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Hydrogen evolution in aqueous solutions containing dissolved H₂S: Evidence of direct electroactive contribution of H₂S.

J. Kittel, F. Ropital, F. Grosjean

*IFP Energies nouvelles, Rond-point de l'échangeur de Solaize BP3, 69360 Solaize,
France*

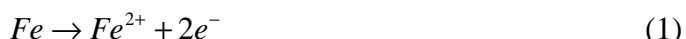
E.M.M. Sutter, B. Tribollet

*Laboratoire Interfaces et Systèmes Electrochimiques, UPR 15 du CNRS, 75252
Paris Cedex 05*

This paper compares the cathodic reactions occurring on steel in an oxygen-free aqueous solution containing dissolved H₂S or dissolved CO₂. It is well admitted that the rate of the cathodic reaction is enhanced in aqueous solutions containing dissolved CO₂, in comparison with strong acid solutions at the same pH [1-6]. In a previous paper [7], the authors have shown that this phenomenon appears only in the mass transfer limitation region, where the transport of carbonic acid is added to the transport of proton. In the case of H₂S containing solutions, this chemical mechanism is no more sufficient to explain the cathodic polarization curves. An additional electrochemical reaction is clearly observed, with strong links with H₂S concentration.

Introduction

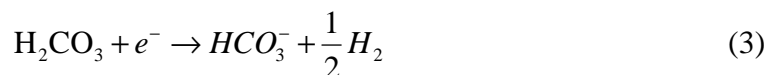
Corrosion in oil and gas environments very often involves water with dissolved CO₂ and H₂S. Once dissolved in water, both CO₂ and H₂S behave like weak acids. As such, they are able to provide oxidizing power and promote iron corrosion, establishing an equilibrium between oxidation and reduction reactions:



The most common reduction reaction in de-aerated acid media is proton reduction:

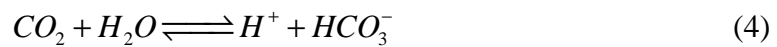


However, additional reactions might take place. This subject has been widely discussed for CO₂, starting several decades ago [1,3-5,8-12]. One particular aspect with CO₂ corrosion is the fact that it is usually enhanced in comparison with strong acid solutions at the same pH. This trend is extremely well established, in particular in the oil and gas industry. However, this mechanism remains poorly understood. Two major theories coexist to explain this additional corrosivity in carbonic acid solutions. Until very recently, the most common assumption consisted in considering that carbonic acid could be reduced:



This cathodic reaction would thus be added to the proton reduction (2), thereby increasing the global cathodic current.

However, recent results obtained by the author's showed that the additional cathodic current could entirely be explained by mass transport and chemical kinetics [7]. The model that was described contains one unique charge transfer reaction (2), while the mass transfer limitation contains the diffusion of H^+ and the diffusion of the weak acid (dissolved CO_2) from the bulk of the solution. Quantitatively, for a pH level and CO_2 partial pressure (P_{CO_2}) typical of oil and gas fields, the transport of acidity at the steel surface is attributed in majority to CO_2 rather than to H^+ : e.g. at ambient temperature under 1 bar CO_2 at pH 4, CO_2 concentration in pure water is 3.3×10^{-2} mol/L, while H^+ concentration is only 10^{-4} mol/L. Thus, CO_2 provides an additional source of protons at the steel surface by transport of CO_2 from the bulk followed by the chemical dissociation reaction:



This dissociation reaction has a slow kinetics: it represents the rate determining step for the CO_2 contribution, rather than CO_2 transport itself.

The same kind of chemical contribution has been demonstrated recently for acetic acid [13].

To our knowledge, only few papers in the literature describe the cathodic reactions in water containing dissolved H_2S . In the 60's, Bolmer proposed a direct reduction reaction as [14]:



Polarization tests were conducted in stagnant condition in near neutral solutions containing different amount of H_2S and HS^- . Bolmer noticed Tafel slopes between 115 mV and 55 mV depending on HS^- concentration. Mass transfer limitation was also observed, but it could not be interpreted quantitatively.

In the eighties, Morris et al. used a carbon steel rotating disc electrode (RDE) to study corrosion in aqueous H_2S systems of acid pH [15]. They concluded that H_2S did not modify the cathodic process in the activation region, but they noticed also that the H^+ diffusion control disappeared gradually with H_2S .

Measurements in controlled turbulent flow conditions were reported by Galvan-Martinez et al. [16], with a rotating cylinder made of carbon steel. They examined the hypothesis of a direct H_2S reduction according to Equation (5), but they noticed that the corrosion potential lied in a region where the cathodic current was under H^+ mass transfer limitation.

Another mechanism of H_2S contribution was proposed by Shoesmith et al. These authors stated that the corrosion reaction of iron with H_2S occurred mainly by a solid state reaction, via the global reaction scheme [17]:



This reaction is still adopted in most of experimental work on iron corrosion in the presence of H_2S , considering that the formation of a protective mackinawite scale is the main parameter for corrosion control, rather than electrochemical kinetics [10,18].

Other studies dealt with cathodic reactions in H₂S containing solutions, but they were focused on the impact of H₂S on hydrogen recombination or charging in the steel, causing embrittlement [5,19-23].

The main objective of this paper is to examine the nature of the impact of H₂S on the cathodic reactions in acidic solution. It will be compared with the reference case of CO₂.

Experimental

Experiments were performed using a 316L rotating disc electrode (RDE). The working electrode surface was polished with 1200 grit paper before each experiment.

The supporting electrolyte was a 0.01M K₂SO₄ solution. Before each experiment, this solution was de-aerated by purging N₂ for at least 2 hours. The solution was then saturated with H₂S at different concentration, by purging N₂ and H₂S with different ratios, from 0.1% H₂S to 5 % H₂S, corresponding respectively to a partial pressure of H₂S (P_{H₂S}) equal to 1 mbar and 50 mbar, or to 10⁻⁴ mol/L to 5x10⁻³ mol/L of dissolved H₂S.

The pH of the test solution was then adjusted to target value between 4 and 6 by KOH or H₂SO₄ addition. Test solution transfer from the preparation tank to the de-aerated electrochemical cell was realized without contacting the solution with air, to avoid any reaction of dissolved H₂S with oxygen, and prevent oxygen reduction contribution.

All experiments were carried out at room temperature (23 +/- 2°C) using a conventional three-electrode cell. A standard Ag/AgCl and a large platinum grid were used as reference and counter electrodes, respectively. The equipment for electrochemical measurement was a Biologic SP200 potentiostat monitored with EC-Lab software. Potential sweeps were performed at a rate of 1 mV/s.

Results and discussion

Theoretical approach

In a very similar manner as the theoretical approach developed for CO₂ in [7], we can propose a simple buffer model for H₂S, consisting in the following reactions and processes:

- transport of H⁺ and H₂S from the bulk to the steel surface
- H₂S dissociation:
$$H_2S \rightleftharpoons H^+ + HS^- \quad (7)$$
- reduction of proton (2)

Quantitatively, in comparison with CO₂, one expects H₂S to be a much more effective reservoir of proton. Indeed, the kinetics of H₂S dissociation is thought to be several orders of magnitude higher than that of CO₂ [11]. Qualitatively, such buffer effect should increase the value of the current plateau at large cathodic overpotential, while the kinetic region under charge transfer control should not be modified in comparison with a strong acid solution at the same pH. If this model is true, the aspect of the stationary cathodic curves should not differ between CO₂ and H₂S. Both should contain only one cathodic Tafel slope, associated with the proton reduction (2). At high cathodic overpotential, where the mass transfer is the limiting step, the current plateau should increase by a greater amplitude with H₂S than with CO₂, due to the higher dissociation rate constant.

On the other hand, if a second reduction reaction with H₂S happened as proposed by several authors, an additional Tafel slope should be observed in the cathodic polarization curves.

These two hypothesis are compared to the experimental measurements in the next section of this paper.

Results and discussion

Typical cathodic experimental stationary polarization curves measured on the 316L steel RDE in solutions at pH 4 and with or without 9 mbar H₂S are presented in Figure 1.

In the absence of H₂S, the polarization curve is characteristic of the proton reduction, followed by water reduction at the lower cathodic potential. A well defined current plateau is observed, which can be ascribed to the mass transport of proton, since it follows strictly the Levich expression:

$$J_{\text{lim},H^+} = 0.62 \times F \times C_{H^+_{\text{bulk}}} \times D_{H^+}^{2/3} \times \nu^{-1/6} \times \Omega^{1/2} \quad (8)$$

where J_{lim,H^+} is the diffusion limited current for H⁺ reduction, F is the Faraday constant (96500 C/mol), $C_{H^+_{\text{bulk}}}$ is the bulk concentration of protons, D_{H^+} is the diffusion coefficient of H⁺, ν is the kinematic viscosity of the liquid, and Ω is the angular rotation speed of the electrode.

The addition of 9 mbar H₂S modifies considerably the polarization curves. A second wave appears at more cathodic potential, which should be attributed to the electroactivity of H₂S. Similar observations were made recently at more acidic pH and with carbon steel rotating cylinder devices, showing also an electrochemical activity of H₂S [24].

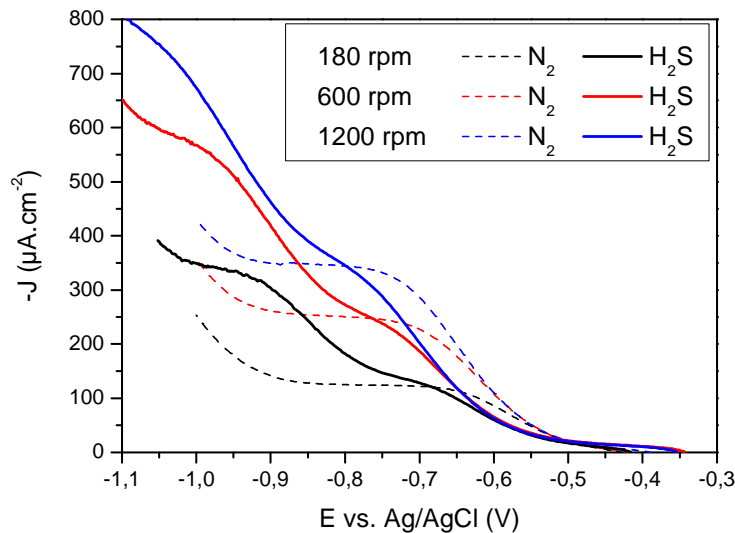


Figure 1 : Stationary cathodic polarization curves measured with a RDE at pH 4 in N₂ purged solution or in H₂S saturated (9 mbar) solution.

In order to characterize in more details the electrochemical reaction associated with H_2S , additional experiments were performed in less acidic solutions, or with different $P_{\text{H}_2\text{S}}$. The corresponding polarization curves are presented in Figure 2 and Figure 3, respectively.

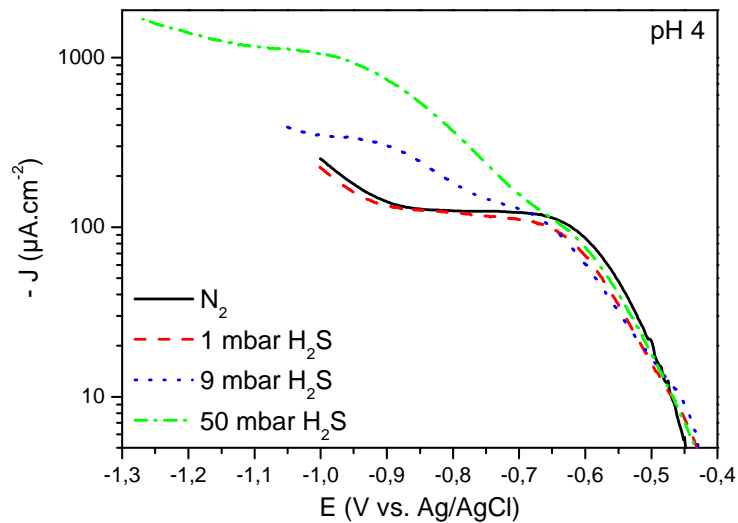


Figure 2: Stationary cathodic polarization curves measured with a RDE at 180 rpm in de-aerated solution containing different amount of H_2S at pH 4.

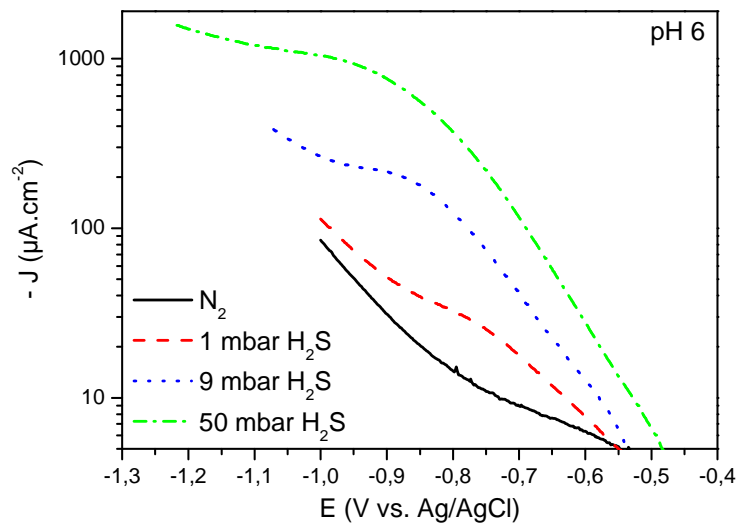


Figure 3: Stationary cathodic polarization curves measured with a RDE at 180 rpm in de-aerated solution containing different amount of H_2S at pH 6.

In the presence of dissolved H_2S , an additional cathodic contribution appears on the polarization curves.

At pH 4, and for $P_{\text{H}_2\text{S}}$ between 1 mbar and 50 mbar, the additional electrochemical reaction associated with H_2S takes place in the potential domain of the mass transport limitation of the proton (Figure 2). With 1 mbar H_2S , the additional contribution is masked by the proton reduction. However, at 9 mbar and 50 mbar H_2S , the second cathodic reaction is well defined,

and its current increases with P_{H_2S} . The cathodic current associated with the proton reduction does not seem to be strongly affected by the presence of H_2S .

At pH 6 and without H_2S , the contribution of H^+ reduction to the global current rapidly vanishes and most of the cathodic current is associated with water reduction.

In the presence of dissolved H_2S , the cathodic contribution of the polarization curves can thus mostly be attributed to H_2S (Figure 3). Even though the plateau is not extremely well defined, the limiting current seems to be proportional with the H_2S concentration. The impact of H_2S on the kinetic part could also be estimated from the results at 9 mbar and 50 mbar of H_2S , which present a linear region at low overpotential. From the values of the cathodic current at -0.6 V vs. Ag/AgCl, the order of the reaction with C_{H_2S} could be estimated as:

$$\frac{\partial \log(J_{0,H_2S})}{\partial \log(C_{H_2S})} \approx 0.5 \quad (9)$$

This reaction order is equivalent to that of the exchange current density of proton reduction in similar environments, as already mentioned by several authors [5,7,23]:

$$\frac{\partial \log(J_{0,H^+})}{\partial \log(C_{H^+})} \approx 0.5 \quad (10)$$

A more detailed analysis of the limiting current is proposed on Figure 4 and Figure 5. For the experiments at pH 6 and with 50 mbar H_2S , the values of the limiting current density measured at -1.05 V vs. Ag/AgCl were plotted versus the square root of the electrode rotation rate (Figure 5). In the same figure, the theoretical mass transport limiting current for H_2S calculated with the Levich expression (11) was also plotted for comparison.

$$J_{lim,H_2S} = 0.62 \times F \times C_{H_2S_{bulk}} \times D_{H_2S}^{2/3} \times \nu^{-1/6} \times \Omega^{1/2} \quad (11)$$

with J_{lim,H_2S} the diffusion limited current for H_2S reduction, $C_{H_2S_{bulk}}$ the H_2S concentration in the bulk of the solution (5×10^{-3} mol/L for $P_{H_2S} = 50$ mbar), and D_{H_2S} the diffusion coefficient of H_2S (1.6×10^{-5} cm²/s [11]).

It appears quite clearly in Figure 5 that the experimental data stay below the theoretical line, and that the difference between the measured and the calculated values seems to increase with the rotation speed. The current limitation is then not just caused by H_2S transport, but might also contain an additional contribution, maybe of chemical nature.

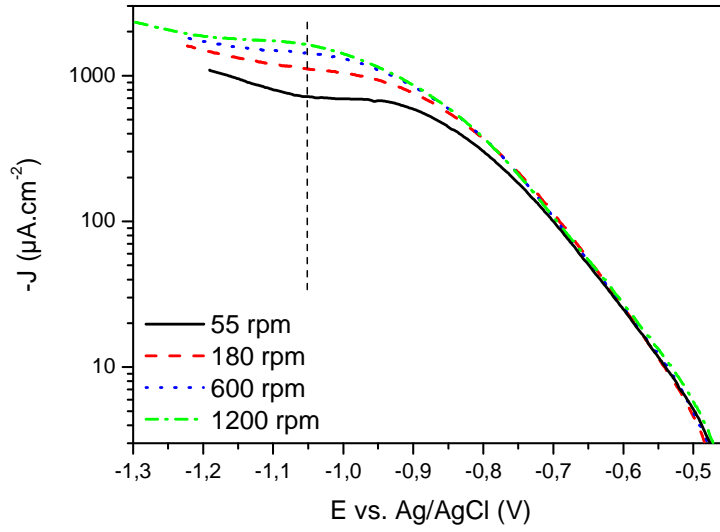


Figure 4: Experimental stationary cathodic polarization curves measured with a RDE at different rotation speed in de-aerated solution containing at pH 6 with 50 mbar H_2S .

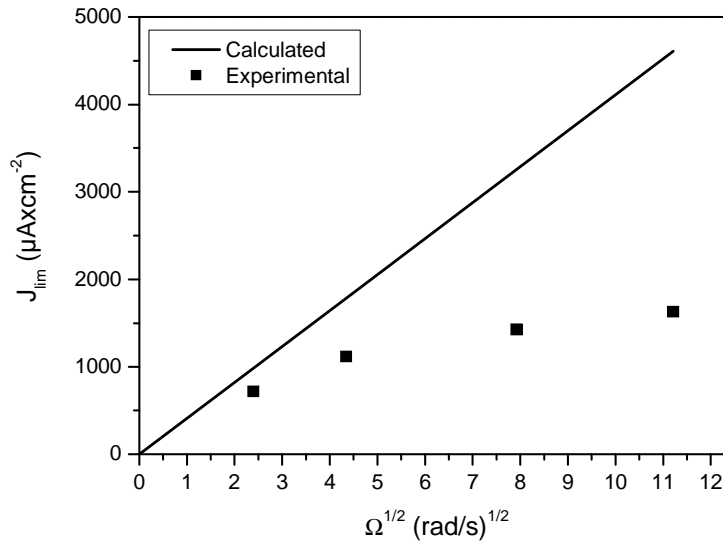


Figure 5: Evolution of the limiting cathodic current with the rotation speed of the electrode in de-aerated solution containing at pH 6 with 50 mbar H_2S .

After the analysis of the plateau region, we examined the apparent kinetic part of the polarization curves related to the reduction reaction involving H_2S . In order to correct for the mass transfer limitation, the Tafel correction was applied in the low overpotential region to calculate the kinetic current density as:

$$J_{k,H_2S} = \frac{J \times J_{lim,H_2S}}{J_{lim,H_2S} - J} \quad (12)$$

where J_{k,H_2S} is the kinetic part of the cathodic current density and J is the global measured current density.

The results are plotted in Figure 6 for different rotation rates, for the experiments at pH 6 and with 50 mbar H₂S. An excellent agreement is found between the different sets of results, and an apparent Tafel slope equal to 152 ± 10 mV is derived. This high value suggests that even for the results of Figure 4, the linear part of $\log(J)$ vs. E is not under pure activation control, but contains an additional contribution. At this stage, it is not possible to precisely define this contribution, but cathodic current due to water and residual H⁺ reduction might have an influence, as well as some residual O₂ reduction in case of small O₂ pollution of the system. A rough estimation of the additional contribution to H₂S reduction could be made from the measurements in pure H₂SO₄ at pH 6 in Figure 3. In the linear region used for the Tafel analysis, between -0.55 and -0.75 mV vs. Ag/AgCl, the residual reduction current due to H⁺, H₂O and other species in the solution varies from 5 to 20 $\mu\text{A}/\text{cm}^2$. This results in an overestimation of the Tafel slope with Equation (12). Unfortunately, the reproducibility of the measurements in strong acid solution at pH 6 was not sufficient to perform a correction of the measured current in Equation (12). Nevertheless, a Tafel value of 120 mV for H₂S is likely, similar to that of the proton reduction.

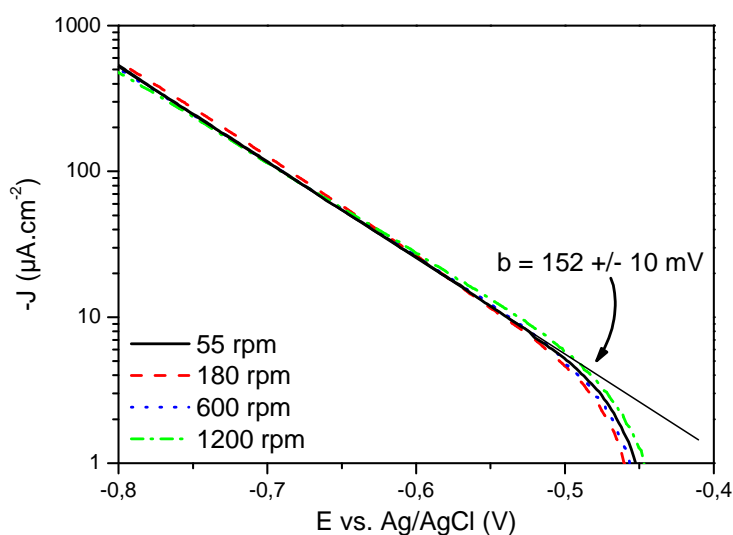


Figure 6 : Tafel plots of the kinetic part of the cathodic current (J_k) in pH 6 solution saturated with 50 mbar H₂S.

Conclusions

The hydrogen evolution reaction in an oxygen free solution with dissolved H₂S is radically different than with dissolved CO₂, even though both dissolved gases are weak acids with comparable solubility and pKa. With dissolved CO₂, proton reduction is the main cathodic reaction. Dissolved CO₂ only contributes to increase the current density in the mass transfer control potential range by a chemical buffer effect. In this potential domain, the transport of the weak acid is added to the transport of proton, and additional interfacial acidity is provided by the weak acid dissociation.

On the contrary, the results presented in this paper demonstrate that the buffer effect is not sufficient to explain the cathodic polarization curves measured in solutions with dissolved

H₂S. An additional cathodic reaction was clearly observed. Although our results did not allow to characterize completely this electrochemical reaction, some apparent features could be determined. This reaction presents strong links with H₂S concentration. The reaction order with C_{H₂S} seems to be close to 0.5. A cathodic current plateau was also observed at high cathodic overpotential, but the relationship with H₂S diffusion was not straightforward. At low cathodic overpotential, a Tafel region was observed, with an apparent slope value of 152 ± 10 mV, suggesting also that the system was not strictly under activation control.

The detailed mechanism of H₂S reduction requires more work to be completely described. Nevertheless, this work emphasizes the fact that weak acids can present extremely different contribution to electrochemical reactivity of the solution. For applications in the petroleum industry, materials testing is very often done in buffered solutions. A better knowledge of the nature of the buffer contribution, either purely chemical like CO₂, or chemical and electrochemical like H₂S, would be of great importance to this community.

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