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Revealing the influence of Cr and Al additions on the corrosion of carbon steel in a supercritical CO₂–SO₂ environment

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The formation mechanism of corrosion product films of X65 and 5Cr2Al steels in CO₂-saturated aqueous phase environments containing 100 ppm and 300 ppm SO₂ impurities was investigated. Under both conditions, the corrosion rate of X65 was approximately ten times that of 5Cr2Al, with the main reaction being the formation of FeCO₃. In the CO₂-100 ppm SO₂ system, the inner layer of 5Cr2Al formed Cr(OH)₃ and Al(OH)₃ layers, while the outer layer formed FeCO₃. When the SO₂ concentration increased to 300 ppm, Cr and Al reacted synergistically with SO₂, forming a double-layer structure with an inner layer composed of Cr(OH)₃ and Al(OH)₃ and an outer layer composed of dense elemental sulfur. This film layer structure exhibited excellent corrosion resistance. *In situ* electrochemical measurement results in supercritical CO₂ environments with 300 ppm SO₂ further reveal that corrosion is aggressive for X65. While a semi-passivation phenomenon occurred for 5Cr2Al steel. This study indicates that a dense S elemental film can form only when Cr and Al are present and the SO₂ concentration reaches 300 ppm. 5Cr2Al is a suitable material choice for the injection tube in a mixed CO₂–SO₂ environment.

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1. Introduction

CO₂ capture and storage (CCS) technology is designed to reduce CO₂ emissions by capturing CO₂ from existing combustion plants, transporting it *via* pipelines under a supercritical state, and ultimately injecting it into deep geological formations *via* an injection tube for long-term storage. There are successful application cases, such as the Sleipner project in Norway. It is recognized as the world's first commercial-scale carbon storage project, storing approximately one million tons of CO₂ annually. CCS technology was proposed by the United Nations Global Climate Change Conference. It has been recognized as a critical solution for controlling CO₂ emissions.¹ It is safe, economical and has good applicability. Pure CO₂ poses almost no corrosion threat to steels.² However, impurities are inevitably present in the captured CO₂ stream (such as SO₂, NO₂, O₂, H₂S, and H₂O).^{3,4} These impurities can damage the structural integrity of pipeline and injection tube. Therefore, it is necessary to explore the role of individual impurities in pipeline corrosion and their specific corrosion mechanisms.

During the injection stage, CO₂ will be injected into deep underground long-term storage layers containing a large amount of chlorides, which are the most preferred storage sites

for CO₂ sequestration.⁵ Water and erosive ions create active environments for corrosion reactions. SO₂, as one of the most common and notorious impurity gases, when dissolved in water, will acidify formation water and cause severe corrosion damage to steels.^{6–8} Sun *et al.*⁹ demonstrated that in the CO₂–H₂O–SO₂ system, even a small amount of water could affect the SO₂ corrosion behavior. SO₂ deteriorated the water chemistry characteristics, making it highly acidic. The water content in the supercritical (SC) CO₂/H₂O/impurities system is far below its solubility limit. A small amount of SO₂ significantly increased the corrosion rate.¹⁰ ISO standard and DYNAMIS project^{11,12} recommend SO₂ should be limited to 100 ppm. It is necessary to study the corrosion behavior when 100 ppm is compared with a higher concentration of SO₂. Besides, most studies on the impact of impurities in CO₂ streams have focused on supercritical (SC) CO₂ gas phases containing a small amount of water.^{13–16} Therefore, it is also necessary to study the effect of impurities on steel in deep saline water under a SC CO₂ environment.

It is estimated that 10 Gt per year of CO₂ will require transportation to geological storage sites by 2050. This scale of deployment would necessitate the construction of an extensive pipeline network, including either 3000 lines of 12-inch diameter or 1000 lines of 20-inch diameter. Carbon steel pipelines are widely considered the most cost-effective solution for large-scale CO₂ transportation.^{17–19} However, the injection of CO₂ transported to geological storage sites into saline aquifers presents more risks, including potential geomechanical

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impacts (e.g., crustal movement, ground deformation) and substantial liquid. As indicated in Table 1, conventional pipeline steels such as grades X65, N80, and P110 exhibit corrosion rates reaching up to 10 mm per year in aqueous phases. Consequently, standard carbon steels are demonstrably inadequate for meeting the operational requirements of such environments. Using corrosion-resistant alloys (CRAs), such as chromium-containing steels, is a promising method for effective corrosion control.²⁰ Under the same high-temperature and high-pressure conditions, using this type of steel can relatively reduce the wall thickness and provide cost savings. Furthermore, these materials also offer stronger collapse resistance and corrosion resistance compared to conventional carbon steels.²¹ 13Cr has the lowest corrosion rate in the liquid phase (Table 1), but it is expensive and has a high investment cost. Extensive research has consequently focused on lower-chromium (1Cr, 2Cr, 3Cr, and 5Cr steels) in the liquid phase of SC CO₂. A chromium content of approximately 3 wt% is sufficient to effectively inhibit localized corrosion under these conditions.²² The addition of Cr content causes the corrosion product film to change from a crystalline to an amorphous structure.²³ The amorphous Cr(OH)₃ corrosion product layer can pre-passivate the steel, thereby inhibiting corrosion.²⁴ Based on traditional low-Cr steel, Al further enhances its corrosion resistance by microalloying. In our previous work, we demonstrated that Fe–Cr–Al steel exhibits excellent corrosion resistance in SC-CO₂, particularly 3Cr2Al and 5Cr2Al,^{25,26} which form a mixed corrosion product film of Cr(OH)₃ and Al(OH)₃. We have also studied the corrosion behavior of 3Cr2Al steel in SC CO₂ environment with 300 ppm SO₂. Even though the formation of a sulfur film has inhibited the corrosion, the corrosion rate is still not up to the ideal value.²⁷ Therefore, to fill the gap in these, corrosion behavior of 5Cr2Al steel will be further studied with 100 ppm/

300 ppm SO₂ impurity. This will also further verify whether 5Cr2Al steel is suitable as a candidate material for CCS injection tubes.

In this paper, the liquid phase corrosion behavior and corrosion mechanism of X65 and 5Cr2Al steel containing 100 ppm and 300 ppm of SO₂ are compared. The interfacial corrosion behavior of X65 and 5Cr2Al was studied by *in situ* electrochemical methods, and their anodic and cathodic corrosion mechanisms were analyzed. The surface morphology of the corrosion products was thoroughly characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The local corrosion rate of X65 and 5Cr2Al steel in supercritical CO₂ gas phase and water-rich phase was analyzed by laser scanning confocal microscopy (LSCM).

2. Experimental methods

2.1 Materials and solution

X65 steel blocks (80 mm long × 30 mm wide × 5 mm thick) were machined from commercial pipes. The novel Al-containing low-Cr steel was prepared based on conventional carbon steel by introducing 5 wt% Cr and 2 wt% Al, which was studied in our previous work.²⁵ Their chemical compositions are detailed in Table 2. The X65 and 5Cr2Al materials were machined into two-dimensional samples with the dimensions

Table 2 Chemical composition of X65 and 5Cr2Al steel (wt%)

Materials	C	Si	Mn	Cr	Mo	Al	S	Fe
X65	0.04	0.20	1.5	≤0.5	≤0.5	—	≤0.003	Bal.
5Cr2Al	0.05	0.20	0.55	5.00	0.15	2.00	≤0.003	Bal.

Table 1 Summary of literature on corrosion rates in supercritical CO₂ environments for various materials

Material	Temperature (K)	Pressure (MPa)	Time (h)	H ₂ O (ppmv)	Impurities	Corrosion rate (mm per year)	Ref.
X65	323.15	8	24	Sat.	—	10.8	Choi <i>et al.</i> ³
			24	Sat.	0.33 MPa O ₂	10.9	
			24	Liq.	—	19.2	
			24	Liq.	0.33 MPa O ₂	19.3	
			120	Liq.	—	10.6	
			120	Liq.	0.33 MPa O ₂	14.1	
13Cr	323.15	8	24	Sat.	—	~0.01	
			24	Sat.	0.33 MPa O ₂	~0.01	
K03014	298.15	8	48	Sat.	200 ppm H ₂ S	0.07	Choi <i>et al.</i> ²⁸
			48	Sat.	200 ppm H ₂ S	0.41	
1Cr	298.15	8	48	Sat.	200 ppm H ₂ S	0.13	
			48	Sat.	200 ppm H ₂ S	0.44	
3Cr	298.15	8	48	Sat.	200 ppm H ₂ S	0.14	
			48	Sat.	200 ppm H ₂ S	0.55	
P110	353.15	9.5	168	Liq.	—	6.12	Zhang <i>et al.</i> ²⁹
N80	333.15	8	96	Liq.	—	12	Zhang <i>et al.</i> ³⁰
1Cr	333.15	10	192	Liq.	—	1.5	Hua <i>et al.</i> ³¹
3Cr	333.15	10	192	Liq.	—	1.8	
5Cr	333.15	10	192	Liq.	—	2.0	
38Mn6/C75	353.15	13.5	96	Liq.	—	11	Zhang <i>et al.</i> ³²
Super 13Cr SS	473	2.85	120	Liq.	—	1.1	Yue <i>et al.</i> ³³



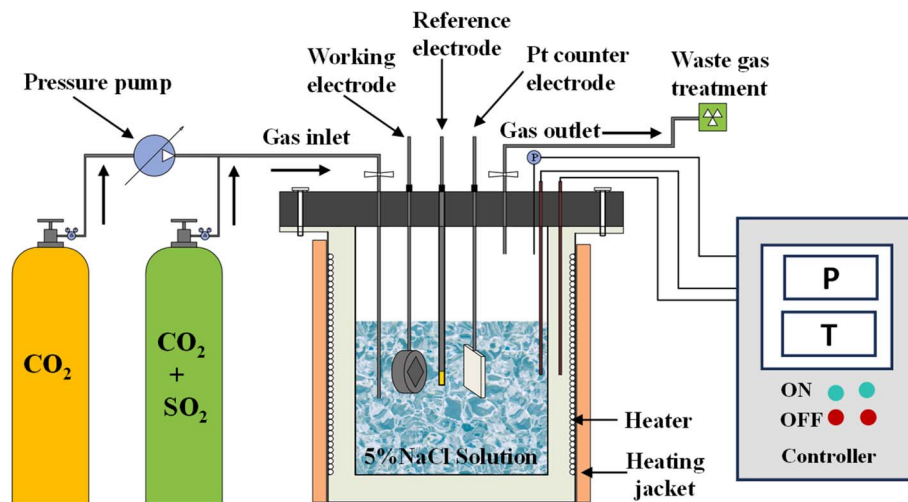


Fig. 1 Schematic diagram of the corrosion test device.

of 3 mm × 3 mm × 10 mm for surface and cross-sectional characterization and 3 mm × 10 mm × 20 mm for the weight loss measurements. Before the corrosion test, each sample was ground with silicon carbide paper of 400, 800, 1200, and 1500 grit, sequentially, then cleaned with deionized water and ethanol. After drying, the specimens were subsequently weighed using an electronic balance with a precision of 0.1 mg (M_{0i}) and measured with a Vernier caliper accurate to 0.01 mm. The test solution simulated a brine environment with a concentration of 5% NaCl. A 2 L NaCl solution was introduced into the autoclave.

2.2 Corrosion tests

The experiments were conducted in a 3 L high-temperature, high-pressure autoclave made of alloy 316L. Before the experiment, deoxygenate 2 L of 5% NaCl solution for 12 h by purging with 99.99% CO₂. Then the autoclave was sealed and degassed with CO₂ for 3 h. The temperature was increased to 80 °C. A mixture of CO₂ + 100/300 ppm SO₂ was charged (as shown in Fig. 1). Continue to pressurize with CO₂ to obtain a total pressure of 8 MPa. After exposure for 168 h, the samples were immediately rinsed with anhydrous ethanol and dried. Then the three parallel specimens were pickled according to the ASTM G1-03 standard. The pickling solution was prepared by dissolving 3.5 g of hexamethylene tetramine in 500 mL of hydrochloric acid, followed by dilution to a final volume of 1000 mL with deionized water. Then, the samples were cleaned for 10 minutes at 20–25 °C. Finally, these samples were rinsed, dried, and weighed again to obtain the final weight (M_{1i}). The corrosion rate was calculated according to:

$$V_{cr} = \frac{87\,600(M_{0i} - M_{1i})}{t\rho S} \quad (1)$$

where V_{cr} is the general corrosion rate in mm a⁻¹; M_{0i} and M_{1i} are the original and final weights of the specimen in g; t is the immersion time in hours; ρ is the steel density in g cm⁻³; and S is the exposed surface area in cm².

2.3 Microstructure characterization and mechanical performance tests

Laser scanning confocal microscopy (LSCM) was employed to analyze the two-dimensional morphology and local corrosion conditions after pickling. The surface and cross-sectional morphologies of the corrosion products were characterized by scanning electron microscopy (SEM, ZEISS MERLIN COMPACT). The atomic composition and distribution were examined by energy dispersive X-ray spectroscopy (EDS). The acceleration voltage is 15 kV and the working distance is 10–15 mm in SEM and EDS. The atomic composition and atomic valence states of the corrosion products were analyzed respectively using X-ray diffraction (XRD, SMARTLAB) and X-ray photoelectron spectroscopy (XPS, ThermoFisher ESCALABXi+).

2.4 In situ electrochemical measurement

Electrochemical measurements were carried out using a Gamry Reference 600+ electrochemical workstation. A three-electrode electrochemical system was used with X65 and 5Cr2Al steel with an exposed area of 1 cm² as the working electrode (WE), platinum as the counter electrode (CE), and a high-temperature and high-pressure Ag/AgCl electrode as the reference electrode (RE). The schematic diagram of the autoclave and the position of WE, CE and RE were shown in Fig. 1. A digital pressure gauge was used to monitor autoclave pressure; a heat controller was applied to monitor and regulate the heating of the autoclave; and a saturated NaOH solution was used as a waste gas treatment device (shown in controller of Fig. 1). The Open circuit potential (OCP) was initially recorded for 1 h to ensure a stable OCP value (a fluctuation less than 5 mV for 2 minutes is considered stability). The polarization resistance (R_p) is obtained through the self-test method, that is, the slope in the linear polarization region is directly equal to the R_p . Electrochemical impedance spectroscopy (EIS) was measured at the OCP with 10 mV AC signals in the range of 0.01–100 000 Hz. The LPR experiments were performed at a scanning rate of



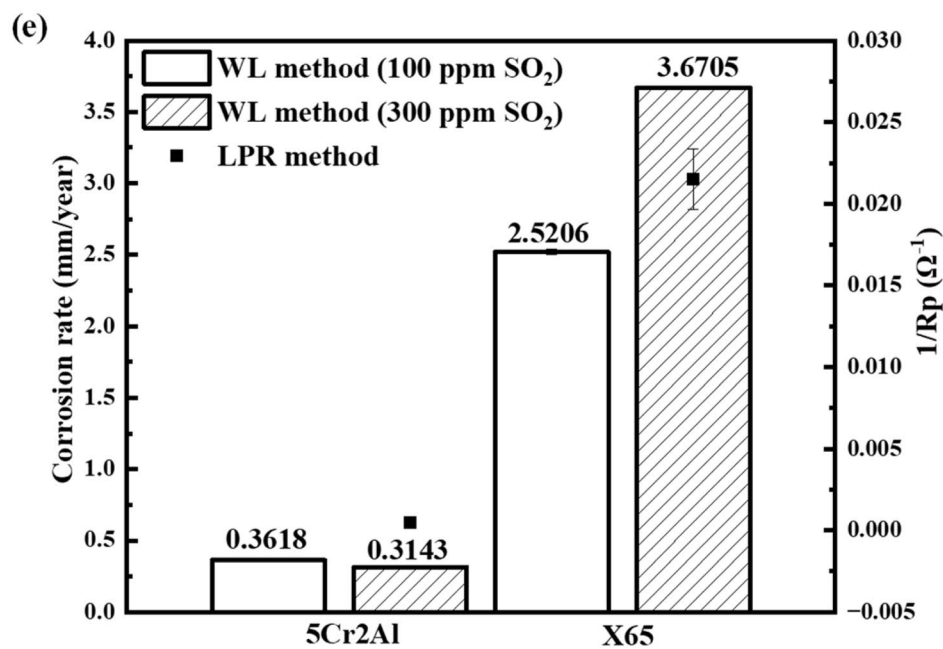
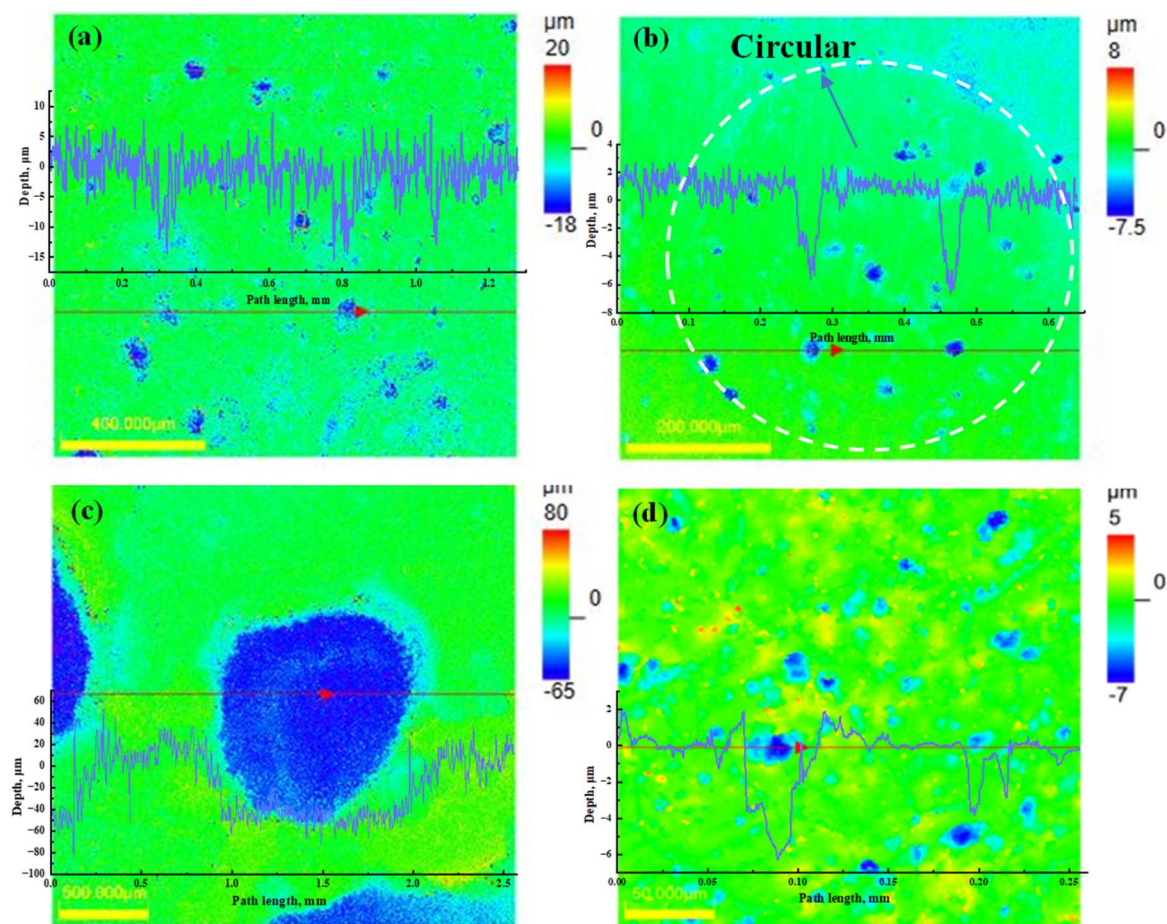


Fig. 2 2D characteristics of X65 and 5Cr2Al steel after acid pickling: (a) X65 steel, 100 ppm SO₂; (b) 5Cr2Al steel, 100 ppm SO₂; (c) X65 steel, 300 ppm SO₂; (d) 5Cr2Al steel, 300 ppm SO₂; (e) overall corrosion rates (note: WL: weight loss; LPR: line polarization resistance).



0.125 mV s⁻¹ in the range of ±10 mV. The polarization curve test ranged from -300 mV to +400 mV vs. OCP at a scan rate of 0.1667 mV s⁻¹. The corrosion rate was obtained with eqn (2):

$$CR = \frac{i_{\text{corr}}(\mu\text{A cm}^{-2})EW(\text{g})}{F \times \rho(\text{g cm}^{-3}) \times A(\text{cm}^2)} \quad (2)$$

where i_{corr} is the corrosion current density in "μA cm⁻²"; E is the number of electrons lost; W is the molar mass in g; F is the Faraday constant; A is the exposed area of the test sample in cm²; and ρ is the sample density in g cm⁻³.

3. Results and discussion

3.1 Corrosion rate and macroscopic film characteristics

Fig. 2(a)–(d) shows the two-dimensional morphology of the X65 and 5Cr2Al steels observed after the removal of the corrosion products. Pitting corrosion of X65 and 5Cr2Al with 100 ppm SO₂ was 0.6257 and 0.2607 mm per year, respectively. In addition, 5Cr2Al presented a morphology similar to the corrosion circular pits in Fig. 3(b₁), with the pitting corrosion inside and at the edge of the circular pits being more severe than the external corrosion product coverage area. No pitting corrosion was observed on the X65 with 300 ppm SO₂ after pickling, but rather step-like corrosion pits. This does not mean that the X65 did not undergo pitting corrosion; it is just that the initially formed pitting corrosion expanded with the progress of corrosion and turned into larger local corrosion. This phenomenon can be explained in combination with the subsequent electrochemical test results. The average pitting corrosion rate of 5Cr2Al with 300 ppm SO₂ is 0.3426 mm per year. The pitting factor is defined as the ratio of the pitting rate to the overall corrosion rate. It is widely used to evaluate the severity and potential threat of localized corrosion to the structural integrity and safety of pipelines and tubing systems. Generally, a pitting factor greater than 5 can be considered a threat to the integrity of steel.²⁰ The

pitting factor of 5Cr2Al in two conditions are lower than 1. It hardly poses a threat to the integrity of steel. Besides, 5Cr2Al steel undergoes pitting corrosion at the initial stage of Cr(OH)₃ and Al(OH)₃ formation, then turns into general corrosion, and no pitting corrosion occurs in the later stage.

Fig. 2(e) presents the overall corrosion rates and polarization resistance (1/R_p) of the X65 and 5Cr2Al steels under aqueous phase with 100 ppm and 300 ppm SO₂. The corrosion rates of the two types of steel with 300 ppm SO₂, measured by the weight loss (WL) method and the line polarization resistance (LPR) method, are comparable. Clearly, the corrosion rate of X65 is 2.5206 mm per year with 100 ppm SO₂. Then it reaches 3.6705 mm per year with 300 ppm SO₂. They are more than ten times higher than those of 5Cr2Al. The addition of SO₂ only promotes corrosion of X65 steel. The corrosion rate of 5Cr2Al in two environments are very low. With 100 ppm SO₂, it is 0.3618 mm per year; interestingly, it decreases to 0.3143 mm per year containing 300 ppm SO₂. This might be attributed to the protective sulfur film formed by the synergistic reaction of Cr, Al and SO₂. The content of 300 ppm of SO₂ might be the threshold of this synergistic reaction. 5Cr2Al could reduce corrosion by nearly 91% compared to X65. Consequently, it poses minimal corrosion threat. The formation mechanism of corrosion products of 5Cr2Al with 300 ppm SO₂ will be further discussed through electrochemical studies in the following text.

3.2 Surface and cross-sectional morphologies

Fig. 3 shows microscopic morphologies and EDS spectra of corrosion film for X65 and 5Cr2Al steels in the aqueous phase with 100 ppm and 300 ppm SO₂. The corrosion products in Fig. 3(a₁) is blocky, mainly composed of Fe and O (points A). Fig. 3(b₁) shows the morphologies and energy spectra of the double-layer structure, which revealed that the inner layer components are elemental Cr, O, Fe and Al (point C). The outer layer contains mainly Fe and O (points B), and a lower amount of

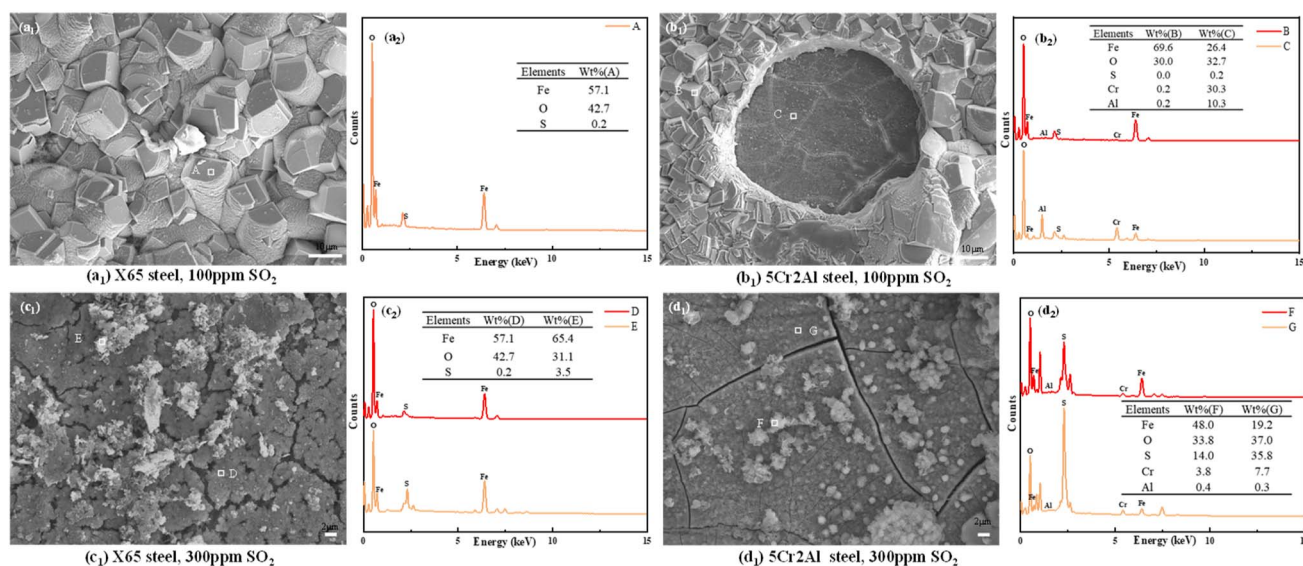


Fig. 3 SEM and EDS of X65 and 5Cr2Al steel exposed to aqueous phase at 8 MPa and 80 °C with different concentration of SO₂: (a₁)–(d₁) SEM images; (a₂)–(d₂) elemental composition of positions A–G.



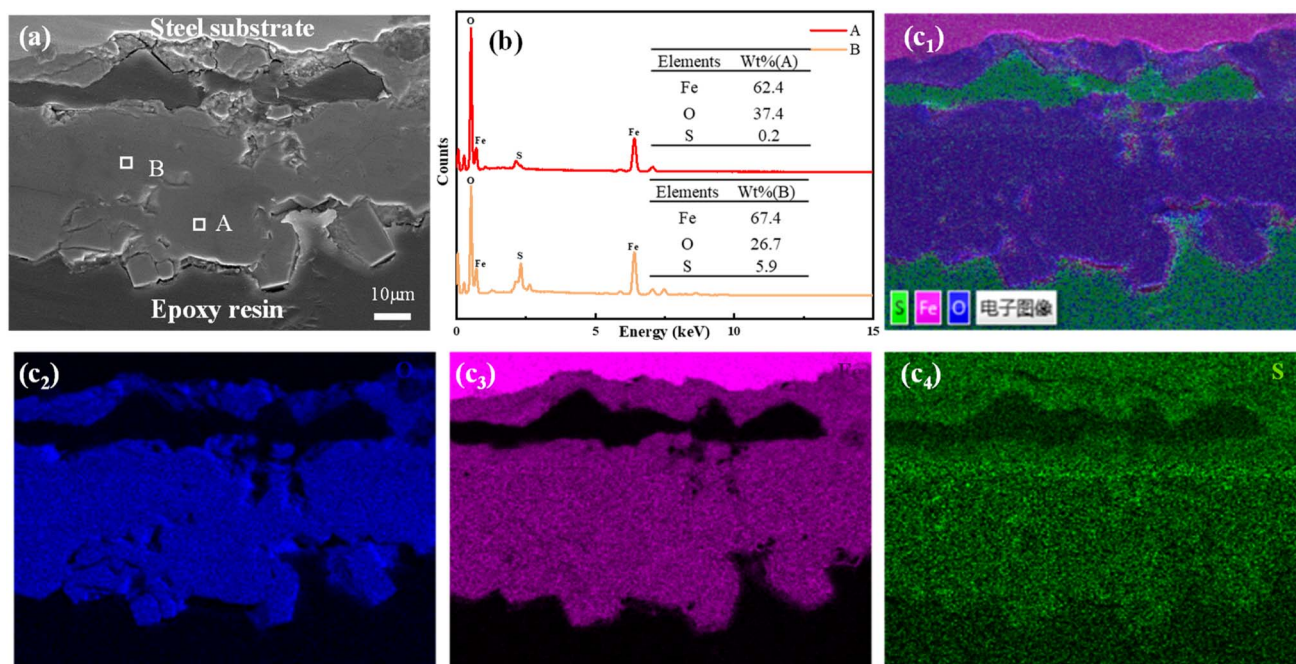


Fig. 4 Cross-sectional morphologies of X65 steel after exposure to aqueous phase with 300 ppm SO_2 at 8 MPa and 80 °C: (a) SEM images; (b) elemental composition of positions A and B; (c₁–c₄) elements surface scans.

sulfide was formed. As shown in Fig. 3(c₁), the whole surface was covered by loose products consisting of Fe and O (point D), which had cracks and cavities. It differs from the morphology in Fig. 3(a₁), with the corrosion product particles being finer. Obviously, Fig. 3(d₁) depicts a denser corrosion product than Fig. 3(c₁). The corrosion products were extremely fine and closely adhered to form an integral corrosion product film which was mainly composed of S and a small amount of Fe, O, Cr and Al (point G). This morphology also indicates superior corrosion resistance. There were a few free ions precipitated on the surface of the corrosion product film in the form of flocculent and spherical corrosion products. Furthermore, due to dehydration occurring during specimen extraction, fine micro-cracks were present on the surface of the corrosion product film.

Fig. 4 presents elemental map scanning for cross-sectional morphologies of X65 steel exposed to the aqueous phase with 300 ppm SO_2 . The corrosion product layer with a thickness of about 86 μm exhibited the characteristic of irregular shape layer, containing Fe, O and S elements (Fig. 4). Epoxy entered the middle of the corrosion products through the cracks, as shown in the dark gray area in Fig. 4(a). According to the EDS point scan, there is only a small amount of S in the corrosion products, indicating that the main reaction occurred between Fe, CO_2 and water during immersion. However, the irregular morphology of the cross-sectional corrosion products suggests that SO_2 contributed to the local corrosion of the steel. Based on XRD and XPS, the main corrosion products of X65 steel in this environment are mainly FeCO_3 , with a small amount of FeSO_3 and FeS .

Fig. 5 shows SEM images and EDS scans for cross-sectional morphologies of 5Cr2Al steel in the aqueous phase with 300 ppm SO_2 . Compared with Fig. 4, the corrosion of 5Cr2Al steel in the CO_2 - SO_2 system was much less. The corrosion product

film consisted of a dense dark gray inner layer and a smooth light gray outer layer, with a thickness of about 9 μm (Fig. 5(a)). The thickness of the double-film layers is much smaller than that of X65. According to EDS line scan and surface scan, the inner dark grey layer is mainly composed of Cr, Al, and O, with a film thickness of approximately 3 μm ; the outer light grey layer is mainly composed of S, with a film thickness of approximately 6 μm . Such a double-layer film structure effectively hinders the further development of the corrosion reaction. According to the EDS point scan (point B), the content of S is 67.1 wt%, and that of Fe is 12.8 wt%. The atomic ratio of S: Fe is approximately 9.5. It is much higher than that of FeS . This indicates that the outer sulfur film is composed of a large amount of elemental sulfur. The presence of SO_2 induced a change in the film structure, forming a dense, integral, and uniform protective sulfur film of a certain thickness on the surface of the original $\text{Cr}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ layers, which inhibited the further progression of corrosion. Obviously, X65 cannot form such an integral and dense S layer.

3.3 XRD analysis

Further analysis in combination with Fig. 6, Strong FeCO_3 peaks were detected in the X65 in two conditions, which should coincide with the element concentrations analyzed in the EDS point scan (Fig. 3). FeCO_3 was the main corrosion product in the aqueous phase.³⁴ Besides the diffraction peaks of FeCO_3 , a small amount of sulfides was also detected in the X65. Notably, for 5Cr2Al, an increase in SO_2 content makes the corrosion products more complex. Compared to 100 ppm SO_2 , in addition to the diffraction peaks assigned to the Fe–Cr base, FeCO_3 , and sulfides, there is also elemental sulfur present. The result is consistent with the EDS result in Fig. 5. XRD can only be applied to the detection of



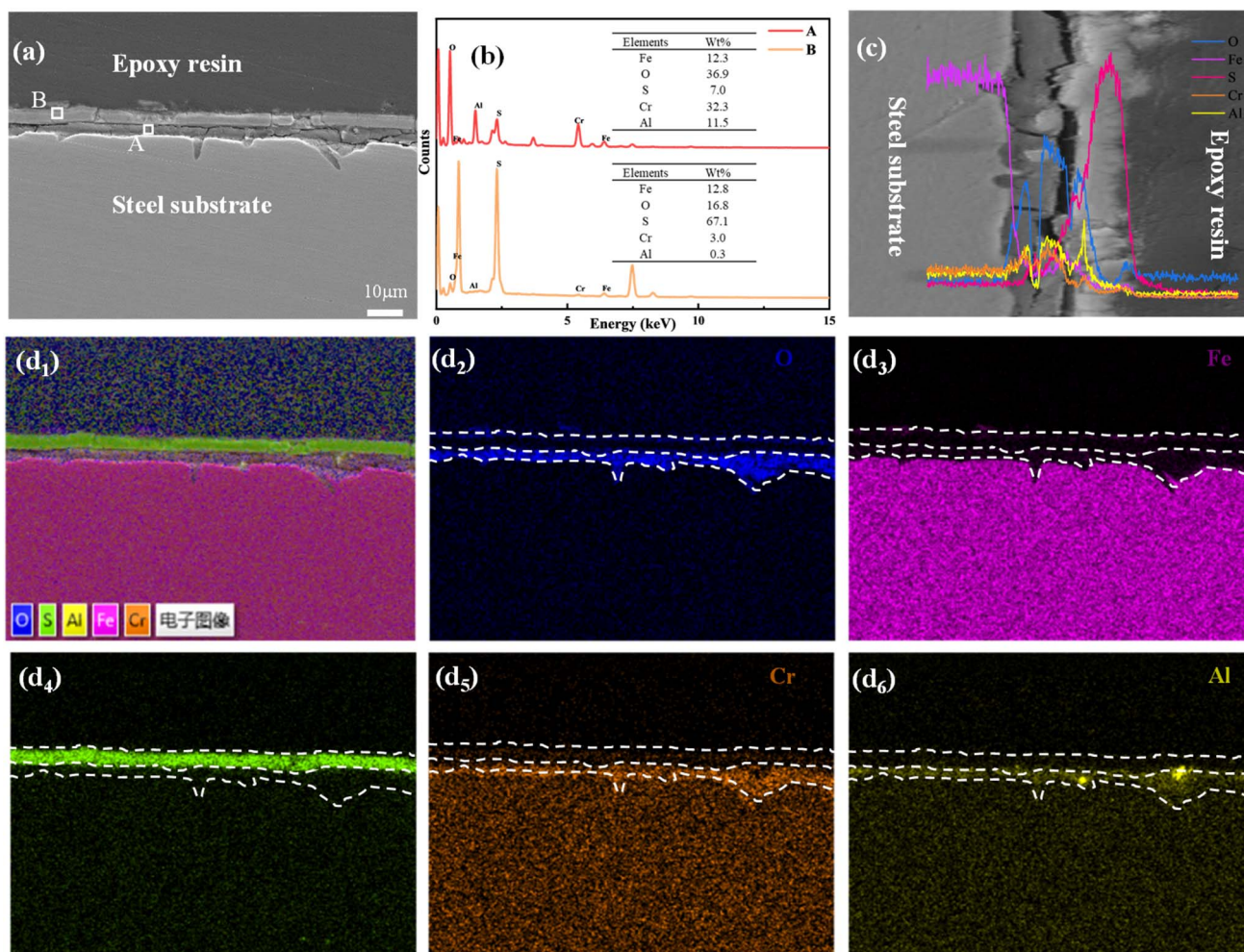


Fig. 5 Cross-sectional morphologies of 5Cr2Al steel exposed to aqueous phase with 300 ppm SO₂ at 8 MPa and 80 °C: (a) SEM images; (b) elemental composition of positions A and B; (c) elements line scan; (d₁–d₆) elements surface scans.

crystalline substances. XPS can detect both crystalline and amorphous corrosion products. We used XPS to conduct further analysis on the corrosion products of these two types of samples.

3.4 XPS analysis

Fig. 7 show a high-resolution XPS spectrum of the corrosion scale of X65 and 5Cr2Al with 300 ppm SO₂. To ensure that all

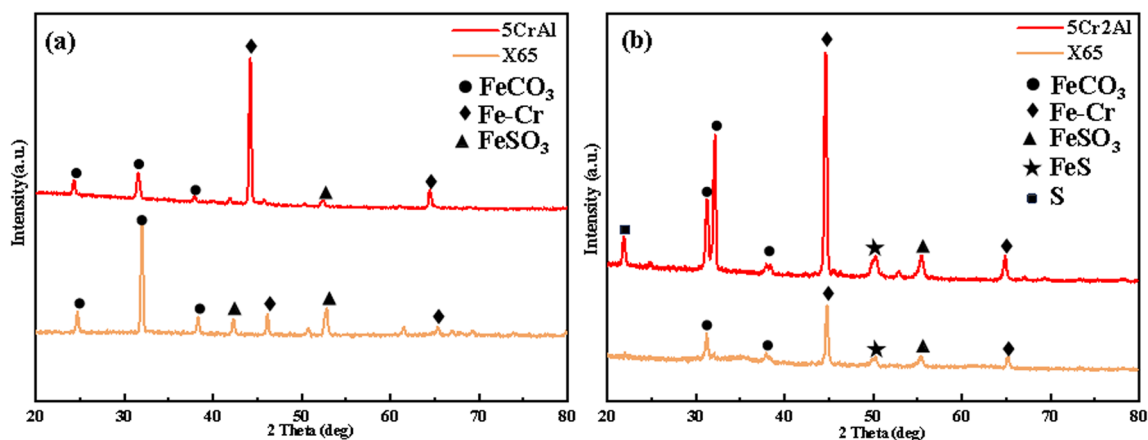


Fig. 6 XRD spectra of the corrosion products formed on X65 and 5Cr2Al steel after exposure to aqueous phase for 168 h at 8 MPa and 80 °C: (a) with 100 ppm SO₂; (b) with 300 ppm SO₂.



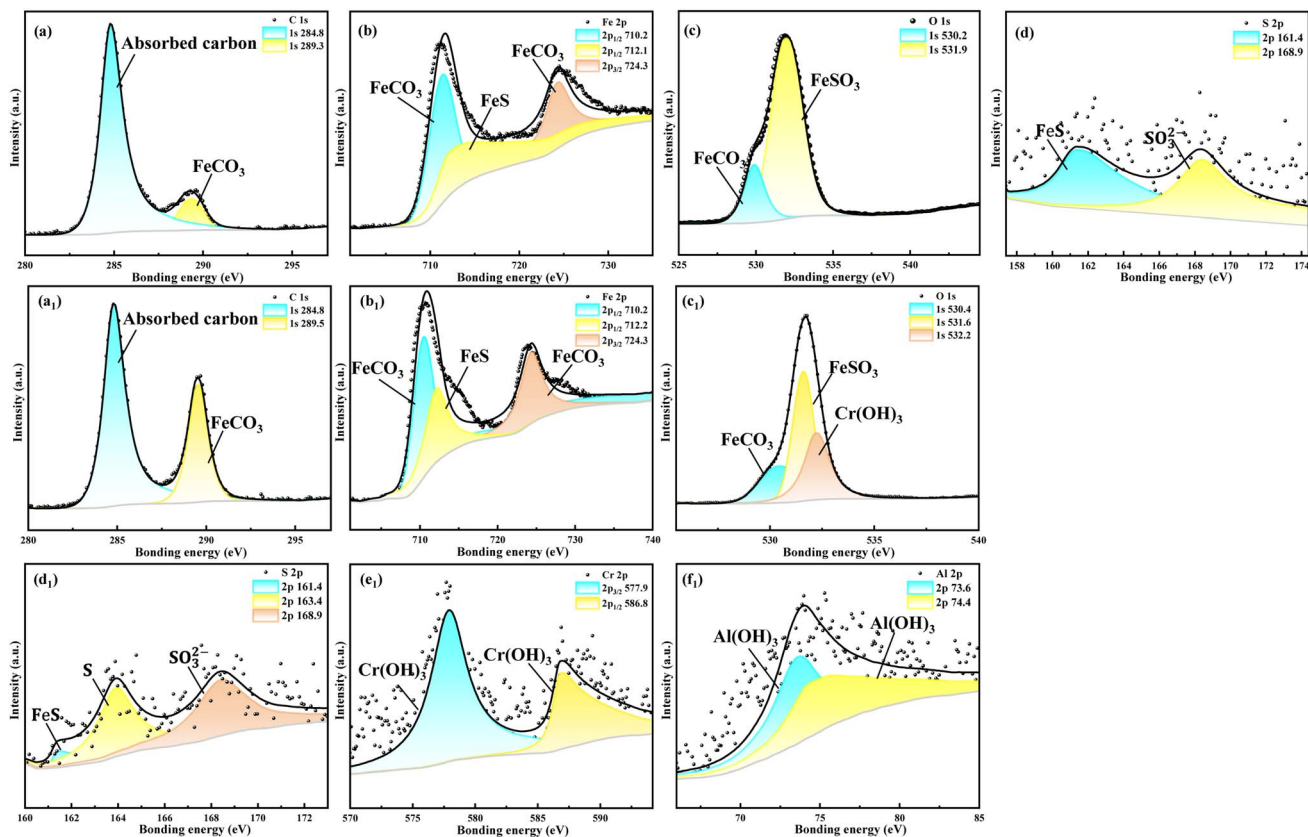


Fig. 7 XPS spectra and peaks deconvolution for various elements of the corrosion product formed on X65 ((a)–(d)) and 5Cr2Al ((a₁)–(f₁)) steel.

types of corrosion products could be detected, the corrosion products were ground into a fine powder and subsequently analyzed by XPS. As shown in Fig. 7((a)–(d)), the C 1s peaks with the binding energy of 284.8 eV correspond to adsorbed carbon. The C 1s peak at 289.3 eV, the O 1s peak at 530.2 eV, the Fe 2p_{1/2} peak at 710.2 eV, and the Fe 2p_{3/2} peak at 724.3 eV were related to FeCO₃.³⁵ The O 1s peak at 531.9 eV and the S 2p peak at 168.9 eV could be assigned to FeSO₃.^{36,37} Meanwhile, the S 2p peak at 161.4 eV and Fe 2p_{1/2} peak at 712.1 eV were correlated to the existence of FeS.^{36,37} Therefore, combining the XRD analysis, the atom ratio of EDS, and XPS results, the main components of X65 steel corrosion products were FeCO₃, FeSO₃, and FeS.

As shown in Fig. 7((a₁)–(f₁)), the C 1s peaks at binding energies of 284.8 eV and 288.4 eV corresponded to adsorbed carbon and FeCO₃, respectively.^{38,39} The O 1s spectrum at the binding energies of 530.4 eV, 531.6 eV and 531.9 eV corresponded to FeCO₃, FeSO₃ and Cr(OH)₃,³⁸ respectively. The Fe 2p spectrum was fitted with three peaks: two components assigned to Fe 2p_{1/2} (724.3 eV) and Fe 2p_{3/2} (710.2 eV) that were both typical of FeCO₃,³⁸ and an additional Fe 2p_{1/2} peak (712.2 eV) associated with FeS.^{36,37} For S 2s, besides the peaks assigned to FeSO₃ (168.9 eV)⁴⁰ and FeS (161.4 eV), a peak appeared at 163.4 eV, which was related to S.^{36,37} Additionally, for 5Cr2Al, the Al 2p_{3/2} peak at 73.9 eV and Al 2p_{1/2} peak at 74.7 eV indicated the presence of Al(OH)₃.⁴¹ The Cr 2p_{3/2} peak at 577.9 eV, the Cr 2p_{1/2} peak at 586.8 eV, and the O 1s peak at 532.2 eV indicated the formation of Cr(OH)₃.^{42,43} Based on the XRD analysis, the atom ratio of EDS, and XPS results, it was concluded that the

corrosion products consisted of Cr(OH)₃, Al(OH)₃, FeCO₃, FeSO₃, FeS, and S for 5Cr2Al.

3.5 Potentiodynamic polarization measurements

From the previous manifestations, due to the low content of 100 ppm SO₂, only a small amount of sulfides was formed. 300 ppm SO₂ formed a sulfur elemental layer in 5Cr2Al steel. To further explore the underlying mechanisms of the formation of

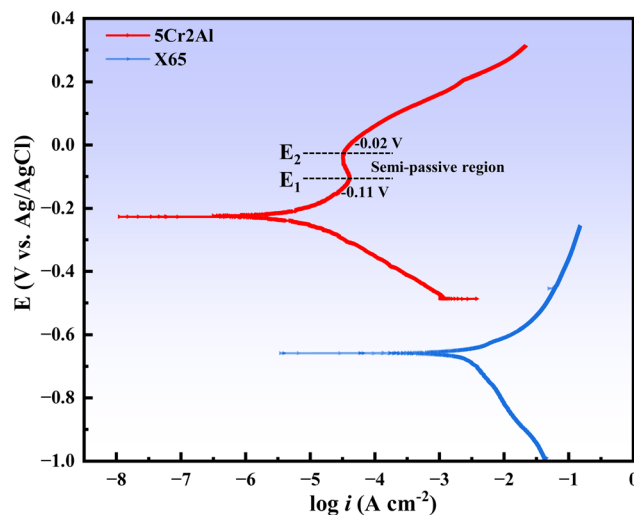


Fig. 8 Polarization curve of 5Cr2Al and X65 steel exposed in water-rich phases with 300 ppm SO₂ at 8 MPa CO₂ and 80 °C for 168 h.



Table 3 Electrochemical parameters of polarization curves of 5Cr2Al and X65 steel exposed in water-rich phases with 300 ppm SO₂ at 8 MPa CO₂ and 80 °C for 168 h

Conditions	E_{corr} (mV vs.)	R_p ($\Omega \text{ cm}^{-2}$)	i_{corr} (A cm^{-2})	CR (mm per year)
X65	-0.64969	46.5	0.002849	3.3172
5Cr2Al	-0.0444	2287.1	0.0000317	0.369

sulfur, polarization curves were measured with X65 and 5Cr2Al when containing 300 ppm SO₂ (Fig. 8). Compared with X65, the OCP of 5Cr2Al moves in a positive direction, shifting from -0.66 V to -0.22 V, and the overall polarization curve shifts to the left. Both the cathodic and anodic processes occurring near the corrosion potential are simultaneously inhibited, leading to a reduced corrosion current. 5Cr2Al exhibits an obvious semi-passivation phenomenon, which is characterized by a decrease in current between E_1 (-0.11 V vs. Ag/AgCl) and E_2 (-0.02 V vs. Ag/AgCl). It is not present in the X65 steel without Cr and Al. The semi-passivation phenomenon of 5Cr2Al is related to the formation of Cr(OH)₃, Al(OH)₃ and a dense sulfur

layer. Table 3 shows that the corrosion current density of 5Cr2Al is two orders of magnitude smaller than that of X65. The R_p of 5Cr2Al is 50 times that of X65 (the value of R_p is self-measured), indicating that the corrosion product film formed on 5Cr2Al has better protective properties. The corrosion rate can be calculated from the corrosion current density, which is consistent with the conclusion obtained by the weight loss method. The corrosion rate of X65 is about 10 times that of 5Cr2Al.

3.6 EIS measurements

To reveal the differences in corrosion mechanism and micro-morphologies between X65 and 5Cr2Al with 300 ppm SO₂, impedance spectroscopy was employed to analyze the formation process of corrosion product films on the two materials. Fig. 9(a₁)–(f₁) presents the EIS results obtained for X65 steel after different immersion times (1–168 h) under conditions of 8 MPa and 80 °C. In the initial stage of corrosion (1–3 h), X65 steel is characterized by a capacitive loop at a high frequency, an inductive loop at an intermediate frequency, and a capacitive loop at a low frequency, which represent three time constants.

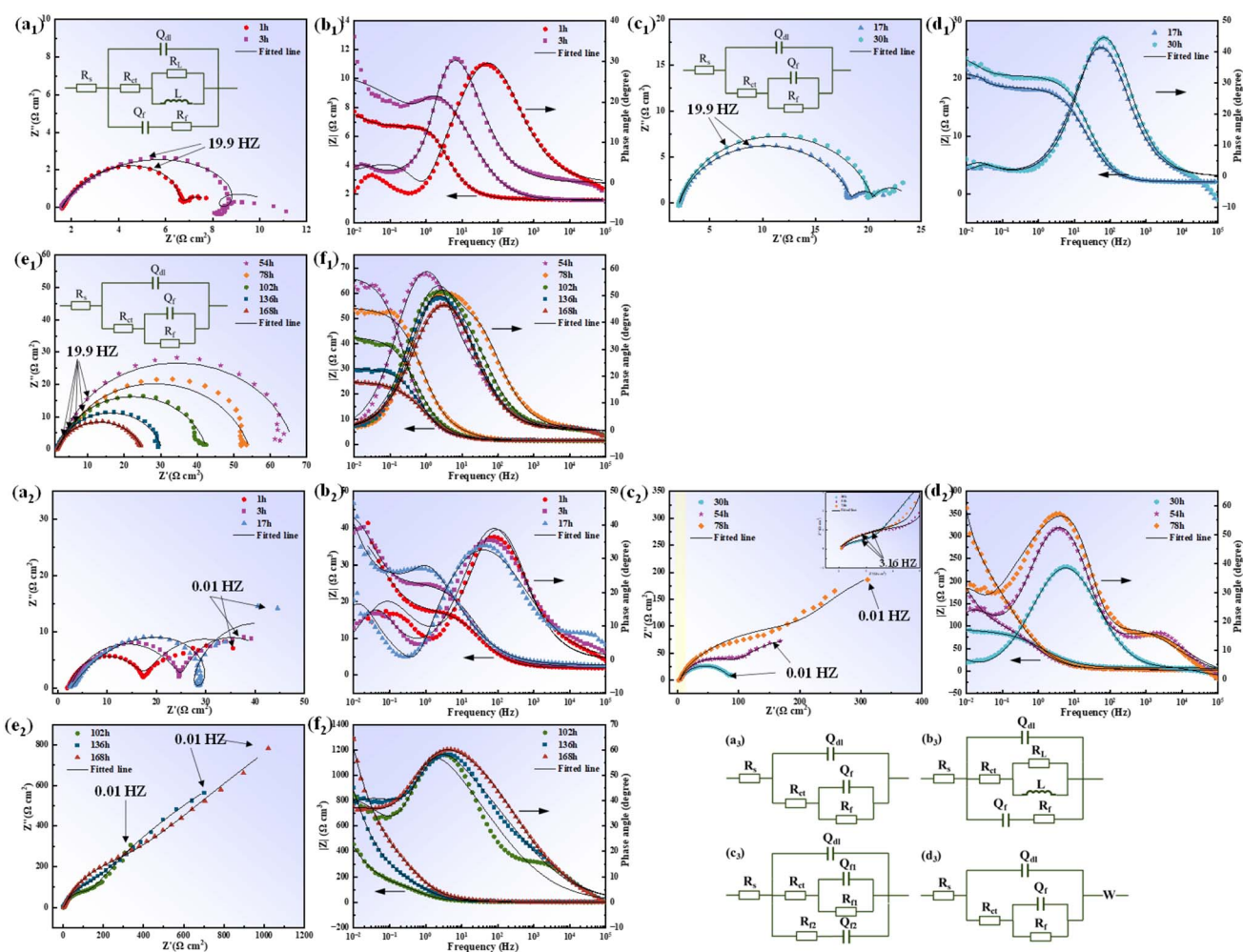


Fig. 9 EIS of steel immersed in aqueous phases at different corrosion periods at 8 MPa and 80 °C with 300 ppm SO₂: (a₁)–(f₁) Nyquist and Bode plot for 1–168 h of X65; (a₂)–(f₂) Nyquist and Bode plot for 1–168 h of 5Cr2Al; (a₃)–(d₃) equivalent circuits for EIS fitting of 5Cr2Al steel ((a₃) 1–3 h; (b₃) 17 h; (c₃) 30–78 h; (d₃) 78–168 h).



The capacitive loop observed at high frequencies can be attributed to the double-layer capacitance and the charge transfer resistance.⁴⁴ The appearance of the medium-frequency inductive loop is due to the local adsorption of OH⁻ on the steel surface to form the intermediate product FeOH_{ads} and the occurrence of pitting corrosion.^{45,46} The capacitive loop observed at low frequencies may be associated with the formation of a corrosion product film.⁴⁴ As the exposure time increases, the diameters of the high-frequency capacitive loop and the low-frequency capacitive loop increase. Then the inductive loop is observed to disappear, with only the high-frequency and low-frequency capacitive loops remaining (17–30 h). The middle and late stages of corrosion (54–168 h) are characterized by two time constants, *i.e.*, a high-frequency capacitive loop and a low-frequency capacitive loop. Interestingly, the diameter of the capacitive loop reaches its maximum at 54 h, and gradually decreases as the corrosion progresses. This indicates that the corrosion products formed on X65 steel, mainly ferrous carbonate, provide very poor protection.

Table S1 lists the fitted parameters obtained from the EIS data with equivalent circuits. The equivalent circuit diagram of the corresponding impedance spectrum is placed in Nyquist. The model elements are defined as follows: R_s is the solution resistance; R_{ct} is the charge-transfer resistance; R_f is the corrosion-product film resistance; Q_{dl} and Q_f are constant-phase elements corresponding to the double-layer capacitance and the film capacitance, respectively; L is the inductance; and R_L is the inductance resistance. It can be seen from Table S1 that the polarization resistance ($R_{ct} + R_f$) increased from 6.26 $\Omega\text{ cm}^2$ at 1 h to 67.05 $\Omega\text{ cm}^2$ at 54 h. The charge transfer was slow and the corrosion process was inhibited. Then the polarization resistance gradually decreased with prolongation of exposure time, dropping to a value of 23.08 $\Omega\text{ cm}^2$ at 168 h. The diameter of the capacitive loop first increased and then decreased with time, indicating that the corrosion process was controlled by charge transfer. In the initial stage of corrosion, the steel dissolved. The formed corrosion products were relatively loose (Fig. 3(c₁) and 4), providing poor protection, and thus the impedance value was small. During the middle stage, the thickness of the corrosion product film gradually increases, thereby enhancing its protective effect and increasing the impedance value. However, the impedance value gradually decreases in the later stage due to the continuous growth of the corrosion product film to a critical thickness, after which the film breaks. This indicates that the FeCO₃ film has almost a non-protective nature in the later stage of corrosion, and the corrosion rate increases rapidly.

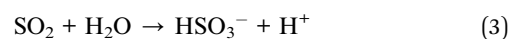
EIS measurements of 5Cr2Al, in the Nyquist and Bode format, are shown in Fig. 9(a₂)–(f₂). At the initial stage, it is characterized by two time constants, one capacitive loop at high frequency, and one capacitive loop at low frequency. With the prolongation of exposure time, the diameter of the impedance loop increases. Subsequently, the inductive loop appears (17 h). Pitting occurs in the initial stage, and no pitting occurs in the later stage. As the corrosion progresses, during the mid-stage of corrosion (30–78 h), the inductive loop disappears and is characterized by three time constants: one capacitive loop at high frequency, one capacitive loop at intermediate frequency, and one capacitive loop at low

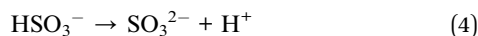
frequency. Due to the accumulation of a certain thickness of Cr(OH)₃ and Al(OH)₃ layers, the diameter of the impedance loop increases by an order of magnitude, and the low-frequency impedance loop gradually approaches the Warburg impedance. In the final stage (102–168 h), the Warburg impedance response becomes clearly distinguishable. This stage is characterized by two time constants. In the previous stage, the first and second capacitive loops merged into one due to their similar time constants, and a Warburg impedance (45° straight line) emerged. Warburg impedance is a diffusion-controlled process that corresponds to pure diffusion with an infinite diffusion layer. The emergence of the Warburg impedance indicates that the system begins to be dominated by diffusion, showing a typical linear diffusion tail in the low-frequency region, and the overall corrosion rate is very slow. According to the previous EDS morphology analysis, it is known that in an environment containing SO₂, 5Cr2Al forms a dense sulfur film. Surprisingly, it acts as a diffusion barrier, with a very small W and an impedance loop diameter reaching four orders of magnitude. Therefore, the increase in impedance is due to the growth of the sulfur film. The high-frequency capacitive loop is associated with the cathodic and anodic reactions occurring on the surface of the solution and corrosion products. The medium-frequency capacitive loop may be associated with the occurrence of pitting corrosion and the adsorption of intermediate products. The low-frequency capacitive loop is related to the corrosion product film. The Warburg impedance corresponds to the diffusion-limited process.

Table S2 lists fitted parameters obtained from the EIS data with the corresponding equivalent circuit. The equivalent circuits for 1–3 h, 17 h, 30–78 h and 102–168 h are fitted by Fig. 9(a₃)–(f₃), respectively. Additionally, W represents the Warburg impedance, which is caused by diffusion of the transferred substance and becomes very obvious after the formation of the sulfur film. Table S2 shows that in the initial corrosion stage (1–17 h), the corrosion reaction occurs rapidly with small R_{ct} and R_f values, but the overall polarization resistance value increases. In the middle stage (30–78 h), the polarization resistance value rapidly increases to 496.88 $\Omega\text{ cm}^2$. Combined with the EDS surface scan analysis, this is due to the rapid growth of the inner layer of Cr(OH)₃ and Al(OH)₃ corrosion products, resulting in an accumulation of thickness. In the later stage (102–168 h), the diffusion polarization impedance value reached 2937.47 $\Omega\text{ cm}^2$, and the Warburg impedance value was 0.0085. The large diffusion impedance indicates that the formation of the sulfur film in the later stage greatly inhibited the diffusion-dominated corrosion. The overall reaction rate was very slow, and only a very small amount of ions could pass through the sulfur film and the Cr(OH)₃ and Al(OH)₃ barriers to exchange substances with the steel substrate.

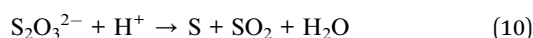
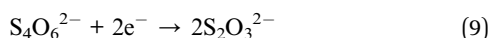
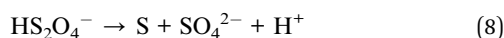
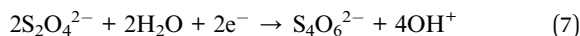
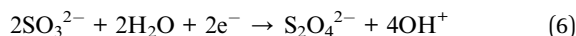
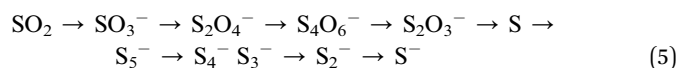
3.7 Discussion of the corrosion mechanism

For X65 steel, when SO₂ dissolves in water, it generates sulfurous acid and other substances, lowering the pH of the solution and encouraging anodic dissolution.

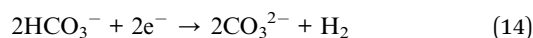
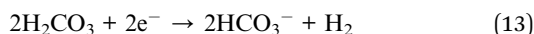




In an anaerobic environment, besides the formation of SO_3^{2-} , the addition of SO_2 also led to the formation of FeS . The specific reactions for the formation of FeS are shown in the reaction eqn (5)–(11).^{47–49} Research⁵⁰ indicated that FeS has certain electrical conductivity and a positive potential relative to the steel substrate. The potential difference between the two will promote corrosion. For X65 steel, the addition of SO_2 promotes corrosion.



Besides, in SC CO_2 environment, the cathodic process may include the reduction of H^+ , H_2CO_3 , HCO_3^- .⁵¹



The anodic reaction is the oxidation of Fe:

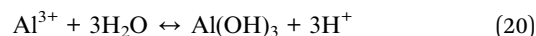
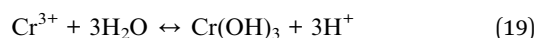


When the concentrations of Fe^{2+} and CO_3^{2-} exceed the solubility product of FeCO_3 ($K_{\text{sp}} = 3.13 \times 10^{-11}$), FeCO_3 precipitation occurs. Although SO_2 lowers the pH and to some extent inhibits the hydrolysis of H_2CO_3 , the corrosion process is mainly controlled by CO_2 in a CO_2 atmosphere. With the increase in impurity SO_2 content, the nucleation sites of FeCO_3 increase, resulting in finer grains. Thus, the corrosion product layer consists mainly of FeCO_3 for X65 steel. Additionally, sulfides promote the anodic dissolution of the steel, resulting in the formation of more Fe^{2+} , which makes it easier to occur the reaction of eqn (16).⁵² Furthermore, when the SO_2 concentration increases from 100 ppm to 300 ppm, the formed FeCO_3 corrosion product becomes finer and the corrosion rate increases. In CO_2 -300 ppm SO_2 system, we have learned through electrochemical research that the formation of FeCO_3 plays a protective role, which leads to an increase in the diameter of the impedance loop in the initial and middle stages. In the later stages, the formation of FeCO_3 mixed with sulfides, which is characterized by being loose and porous (Fig. 3c₁) and having a certain degree of conductivity, accelerates the corrosion. The

amplitude of the impedance loop weakens, and the charge transfer process is considered to accelerate the cathodic process.^{46,53} The decrease in R_f indicates that the weakened protective effect of the corrosion product film increases with immersion time. In addition, the anodic polarization curve is very smooth, indicating that no passive film is formed.



For 5Cr2Al steel in a CO_2 -100 ppm SO_2 system, there is a higher reactivity of Cr and Al compared to Fe. Thus, Cr and Al dissolve preferentially (eqn (17) and (18)).⁵⁴ $K_{\text{sp}}(\text{Al}(\text{OH})_3) = 1.3 \times 10^{-33}$, $K_{\text{sp}}(\text{Cr}(\text{OH})_3) = 6.3 \times 10^{-31}$, $K_{\text{sp}}(\text{FeCO}_3) = 3.13 \times 10^{-11}$. Due to the smaller K_{sp} of $\text{Cr}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$, they precipitate preferentially, forming a thin layer of $\text{Cr}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ (eqn (19) and (20)). An outer layer of corrosion products is mainly composed of FeCO_3 (Fig. 3(b₁)). In a CO_2 -300 ppm SO_2 system, an increase in SO_2 content with Cr and Al elements alters the type of corrosion products, which is not observed in X65 steel without Cr and Al. It also forms a layer of $\text{Cr}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ (Fig. 5). Based on the electrochemical data analysis, the impedance loop initially shows a double capacitive loop, indicating that the formed $\text{Cr}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ are protective. Cr and Al continuously precipitate with exposure time, forming a $\text{Cr}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ layer with a thickness of 3 μm . The pH value near the steel surface will decrease.²⁴ In an anaerobic environment, SO_2 will also cause the reactions of eqn (3) and (4). The pH will also decrease accordingly. In a lower pH environment, the ionization of H_2CO_3 is almost inhibited, so there is almost no formation of FeCO_3 (Fig. 5). When the pH reaches the conditions for sulfite ion to occur the reactions of eqn (5)–(10), a large amount of elemental sulfur is formed, and the sulfur film blocks the exchange of substances between the steel substrate and the solution. It effectively hinders the diffusion of Fe^{2+} , Cr^{2+} , and Al^{2+} from the oxide film/matrix interface to the oxide film/solution interface, and reduces the concentration of ions above the inner oxide film. Correspondingly, the impedance loop gradually shows the Warburg impedance. At this time, the R_f also reaches four orders of magnitude, which indicates an artefact of the slow migration of species to and from the sulfur film surface. The formation of this more protective film leads to a semi-passivation phenomenon in the corresponding polarization curve.



We used the OLI software to calculate the solubility of 300 ppm SO_2 at different temperatures and pressures (Fig. 10). In the aqueous phase, it can be observed that CO_2 dissolved in the solution increases with pressure and decreases with temperature. This indicates that the solubility of CO_2 in water increases as pressure increases, and it decreases as temperature



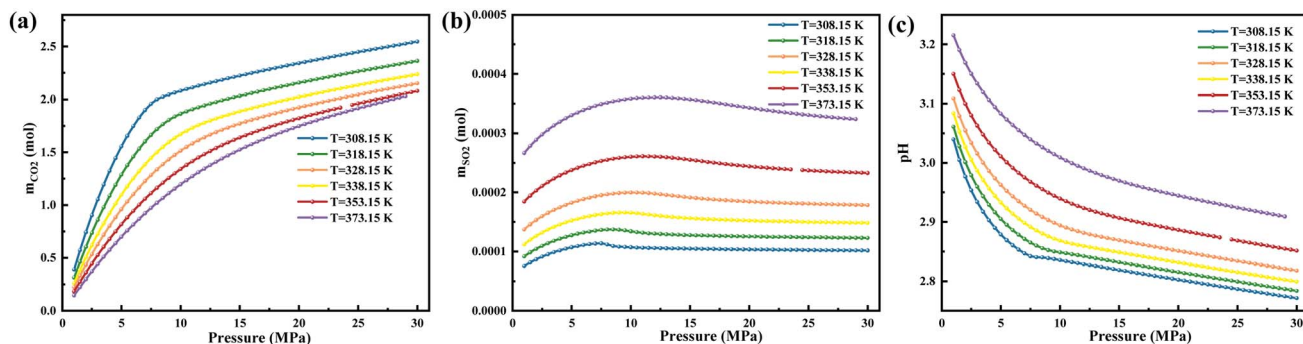


Fig. 10 The concentrations of CO₂ and SO₂ dissolved in water and the variation of pH with temperature and pressure: (a) CO₂; (b) SO₂; (c) pH.

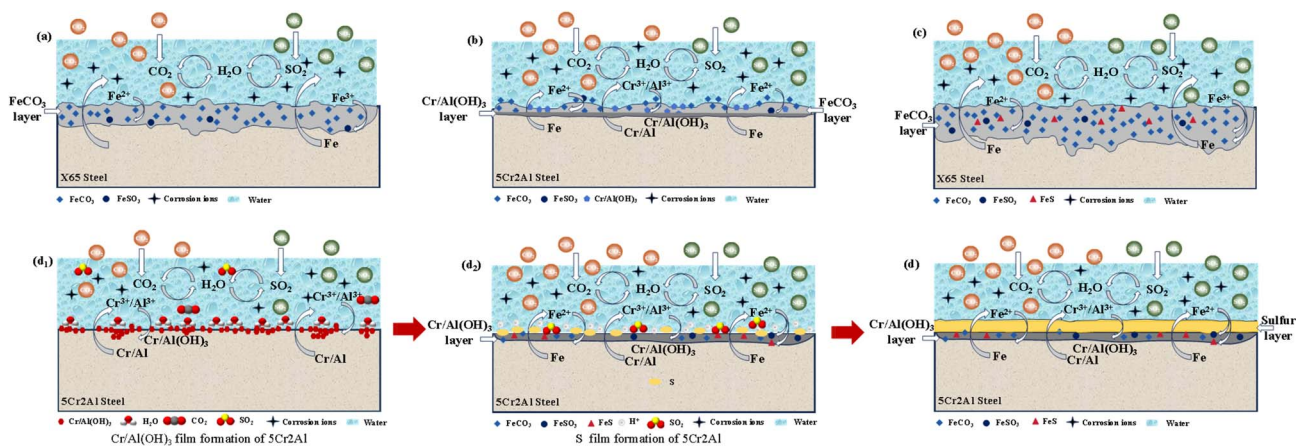


Fig. 11 Schematic diagram of corrosion film formation: (a) X65 with 100 ppm SO₂; (b) 5Cr2Al steels with 100 ppm SO₂; (c) X65 with 300 ppm SO₂; (d) 5Cr2Al with 300 ppm.

risers. The calculated trends are consistent with the findings of previous studies.⁵⁵ However, the solubility of SO₂ in water shows an opposite trend. It increases first and then decreases with the increase of pressure, and increases with the increase of temperature. The pH gradually decreases as pressure increases, which is related to the dissolution of more CO₂. When the pressure is lower than 8 MPa, the pH drops more rapidly, which is associated with the dissolution of more SO₂ at this time. The pH increases with the rise in temperature, which is related to the variation trend of CO₂ solubility with temperature. In this study, approximately 0.00026 mol of SO₂ was dissolved in water, almost reaching the dissolution peak, which made a great contribution to the reduction of pH. Additionally, due to the precipitation of Cr and Al in 5Cr2Al steel and their combination with water, the pH would be further reduced to a greater extent, which would be conducive to the formation of a sulfur film.

The corrosion mechanism model of X65 and 5Cr2Al steel in aqueous phases with 100 ppm and 300 ppm SO₂ at a total pressure of 8 MPa and 80 °C are shown in Fig. 11. The corrosion mechanism of the two types of steel with 100 ppm and 300 ppm SO₂ shows significant differences. In a CO₂-100 ppm SO₂ system, X65 undergoes a reaction dominated by the formation of FeCO₃. A small amount of sulfides is also produced (Fig. 11(a)). The inner layer of 5Cr2Al consists of a thin film of

Cr(OH)₃ and Al(OH)₃ corrosion products (Fig. 11(b)). Given the minimal impact of 100 ppm SO₂ on pH, the precipitation of FeCO₃ is hardly inhibited, resulting in an outer layer predominantly composed of dense FeCO₃ with minor sulfide inclusions. In a CO₂-300 ppm SO₂ system, SO₂ merely accelerates the corrosion of X65 steel, and the type of corrosion products remains unchanged (Fig. 11(c)). However, for 5Cr2Al steel, the type of corrosion products changed, forming a double-layer structure with Cr(OH)₃ and Al(OH)₃ as the inner layer and elemental S as the outer layer, which inhibited the progress of corrosion (Fig. 11(d)-(d₂)). We found that only when Cr and Al are present and the SO₂ concentration reaches 300 ppm can a dense S elemental film be formed compared to 100 ppm SO₂.

4. Conclusions

(1) In the CO₂-100 ppm SO₂ system, X65 occur a reaction dominated by the formation of FeCO₃. SO₂ significantly accelerates both general and localized corrosion of X65 steel compared to 5Cr2Al steel. 5Cr2Al forms a double-layer structure with Cr(OH)₃ and Al(OH)₃ as the inner layer and FeCO₃ as the outer layer.

(2) In the CO₂-300 ppm SO₂ system, the corrosion rate of X65 is 1.5 times greater than that at 100 ppm. The corrosion



products formed on X65 steel have a certain protective effect in the initial and middle stages. However, in the later stage, the corrosion product layer loses its protective property due to its porous and loose structure as well as crack formation. SO₂ only accelerates corrosion in X65 without added Cr and Al.

(3) 300 ppm SO₂ is a concentration that will have a synergistic reaction with Cr and Al. It changes the corrosion mechanism and enhances the corrosion resistance of steel. This study found that only when Cr and Al are present and the SO₂ content reaches 300 ppm can a synergistic effect occur, which inhibits corrosion attack on the steel surface by forming a dense sulfur film on the outer surface of the thin Cr(OH)₃ and Al(OH)₃ layers.

(4) 5Cr2Al can reduce corrosion by nearly 91% when compared to X65. Therefore, 5Cr2Al steel is an important option for material selection in the injection tube of Carbon capture, utilization and storage (CCUS). X65 steel can be used for transporting CO₂ on ground with less water content.

Author contributions

Rongdie Zhu: investigation, formal analysis, validation, visualization, writing – original draft, methodology, software. Jinyang Zhu: conceptualization, data curation, funding acquisition, methodology, project administration, resources, supervision, writing – review & editing, investigation, validation. Hangrui Shi: investigation, software. Lining Xu: conceptualization, methodology, software, supervision. Yunan Zhang: conceptualization, methodology, supervision. Zhile Yang: methodology, software, validation. Yuanliang Liu: investigation, software. Hangqi Li: investigation, software.

Conflicts of 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.

Data availability

Data will be made available on request.

Supplementary information: specific data of the electrochemical impedance spectrum. See DOI: <https://doi.org/10.1039/d5ra09269h>.

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