

Investigation of Cathodic Reaction Mechanisms of H₂S Corrosion Using a Passive SS304 Rotating Cylinder Electrode

Yougui Zheng, Jing Ning, Bruce Brown, and Srdjan Nescic
Institute for Corrosion and Multiphase Technology, Ohio University
342 West State Street
Athens, OH, 45701, USA

ABSTRACT

The internal corrosion of pipeline steel in the presence of hydrogen sulfide (H₂S) represents a significant problem in oil and gas industry. Its prediction and control pose a challenge for the corrosion engineers. In previously published research by the same authors, an electrochemical model of H₂S corrosion was developed in both pure H₂S and H₂S/CO₂ aqueous systems. An additional electrochemical cathodic reaction, direct H₂S reduction, was uncovered based upon the carbon steel corrosion experimental results. However, in the carbon steel corrosion experiments, the cathodic sweeps experienced interference by the anodic iron dissolution reaction, making the kinetics of cathodic reactions unclear. In the present study, experimentation was conducted to better resolve the direct reduction of H₂S while minimizing the effect of the anodic reaction by using a passive stainless steel working electrode. The electrochemical kinetics parameters for H₂S reduction (i.e. Tafel slope, exchange current density, and reaction order with H₂S concentration) were determined. Moreover, the electrochemical kinetics parameters for H⁺ reduction were also revisited.

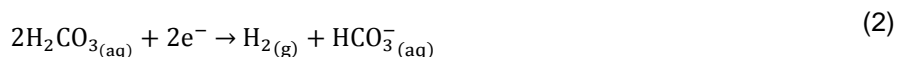
INTRODUCTION

The internal corrosion of pipeline steel in the presence of hydrogen sulfide (H₂S) represents a significant problem in oil and gas industry. Its prediction and control pose a challenge for the corrosion community. The aqueous H₂S corrosion of carbon steel is an electrochemical process occurring at the steel surface. The overall reaction is dependent on the kinetics of different electrochemical reactions, which are composed of two simultaneous electrochemical half-reactions: anodic (oxidation) and cathodic (reduction). The present study is focused on cathodic reactions in H₂S corrosion of carbon steel.

The best known cathodic reaction in aqueous solution is hydrogen evolution or hydrogen ion (H⁺) reduction, Reaction (1), which has been intensely investigated in strong acid solutions with different substrates. The same kinetics has been assumed to hold in both CO₂ and H₂S corrosion models.



When there are other reducible species in an aqueous solution, additional cathodic reactions may occur. In a CO₂ environment, an additional cathodic reaction, the direct reduction of carbonic acid^{1,2}, has been assumed:



However, recent results obtained by Remita *et al.*³ and Tran *et al.*⁴ showed that the direct reduction of carbonic acid is insignificant and the dominant cathodic reaction is the H⁺ reduction on the steel surface. Carbonic acid, produced from a slow CO₂ hydration, only acts as an additional reservoir of hydrogen ions and enhances the mass transport process.

Aqueous H₂S, which is a weak acid, can also act as an additional reservoir of hydrogen ions and promote H⁺ reduction at the metal surface. Moreover, aqueous H₂S is also an excellent electron acceptor⁵, meaning that it is easy for aqueous H₂S to receive electrons and reduce at the steel surface. This occurs due to a strong chemisorption of H₂S on iron via the sulfur atom⁶ which places the hydrogen close to the metal surface and enables conversion of H⁺ to an adsorbed H atom without prior dissociation. The direct reduction of H₂S is written as follows:



Morris, *et al.*⁷ found that a cathodic limiting current density in an acidic solution gradually vanishes as the concentration of H₂S is increased. They concluded that the cathodic reaction process was under activation control and the Tafel slope didn't change with H₂S concentration, staying consistently in the range of 110 - 116 mV/decade.

Kittel, *et al.*⁸ conducted cathodic stationary polarization in a 316L steel rotating disk electrode (RDE) in solutions at pH 4 and pH 5. They observed the additional cathodic reaction for direct H₂S reduction and reported a reaction order to C_{H₂S} close to 0.5 with a Tafel slope of 145 ± 10 mV/decade. A clear discrepancy with the Levich law in the limiting current of H₂S reduction was observed.

In the previous research by the current authors^{9,10}, the direct reduction of H₂S as an additional cathodic reaction was also clearly observed for a carbon steel rotating cylinder electrode (RCE) in an aqueous H₂S corrosion system. The kinetics parameters of this charge transfer reaction were obtained based on carbon steel corrosion experiments. The limiting current density of H₂S reduction was found to be in good agreement with the theoretical values calculated by using the Eisenberg expression. An electrochemical model based on these findings was developed in both pure H₂S and H₂S/CO₂ systems to account for the effect of P_{H₂S}, flow rate, pH, and temperature on H₂S corrosion. However, the cathodic sweeps experienced interference by the anodic reaction of iron dissolution in the carbon steel corrosion experiments. Further investigation on the details of electrochemical kinetics related to an H₂S/iron system is still needed.

Considering the existing discrepancies in the open literature in the electrochemical kinetics parameters for H₂S reduction, a passive SS304 (UNS S30400) rotating cylinder electrode was used in the present work, with the goal to determine these parameters by avoiding the interference by the anodic reaction of iron dissolution. Moreover, the electrochemical kinetics parameters of H⁺ reduction were also revisited.

EXPERIMENTAL

Experimental Methodology

X65 carbon steel was used in the previous studies^{9,10} by the current authors. The electrochemical parameters for H₂S reduction were difficult to determine with accuracy as the charge transfer region for cathodic reactions overlaps with the region where the dominant reaction is the anodic dissolution of iron. Therefore, a passive stainless steel was used here to avoid the interference from the iron dissolution reaction. Figure 1 below shows a reasonable agreement obtained between the cathodic sweeps on the two steels (UNS S30400 and X65) under the same conditions. Based on these results, stainless steel can be considered to be “similar enough” to mild steel as a substrate to study cathodic reactions under these environmental conditions.

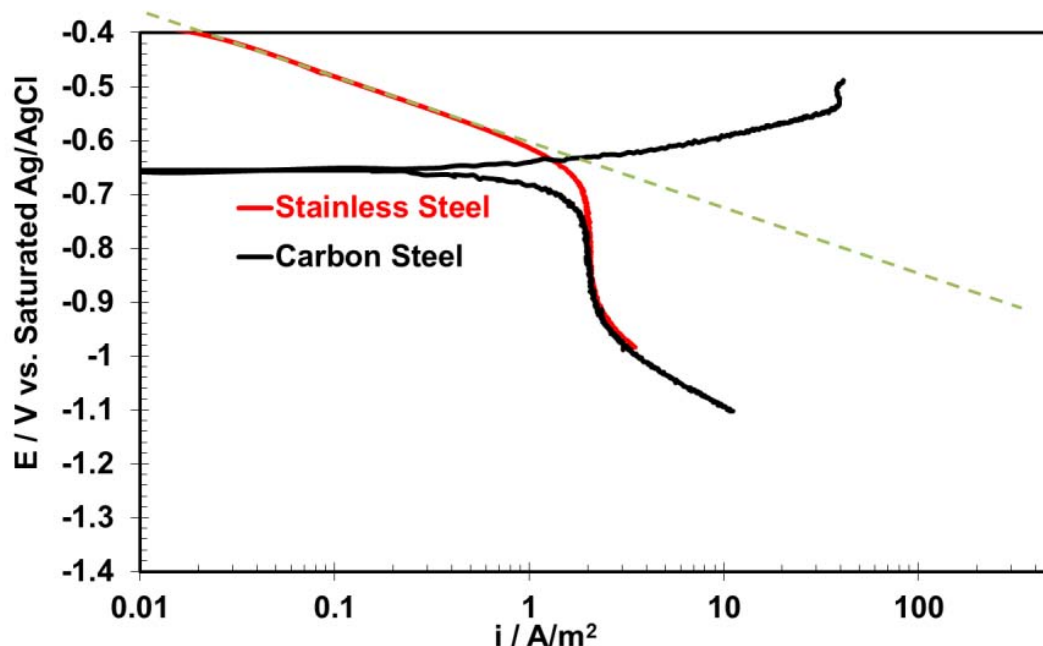


Figure 1. Comparison of the cathodic sweeps obtained on X65 and stainless steel (UNS S30400) at 30°C, pH 4.0, aqueous solution saturated with N₂ with 1 wt% NaCl, RCE rotating speed 1,000 rpm

Experimental Apparatus and Procedure

Experiments were performed in a 2-liter glass cell filled with 1 wt. % sodium chloride (NaCl) electrolyte. The experimental set-up is a typical three-electrode system, which was described in the previous work^{9,10}. The carbon steel RCE was replaced by stainless steel RCE. The test matrix is shown in Table 1.

The aqueous solution was initially deoxygenated by continuously purging N₂ gas for at least 3 hours. After the solution was deoxygenated, H₂S was added to the purge for at least 30 mins to saturate the solution at the required partial pressure of H₂S. The pH was adjusted by adding deoxygenated hydrochloric acid (HCl) or sodium hydroxide (NaOH). Prior to immersion, the cylindrical stainless steel specimen surfaces were polished sequentially with 400 and 600 grit sandpaper, while being cooled simultaneously with isopropyl propanol, then each specimen was cleaned with isopropyl propanol in an ultrasonic cleaner and dried with an air blower.

All the experiments were performed at room temperature (30 ± 1 °C). Cathodic sweeps started after the OCP stabilized within ± 1 mV over a period of five minutes or more, scanning from the OCP in the negative direction with a scan rate of 1 mV/s. The EIS measurements were conducted mainly to get the solution resistance and corrected the cathodic sweeps results.

Table 1. Test matrix for electrochemical experiment using stainless steel electrode

Description	Parameters
Material	SS 304 (UNS S30400) Rotating Cylinder Electrode
Solution	1 wt% NaCl Solution
Purged Gas (H ₂ S volume fraction in H ₂ S/N ₂)	0 -10%(v) (0 – 0.1 bar)
Rotating Speed	1000 rpm
Total Pressure	1 bar
Temperature	30°C
pH	3, 4, 5, 6
Measurement Methods	EIS, Potentiodynamic Sweeps

EXPERIMENTAL RESULTS

Investigation of H⁺ reduction without H₂S

Hydrogen ions (H⁺) always exist in an aqueous solution, so the reduction of H⁺ is the most important cathodic reaction in acidic environments. To differentiate H₂S reduction from the H⁺ reduction reaction, the electrochemical kinetics of H⁺ reduction was investigated first.

Figure 2 shows the cathodic experimental sweeps measured on a SS304 RCE in solutions at different pH. Except for the experiment at pH 6, all the potentiodynamic sweeps show a well-defined current plateau due to H⁺ reduction, followed by a water reduction in the lower potential range. At pH 6, the cathodic sweep appears almost as a straight line; no mass transfer-limiting current plateau was observed. That is because the contribution of H⁺ reduction vanishes and most of the cathodic current is from direct water reduction. From pH 3 to pH 5 in testing where the pH was incrementally increased by 1 unit, the limiting current decreased by a factor of 10, which is also in good agreement with the theoretical values calculated by using the Eisenberg expression. This is evident that H⁺ reduction is a mass transfer limiting reaction.

The general expression for the charge current density for H⁺ reduction without considering a temperature effect is:

$$i_{H^+} = i_{H^+ ref} (C_{H^+})^{\alpha_{H^+}} 10^{\left(\frac{-E}{b_{H^+}}\right)} \quad (4)$$

Where: α_{H^+} is the reaction order, C_{H^+} is the hydrogen ion concentration, mol/L; E is the electrode potential, and b_{H^+} is the cathodic Tafel slope, and $i_{H^+ ref}$ is the reference H^+ reduction current at reference conditions of 1 mol/L H^+ concentration, 0 V (SHE) electrode potential and 30 °C reference temperature.

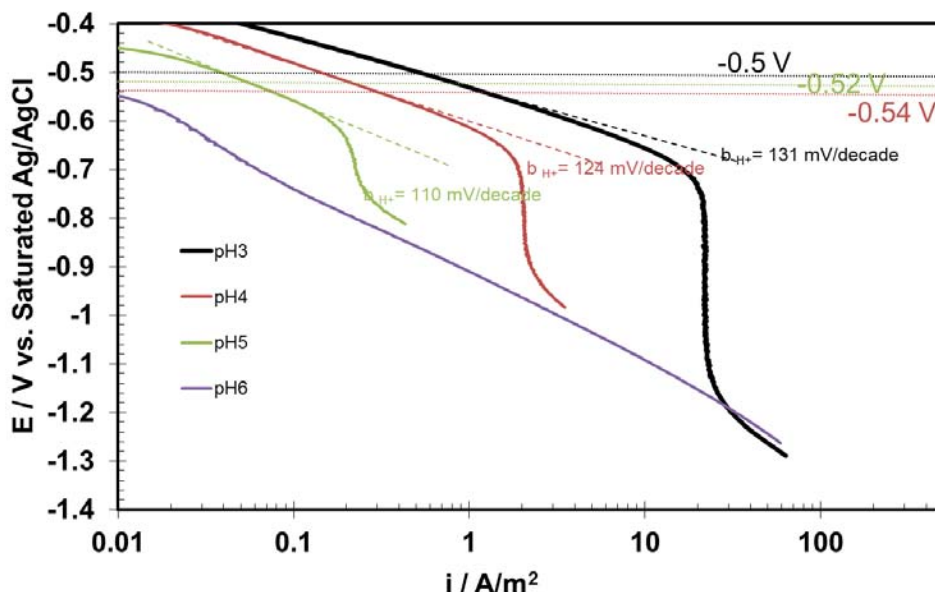


Figure 2. Comparison of the cathodic sweeps obtained on stainless steel (UNS S30400) at various pH, 30°C, 1 wt% NaCl aqueous solution saturated with N_2 , RCE rotating speed 1,000 rpm, 1 bar total pressure. The dashed lines are trend lines by linear regression to get the Tafel slopes of H^+ reduction. The dotted lines are used for the charge current density at different potentials and for the determination of reaction order.

Tafel slope b_{H^+} was obtained from the linear regression of the charge transfer control region of the sweep (-0.48 to -0.5 V) related to H^+ reduction at different pH values, shown in Figure 2. The measured Tafel slope was 121 ± 11 mV/decade. These results agreed well with the findings by Bockris, *et al.*¹¹ and Stern, *et al.*¹² along with the theoretical calculation of $2.303 RT/(0.5F)$ as well.

In order to find the reaction order with respect to H^+ concentration, α_{H^+} , three dotted lines, representing different electrode potential (-0.50 V, -0.52 V and -0.54 V vs Sat. Ag/AgCl) in the charge control region, were drawn to obtain the current density for H^+ reduction. When pH is increased by 1 unit, the charge transfer current density for H^+ reduction decreased approximately 3 times. The log values of the current density were plotted versus pH value (Figure 3). The linear regression was applied to these data and shows the reaction order to be between 0.57 and 0.60. Considering the error and the simplification, the reaction order for H^+ order was taken as 0.5, expressed by the equation:

$$\left(\frac{\partial \log i_{H^+}}{\partial pH} \right)_E = -0.5 \quad (5)$$

This reaction order agrees with the measurements from Tran *et al.* and Kittel *et al.*⁸ on stainless steel electrodes and with Stern *et al.*¹² on an iron electrode. It is different from the measurement by Bockris, which was also used by Nescic *et al.*¹³ for a CO_2 corrosion model and Zheng *et al.*^{9,10} for an H_2S

corrosion model. Given by Bockris's experimental results¹¹, $\frac{\partial \log i_{0,H^+}}{\partial pH} = -0.5$ (i_{0,H^+} is the exchange current density at the equilibrium potential), Nescic *et al.*¹³ derived the expression for H⁺ reduction current density:

$$i_{H^+} = i_{H^+ ref} \left(\frac{C_{H^+}}{C_{H^+ ref}} \right)^{0.5} 10^{\left(\frac{-(E-E_{rev})}{b_{H^+}} \right)} \quad (6)$$

Here $C_{H^+ ref}$ is the reference concentration as 10^{-4} mol/L and the reversible potential $E_{rev} = -\frac{2.303RTpH}{F}$, and $b_{H^+} = \frac{2.303RT}{0.5 * F}$. Combining all the expressions, Equation (6) becomes:

$$i_{H^+} = i_{H^+ ref} \left(\frac{C_{H^+}}{C_{H^+ ref}} \right)^{0.5} C_{H^+}^{0.5} * 10^{\left(\frac{-E}{b_{H^+}} \right)} = i_{H^+ ref} * 100 * C_{H^+} * 10^{\left(\frac{-E}{b_{H^+}} \right)} \quad (7)$$

This equation shows that the reaction order for the H⁺ ion concentration at a fixed potential is 1, which is different from current results. With careful examination of the Bockris' results, the determination of the exchange current density was questionable. One can argue that it is not accurate to extract the Tafel line from the polarization curves on an iron electrode without any modification of the experiments, such as increasing limiting current density by either increasing flow rate or by adding more buffer acid to the solution. Actually, Stern *et al.*¹² added citric acid or malic acid to the solution and observed higher limiting current density, making their results more convincing.

After the Tafel slope and reaction order of H⁺ concentration were determined, the reference current density ($i_{H^+ ref}$) was calibrated to be 0.045 A/m² at 30 °C. Considering the temperature effect with Arrhenius equation using 30 kJ/mol activation energy from public literature, the reference current density $i_{H^+ ref}$ would be 0.03 A/m² at 20 °C and 0.041 at 25 °C, which is slightly smaller than 0.05 at 25°C used for carbon steel corrosion model by Nescic *et al.*¹³, but slightly higher than 0.03 at 25 °C used in the current Freecorp* software¹⁴.

* Trade Name

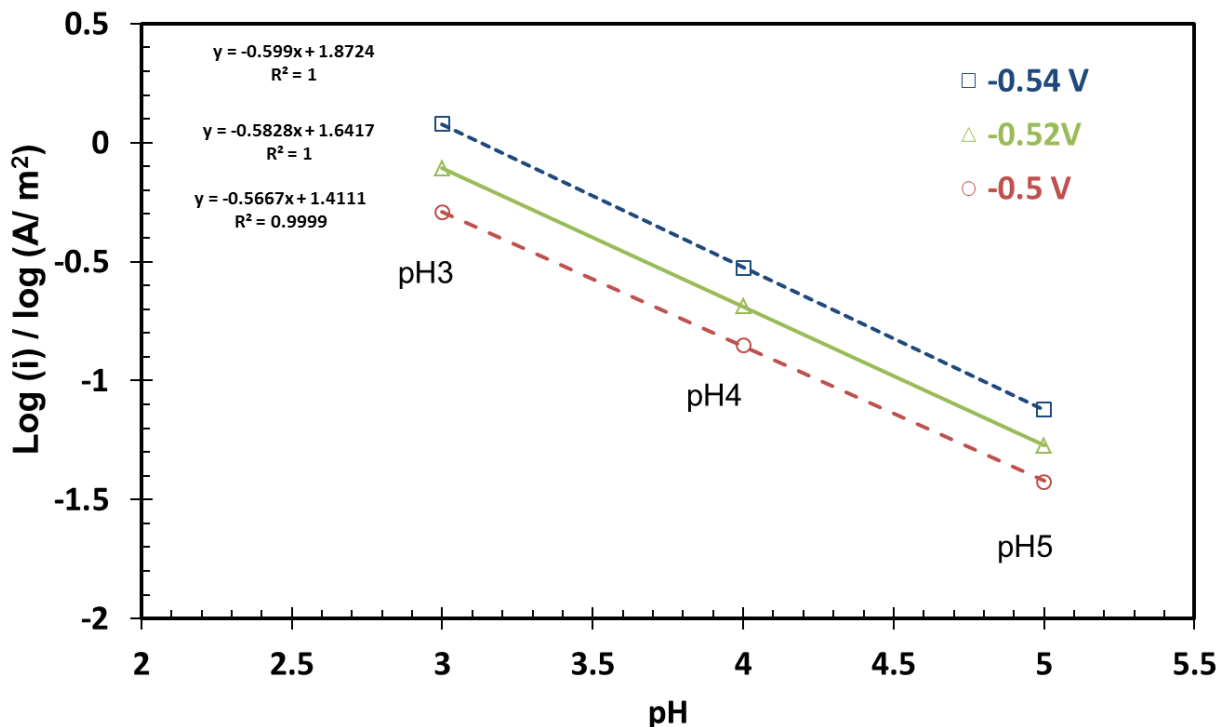


Figure 3. Plot of the log values of the H⁺ reduction current density with the pH of the solution, 30°C, 1 wt% NaCl aqueous solution saturated with N₂, RCE rotating speed 1,000 rpm, 1 bar total pressure. The lines are trend lines by linear regression.

Investigation of electrochemical kinetics of H₂S reduction

After H⁺ reduction kinetics has been investigated, the electrochemical kinetics parameters related to H₂S reduction are addressed in this section.

The first question to be asked is: whether there truly is a direct reduction of H₂S on the steel surface. Although this question has been answered by Kittel *et al.*⁸ using stainless steel RDE and Zheng *et al.*⁹ using carbon steel RCE, it is still meaningful to confirm this answer in the present study using stainless steel RCE. It can be hypothesized that if there is a direct reduction of H₂S on the steel surface, the charge-current should increase with an increase of H₂S concentration. Figure 4, Figure 5, and Figure 6 show comparison of cathodic potentiodynamic sweeps at different pH_{H₂S} (0 to 0.1bar) and different pH (pH 4 to pH 6).

At pH 4 and pH 5 (Figure 4 and Figure 5, respectfully) the addition of H₂S didn't increase the charge transfer current, rather it appears to have a small retardation on charge transfer current which may be related to the chemical adsorbed layer of H₂S on the steel surface. This small effect could be also just due to experimental error and needs further investigation. At pH 5, it was observed that the addition of 1000 ppm H₂S gas modified the cathodic polarization curve. A second wave appears at more cathodic potentials, which was apparently due to the direct reduction of H₂S on the steel surface. Therefore, the only explanation for the lack of increase in the charge transfer current after the introduction of H₂S is that the increase was too small and within the experimental error; the dominant cathodic reaction at these conditions remained H⁺ reduction. This explanation was proven to be right from the potentiodynamic sweep measurements at pH 6 (Figure 6). At pH 6, the contribution from H⁺ reduction was so small that even with the addition of a low concentration of H₂S (100 ppm or 1000 ppm), the increase of the charge current was easily observed. These experiments clearly indicated that there was a direct reduction of H₂S on the steel surface.

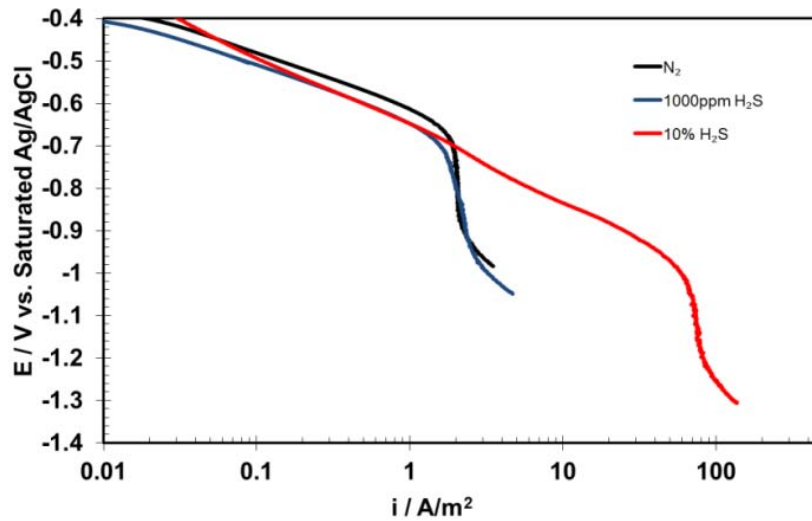


Figure 4. Comparison of the cathodic sweeps obtained on stainless steel (UNS S30400) in the 1 wt% NaCl aqueous solution saturated with different gas concentration of H₂S/N₂, 30°C, pH 4.0, RCE rotating speed 1,000 rpm, 1 bar total pressure.

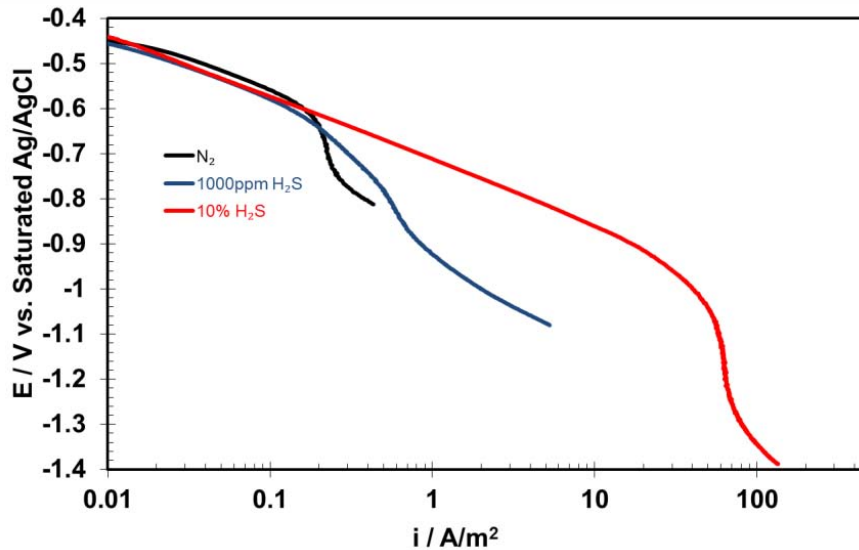


Figure 5. Comparison of the cathodic sweeps obtained on stainless steel (UNS S30400) in the 1 wt% NaCl aqueous solution saturated with different gas concentration of H₂S/N₂, 30°C, pH 5.0, RCE rotating speed 1,000 rpm, 1 bar total pressure.

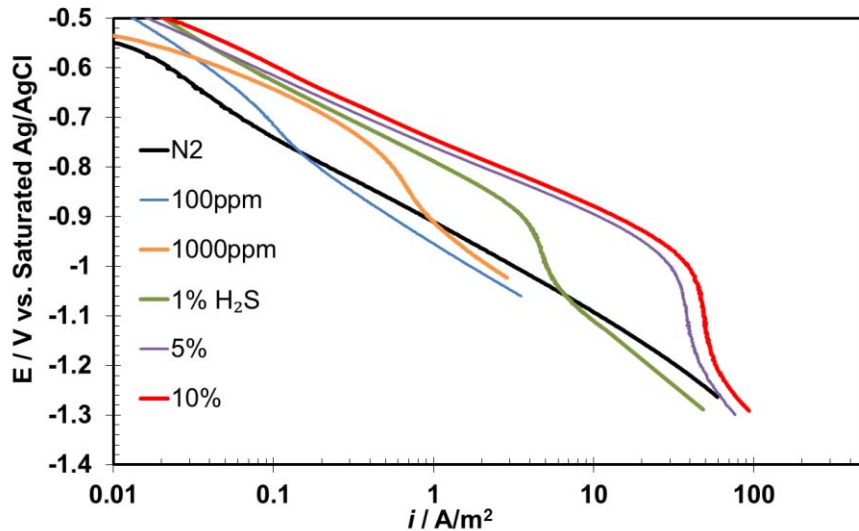


Figure 6. Comparison of the cathodic sweeps obtained on stainless steel (UNS S30400) in the 1 wt% NaCl aqueous solution saturated with different gas concentration of H₂S/N₂, 30°C, pH 6.0, RCE rotating speed 1,000 rpm, 1 bar total pressure.

The second question is related to the mass transfer rate for the reaction involving direct reduction of H₂S. In Zheng *et al.*'s study⁹ on carbon steel corrosion, the measured values of mass transfer limiting current density agreed very well with the calculation of mass transfer rates by Eisenberg correlation using an RCE. However, in Kittel *et al.*⁸ and Tribollet *et al.*'s research¹⁵, the measured limiting current density of H₂S reduction was lower than the calculation by the Levich law. One of their suspicions was related to the use of different materials: carbon steel vs. stainless steel. Assuming the limiting currents of H⁺ reduction and H₂S reduction are additive, Table 2 shows the comparison between the calculated and measured limiting current density. The calculated limiting current densities are in a good agreement with the measured limiting currents within a 15% error.

Table 2: Comparison between calculated and experimental limiting current density at different pH and gaseous H₂S concentrations (1 bar total pressure).

Gaseous H ₂ S concentration	Measured limiting current density [†] (A/m ²)	Calculated limiting current density (A/m ²)
pH4		
0	2±10%	1.90
1000 ppm	2.05±10%	1.95
10%	60±10%	53.0
pH5		
0	0.18±10%	0.19
1000 ppm	0.52±10%	0.60
10%	54±10%	51.4
pH6		
0	0.02±30%	0.019
100 ppm	0.1±20%	0.079
1000 ppm	0.5±10%	0.53
1%	5±10%	5.14
5%	32±10%	25.62
10%	50±10%	51.22

[†] Note: the uncertainty of the "Measured limiting current density" was determined from the potentiodynamic sweep data.

The general expression for the charge current density for H₂S reduction without considering temperature effect is:

$$i_{H_2S} = i_{H_2S_{ref}} (C_{H_2S})^{\alpha_{H_2S}} 10^{\left(\frac{-E}{b_{H_2S}}\right)} \quad (8)$$

Where: α_{H^+} is the reaction order C_{H_2S} is the H₂S concentration, mol/L; E is the electrode potential, and b_{H_2S} is the cathodic Tafel slope, $i_{H_2S_{ref}}$ is the reference current density at reference conditions: 1 mol/L aqueous H₂S concentration, 0 V (SHE) electrode potential and 30 °C temperature.

Similarly, Tafel slope b_{H_2S} was obtained by linear regression in the charge transfer control region of the potentiodynamic sweeps, related to H₂S reduction at different pH, as shown in Figure 7. The measured Tafel slope was 135 ± 5 mV/decade, which is a little higher than the theoretical calculated value for H⁺ reduction, $2.303 RT/(0.5F)$.

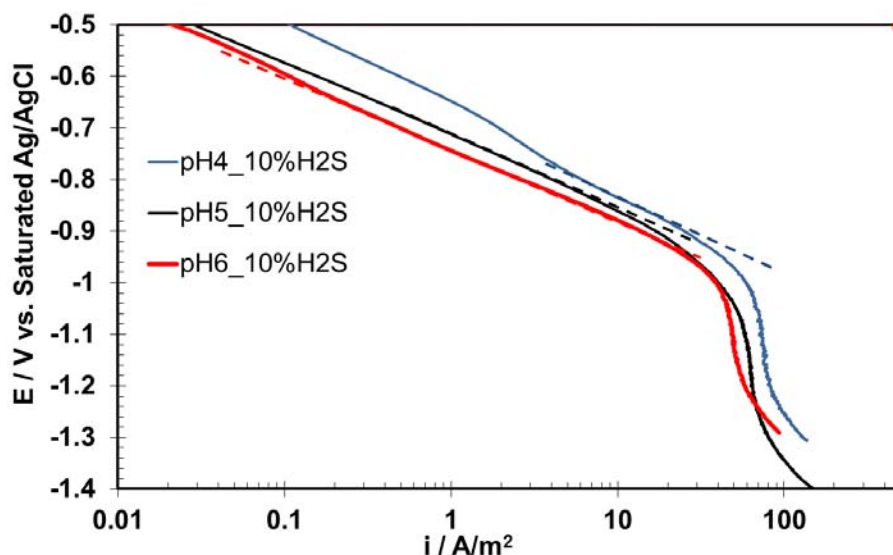


Figure 7: Comparison of the cathodic sweeps obtained on stainless steel (UNS S30400) at various pH, 10% H₂S, 30°C, 1 wt% NaCl aqueous solution saturated with N₂, RCE rotating speed 1,000 rpm, 1 bar total pressure.. The dashed lines are trend lines by linear regression to get the Tafel slopes of H₂S reduction.

The reaction order of H₂S concentration was also obtained from the charge region of the cathodic sweep at different H₂S concentrations at pH 6. The results are shown in Figure 8. The reaction order is between 0.18 and 0.23, which is different from the previously reported value of 0.5.

Finally, the reference current density of H₂S reduction was calibrated to be close to 0.0001 A/m² at 30°C.

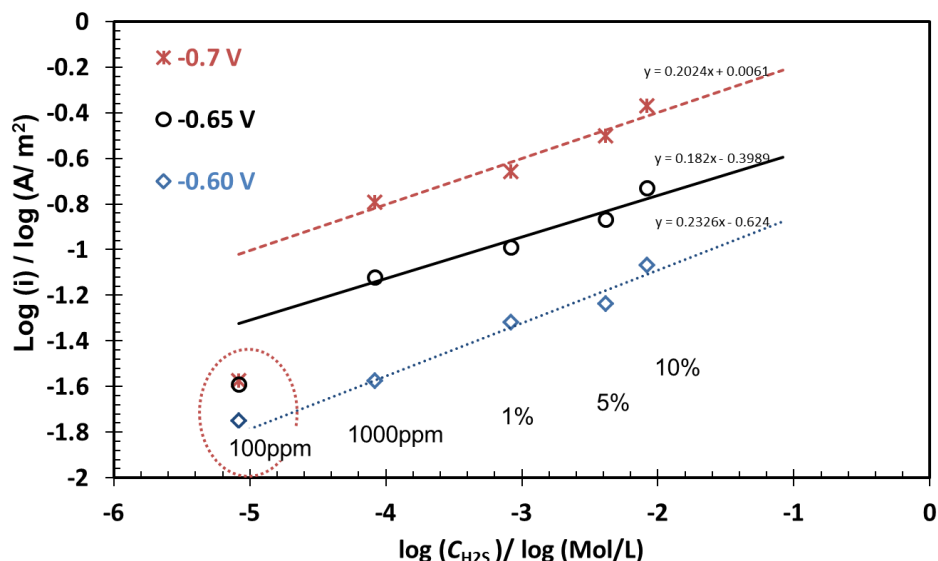


Figure 8. Plot of the log values of the H₂S reduction current density with the pH of the solution, 30°C, 1 wt% NaCl aqueous solution saturated with different gas concentrations, RCE rotating speed 1,000 rpm, 1 bar total pressure. The lines are trend lines drawn by linear regression. The data at 100 ppm was not used for the regression.

CONCLUSIONS

Direct reduction of H₂S in an aqueous systems has been confirmed. Tafel slope for direct reduction of H₂S is 135±5 mV/decade, which is a little higher than the theoretical calculated value for H⁺ reduction, 2.303 RT/(0.5F). Other electrochemical kinetics parameters for both H⁺ reduction and direct H₂S reduction were obtained in this study, shown by the following two equations at 30 °C:

$$\text{H}^+ \text{ reduction: } i_{H^+} = 0.045(C_{H^+})^{0.5} 10^{\left(\frac{-E}{b_{H^+}}\right)}$$

$$\text{H}_2\text{S reduction: } i_{H_2S} = 0.0001(C_{H_2S})^{0.2} 10^{\left(\frac{-E}{b_{H_2S}}\right)}$$

Measured mass transfer limiting currents agree with the calculated values by using standard correlations.

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