

Electrocatalysis of the hydrogen evolution reaction by thermally formed sulfides on steels

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The electrocatalytic activity of sulfides, formed by thermal sulfidization of various commercially available steels, for the cathodic evolution of hydrogen from sodium chloride is dealt with in this paper. The effects of certain surface active anions on the hydrogen evolution reaction on these sulfidized steels have also been studied.

It has been shown that sulfidization of carbon steels and silicon steels increases their electrocatalytic activity with respect to cathodic hydrogen evolution and thereby reduces the overpotential in sodium chloride solutions (typically about 100 - 150 mV at 0.5 A cm⁻²).

The anomalously high Tafel slopes observed for h.e.r. on steels during brine electrolysis is explained as due most probably to the presence of a hydride film on the steel surface at high cathodic potentials. A comparison of the hydrogen overpotentials and corrosion currents reveals that carbon steels—both in their plain and sulfidized forms—are better cathodes for brine electrolysis.

Key words: Hydrogen evolution, sulphide steel, galvanostatic polarisation

INTRODUCTION

In recent years, increasing attention has been directed towards reducing the overpotential for the hydrogen evolution reaction (h.e.r.) which is a common cathodic reaction in industrial electrolytic processes. In addition to having a low hydrogen overpotential (η_H), a cathode should be constructed from materials that are inexpensive, easy to fabricate, mechanically strong and capable of withstanding the environmental conditions in the electrolytic cell. Iron and steels have been the traditional materials used for commercial cathode fabrication, e.g. in the chlor-alkali industry. Efforts to decrease η_H on steels have generally been focussed on improving the catalytic effect of the steel surface or providing a larger effective surface area. This paper presents a comparative study of some commercially available steels, both in their plain and sulfidized forms, as cathodes in 30% NaCl solutions with and without additives (5g l⁻¹ of Na₂MoO₄ or Na₂Cr₂O₇).

EXPERIMENTAL

The following commercially available steels have been employed in the present study: cold rolled low-carbon steel (IS 513), cold rolled high-carbon steel (IS 7226), cold rolled grain oriented silicon steel, CRGO (AISI:M-8), cold rolled nongrain oriented silicon steel, CRNGO (AISI:M-14), hot rolled nongrain oriented silicon steel, HRNGO (AISI:M-

22) and stainless steel (ASTM 304).

The working electrodes were rectangular pieces of geometrical area 7.18 cm², cleaned and degreased according to procedures described elsewhere [1]. The reference electrode used was Hg₂Cl₂/30% NaCl. Thermal sulfidization of the steels was effected by dipping clean specimens of the steels in molten sulfur at 523 ± 5K for 15 minutes. The excess unreacted sulfur on the steel surface was removed by dipping in a 20% solution of NaOH for one hour. The specimens were then washed thoroughly with water and dried.

STEADY-STATE CATHODIC GALVANOSTATIC POLARIZATION IN SODIUM CHLORIDE SOLUTIONS

The steady-state cathodic galvanostatic polarization curves of the steels in the various solutions are characterized by the three regions marked I, II and III in Fig. 1 which shows typical curves for IS 513 and IS 513-S in 30% NaCl. Region I corresponds to that around E_{corr}. II is the region corresponding to the "low" c.d. range. Region III covers the "high" c.d. range.

Further, the Tafel slope for the region II is unusually high (500 - 1000 mV). The Tafel slope for region III is also high, typically 200 - 250 mV (Table I).

Table II shows that the E_{corr} of the plain and sulfidized

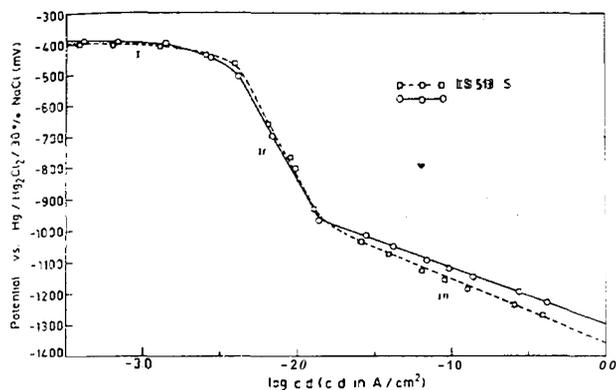


Fig. 1: Typical steady-state cathodic galvanostatic polarization curves of IS 513 and IS 513-S in 30% NaCl

steels are in the range of -0.3 V to -0.45 V vs the reference. Assuming a concentration of about 10^{-3} M for Fe^{2+} ions in solution,

$$E_{\text{Fe}}^r \sim -0.77 \text{ V vs Hg/Hg}_2\text{Cl}_2/30\% \text{ NaCl.}$$

At a pH of 6.5 and at a partial pressure of 1 atmosphere for H_2 ,

$$E_{\text{H}}^r \sim -0.66 \text{ V vs Hg/Hg}_2\text{Cl}_2/30\% \text{ NaCl.}$$

If the above values of E_{corr} , E_{Fe}^r and E_{H}^r are taken into account, it follows that (i) E_{corr} is a mixed potential sustaining the dissolution of iron and oxygen reduction reaction. (ii) a significant concentration of Fe^{2+} ions is likely to be present in the solution contacting the working electrode for some time. (iii) h.e.r. can (and will) occur only on cathodic polarization of the working electrode in region III (iv) deposition of iron will occur at increasing rates concurrently with h.e.r. in region II until the limiting current is reached corresponding to the bulk concentration

TABLE-I: Tafel slopes (mV) for h.e.r. at high c.d. for plain and sulfidized steels (pH = 6.5 ± 0.1 ; T = $343 \pm 1 \text{ K}$)

Solution	300 g NaCl/l		(300g NaCl + 5g Na_2MoO_4)/l		(300g NaCl + 5g $\text{Na}_2\text{Cr}_2\text{O}_7$)/l	
	Plain	-S	Plain	-S	Plain	-S
IS 513	202	180.5	185	152	194	120
IS 7226	200	184	208	191	170	159
CRGO	248.5	252.5	229	234.5	222	192
CRNGO	246.5	254	252	241.5	241.5	171
HRNGO	254	221.5	251	245	245	182
ASTM 304	235	240.5	258	270	244	251

--S denotes sulfidized sample

IS 7226	-344	-340	-332	-352	-308	-332
CRGO	-354	-368	-346	-342	-336	-356
CRNGO	-342	-348	-362	-383	-332	-344
HRNGO	-387	-395	-364	-358	-360	-383
ASTM 304	-292	-294	-286	-289	-272	-272

E_{cor} : $\pm 1 \text{ mV, min}^{-1}$ after one hour waiting time

TABLE-III: Exchange current densities ($A.cm^{-2}$) for h.e.r. on plain and sulfidized steels
(pH = 6.5 ± 0.1 ; T = $343 \pm 1K$)

Solution	300g NaCl/l		(300g NaCl + 5g Na ₂ MoO ₄)/l		(300g NaCl + 5g Na ₂ Cr ₂ O ₇)/l	
	Plain	-S	Plain	-S	Plain	-S
IS 513	3.89×10^{-4}	3.16×10^{-4}	3.80×10^{-4}	1.82×10^{-4}	3.47×10^{-4}	7.76×10^{-5}
IS 7226	3.16×10^{-4}	2.75×10^{-4}	5.62×10^{-4}	5.62×10^{-4}	2.69×10^{-4}	4.17×10^{-5}
CRGO	1.20×10^{-3}	1.58×10^{-3}	1.58×10^{-3}	1.41×10^{-3}	5.75×10^{-4}	5.45×10^{-4}
CRNGO	1.55×10^{-3}	8.51×10^{-4}	2.04×10^{-3}	2.09×10^{-3}	1.38×10^{-3}	4.68×10^{-4}
HRNGO	1.10×10^{-3}	7.76×10^{-4}	2.51×10^{-3}	2.75×10^{-3}	3.02×10^{-3}	9.77×10^{-4}
ASTM 304	2.29×10^{-5}	2.29×10^{-5}	6.31×10^{-5}	1.02×10^{-5}	1.38×10^{-5}	1.45×10^{-5}

of Fe²⁺ ions under the given conditions of stirring, and (v) the end of region II marks the limiting current region for the deposition of iron. Beyond this region, that is in region III, h.e.r. will occur exclusively—as evidenced by visible and vigorous hydrogen evolution and conspicuous disappearance of a brown iron oxide/hydroxide film on the cathode.

Based on the reasoning above, it can be concluded that the Tafel slopes for h.e.r. on the steel is obtained in the region III. Correspondingly, i_0 for h.e.r. (Table III) and i_{cor} have to be obtained by back extrapolation of only the "high" c.d. Tafel line to E_H^r and E_{cor} respectively. The "low" c.d. Tafel line is, therefore, not a Tafel line—it being only a distorted limiting current region comprising of mainly the deposition of iron with some contribution from h.e.r.

ANOMALOUS TAFEL SLOPES

The question to be resolved now is that of the Tafel slope in the region III which is typically between 200 mV

and 250 mV. In such cases, where an unusually high Tafel slope is obtained, the anomaly has been attributed to the experimentally observed surface films, presumably semiconducting (e.g. [2-5]). If η is the total overpotential and η_f the overpotential across the film, it can be shown [5] that the Tafel slope for the cathodic process is

$$\frac{\partial \eta}{\partial \log i} = -2.3 RT/\beta n F [1 - (d\eta_f/d\eta)] \quad (1)$$

It is clear that the values of about 200-250 mV for the present experimental Tafel slopes may be obtained if η_f is between 0.40η and 0.52η . This interpretation is different from that of Meyer [4] who considers activation barriers of equal "height" in series for one act of the overall reaction which, however, appears quite unlikely.

A close observation of the cathode surface at high c.d. shows a gray-black layer which disappears on standing. This is presumably due to a semiconducting/insulating hydride films or hydrogen embrittled surface layer on the steel.

TABLE-IV: Logarithm of corrosion currents ($A.cm^{-2}$) for plain and sulfidized steels
(pH = 6.5 ± 0.1 ; T = $343 \pm 1K$). In parantheses are presented the F.O.M.

Solution	300g NaCl/l		(300g NaCl + 5g Na ₂ MoO ₄)/l		(300g NaCl + 5g Na ₂ Cr ₂ O ₇)/l	
	Plain	-S	Plain	-S	Plain	-S
IS 513	-5.21(5)	-5.00(4)	-5.17(5)	-5.36(4)	-5.27(4)	-5.97(4)
IS 7226	-5.01(4)	-5.21(5)	-4.92(3)	-4.94(3)	-5.48(5)	-6.07(5)
CRGO	-4.02(1)	-4.99(3)	-4.10(3)	-4.32(2)	-4.74(3)	-4.92(2)
CRNGO	-4.42(3)	-4.09(1)	-4.95(2)	-3.90(1)	-4.17(2)	-5.26(3)
HRNGO	-4.09(2)	-4.32(2)	-3.94(1)	-3.90(1)	-3.78(1)	-4.61(1)
ASTM 304	-6.53(6)	-6.47(6)	-5.78(6)	-5.66(6)	-5.95(6)	-5.71(6)

TABLE-V: Potentials (mV) vs Hg/Hg₂Cl₂/30% NaCl for h.e.r. at a c.d. of 0.5 A.cm⁻² (pH = 6.5 ± 0.1; T = 343 ± 1K). In parantheses are given the F.O.M.

Solution	300 g NaCl/l		(300g NaCl + 5g Na ₂ MoO ₄)/l		(300g NaCl + 5g Na ₂ Cr ₂ O ₇)/l	
	Plain	-S	Plain	-S	Plain	-S
IS 513	624(5)	569(6)	572(4)	519(5)	610(3)	454(5)
IS 7226	609(6)	572(5)	599(2)	561(3)	549(4)	444(6)
CRGO	712(2)	629(3)	569(5)	569(2)	694(2)	564(2)
CRNGO	679(3)	634(2)	597(3)	569(2)	610(3)	511(3)
HRNGO	672(4)	616(4)	541(6)	524(4)	549(4)	493(4)
ASTM 304	1658(1)	1678(1)	1698(1)	1732(1)	1648(1)	1683(1)

RELATIVE CORROSION BEHAVIOUR OF THE STEELS

A perusal of Tables II and IV reveals that the silicon steels are more prone to corrosion than of the carbon steels and that stainless steel is the least prone. Added chromate shifts E_{cor} to more positive values. But the expected inhibitory action of molybdate ion is not supported by the above data. Probably, the adsorption of molybdate ion is weak.

RELATIVE ELECTROCATALYTIC PERFORMANCE FOR H.E.R.

It can be seen from Tables III and V that all sulfidized steels show lower η_H compared to their unsulfidized counterparts (except in the case of ASTM 304). Chromate ion aids in the reduction of η_H more than molybdate ion. The maximum lowering of η_H is obtained when a sulfidized steel is employed in a chromate added electrolyte (the exception being ASTM 304-S).

As may be seen from Table V, the electrocatalytic performance of the various steels for h.e.r. follows the general trend carbon steels > silicon steels > stainless steels.

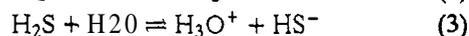
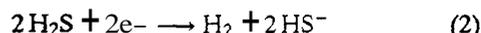
EFFECT OF SULFIDIZATION OF THE STEELS ON THE OVERPOTENTIAL FOR R.E.R.

Sulfidization does not have any effect on the η_H on stainless steel. This probably is an indication that under the present conditions of sulfidization, the protective film on the steel remains impervious to attack by molten sulfur on the metallic components of the steel.

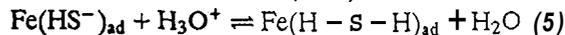
At the c.d. of 0.5 A.cm⁻² the decrease in η_H due to sulfidization for carbon steels and silicon steels is of the order of 40 to 80 mV in plain NaCl solution, between 0

and 50 mV in molybdate added solution and about 50 to 150 mV in chromate added solution. There is apparently a role for chromate ion in the kinetics of h.e.r.

The role of sulfidization in lowering the overpotential for h.e.r. may be explained as follows. The sulfidized steels have a layer of iron sulfide on them. During cathodic polarization a film of iron sulfide gets reduced to H₂S which readily gets adsorbed on the steel surface. The H₂S moiety can now be reduced in HS⁻ through one of the following reactions:



The HS⁻ species now get chemisorbed on the steel surface. An interaction ensues between the HS⁻ ions on the metal surface and H₃O⁺ ions in solution resulting in the formation of a catalyst: the molecular surface complex Fe(H-S-H)_{ad} [6]. Upon cathodic polarization, the protons of this complex are reduced to hydrogen atoms, some of which may recombine while others diffuse into the metal causing hydrogen embrittlement.



After the reduction of proton from the complex, the HS⁻ ions are regenerated on the metal surface and once again the molecular surface complex is formed according to reaction (5).

The steps (4) and (5) are quasi-reversible and proceed faster than step (6) which is the one that determines the general rate of the cathodic process [6,7].

TABLE-VI: Comparison of the "figures of merit" for the various steels

Steel	Plain		Sulfidized		Total F.O.M.	
	F.O.M. w.r.t. η_H	F.O.M. w.r.t. i_{cor}	F.O.M. w.r.t. η_H	F.O.M. w.r.t. i	Plain	-S
IS 513	12	14	16	12	26	28
IS 7226	12	13	14	13	25	27
CRGO	9	7	7	7	16	14
CRNGO	9	7	7	5	16	12
HRNGO	14	4	12	4	18	16
ASTM 304	3	18	3	17	21	20

COMPARATIVE PERFORMANCE OF STEELS -

Taking i_{cor} as a measure of the tendency of steels to corrode in a given medium and η_H at 0.5 A.cm^{-2} as a measure of the electrocatalytic behaviour of the steels, a "figure of merit" (F.O.M.) can be assigned to each steel in a given medium to strike a balance between these two opposing requirements. The F.O.M. w.r.t. η_H (Table V) is assigned as follows: since the steel with the lowest η_H has the highest electrocatalytic activity for h.e.r., the highest value for the F.O.M. is assigned to that steel. As the η_H value increases, the F.O.M. value decreases. Similarly, since the least corroding cathode system is the most desirable, the steel that has the lowest corrosion current is assigned the highest value for the F.O.M. and vice versa (Table VI). Adding the numerical values of the "figures of merit" for the electrocatalytic activity as well as those for the corrosion behaviour, and taking the total F.O.M. as an index of the usefulness of the steels as cathodes in brine electrolysis, the following trend is obtained: carbon steels > silicon steels > stainless steel. The steels with the highest figures of merit are the best among the ones studied.

CONCLUSION

Thermal sulfidization of steels is a convenient method of modifying the surface of steels to achieve a reduction in hydrogen overpotential in brine electrolysis. The anomalously high Tafel slopes for h.e.r. on steels during brine electrolysis is possibly due to the presence of a "hydride" film on the steel surface at high

cathodic potentials. The carbon steels exhibit greater electrocatalytic activity than the silicon steels and stainless steel.

The best performance is obtained with sulfidized steels in chromate-containing brine solution. Except for stainless steel, all steels show a reduction of hydrogen overpotentials on sulfidization. A comparison of the hydrogen overpotentials and the corrosion currents reveals that carbon steels (both in their plain and sulfidized forms) are better suited to be employed as cathodes in brine electrolysis.

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