



## New hypotheses for hydrogenase implication in the corrosion of mild steel

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### ABSTRACT

The influence of [Fe]-hydrogenase from *Clostridium acetobutylicum* was studied on the anaerobic corrosion of mild steel. Two short-circuited mild steel electrodes were exposed to the same solution and hydrogenase was retained on the surface of only one electrode thanks to a dialysis membrane. The galvanic current and the electrode potential were measured as a function of time in order to monitor the difference in electrochemical behaviour induced by the presence of hydrogenase. A sharp potential decrease of around 500 mV was controlled by the deoxygenating phase. When hydrogenase was introduced after complete deoxygenation, significant heterogeneous corrosion was observed under the vivianite deposit on the electrode in contact with hydrogenase, while the other electrode only showed the vivianite deposit, which was analysed by MEB and EDX. The effect of hydrogenase was then confirmed by monitoring the free potential of single coupons exposed or not to the enzyme in a classical cell after complete deoxygenating. In both phosphate and Tris–HCl buffers, the presence of hydrogenase increased the free potential around 60 mV and induced marked general corrosion. It was concluded that [Fe]-hydrogenase acts in the absence of any final electron acceptor by catalysing direct proton reduction on the mild steel surface.

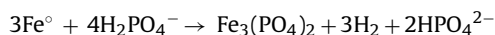
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### 1. Introduction

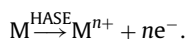
Corrosion costs 4% of the GNP of industrialized countries out of which 10% are due to biocorrosion [1]. It is now commonly agreed that sulfate-reducing bacteria and thiosulfate-reducing bacteria (SRB/TRB) are the main causes of anaerobic microbially influenced corrosion (MIC) [2–6]. Many mechanisms have been proposed to explain anaerobic MIC by SRB and TRB: precipitation of iron sulphide, which next catalyses proton reduction into molecular hydrogen and acts as a cathode in a galvanic couple with metallic iron; anodic depolarization resulting from the local acidification at the anode [7]; possible production of corrosive phosphides containing metabolite PH<sub>3</sub> that enhances the dissolution of metal under anaerobic conditions [8]; metal ion complexation by extra cellular polymer substances [9]; diminution of the pH and metabolism of reducing thiosulfate to sulphide [10].

The involvement of hydrogenases, which are either present in bacteria or free in solution, remains subject to many debates. While it has been claimed that a hydrogenase negative strain of SRB was more corrosive than hydrogenase positive strains [11], other studies have demonstrated that there is a direct correlation between the presence of hydrogenase in SRB and corrosion [12]. The same

authors found that hydrogenase increased the corrosion rate when used in a phosphate solution and proposed the following chemical reaction between steel and phosphate ions [13]:

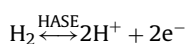


Also, the ability of hydrogenases from *T. roseopersicina* and *L. modestohalophilus* to oxidize metals even without the need for a mediator has been confirmed [14]:



Moreover, it has been claimed that [Ni–Fe]-hydrogenase from *Ralstonia eutropha* is an effective trigger of mild steel corrosion when used in phosphate solution with no need for a mediator [15,16].

Hydrogenases are enzymes that catalyse the reversible oxidation of molecular hydrogen:



They are divided into three groups according to the composition of their active site: [NiFe]-, [Fe]- and transition metal free hydrogenases [17,18]. The [NiFe]- and [Fe]-constitute the vast majority and both contain a binuclear metal active site. The [NiFe]-hydrogenases have a minimum of two subunits: the catalytic site that contains the active site, and the electron transferring subunit that contains one or more iron–sulfur centres. The [Fe]-hydrogenases may be constituted by only one subunit, which may include the catalytic

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and electron transferring domains [19]. [Fe]-hydrogenases are known to have 100 times more  $H_2$  production specific activity than [NiFe]-hydrogenases [20], therefore a [Fe]-hydrogenase from *Clostridium* was chosen here, suspecting that it might be more effective in MIC than the [NiFe]-hydrogenase studied previously. The aim of this work was to determine the possible influence of this enzyme on anaerobic MIC of mild steel. In the first phase of the study, two short-circuited mild steel electrodes were exposed to the same phosphate solution and hydrogenase was retained on the surface of only one electrode thanks to a dialysis membrane. It was expected that the galvanic current between both electrodes gives a measure of the electrochemical disturbance induced by the presence of hydrogenase on the surface of one electrode only. In the second phase, experiments were conducted with a single electrode in order to avoid any disturbance due to the deoxygenating phase. The influence of the buffer solutions phosphate and Tris-HCl and possible mechanisms were discussed. The surface deposits on the electrodes were examined and the influence of the buffer was also investigated.

## 2. Experimental

### 2.1. Chemicals and biochemicals

Sodium dihydrogenophosphate was purchased from Prolabo, tris(hydroxymethyl) aminomethane from Acros Organic, sodium dithionite and desthiobiotine from Sigma. *Clostridium acetobutylicum* cultures and hydrogenase preparation were carried out at the LISBP as reported elsewhere [21].

### 2.2. Electrochemical measurements

Working electrodes were 2 cm diameter cylinders of XC45 mild steel purchased from Thyssen (elemental composition by weight

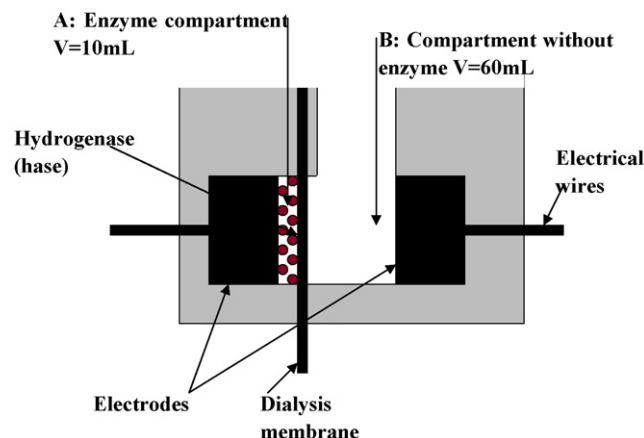


Fig. 1. Scheme of the galvanic cell.

percentage: 0.46 C, 0.31 Si, 0.65 Mn, 0.01 P, 0.032 S, 0.1 Cr, 0.1 Ni, 0.02 Mo, 0.05 Al, and 0.11 Cu) embedded in resin (Resipoly Chryсор). Electrical connection was made through titanium wire protected with resin. Coupons were polished successively with SiC papers of P120, P180, P400, P800, P1200, P800/2400, and P1200/4000 grit (Lam Plan) and rinsed thoroughly with distilled water.

The galvanic cell was composed of two compartments separated by a dialysis membrane (Cellu Sep T4 12–14 kDa) as shown in Fig. 1. Compartment A, where the enzyme was injected, and B had volumes of 10 and 60 mL, respectively. Electrodes were put face to face in the galvanic cell and coupled through a Keithley 2000 picoammeter. The dialysis membrane confined the enzyme near the surface of only one electrode (compartment A) while both electrodes were exposed to the same solution. Oxygen was removed

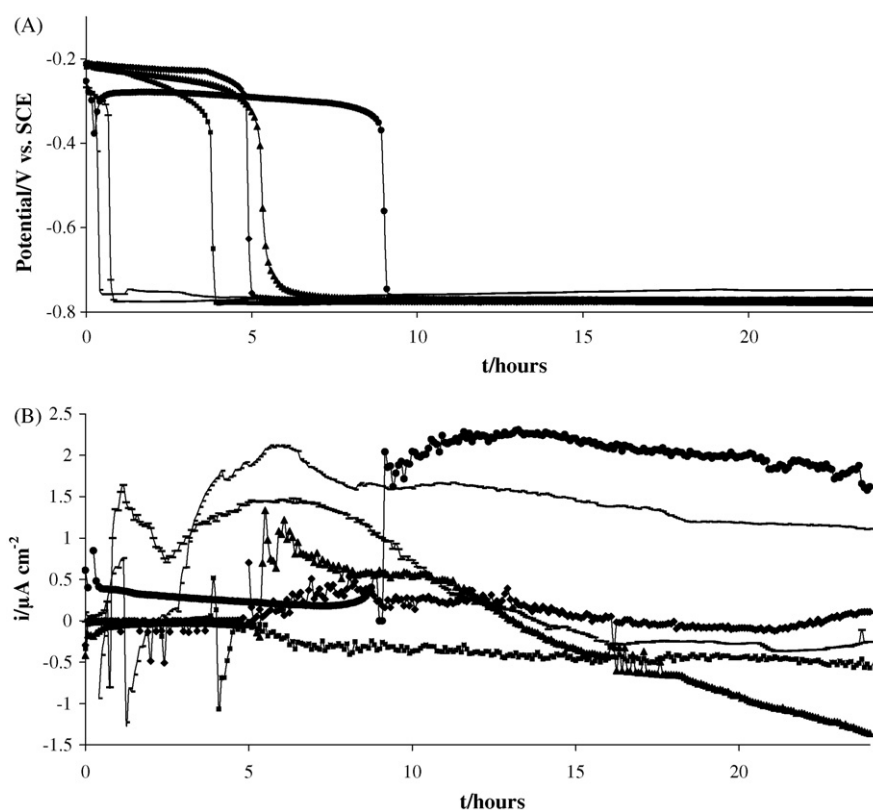


Fig. 2. Evolutions of the potential (A) and the galvanic current (B) as a function of time obtained with two XC45 coupled electrodes in a 100 mM phosphate solution pH 8.0, under deoxygenation but without hydrogenase addition.

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