

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

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Appendix A: Supplementary data

Scheme of measurements in electrochemical cells.

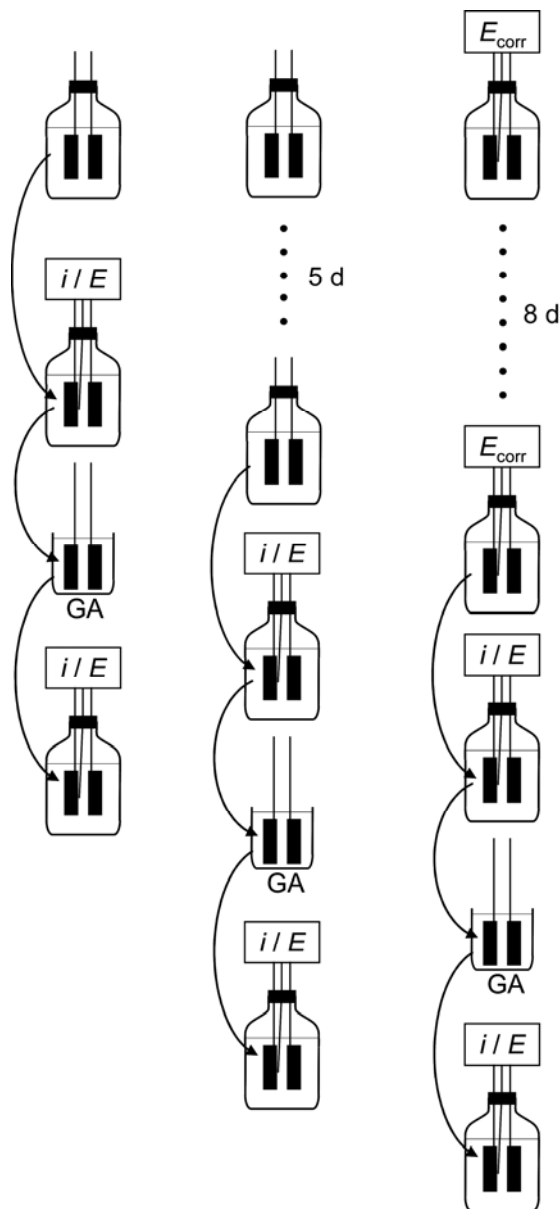


Fig. S1. Three electrochemical cells were prepared for each strain. One cell was used for the LSV measurements (“ i/E ”) directly after inoculation (left column) and the second cell after five days (middle column); the third cell (right column) was first used to record the development of E_{corr} over eight days and subsequently used for potentiodynamic measurements. The first LSV measurements were followed by chemical inactivation, viz. the transfer in glutaraldehyde containing medium and washing steps indicated by “GA”. This procedure sacrificed the colonized electrodes. Afterwards the inactivated electrodes were transferred in fresh electrolyte and subsequently investigated by a second LSV measurement.

Efficiency of chemical sterilization procedure

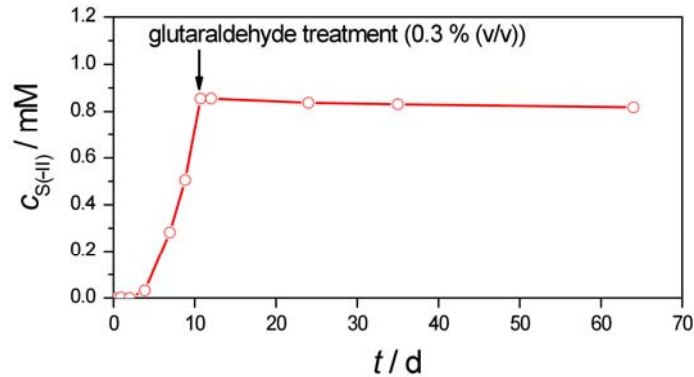


Fig. S2. Production of sulfide (calculated from sulfate loss) in a culture of strain IS4. Corrosion coupon (crust-covered) was treated with 0.3 % glutaraldehyde (v/v) on day 10 and further incubated in fresh ASW.

LSV of strain HS3 after three days

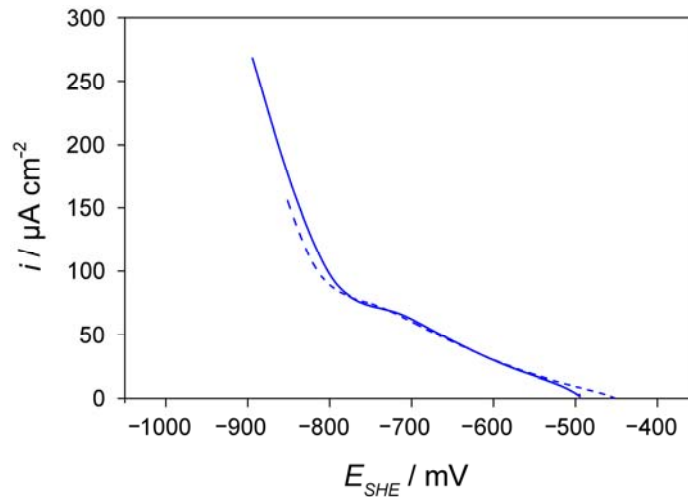


Fig. S3. Voltammograms of an iron electrode incubated in a culture of strain HS3 for three days. Measurements were performed in fresh artificial seawater medium as electrolyte with viable cells (solid line) and after sterilization with glutaraldehyde (dashed line). The potential sweep with 1 mV s^{-1} ranged from the free corrosion potential (E_{corr} ; start) to -400 mV below E_{corr} . In the first days of incubation cathodically active iron sulfides with a correspondingly higher rate of H_2 formation may form. These curves support this assumption showing increased corrosion currents independent of the microbial activity.

LSV at different scan rates

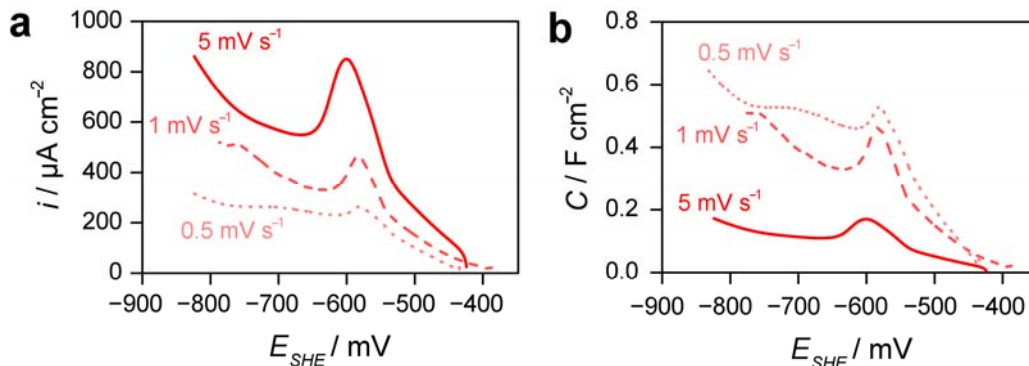


Fig. S4. Voltammograms of an iron electrode incubated in a culture of strain IS4 for twelve days. A thick precipitate crust was established on the surface. The potential sweep ranged from the free corrosion potential (E_{corr} ; start) to -400 mV below E_{corr} with a scan rate of 1 mV s^{-1} (first sweep), 0.5 mV s^{-1} (second sweep) and 5 mV s^{-1} (third sweep). A pure Faradaic current would be independent of the scanrate, but actual polarization behaviour (a) indicates an additional non-Faradaic current, e.g. due to charging effects of the semiconductive crust. This current is however also not pure non-Faradaic as the capacitance (current density divided by scanrate, (b)) is not independent of the scanrate. Additional potential sweep experiments had demonstrated that polarization behaviour in general is reproducible for one scanrate.

Impedance spectra (Nyquist plots)

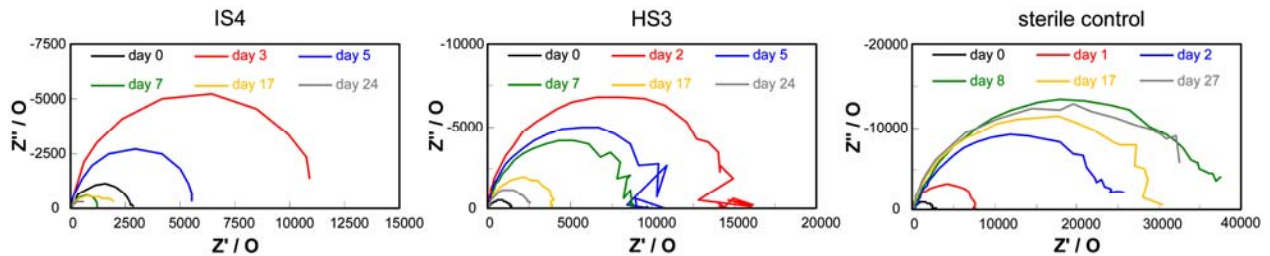


Fig. S5. Impedance spectra (Nyquist representation) of iron wire electrodes incubated in cultures of strain IS4, strain HS3 and without bacteria (sterile control).

Table S1. Free energies of formation used for calculation of equilibrium redox potentials

Species (state)	$\Delta_f G^\circ / (\text{kJ mol}^{-1})$	Source
H ₂ (g)	0.00	By definition
H ⁺ (aq)	0.00	By definition
H ₂ O (lq)	-237.18	[1]
HCO ₃ ⁻ (aq)	-586.8	[1]
H ₂ S (aq)	-27.87	[1]
SO ₄ ²⁻ (aq)	-744.6	[1]
Fe (c)	0.00	By definition
Fe ²⁺ (aq)	-90.5	[2]
FeCO ₃ (c)	-666.7	[1]
FeS (c)	-100.4	[3]

Estimation of activities

The used seawater medium was provided with HCO₃⁻ at 0.030 mol l⁻¹ and SO₄²⁻ at 0.028 mol l⁻¹, which were partly reduced or precipitated, respectively, during incubation. Based on chosen activity coefficients in seawater of 0.55 and 0.11 l mol⁻¹ [1], respectively, we used for convenient calculation $a_{\text{HCO}_3^-} = 10^{-2}$, and $a_{\text{SO}_4^{2-}} = 10^{-2.5}$. The slightly reduced activity of H₂O in seawater was not considered (i.e. we used $a_{\text{H}_2\text{O}} = 1$).

References for Supplement

- [1] W. Stumm, J.J. Morgan, Aquatic Chemistry, 2nd edn., John Wiley & Sons, New York (1981)
- [2] D. Rickard, G.W. Luther, (2007) Chemistry of iron sulfides, Chem. Rev. 107 (2007) 514–562
- [3] P. Atkins, J. De Paula, Physical Chemistry, 8th edn., Oxford University Press, Oxford (2006)