating region (E) was particularly high, reaching up to 27.9%, whereas both typical regions of the 20W-MoS₂ coating exhibited a significantly lower O content. These findings indicated that the W-MoS₂ coatings underwent oxidation reactions under the influence of a 3.5 wt.% NaCl solution, resulting in the formation of oxides. The 20W-MoS₂ coating demonstrated the lowest degree of oxidation and the strongest corrosion resistance.

Table 8. EDS results of W-MoS₂ coatings.

Sample	Position		Composition(wt.%)				
			W	S	Mo	Fe	O
10W-MoS ₂	original	white	86.7	3.7	7.4	2.2	-
		gray	61.2	8.5	8.3	22.0	-
	corroded	A	37.1	4.5	0	37.6	20.8
		B	45.6	9.8	5.4	26.4	12.8
20W-MoS ₂	original	white	79.9	6.6	10.1	3.4	-
		gray	53.4	11.1	15.0	20.5	-
	corroded	C	35.8	23.2	9.5	24.4	7.1
		D	41.2	24.6	8.8	22.1	3.3
30W-MoS ₂	original	white	59.0	8.6	27.0	5.4	-
		gray	43.5	18.5	34.5	3.5	-
	corroded	E	32.2	17.0	0	22.9	27.9
		F	19.8	6.1	8.1	56.2	9.8

To thoroughly analyze the evolution of coating composition and reveal the corrosion mechanism, a comparative analysis was conducted on the EDS results, with specific data presented in Table 9. As indicated in Table 9, all coatings exhibited losses of W and Mo, along with an increase in Fe content, following corrosion. Notably, the loss of W was significantly higher in the white bright areas compared to the gray dark areas. In particular, the Mo content in the white regions rich in the W(Mo)-rich metallic phase of the 10W-MoS₂ and 30W-MoS₂ coatings decreased from 7.4% and 27% to 0, respectively, while their residual Mo remained relatively high after corrosion. Although the lubricating phases MoS₂ and WS₂ were highly prone to oxidation in humid environments, with their reaction product H₂SO₄ causing a loss of S, in this experiment, except for the gray area

of the 30WMoS₂ coating (F), the S content increased in all areas of the coatings after electrochemical corrosion.

Table 9. Analysis of EDS composition changes in typical areas of W-MoS₂ coatings.

Sample	Position	Content Variation Before and After Corrosion/wt.%						Residue After Corrosion/wt.%			
		O	Fe	W	Mo	W + Mo	S	W	Mo	S	Fe
10WMoS ₂	ΔA	0 → 20.8	↑ 35.4	↓ 49.6	↓ 7.4	↓ 57.0	↑ 0.8	37.1	0	4.5	37.6
	ΔB	0 → 12.8	↑ 4.4	↓ 15.6	↓ 2.9	↓ 18.5	↑ 1.3	45.6	5.4	9.8	26.4
20WMoS ₂	ΔC	0 → 7.1	↑ 21	↓ 44.1	↓ 0.6	↓ 44.7	↑ 16.6	35.8	9.5	23.2	24.4
	ΔD	0 → 3.3	↑ 1.6	↓ 12.2	↓ 6.2	↓ 18.4	↑ 13.5	41.2	8.8	24.6	22.1
30WMoS ₂	ΔE	0 → 27.9	↑ 17.5	↓ 26.8	↓ 27	↓ 53.8	↑ 8.4	32.2	0	17	22.9
	ΔF	0 → 9.8	↑ 52.7	↓ 23.7	↓ 26.4	↓ 50.1	↓ 12.4	19.8	8.1	6.1	56.2

The observed phenomena can be summarized as follows: The white regions consisted of W(Mo)-rich metallic regions with an exceptionally high W content. When exposed to a 3.5 wt.% NaCl solution, the W(Mo)-rich metallic phase exhibited preferential oxidation characteristics. Among its components, W with a high content and Mo with a low content preferentially underwent oxidative dissolution, acting as the anode. This led to a greater loss of W in the white regions, indicating that the lost W primarily originated from the W(Mo)-rich metallic phase. Meanwhile, the elevated S content suggested that the lost Mo also predominantly came from the W(Mo)-rich metallic phase rather than from MoS₂. Furthermore, considering WS₂'s superior oxidation resistance compared to MoS₂ and the observed increase in S content, it can be inferred that WS₂ remained retained within the coatings. Consequently, both MoS₂ and WS₂ were effectively protected by the W(Mo)-rich metallic phase, resulting in significantly enhanced oxidation resistance.

Furthermore, although the Fe content increased following coating corrosion, it remained considerably lower than that of the substrate. Based on the results of the single time constant test (Figure 5c), it can be concluded that during corrosion, the electrolyte diffused from the surface into the interior of the coating. This process led to the oxidative dissolution of the Fe that had diffused from the substrate into the original coating, resulting in the formation of Fe oxide, while the substrate itself remained unexposed.

The gray zone of the 30WMoS₂ coating (F in Figure 7) showed an abnormal decrease in S content and a sharp increase in Fe content. This phenomenon indicated that structural defects, such as deep grooves and wide cracks, facilitated rapid penetration of the electrolyte, triggering severe internal corrosion. Consequently, oxidation reactions occurred in MoS₂ and WS₂ within the defect region, leading to the formation of H₂SO₄ and resulting in the loss of S. Meanwhile, the internal Fe formed Fe oxides, which caused the dramatic rise in Fe content. The intensified corrosion in these regions directly reduced the coating's anti-corrosion performance.

A comprehensive comparison of the coatings revealed that the 20WMoS₂ coating demonstrated the lowest total loss of W and Mo in the gray-white regions, the highest retention of Mo and S, and the smallest increase in Fe and O content. The results indicated that this coating could effectively prevent electrolyte penetration and inhibit the dissolution of the metal phase and the formation of oxidation products, thereby achieving optimal corrosion resistance performance. Although electrolyte infiltration exacerbated the oxidation and dissolution of Fe in the 10WMoS₂ and 30WMoS₂ coatings, leading to significant elemental loss and weakened corrosion resistance, none of the coatings exposed the underlying substrate after corrosion. Overall, the protective performance of the W-MoS₂ coating system was reliable.

Cross-sectional EDS maps before and after corrosion would further clarify electrolyte penetration paths and the through-thickness redistribution of W, Mo, S, Fe, and O. In the present study, the corrosion interpretation is based on the available as-deposited cross-sectional morphology, post-corrosion surface SEM/EDS, XPS, and electrochemical data. Thus, the depth-resolved corrosion behavior should be regarded as a limitation of the current dataset and will be examined by cross-sectional EDS mapping in subsequent work.

The XPS analysis results are shown in Figure 8, which indicates that the corrosion products of the W-MoS₂ coating primarily consisted of a series of metal oxides formed by W, Mo, and Fe. Notably, no chlorides were identified in the XPS spectra. This phenomenon was ascribed to electrochemical corrosion reactions initiated by active agents such as O₂, H₂O, and Cl[−]. However, due to the solubility of chlorides, they had difficulty persisting on the coating surface. Meanwhile, the detection of MoS₂ and WS₂ signals further indicated that although the W-MoS₂ coating underwent electrochemical corrosion, the W(Mo)-rich metallic phase likely participated preferentially in the oxidation process. This significantly curbed the oxidative consumption of the lubricating phases, enabling them to remain intact. This mechanism was also a crucial factor allowing the W-MoS₂ coating to maintain excellent protective performance in a 3.5 wt.% NaCl solution.

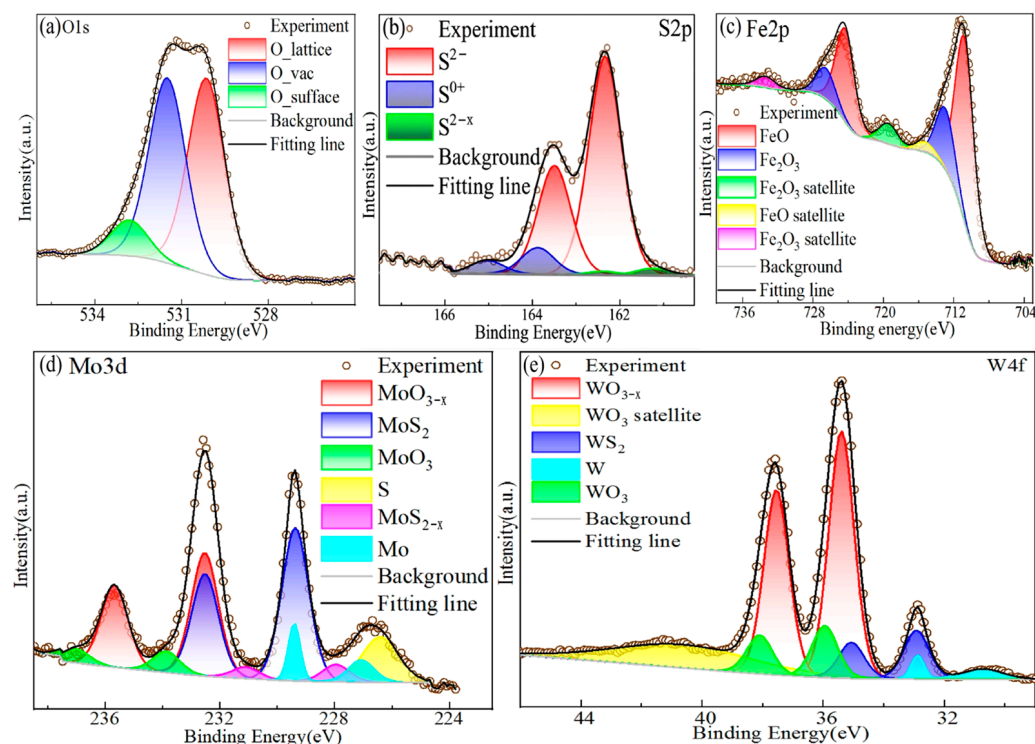


Figure 8. XPS spectra of 20W-MoS₂ coating surface in 3.5 wt.% NaCl solution: (a) O1s, (b) S2p, (c) Fe2p, (d) Mo3d, (e) W4f.

3.6. Corrosion Mechanism of W-MoS₂ Coating

On the basis of the SEM/EDS/XRD/XPS and electrochemical results, the corrosion mechanism of the W-MoS₂ coatings can be summarized as follows: The MoS₂/WS₂ lubricating phases provide relatively high-resistance regions, while the W(Mo)-rich metallic regions and the rapidly solidified ESD microstructure form a composite layer with tortuous electrolyte-transport paths. Because the electrochemical activity of W and Mo is lower than that of Fe in the CrNi3MoVA substrate, the coatings exhibit higher impedance and significantly lower I_{corr} than the uncoated steel under the present short-term 3.5 wt.% NaCl test. Compared with MoS₂-containing organic barrier coatings, where MoS₂ mainly im-

proves corrosion resistance by increasing the tortuosity of the layered barrier [18], the present ESD coating combines W(Mo)-rich metallic regions with MoS₂/WS₂ lubricating phases. The results also complement recent studies on tungsten-based dichalcogenide corrosion-inhibition systems [21], because they demonstrate that the corrosion resistance of W-containing sulfide coatings is governed not only by the intrinsic chemical stability of the sulfide phases but also by the compactness and defect distribution determined by the W/MoS₂ ratio.

Furthermore, the W/MoS₂ ratio strongly influenced corrosion resistance. The 10WMoS₂ coating exhibited a relatively low R_{ct} because of its low lubricating-phase content, high W content, rough surface, and uneven phase distribution. It had the lowest CPE exponent *n* and a relatively high C_{ct}, indicating stronger interfacial non-ideality and a larger effective wetted area rather than the maximum C_{ct} among all coatings. The concentration of W(Mo)-rich metallic regions in the upper part of the coating, together with pores and microcracks, facilitated local electrolyte penetration and the formation of oxygen-concentration cells. At these defects, W and Mo-containing corrosion products could not form a continuous protective layer, and Cl[−] further destabilized the locally passivated regions. The electrolyte therefore penetrated the porous corrosion products and promoted internal Fe oxidation, weakening the overall protective performance.

The 20WMoS₂ coating, featuring a homogeneous and dense structure, effectively hindered the penetration of the electrolyte. It achieved the highest *n*, the lowest C_{ct} among the coatings, and the maximum capacitive reactance. Meanwhile, the optimal ratio of MoS₂ and W contents significantly increased the charge transfer resistance. As a result, during the electrochemical corrosion process, the 20WMoS₂ coating formed relatively stable corrosion products and demonstrated the highest R_{ct} and |Z|, thereby providing the best protective performance.

For the 30WMoS₂ coating, the higher MoS₂ fraction was expected to increase charge-transfer resistance, but excessive MoS₂ also promoted agglomeration during ESD and produced deep grooves or wide cracks. These defects reduced surface uniformity, decreased the CPE exponent *n*, and increased the effective electrolyte-contact area, resulting in a higher C_{ct} and lower capacitive impedance. The cracks also provided faster channels for electrolyte penetration and promoted O concentration-gradient microcells. Under the combined action of Cl[−] erosion and localized defect-assisted transport, the protective performance of the 30WMoS₂ coating was weakened.

The quantitative roughness measurements provide direct support for this composition-dependent mechanism. The higher Ra, Rq, and Rz values of the 10WMoS₂ and 30WMoS₂ coatings increase the real electrolyte-contact area and the number of sites available for localized corrosion, whereas the smoother 20WMoS₂ coating limits electrolyte accumulation and helps maintain a higher impedance response.

As summarized in Figure 9, the transient spark discharge melts and transfers W-MoS₂ electrode material to the steel surface, producing a rapidly solidified composite layer. During corrosion, electrolyte first contacts surface pores, grooves, and phase boundaries. For the 20WMoS₂ coating, the denser morphology and more favorable phase distribution delay electrolyte penetration and charge transfer. In contrast, excessive W-rich aggregation in 10WMoS₂ and MoS₂-related agglomeration/grooves in 30WMoS₂ provide easier channels for localized corrosion.

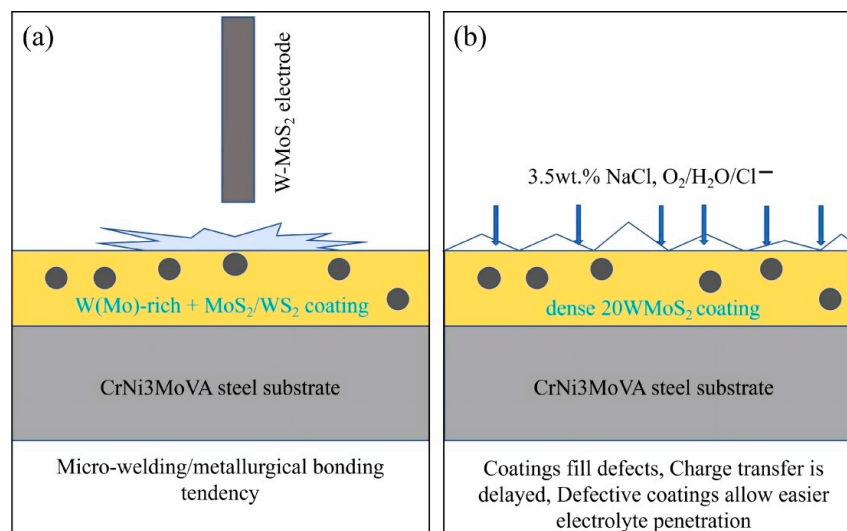


Figure 9. (a) Schematic illustration of the ESD preparation process, (b) the short-term corrosion response of W-MoS₂ coatings in 3.5 wt.% NaCl solution.

4. Conclusions

This study systematically investigated the electrochemical corrosion behavior of W-MoS₂ coatings in 3.5 wt.% NaCl solution under short-term laboratory conditions. The main conclusions are as follows:

(1) Compared to the substrate, the E_{corr} values of the 10WMoS₂, 20WMoS₂, and 30WMoS₂ coatings all exhibited a slight negative shift. However, their I_{corr} decreased significantly, dropping from $8.65 \mu\text{A}\cdot\text{cm}^{-2}$ to $3.31 \mu\text{A}\cdot\text{cm}^{-2}$, $2.82 \mu\text{A}\cdot\text{cm}^{-2}$, and $3.30 \mu\text{A}\cdot\text{cm}^{-2}$, representing reductions of 61.7%, 67.4%, and 61.8%, respectively. Therefore, among the three coatings, the W-20 wt.% MoS₂ coating demonstrates the best corrosion resistance due to it having the highest E_{corr} and lowest I_{corr} .

(2) The R_{ct} values of the 10WMoS₂, 20WMoS₂, and 30WMoS₂ coatings increased to 1416, 1968 and 1747 $\Omega\cdot\text{cm}^2$, respectively. These represent increases of 71.7%, 1.39 times, and 1.12 times compared to the substrate ($824.8 \Omega\cdot\text{cm}^2$), primarily due to the reduced I_{corr} of the W-MoS₂ coatings.

(3) Due to surface inhomogeneity, pores, and wide cracks, the 10WMoS₂ and 30WMoS₂ coatings exhibited decreased values of n (0.58 and 0.59, respectively) and higher C_{ct} values ($10.77 \times 10^{-4} \text{ F}\cdot\text{cm}^{-2}$ and $15.94 \times 10^{-4} \text{ F}\cdot\text{cm}^{-2}$, respectively), leading to severe localized corrosion. In contrast, the 20WMoS₂ coating displayed a more uniform and denser structure, demonstrating the highest n value and the smallest C_{ct} value. Its $|Z|$ reached a maximum of $767.5 \Omega\cdot\text{cm}^2$ (approximately 16% higher than that of the substrate), indicating the strongest corrosion resistance and the least severe corrosion morphology.

(4) Quantitative roughness measurements further linked surface morphology with electrochemical behavior. The lower R_a , R_q , and R_z values of the 20WMoS₂ coating reduced the real electrolyte-contact area and the number of localized corrosion sites, supporting its higher impedance response and superior corrosion resistance.

(5) The present work demonstrates the feasibility of using W-MoS₂ ESD coatings to improve the short-term chloride-corrosion resistance of CrNi3MoVA steel while retaining self-lubricating phases. Nevertheless, quantitative adhesion testing, long-term immersion/cyclic salt-spray exposure, and field-performance evaluation should be carried out in future work before the coating is recommended for long-term marine service. In particular, direct friction/wear tests, tribocorrosion evaluation, and cross-sectional EDS mapping

before and after corrosion are required to fully verify the self-lubricating function and corrosion-penetration behavior of the present W-MoS₂ coatings.

Author Contributions: Conceptualization, X.Z., H.J., G.Z. and C.G.; Methodology, X.Z., C.J., L.Z., H.J., X.L. and J.Z.; Software, X.Z., F.L., L.Z., M.B. and H.J.; Validation, C.J.; Formal analysis, M.B. and F.L.; Investigation, C.J. and C.G.; Resources, X.Z., C.J., H.J., G.Z. and C.G.; Data curation, M.B. and F.L.; Writing—original draft, X.Z.; Writing—review & editing, X.L., G.Z. and C.G.; Visualization, J.Z.; Supervision, F.L., L.Z., H.J. and G.Z.; Project administration, F.L., X.L., G.Z., C.G. and J.Z.; Funding acquisition, X.L. and J.Z. All authors have read and agreed to the published version of the manuscript.

Funding: The study is supported by the Research Project of the Education Department of Liaoning Province of China (1030040000675), Research support funding for attracting high-level talents in 2025 (6030109777), 2026 Liaoning Province Doctoral Research Launch Project, Shenyang Municipal Special Project for Scientific and Technological Talents (RC23095), Special Fund of Basic Scientific Research Operating Expense of Undergraduate Universities in Liaoning Province (LJ212410144077), Financial support of the Key R&D Project of the Joint Science and Technology Program of Liaoning Province (2025JH2/101800434).

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding authors.

Conflicts of Interest: Authors Chunmao Jiang, Fengsheng Lu, Lei Zhang were employed by North Huaan Industry Group Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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