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Accelerated cathodic reaction in microbial corrosion of iron due to direct electron uptake by sulfate-reducing bacteria

Hendrik Venzlaff [a,*], Dennis Enning [b], Jayendran Srinivasan [a], Karl J.J. Mayrhofer [a,*], Achim Walter Hassel [c], Friedrich Widdel [b], Martin Stratmann [a]

[a] Max Planck Institute for Iron Research, Max-Planck-Straße 1, 40237 Düsseldorf, Germany
[b] Max Planck Institute for Marine Microbiology, Celsiusstraße 1, 28359 Bremen, Germany
[c] Institute for Chemical Technology of Inorganic Materials, Johannes-Kepler University, Altenberger Straße 69, 4040 Linz, Austria

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ABSTRACT

Microbially influenced iron corrosion by sulfate-reducing bacteria (SRB) is conventionally attributed to the chemical corrosiveness of H_2S, facilitated abiotic H^+-reduction at deposited FeS, and biological consumption of chemically formed ('cathodic') H_2. However, recent studies with corrosive SRB indicated direct consumption of iron-derived electrons rather than of H_2 as a crucial mechanism. Here, we conducted potentiodynamic measurements with iron electrodes colonized by corrosive SRB. They significantly stimulated the cathodic reaction, while non-corrosive yet H_2-consuming control SRB had no effect. Inactivation of the colonizing bacteria significantly reduced current stimulation, thus confirming biological catalysis rather than an abiotic cathodic effect of FeS.

1. Introduction

Whereas iron corrosion by oxygen from air is, to our present knowledge, a purely electrochemical process, iron corrosion in neutral media in the absence of air (as, for instance, in aqueous underground or inside iron pipes) is largely biologically influenced. Sulfate-reducing bacteria (SRB) are commonly considered to be the main originators of this microbiologically influenced corrosion (MIC) [1,2]. SRB gain their biochemical energy for growth by reducing sulfate (SO_4^{2-}) to sulfide (H_2S, HS^-) with natural organic compounds as electron donors that are oxidized to CO_2 (also referred to as sulfate respiration). In addition, many SRB can also utilize molecular hydrogen (H_2), a common product of other bacteria involved in the biological breakdown of organic compounds in oxygen-free aquatic systems such as sewers, sediments and swamps.

The mechanisms by which SRB act upon metallic iron have been controversially discussed in literature [3–6]. The basic feature of previously described models is always the low-potential electron release by the metal according to

$$Fe^{2+} + 2e^- \rightleftarrows Fe$$

$$E_{SHE,298K} = -0.47 + 0.0296\ \log(a_{Fe^{2+}}) \quad (1)$$

(the previous redox potential ($E^0_{SHE} = -0.44$ V) has been revised according to [7]). The sulfide formed by SRB behaves as a chemically aggressive compound [3,8,9], resulting in the bulk equation $Fe + H_2S \rightarrow FeS + H_2$; for review see also Ref. [2]. In this way, SRB act indirectly by chemical reaction of their metabolic end product (chemical microbially influenced corrosion, CMIC).

A fundamentally different, traditional mechanistic proposal is based on the inherent ability of many SRB to utilize H_2 as electron donor ($4H_2 + SO_4^{2-} + 2\ H^+ \rightarrow H_2S + 4H_2O$). Reduction of protons in water to hydrogen according to

$$2H^+ + 2e^- \rightleftarrows H_2$$

$$E_{SHE,298K} = 0.00 - 0.0296\ \log(a_{H_2}) - 0.0592\ pH \quad (2)$$

can in principle be linked with iron oxidation (Eq. (1)) and results in the net reaction

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2. \quad (3)$$

Early investigators speculated that in the absence of microorganisms, the H_2 formed builds up a 'hydrogen film' at the metal surface, ultimately impeding reaction (3) and thus iron dissolution to progress [4,10]; traditionally, this impediment is often referred to as 'polarization'. In the presence of microorganisms with the capability of H_2 utilization such as SRB, their effective scavenging of H_2 was suggested to lower the local partial pressure and through such 'depolarization' allow iron dissolution to proceed. This proposal became therefore known as 'cathodic depolarization theory'.

* Corresponding authors. Tel.: +49 211 6792 160; fax: +49 211 6792 218.
E-mail addresses: venzlaff@mpie.de (H. Venzlaff), mayrhofer@mpie.de (K.J.J. Mayrhofer).

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Because H_2S combines with Fe^{2+} ions from the primary dissolution (Eq. (1)), the net reaction (including bicarbonate that is readily available in many water systems) is

$$4Fe + SO_4^{2-} + 3HCO_3^- + 5H^+ \rightarrow FeS + 3FeCO_3 + 4H_2O. \quad (4)$$

From a merely thermodynamic perspective, however, the above considerations may be questioned. The redox potential of the electron donor (Eq. (1)) is more negative than that of the electron acceptor (Eq. (2)). Accordingly, the free energy of reaction (3) under standard conditions (except that $(a_{H^+} = 10^{-7})$ is $\Delta G^0_{pH7} = -10.6$ kJ mol^{-1}, and the reaction can, in principle, proceed spontaneously. At environmentally relevant activities of Fe^{2+}(aq) that are significantly below standard activity, the Fe^{2+}/Fe redox couple is even more negative, often $E_{environ} \leqslant -0.6$ V vs. standard hydrogen electrode (SHE), so that $\Delta G_{environ} \leqslant -36.7$ kJ mol^{-1}. For a thermodynamic halt ($\Delta G \geqslant 0$) of iron dissolution according to reaction (3), one would have to assume a 'hydrogen film' with a local fugacity corresponding to $p_{H_2} > 10^{11.3}$ Pa. Considering the extremely fast diffusion of H_2, viz. of the hydrogen species that is used by bacteria, such local build-up of a hydrogen film appears very unrealistic. If SRB have a direct influence on corrosion, an understanding can be only expected from the viewpoint of electrokinetics, in particular of H^+ reduction to H_2, rather than *via* mere thermodynamic considerations. H_2 formation on iron in circumneutral water is inherently slow, a 'kinetic bottle neck' due to limitations in proton availability and combination reactions forming H_2 [11–13]. Still, several hydrogenase-positive cultures of sulfate-reducing bacteria apparently stimulated the cathodic current ('depolarization') on mild steel electrodes [5,14,15]. The authors attributed this to bacterial H_2-uptake from the electrode surface and, hence, interpreted the observation in favor of the 'classical' depolarization theory. The ability of SRB for scavenging H_2 from corroding iron and water has indeed been shown [6,16,17].

However, an experimental misconception in the early electrochemical study of the postulated direct mechanism involving H_2 with conventional SRB strains was the addition of lactate, a routine, excellent cultivation substrate of SRB [5,14,15]. Lactate represents a competitive electron donor in addition to 'cathodic' H_2 and, more importantly, leads to excessive concentrations of aggressive sulfide causing chemical corrosion (CMIC) and altering the electrode surface drastically. Costello [3] and Hardy [6] therefore omitted lactate and gave proof that cathodic depolarization did not occur in SRB cultures with metallic iron as the only source of electrons for the organisms; rather, acceleration of the cathodic reaction was shown to result from the reactivity of dissolved sulfide. Accelerated corrosion due to bacterial H_2-uptake from the metallic iron surface was consequently questioned by several authors, particularly as SRB incubated with iron alone did not accelerate corrosion [18–20].

In another model of SRB-induced corrosion, stimulation of H^+-reduction to H_2 by catalytically active ferrous sulfides on the iron electrode was suggested [21,22]. Hence, SRB were thought to scavenge H_2 from FeS rather than from the metallic surface. Chemically prepared, fine suspensions of FeS transiently accelerated the cathodic reaction and iron loss even in the absence of bacteria, viz. if H_2 was not consumed [22,23]. However, a variety of both amorphous and crystalline iron sulfides exist which exhibit very different properties with regard to the corrosion of iron. Neither their properties nor the extent of their contribution to anaerobic iron corrosion are completely understood at the moment [24].

In another approach towards a mechanistic understanding of anaerobic corrosion, SRB were directly enriched and isolated with metallic iron as the only source of electrons (viz. without an organic substrate such as lactate) for sulfate reduction [19]. They severely corroded the metallic substrate with a rate of up to 0.7 mm Fe^0 yr^{-1}, corresponding to 61 μA cm^{-2} [25]. The corrosion rate could not be explained by dependency on H_2, the chemical formation of which from iron and water was by far too slow [19,25]. This and the significant conductivity of the deposited FeS-containing crust [25] indicated a direct electron uptake (i.e., electrical microbially influenced corrosion, EMIC) by the attached cells according to

$$8e^- + SO_4^{2-} + 10H^+ \rightarrow H_2S + 4H_2O \quad (5)$$

$$E_{SHE,average,298K} = 0.30 + 0.0074\ \log(a_{SO_4^{2-}}/a_{H_2S}) - 0.074\ pH$$

(underlying data in Supplementary material) and thus an effective by-pass of the H_2-formation reaction. The net reaction (combination of Eq. (1) and (5)), which is the same as Eq. (4), results in significant mineral precipitation on the iron.

Such a postulated direct electron uptake urges upon corroboration by electrochemical measurements. If the novel SRB accelerate corrosion by direct electron uptake, this should be obvious from a shift of the free corrosion potential and from an increase of the cathodic current of iron electrodes in potential-controlled experiments. In the present study these effects were investigated using iron coupons colonized and encrusted (Eq. (4)) by the corrosive SRB *Desulfopila corrodens* (tentative name) strain IS4 for electrochemical measurements in defined electrolyte. No organic electron donor was added, viz. all electrons for sulfate reduction were provided through the metal. Moreover, to distinguish between the impact of bacterial activity and their deposited iron sulfides, the current–potential relationship was measured prior to and after chemical inactivation of the colonizing bacteria. *Desulfovibrio* sp. strain HS3, an organism similar to SRB investigated in former 'depolarization' studies and growing well with H_2 served as control culture. The expected electrokinetic effects of strain IS4 were indeed observed, thus fully supporting the postulated enhancement of corrosion by direct biological electron uptake rather than by H_2-consumption.

2. Materials and methods

2.1. Chemicals and organisms

All solutions and culture media were prepared from chemicals of analytical grade and ultrapure deionised water (Purelab Plus by Elga Labwater, Celle, Germany). Culture liquids were sterilized in an autoclave at 121 °C for 25 min. Pre-cultures of the two isolated SRB strains used in this study, *D. corrodens* strain IS4 and *Desulfovibrio* sp. strain HS3 [19,25], were incubated in butyl-rubber-stoppered glass bottles with artificial seawater medium (ASW) [26] buffered by CO_2/$NaHCO_3$, and provided with an anoxic headspace of CO_2/N_2 (10:90, v/v). ASW contained typically 28 mM sulfate as an electron acceptor and no oxidizable organic substrates. For the experiments including sulfate analysis, the sulfate concentration was lowered to 5 mM for more precise detection of its consumption. Pre-cultures of SRB strains were grown on H_2 and subsequently flushed with CO_2/N_2 for 30 min to prevent transfer of dissolved sulfide and H_2 into the incubations. The cell density in inocula was determined by acridine orange (0.1 mg ml^{-1}) staining and epifluorescent microscopy (Zeiss Axiophot, Carl Zeiss MicroImaging, Göttingen, Germany), so that all experiments could be started with identical cell numbers.

2.2. Free corrosion potential and potentiodynamic measurements

2.2.1. Electrochemical cell setup and incubation

Electrochemical cells were constructed as follows: Sheets of pure iron (composition in wt.%: 99.877% Fe; <0.06% Mn, <0.03%