**Supporting Information**

# Improvement of hydrogen permeation barrier performance by iron sulphide surface films

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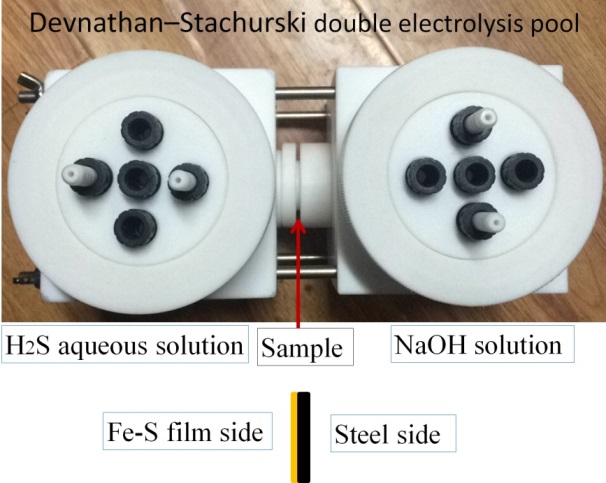


Fig.S1. Devnathan–Stachurski double electrolysis pool.



Fig.S2. Macroscopic photographs of prepared Fe–S films on steel.



Fig.S3. Permeation curves of bare steel in H2S environment at 18°C.

## The calculation of hydrogen diffusion coefficient using time lag method

Assuming that hydrogen diffuses in one dimension perpendicular to the surface of the sample, the hydrogen diffuses in the sample in accordance with Fick’s law.

 （S1）

where *D* is the hydrogen diffusion coefficient, and *c*(*x, t*) is the concentration distribution function of hydrogen in steel. Assuming that the initial hydrogen distribution in the sample is uniform, the hydrogen concentration on the hydrogen charging side of steel increases to *C*0 at *t* = 0, and then remains stable at a certain value. At the hydrogen evolution side of steel, the hydrogen concentration remains 0, and the hydrogen concentration distribution in the sample must meet the following conditions:

Initial conditions: *t* = 0；*c*(*x*,0) = 0；

Boundary conditions: *t* > 0; *c*(0, *t*) = C0, *c*(*L*,*t*) = 0;

From the above initial and boundary conditions, *D* can be obtained:

 (S2)

where *t*0.63 is the time when the instantaneous hydrogen permeation current reaches 0.63 times the steady-state hydrogen permeation current, which is labeled as *tL*, also known as lag time, and the unit is s. *L* is the thickness of the sample the unite of which is cm. The steady-state hydrogen permeation current density *i*max is obtained from the measured hydrogen permeation curves. The steady-state hydrogen diffusion flux *J*∞

(S3)

The Faraday constant *F* = 96485 C·mol–1, which is the electron transferred during the reaction *n* = 1. Hydrogen permeability can be calculated using formula 4.

 (S4)

The adsorption of hydrogen (Capp.) on the surface of the sample can be calculated using formula 5:

*C*app*=*  (S5)

The basic reactions occurred in the steel–H2S–H2S system

(i) Ionization reaction of H2S [52]:

(S6)

(S7)

(S8)

H2S dissolves in water to generate H+ and HS- ions in the first ionization process. Then, HS- ions undergo secondary ionization to form H+ and S2–. and K*i* (*i* = 1, 2) are the solubility constants and ionization constants for H2S, respectively.

(ii) Anode reactions: the dissolution of iron in acidic solution [53–54]:

(S9)

(S10)

(S11)

(S12)

(S13)

(S14)

where FeSH–ads and FeSHads are adsorbed mesophases, k*i* (*i* = 1, 2, 3, 4) is the equilibrium constant, and FeSads is the adsorbed amorphous FeS. These reactions represent the active dissolution of iron based on the intermediate product FeSads adsorbed on the surface.

(iii) Cathode reaction [53]:

(S15)

(S16)

(S17)

The cathode reactions are constituted by a series of depolarization processes involving H2S, HS-, and H+. The H+ ions generated by the ionization of H2S are ultimately reduced to H2.