Investigation of the deterioration of passive films in H₂S-containing solutions

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Abstract: The effect of H₂S on the corrosion behavior of 316L stainless steel was investigated using electrochemical methods by changing the gas condition from CO₂ to H₂S and then back to CO₂. The presence of H₂S showed an acceleration effect on the corrosion of 316L stainless steel in comparison with CO₂. The acceleration effect remained even after the complete removal of H₂S by CO₂, indicating that the passive film was irreversibly damaged. X-ray photoelectron spectroscopy (XPS) analysis indicated that the passive film was composed of Cr₂O₃, Fe₂O₃, and FeS₂ after being immersed in H₂S-containing solutions. The semiconducting property of the passive film was then investigated by using the Mott–Schottky approach. The presence of sulfides resulted in higher acceptor and donor densities and thus was responsible for the deterioration of passive films.

Keywords: stainless steel; passive films; hydrogen sulfide; corrosion

1. Introduction

Accelerated energy demands have boosted the exploitation of much deeper and sourer oil-gas fields that require excellent corrosion-resistant alloys (CRAs) for oil country tubular goods [1–2]. The presence of H₂S may lead to severe corrosion failure of materials, such as pitting and stress corrosion cracking (SCC) [3–5]. Therefore, CRAs are widely used in sour conditions to meet exploitation requirements. Austenitic stainless steels, especially 316L stainless steel, are widely used as structural materials because of their good corrosion resistance and mechanical properties [6–9].

The high resistance of stainless steels is due to the thin and dense passive film that formed on the surface [10–12]. The passive film is believed to have a bilayer structure with varying composition that depends on the environment. Generally, the passive film consists mainly of Fe₂O₃, Fe(OH)₃, and Cr₂O₃ [13]. Banas *et al.* [14] found that CO₂ could stimulate the dehydroxylation of the outer part of the oxide film. Liang *et al.* [15] found that the surface film was composed of Cr₂O₃, MoO₃, FeS, FeS₂, Fe(OH)₂, and FeO after immersing the sample in a sulfate-reducing bacteria medium.

The variation in the chemical composition of passive films can eventually lead to a change in corrosion resistance.

For carbon steels, the presence of H₂S can have either an acceleration or inhibition effect on the corrosion behavior depending on the partial pressure [16]. However, the inhibition effect of H₂S on stainless steels has seldom been reported. To date, several investigations have been conducted with regard to the corrosion behavior of stainless steels in the presence of H₂S. Banas *et al.* [14] found that the presence of H₂S in thermal water could lead to the decrease in the stability of the passive film on high alloyed stainless steels by inhibiting the formation of oxides. Ge *et al.* [17] found that the addition of sodium sulfide to cooling water could affect the Cr oxide in the inner passive film, thereby resulting in an increased acceptor density. He *et al.* [18] found that H₂S had little effect on the semiconductor properties of oxide films. Ding *et al.* [1] discovered that the presence of H₂S in Cl[−] solutions could accelerate both cathodic and anodic current densities and increase susceptibility to corrosion. However, no direct evidence has been reported about the H₂S effect on the protectiveness of passive films. The reversibility of corrosion resistance due to the addition of H₂S has not been investigated.

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Electrochemical Impedance Spectroscopy (EIS) is an *in situ* and non-disturbing technique when conducted at the open circuit potential (OCP). It is a very powerful technique for characterizing surface layers and identifying H₂S corrosion mechanisms [19], especially when time effects are considered. The objective of this paper is to investigate the effect of H₂S on the passive behavior of austenitic stainless steel. With the gas condition changed from CO₂ to H₂S and then back to CO₂, the evolution of corrosion behavior was monitored using OCP and EIS measurements. The irreversible corrosion behavior was observed from the analysis of EIS results. Mott–Schottky, cyclic polarization measurements, and XPS analysis were then employed to further investigate the deterioration of the passive film induced by H₂S.

2. Experimental

2.1. Materials and solutions

All test specimens were cut from a hot-rolled 316L stainless steel plate, whose chemical composition is shown in Table 1. The specimens were cut to a size of 10 mm × 10 mm × 3 mm and then mounted in epoxy resin, leaving a working area of 1 cm². Prior to the experiments, the specimens were successively polished with SiC paper up to 2000 grit to obtain a fine specimen surface and minimize the errors caused by surface roughness. After polishing, the specimens were cleaned using distilled water and ethanol, and then dried by cool air. All specimens were then exposed in the air for more than 24 h so that the protective passive film

formed. Test solutions for electrochemical measurements contained 5000 mg·L⁻¹ Cl⁻, which was prepared using deionized water and analytically pure NaCl.

2.2. Electrochemical measurements

All the electrochemical measurements were performed in a conventional three-electrode cell. A platinum plate and a saturated calomel electrode (SCE) connected to the cell via a Luggin's capillary were used as the counter and reference electrodes, respectively. All tests were conducted in 5000 mg·L⁻¹ Cl⁻ solutions at room temperature (approximately 25°C) and atmospheric pressure. The electrochemical measurements include three steps: (1) the test system was deaerated by pure CO₂ for 50 h to deoxygenate and stabilize the system; (2) H₂S was bubbled through the media for approximately 110 h to investigate its effect on corrosion; (3) CO₂ was bubbled through the media for 140 h. This prolonged CO₂ bubbling process was performed to remove H₂S as completely as possible and to investigate the corrosion behavior of stainless steel after the removal of H₂S. During these stages, OCP and EIS measurements were employed at regular intervals to monitor the corrosion behavior. At the end of each stage, cyclic potentiodynamic polarization and Mott–Schottky measurements were performed on the samples. Cyclic potentiodynamic polarization and Mott–Schottky measurements were conducted on different specimens to avoid damage to the working electrodes during the polarization process. The experimental procedure for this study is shown in Fig. 1.

Table 1. Chemical composition of 316L austenitic stainless steel

								wt%
C	Si	Mn	P	S	Cr	Mo	Ni	Fe
0.022	0.47	1.07	0.024	0.001	18.5	2.13	11.0	Bal.

Fig. 1. Experimental procedure for the study.

EIS measurements were performed at the OCP by using an alternating current voltage amplitude of 10 mV. The frequency varied from 100000 to 0.01 Hz. The

Mott–Schottky measurements were performed on the passive film from -0.7 to 0.6 V vs. SCE with a potential step of 50 mV. The high sweep rate was used to ensure

that the film thickness, composition, and defect density remain constant during the test [20]. The frequency was maintained at 1000 Hz, and an AC voltage amplitude of 10 mV was employed.

The potentiodynamic polarization curves were recorded from -0.1 V vs. OCP in the positive direction with a potential sweep rate of $0.167 \text{ mV}\cdot\text{s}^{-1}$. The reversing current density was $5 \text{ mA}\cdot\text{cm}^{-2}$. All measurements were performed at least two times.

2.3. XPS analysis

The composition of the passive films formed in natural air and H₂S-containing solutions was analyzed by XPS with an AXIS-UltraDLD instrument (monochromatic Al K α , $h\nu = 1486.6 \text{ eV}$). In addition, the C1s peak at 284.8 eV was used as a reference to adjust the shifted charge. An analysis of the peaks on the measured curves was conducted via the commercial software XPSpeak version 4.1.

3. Results and discussion

3.1. OCP and EIS results

OCP and EIS measurements were conducted on the same sample at regular intervals during the entire test to monitor the corrosion behavior. The OCP results are shown in Fig. 2(a). During the first 20 h in stage 1, the OCP decreased sharply from -0.298 to -0.453 V vs. SCE. This phenomenon was thought to be related to the decrease in oxygen content in the solution and the acceleration effect of CO₂ on the anodic reaction. Afterwards, the OCP reached a steady

state (OCP decreased 10 mV in 24 h). At the transition from stage 1 to stage 2, once H₂S was bubbled into the CO₂-saturated solution, the OCP immediately shifted in the negative direction (Fig. 2(b)). The negative movement of OCP suggests that the anodic process was accelerated, which will be further discussed in the following section. The OCP then gradually increased toward higher values. In stage 3, the OCP returned to a more positive value (-0.485 V vs. SCE), but was still slightly lower than that at the end of stage 1 (-0.473 V vs. SCE).

EIS is an *in situ* and non-disturbing technique when conducted at the OCP, thereby making it a powerful means to investigate the evolution of corrosion behavior. EIS measurements were conducted at the OCP at each stage. Figs. 3(a), 3(b), and 3(c) show the Nyquist plots measured during each stage. At the beginning of stage 1, when CO₂ was bubbled through for 4 h, the Nyquist plot was characterized by a single capacitive semicircle, which is related to the charge transfer in the electrode/electrolyte interface. When the electrode was immersed in an aqueous solution for 4–8 h, the Nyquist impedance diagrams presented two capacitive reactance arcs. The capacitive reactance arc in the high-frequency region corresponded to the charge transfer process at the interface, whereas the incomplete capacitive reactance arc was related to the passive film in the low-frequency region. The Nyquist plots overlapped after the electrode was immersed for 32 h, indicating that steady state was reached. In stages 2 and 3, the diameter of Nyquist plots decreased slightly at the beginning and then stabilized at the end.

Fig. 2. OCP (E_{oc}) variations of 316L stainless steel vs. time: (a) stages 1, 2, and 3; (b) the transition from stage 1 to stage 2.

Fig. 3(d) shows the EIS diagrams measured at the beginning and the end of each stage. Two time constants evidently exist in the EIS curve for all impedance spectra, i.e., two capacitive reactance arcs, except for that obtained at 4 h. The EIS data were fitted with the electrochemical

equivalent circuit. After comparing multiple equivalent circuit diagrams, the diagram with the smallest error was chosen. The electrochemical equivalent circuits are shown in Fig. 4. The equivalent circuit at 4 h is illustrated in Fig. 4(a), where R_s is the solution resistance, R_t is the charge

transfer resistance, and Q_{dl} represents the double-layer capacitance. The other impedance data were fitted by an equivalent circuit shown in Fig. 4(b), where R_f and Q_f are the resistance and capacitance of the passive film, respectively. In the above circuits, Q is the constant-phase ele-

ment (CPE). The CPE is commonly used in the case of an uneven current distribution at the surface or in the event of increased surface roughness. The impedance of CPE is given by

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

Fig. 3. Nyquist plots of 316L stainless steel in Cl^- -containing solutions at room temperature during various stages: (a) stage 1; (b) stage 2; (c) stage 3; (d) the beginning and the end of each stage.

Fig. 4. Equivalent circuit for simulating EIS results.

where Y_0 is a proportionality constant, $j^2 = -1$, and n is an empirical exponent between 0 and 1. When $n = 1$, the CPE

represents a pure capacitive element; when $n = 0$, the CPE represents a resistor; and when $n = 0.5$, the CPE represents the Warburg impedance. ω is the angular frequency.

The values of the equivalent circuit elements for each stage are presented in Table 2. Combined with the results in Fig. 3, the stable values of R_t and R_f are 140 and 54.4 $k\Omega \cdot cm^2$, respectively, in stage 1, i.e., CO_2 -saturated condition. Moreover, the R_t and R_f values sharply decreased with the presence of H_2S from 140 to 9.94 $k\Omega \cdot cm^2$ and 54.4 to 17.3 $k\Omega \cdot cm^2$, respectively, thereby indicating the acceleration effect of H_2S on the corrosion of 316L. However, after CO_2 was bubbled into the solution once again ($t > 162$ h), the R_t and R_f values did not change significantly even though H_2S was completely removed at 301 h. This result was thought to be related to the deterioration of the passive film, which will be illustrated in the following sections.

Table 2. Calculated equivalent circuit parameters

Condition	$R_s / (\Omega\text{-cm}^2)$	Q_{dl}			$R_t / (\text{k}\Omega\text{-cm}^2)$	Q_r			$R_f / (\text{k}\Omega\text{-cm}^2)$
		$Y_0 / (\Omega^{-1}\text{-cm}^{-2}\cdot\text{s}^n)$	n			$Y_0 / (\Omega^{-1}\text{-cm}^{-2}\cdot\text{s}^n)$	n		
Stage 1	4 h	21.3	8.10×10^{-5}	0.88	268.9	—	—	—	—
	48 h	14.9	6.94×10^{-5}	0.86	140.0	7.15×10^{-4}	0.88	54.4	—
Stage 2	52 h	19.4	7.92×10^{-5}	0.85	9.94	5.44×10^{-3}	1.00	17.3	—
	160 h	18.2	7.33×10^{-5}	0.86	7.37	2.91×10^{-3}	0.89	15.6	—
Stage 3	162 h	17.4	7.03×10^{-5}	0.86	7.68	3.88×10^{-3}	1.00	11.2	—
	301 h	17.6	7.09×10^{-5}	0.86	6.52	2.44×10^{-3}	0.91	11.9	—

3.2. Cyclic potentiodynamic polarization curves

The cyclic potentiodynamic polarization curves for austenitic stainless steel 316L obtained at the end of each stage are shown in Fig. 5. In stage 1, the i - E curve exhibits a current plateau, which is a typical characteristic of the passive behavior of stainless steel. In stages 2 and 3, the cyclic polarization curves are similar in shape when the applied potential is lower than -0.06 V vs. SCE. When higher than -0.06 V vs. SCE, the current density sharply increased for stage 2. In addition, the passive current densities increase with the applied potential for both curves. This phenomenon is also reported and considered the result of additional reactions on the surface [18].

Fig. 5. Cyclic polarization curves of 316L stainless steel in Cl⁻-containing solutions at room temperature measured at the end of each stage.

Generally, a sharp increase in current density at more positive potentials can be regarded as the indication of (1) transpassivity, (2) oxygen evolution, or (3) localized corrosion (pitting and/or crevice corrosion). In cases (1) and (2), no hysteresis loop can be observed because no irreversible damage occurs at certain critical potentials. Nevertheless, once localized corrosion occurred on the electrode surface at a certain anodic potential, repassivation in this location will be more difficult due to the local acidity in pits or crevice.

Therefore, at the same potentials, current densities during the reversing scan will be higher than those during the forward scan. This condition eventually leads to the presence of hysteresis loop in cyclic polarization curves. Accordingly, the potential that corresponds to the sharp increase in current density in Fig. 5 is interpreted as the pitting potential. This finding is also verified by the observed pits on the specimens after the cyclic polarization tests. The parameters extracted from the anodic branch, including corrosion potentials (E_{corr}), passive current densities (i_p), pitting potentials (E_p), and repassivation potentials (E_{rp}), are listed in Table 3. Here all the i_p values are measured at -0.15 V vs. SCE. The repassivation potential (E_{rp}) is defined as the potential at which the current density becomes equal to the passive current density during a cyclic polarization test. The i_p value was approximately two times larger for stages 2 and 3 than that for stage 1, thereby indicating that the passive film degraded after H₂S bubbled through the cell. This result is in accordance with the EIS analysis.

Table 3. Corrosion parameters extracted from the cyclic polarization curves

Condition	$E_{\text{corr}} / \text{V}$	E_p / V	E_{rp} / V	$i_p / (\mu\text{A}\cdot\text{cm}^{-2})$
Stage 1	-0.499	0.338	0.025	0.80
Stage 2	-0.547	-0.053	-0.255	1.96
Stage 3	-0.539	0.134	-0.321	1.66

The corrosion rate of stainless steels in passive state is known to always be under anodic control, i.e., the corrosion rate of stainless steel is mainly controlled by the anodic reaction. Therefore, at the beginning of stage 2, the decreasing diameter of the Nyquist plot indicates the increase in anodic reaction rate. The slight injection of H₂S at the very beginning may not have a considerable influence on the cathodic reaction. As shown in Fig. 5, cathodic reactions did not even show a significant difference at the end of each stage. Accordingly, the OCP variation in stage 2 is mainly attributed to the anodic acceleration effect.

Combined with the EIS and cyclic polarization results, the variation of OCP (Fig. 2) can be illustrated. As illustrated in Fig. 6(a), the ideal anodic and cathodic polarization curves intersect at the corrosion potential, E_{corr1} . The intersection locates in the passive region of the ideal anodic branch 1 due to the absence of an active-passive transition in the actual polarization curves, as shown in Fig. 5. The acceleration of the anodic process results in the increase in current densities, i.e., the anodic branch 1 moves toward the right direction to anodic branch 2. If the cathodic process did not show much difference, then E_{corr2} is much lower than E_{corr1} , i.e., the acceleration of the anodic process results in the negative movement of corrosion potential. In addition, if the pH variation is taken into account at the transition from stage 1 to stage 2, then one can easily infer that the in-

creased pH at the end of stage 2 can also promote the negative movement of corrosion potential, as illustrated in Fig. 6(b). The increasing pH value will decrease the equilibrium potential of the H^+ reduction reaction according to the Nernst equation, which can lead to the downward movement of the cathodic branch. Therefore, E_{corr3} is more negative than E_{corr1} . At the end of stage 3, H_2S was completely removed by CO_2 , which resulted in the slight decrease in pH value and thus the acceleration of the cathodic branch and the increase in OCP (in comparison with stage 2). Moreover, the E_{corr} values listed in Table 3 are more negative than the OCP values shown in Fig. 2(a). However, this difference may be reasonable because E_{corr} was measured after the specimens were cathodically polarized.

Fig. 6. Schematic diagrams of the corrosion potential variation caused by the movement of anodic (a) and cathodic (b) branches.

Obviously, the passive region was much larger in stage 1 than in stage 2, indicating a better pitting resistance of the 316L stainless steel in CO_2 condition. Furthermore, the pitting potential of stage 3 exhibited an anodic shift of 187 mV in comparison with stage 2, although it was still 204 mV lower than in stage 1. To some extent, the difference in the passive region at the end of stage 3 was diminished compared with stage 1. Through a comparison between the passive regions of stages 1 and 3, the deterioration of the passive film can be easily inferred. H_2S has been reported to have a positive effect on the pitting initiation [21]. The presence of H_2S in stage 2 may inhibit the formation of oxides during the anodic polarization process, thereby eventually leading to the thinning and local breakdown of the passive film at lower potentials than in stage 3.

However, some doubt may exist as to whether the irreversibility of passive film damage was not real but rather caused by the change of solution composition or the residual H_2S at the end of stage 3. First, stainless steel 316L in this condition is still of high corrosion resistance. From the passive current density, the highest corrosion rate is roughly

calculated to be $0.023 \text{ mm}\cdot\text{a}^{-1}$, which means that after the entire experiment (300 h), the dissolved metal can increase the solution concentration by only about $5 \times 10^{-7} \text{ mg}\cdot\text{L}^{-1}$ at most. This value is too small to affect the corrosion behavior. Second, in our experience, H_2S will drop to ppm level by bubbling CO_2 for only 10 h. The CO_2 bubbling process was extended to 140 h to remove H_2S as completely as possible. Finally, although the complete removal of H_2S at the end of stage 3 cannot be guaranteed, the H_2S content should be no more than ppm level. The corrosion behavior of stainless steel 316L in trace amounts of H_2S -containing solution should certainly be different from that in the H_2S -saturated condition [1], which is not in agreement with the EIS and cyclic polarization results. Therefore, the irreversibility of corrosion behavior is thought to be related with the deterioration of passive films.

3.3. XPS analysis

XPS analysis was employed to investigate the deterioration of passive films by clarifying the chemical composition of the passive films formed under H_2S -containing conditions.

XPS samples were prepared after 24 h exposure in the air. Then XPS analysis was employed on the samples to investigate the chemical composition of the passive film formed under natural air condition. The other samples were immersed in the corrosive system and then extracted at the end of stage 3. A comparison of the above XPS results can provide information on the evolution of the passive film. Fig. 7 shows the high-resolution spectra for Cr 2p_{3/2} (Fig. 7(a)), O 1s (Fig. 7(b)), and Fe 2p_{3/2} (Fig. 7(c)) recorded on the samples exposed in the air for 24 h. The Cr 2p_{3/2} peak at a binding energy of 576.4 eV can be attributed to Cr₂O₃ [15,22]. The O 1s spectrum shown in Fig. 7(b) is fitted to three peaks,

namely, Fe₂O₃ (529.5 eV), Cr₂O₃ (530.7 eV), and OH⁻ (531.6 eV). The curve fitting in Fig. 7(c) shows that the peak at 710.7 eV is attributed to Fe³⁺ [13]. Combined with the O 1s spectrum, the passive film formed in natural air mainly consists of Fe₂O₃, Fe(OH)₃, and Cr₂O₃. In addition, the XPS results show that the atomic ratio of Fe to Cr is approximately 12, which indicates an enrichment of element Fe in the outer layer. This result is consistent with the current understanding of passive films, which is a bilayer composed of an n-type outer region of iron oxide (Fe₂O₃) and hydroxide near the solution interface and a p-type inner region of chromium oxide (Cr₂O₃) near the metal surface [13].

Fig. 7. XPS spectra of the passive films formed on 316L stainless steel under natural air condition: (a) Cr 2p_{3/2}; (b) O 1s; (c) Fe 2p_{3/2}.

Fig. 8 shows the XPS results of the passive film formed at corrosion potential at the end of stage 3. As shown in Fig. 8(a), the Cr 2p_{3/2} spectrum shows the same peak position as in Fig. 7(a), indicating that the composition of Cr species remains as Cr₂O₃. The O 1s spectrum (Fig. 8(b)) can be separated into three peaks, namely, Fe₂O₃ (529.5 eV), Cr₂O₃ (530.7 eV), and SO₄²⁻ (532.2 eV). The presence of SO₄²⁻ may be due to the partial oxidation of iron sulfides during sample transfer [23]. In comparison with Fig. 7(c), the average peak of Fe shifted toward a more negative binding energy to 709.5 eV. This condition generally indicates the presence of Fe²⁺ [15]. The other two peaks corresponded to

Fe⁰ (706.7 eV) and Fe³⁺ (710.7 eV), respectively. The presence of the metallic states of iron indicates that the passive film is thinner in comparison with the film formed under natural gas conditions [24]. The S 2p_{3/2} spectrum was fitted with one doublet with S 2p_{3/2} at a binding energy of 161.7 eV and one singlet peak component at 167.84 eV corresponding to S₂²⁻ and SO₄²⁻, respectively [23]. The above analysis shows that the passive film formed at the end of stage 3 was composed of Cr₂O₃, Fe₂O₃, FeS₂, and FeSO₄, indicating the sulfidation of passive films. However, the atomic ratio of Fe to Cr is decreased to approximately 1.

Fig. 8. XPS spectra of the passive films formed on 316L stainless steel at the end of stage 3: (a) Cr 2p_{3/2}; (b) O 1s; (c) Fe 2p_{3/2}; (d) S 2p_{3/2}.

The XPS results show a decreasing trend of Fe content in the passive film in the corrosion process. This decreasing trend is attributed to the fact that Fe₂O₃ is less stable than Cr₂O₃. When immersed in H₂S-containing solutions, the Fe species dissolved preferentially. Moreover, the migration of S²⁻ into the passive film can prevent the formation of Fe₂O₃ by forming iron sulfides. Therefore, less Fe₂O₃ was identified on the outer layer from the Fe 2p_{3/2} spectra at the end of stage 3. The schematic diagram of the passive film formed in H₂S-containing solutions is shown in Fig. 9. The continuous depletion of Fe finally resulted in the enrichment of Cr in the passive film. This enrichment might induce the increase in OCP in stage 2 after 81 h.

Fig. 9. Schematic diagram of the passive film formed in H₂S-containing media.

3.4. Mott–Schottky measurements

Mott–Schottky measurements are often used to investigate the semiconductive behavior of passive films. Through this method, the relationship between the passive film composition and its protectiveness can be established. The Mott–Schottky relation is given as [25–27]

$$\frac{1}{C^2} = \pm \frac{2}{eN\epsilon\epsilon_0} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (2)$$

where C is the capacitance of the space charge, ϵ is the dielectric constant of the oxide film ($\epsilon = 15.6$ has been assumed in this study [28]), ϵ_0 is the vacuum permittivity constant (8.854×10^{-14} F·cm⁻¹), e is the electron charge (1.602×10^{-19} C), N is the donor or acceptor density (electron donor concentration for n-type semiconductors or hole acceptor concentration for p-type semiconductors), T is the absolute temperature, k is the Boltzmann constant (1.38×10^{-23} J·K⁻¹), E is the applied potential, and E_{fb} is the flatband potential. The donor or acceptor densities can be calculated from the slope of the experimental C^{-2} vs. E plots. For a p-type semiconductor, C^{-2} versus E should be linear with a negative slope that is inversely proportional to the acceptor density. Conversely, an n-type semiconductor yields a positive slope that is inversely proportional to the donor density.

Fig. 10 presents the Mott–Schottky plots for the passive

films formed on 316L stainless steels at the end of each stage. The plots are qualitatively similar. Therefore, the passive films can be inferred to exhibit the same electronic character regardless of the gas conditions. The passive film of 316L stainless steel showed n-type semiconducting behavior in potential regions A (lower than -0.4 V vs. SCE) and C (higher than -0.08 V vs. SCE), whereas it exhibited p-type behavior in potential region B. The modification of semiconducting behavior of passive films is always related to its composition. As mentioned above, iron oxide in the outer layer shows n-type behavior, and chromium oxide in the inner layer exhibits p-type behavior. Hence, the capacitance response in region A is controlled by the electric structure of iron oxide, while region B is controlled by chromium oxide. The n-type behavior in higher potential region C is probably due to the presence of additional free charge carriers (electrons) from an oxidation reaction [29], for example, S^{2-} to S, or due to the variation of the chemical composition of passive films during the polarization process [1].

Fig. 10. Mott-Schottky plots for 316L stainless steel electrodes immersed in Cl[−]-containing solutions at the end of each stage.

The electron donor concentration (N_d) and hole acceptor concentration (N_a) of the n-type and p-type semiconducting regions of the passive films at each stage were calculated from the slopes of the corresponding linear segments of the Mott-Schottky plots. The results are listed in Table 4. The calculated donor and acceptor densities are of the same order of magnitude (10^{21} cm^{−3}) as those in other studies [30–33]. As seen in Table 4, both N_d and N_a values were higher for stages 2 and 3 than for stage 1, indicating the negative effect of H₂S on the protectiveness of the inner and outer layers.

According to the point defect model (PDM) the electron donors are mainly oxygen vacancies and metal interstitials, whereas the dominated acceptor species are cation vacancies [34–35]. The electronic structure of passive films can be significantly affected by its chemical composition [26].

The presence of different elements in the passive film can either accelerate or suppress the corrosion rate by altering the donor and acceptor concentrations, as reported in Refs. [26] and [36], respectively. The presence of H₂S in solution can increase both N_a and N_d values, as shown in Table 4. On the one hand, H₂S can facilitate the formation of FeS₂ so that the chemical composition of the outer layer is changed. In addition, FeS₂ is known to have a more defective structure than Fe₂O₃, which can lead to the increase in N_d values. On the other hand, the penetration of S^{2-} into the passive film may further aggravate the disordered nature of the passive film. Therefore, the N_d and N_a values increased after immersion in H₂S-containing solutions. Acceptor and donor densities have been reported to increase with increasing conductivity of passive films [37], which implies that high acceptor or donor densities will lead to high values of passive current density. Accordingly, the anodic process was accelerated by the sulfidation of the passive film regardless of the presence or absence of H₂S in stages 2 and 3.

Table 4. Calculated donor and acceptor densities from Mott-Schottky plots at different stages

Stage	N_d / cm ^{−3}	N_a / cm ^{−3}
Stage 1	2.07×10^{21}	1.55×10^{21}
Stage 2	2.99×10^{21}	3.12×10^{21}
Stage 3	3.46×10^{21}	3.00×10^{21}

4. Conclusions

The effect of H₂S on the passive behavior of austenitic stainless steel in Cl[−]-containing solutions was investigated by OCP, EIS, cyclic polarization, XPS, and Mott-Schottky measurements. The conclusions are presented as follows:

(1) The EIS and cyclic polarization results show that the presence of H₂S in solution has an acceleration effect on the corrosion behavior of 316L stainless steel. This effect is not weakened after the removal of H₂S.

(2) The immediate movement of OCP to the negative direction at the transition of Stage 2 was attributed to the acceleration of the anodic process.

(3) The passive film was composed of Cr₂O₃, Fe₂O₃, and FeS₂ after immersion in the H₂S-containing solution.

(4) The presence of sulfides in the passive film increased the acceptor and donor densities and thus resulted in the irreversible deterioration of the passive film.

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