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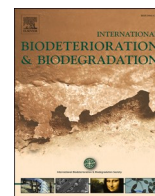
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Microbially influenced corrosion: Towards an interdisciplinary perspective on mechanisms

Brenda J. Little^a, Jamie Hinks^{b,*}, Daniel J. Blackwood^c

^a BJ Little Corrosion Consulting, LLC, Diamondhead, MS, 39525, USA

^b Singapore Centre for Environmental Life Sciences Engineering (SCELESE), Nanyang Technological University, 60 Nanyang Drive, 637551, Singapore

^c Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, 117576, Singapore

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ABSTRACT

A perspective is provided on mechanisms for microbially influenced corrosion by sulfate-reducing bacteria and metal-oxidizing bacteria. The authors discuss the confusion introduced by cross-disciplinary discussions of MIC mechanisms and the divergent terminologies used by microbiologists and electrochemists, e.g. “anaerobic” and “direct electron transfer.” Examination of the cathodic depolarization theory for corrosion of carbon steel by sulfate-reducing bacteria suggests that the theory cannot explain the observations. Stainless steels containing <20% chromium are vulnerable to pitting in the presence of iron and manganese oxides produced by iron- and manganese-oxidizing bacteria, respectively. However, mechanisms for pitting differ between the two oxides. In all cases, understanding mechanisms for microbially influenced corrosion must consider the environment, i.e., the composition of the electrolyte, in addition to the vulnerability of the material in the presence of putative microorganisms. Significant opportunity exists for more integrated approaches to interdisciplinary research and open discourse.

1. Introduction

Microbially influenced corrosion (MIC) is not a mechanism for corrosion. Instead microorganisms influence multiple mechanisms, both directly and indirectly. Numerous compendia provide lists of microorganisms typically associated with microbially influenced corrosion. It follows that these microorganisms are often referred to as “corrosive.” The current trend to identify specific microorganisms associated with MIC by molecular microbiological methods, i.e., hybridization, polymerase chain reaction and sequencing, has demonstrated the microbial diversity in MIC and added to the list of “corrosive” microorganisms. However, molecular microbiological methods have not provided insight into corrosion mechanisms. Lists of “corrosive” microorganisms are of limited practical value in the absence of specific information regarding the composition of the electrolyte and the corroding material.

Corrosion mechanisms are microorganism/electrolyte/metal-specific (Jigletsova et al., 2004). Electrochemistry has been used to demonstrate metal-specific reactions in the presence of identical electrolyte/microorganism exposures (Javed et al., 2017). Mehanna et al. (2010) demonstrated that pitting of 304L stainless steel (SS) due to biofilms of *Geobacter sulfurreducens* “... drastically depended on the

composition of the medium ...”. *G. sulfurreducens* biofilms enhanced pit depth when the growth medium was deficient in electron donor. In contrast, at a low concentration of sodium fumarate (electron acceptor) the presence of *G. sulfurreducens* protected 304L SS against pitting (Mehanna et al., 2010). Specific mechanisms are most often linked to electron donor and acceptor reactions, e.g., iron oxidation or sulfate reduction. However, corrosion mechanisms cannot be assumed based on the identification of a specific group of bacteria or a single electron donor or acceptor. For example, the following corrosion mechanisms have been attributed to sulfate-reducing bacteria (SRB): cathodic depolarization by hydrogenase⁺ microorganisms; formation of non-tenacious cathodic sulfide layers; sulfide induced stress-corrosion cracking and direct electron uptake from Fe⁰ (electroactive behavior) (Enning and Garrelfs, 2014). The identification of specific organisms has not yet been used as a proactive approach for controlling the microbial processes that result in corrosion (Javaherdashti, 2017). In contrast, manipulating electrolyte composition and operating conditions has been used in attempts to prevent some MIC mechanisms e.g., nitrate addition and manganese removal (Hubert et al., 2005; Dickinson and Wiart, 2013).

The study of MIC mechanisms is dominated by two disciplines, i.e.,

* Corresponding author.

E-mail addresses: brenda.little@att.net (B.J. Little), JHinks@ntu.edu.sg (J. Hinks).

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electrochemistry and microbiology. To date the result has been cross-disciplinary research, viewing one discipline from the perspective of the other. Despite attempts to reconcile differences in fundamental concepts, misunderstandings persist. In most cases, explanations have been proposed and accepted by microbiologists for electrochemical observations. For example, most MIC mechanisms are described as either aerobic or anaerobic. From an electrochemical perspective, the crucial aspect is the nature of the cathodic reaction, which in most aqueous environments is the reduction of either dissolved oxygen or protons/water. It therefore makes sense to describe “aerobic” as the condition in which reduction of dissolved oxygen (DO) is the cathodic reactant. In the absence of DO, “anaerobic” is the condition in which an alternative reactant, e.g., water, is reduced to support the corrosion reaction. These definitions for anaerobic and aerobic conditions are metal-specific, depending on the corrosion rate rather than the bulk DO concentration. For example, a single electrolyte can be anaerobic to an active metal, and aerobic to a passive one (Blackwood, 2001). Using the electrochemical definitions, one can categorize an environment as being aerobic or anaerobic by comparing the open-circuit potential (OCP) to the value for the reversible hydrogen electrode (RHE). Values positive to RHE indicate an aerobic metal/electrolyte interface, while values that are negative to RHE indicate an anaerobic interface.

In contrast, environmental microbiologists use the terms “aerobic” and “anaerobic” to make the distinction between respiratory strategies that use oxygen and those that do not, respectively. Use of the term “anaerobic” does not always mean the absence of free oxygen or reducing conditions which is an absolute requirement for some microbes (Hungate, 1969; Tanner, 2007). In reality, anaerobic and aerobic metabolic strategies can occur simultaneously as microbes arrange themselves in mutualistic biofilms which impose chemical gradients that create microenvironments, including anaerobic microniches. Although the oxygen concentration at the bottom of biofilms has been described as “zero,” the authors are reporting that the DO concentration is below the detection limit for the measurement technique (e.g., typically 10 ppb for amperometric DO sensors) (Jo et al., 2017).

Similarly, many MIC experiments are conducted in media where the DO has been reduced by purging with a replacement gas so that DO is below detection limits with an oxygen meter or probe. In the latter case, an electrolyte is defined as anaerobic based on the absence of detectable DO in the medium. The result is published claims of anaerobic conditions and conclusions about anaerobic mechanisms derived from media with residual oxygen. In such conditions, a microbiologist would use the term anaerobic but the electrochemical consequences of ppb levels of oxygen in MIC experiments are well-documented and may influence MIC mechanisms in addition to inhibiting microbes that require strict reducing conditions.

The previous discussion, involving definitions, is just one example of semantic and experimental conflict between disciplines in the study of MIC. The following discussion is not meant to be a comprehensive coverage of MIC mechanisms. Instead, examples for two groups of microorganisms, i.e., SRB (typically defined as anaerobes) and iron- and manganese-oxidizing bacteria (FeOB and MnOB, respectively) (typically defined as aerobes) are presented to demonstrate that mechanisms for MIC are microorganism/electrolyte/metal-specific.

2. Sulfate-reducing bacteria SRB

In aqueous environments virtually all the important structural metals form oxide films, which is the basis of passivity that allows thermodynamically unstable metals to be used in construction (Macdonald, 1999). Carbon steel and copper alloys are vulnerable to MIC by SRB because the metal oxides on these materials can react with sulfide produced by SRB to produce metal sulfides. McNeil and Odom (1994) developed a thermodynamic model for predicting the vulnerability of metals and alloys to MIC by SRB based on susceptibility of the metal oxide to react with sulfides (McNeil and Odom, 1994). If the reaction to

produce a metal sulfide from a metal oxide has a negative Gibbs free energy (ΔG), the sulfide can form, although whether it forms will depend on the reaction kinetics. If the reaction has a positive ΔG the metal sulfide cannot form. McNeil and Odom (1994) reported that corrosion rates for stainless steels (SS) derivatized by sulfides would be slower than those for carbon steel and that SS containing 6% or more molybdenum will be “very resistant” to SRB influenced MIC. Reinforcing that prediction, Webster and Newman (1994) demonstrated that SRB influenced corrosion of a stainless steel (Fe–15Cr–10Ni) required specialized “test media and test methods.” They reported that the following were necessary: an anion ratio of $[Cl^-]: \Sigma$ [all other anions] of 5:1; inclusion of NaCl and removal of ferrous ions. Removal of reducing agents, e.g., ascorbic acid, sodium thioglycolate and yeast extract (YE) eliminated, “nearly all interferences of medium composition on electrochemical measurements ...” in a deaerated medium (Webster and Newman, 1994).

Blackwood (2018) recently reviewed SRB influenced corrosion mechanisms and concluded that two of the explanations for existing mechanisms were not satisfactory, as outlined in sections 2.1 and 2.2. He provided detailed electrochemical perspectives on both the oldest (von Wolzogen Kühr and van der Vlugt, 1964) and the newest (Venzlaff et al., 2013) hypotheses for SRB influenced corrosion, i.e., cathodic depolarization (CDP) and direct electron uptake, respectively (Blackwood, 2018).

2.1. The CDP hypothesis

The OCP is the potential at which the anodic corrosion current is exactly balanced by the supporting cathodic current. Further, any observed increase in the corrosion rate means there must also have been an increase in the rate of the cathodic reaction. In most abiotic environments the nature of the cathode does not change with time and so increased corrosion rates are usually associated with negative shifts in OCP (higher driving force for the cathodic reaction). In contrast, with MIC increased corrosion rates can be associated with positive shifts in OCP, which implies faster kinetics for the cathodic reaction that can be achieved by one of two routes: (i) a change in the mechanism of the cathodic reaction; or (ii) a change in the nature of the cathode, such that it becomes a better catalyst.

The CDP hypothesis was developed to explain observations of a positive shift in OCP during corrosion of iron by SRB, i.e., a depolarization, and is based on the first of the two above mechanisms, i.e., a change in the mechanism of the cathodic reaction. The depolarization was originally attributed to the removal of hydrogen (H_2) at the cathode by hydrogenase⁺ SRB. The theory assumes that biological oxidation of H_2 would accelerate the cathodic reaction, thereby depolarizing OCP (i.e., causing a positive shift) and leading to increased corrosion rates. Although the CDP theory with the original interpretation has been criticized for over a decade, it is routinely reported as a potential mechanism attributed to SRB (Imo et al., 2016; Kakooei et al., 2012; Procópio, 2019). However, Blackwood (2018) delineated the following major problems with the original interpretation. The rate determining step for H_2 evolution on carbon steels is the adsorption step not the desorption step, meaning that the removal of the H_2 from the surface is not rate-limiting and not likely to accelerate the cathodic reaction (Frankenthal and Milner, 1986). Furthermore, hydrogenase⁺ SRB do not affect corrosion rates any more than hydrogenase⁻ SRB (Dinh et al., 2004; Mori et al., 2010; Hardy, 1983; Spruit and Wanklyn, 1951).

Blackwood (2018) reviewed more plausible explanations to account for the shift in OCP, commonly observed in SRB corrosion of iron based on the second of the above two mechanisms, i.e., a change in the nature of the cathode, such that it is a better catalyst for the cathodic reaction. King and Miller (1973) suggested that the reaction of iron oxide with H_2S caused the development of a conductive iron sulfide layer that acts as an extended cathode leading to the positive shift in the corrosion potential (cathode depolarization) (King et al., 1973). Costello et al.

(1974) proposed that H_2S provided an additional cathodic reduction pathway (Costello, 1974). However, this hypothesis has since been disproved (Kahyarian and Nescic, 2019). All of the characteristic behaviour of cathodic currents in H_2S environments can be modelled with H^+ reduction as the sole cathodic reaction. Further support for the lack of an additional cathodic reduction pathway was recently provided by Jia et al. (2018) who demonstrated that H_2S was not a major contributor in the MIC process in near-neutral pH environments.

In practice, iron and copper sulfide films are not tenacious and do not provide long-term corrosion protection for the substrata. In the presence of mechanical stress, e.g. turbulence, loosely adherent sulfide films are removed, exposing fresh substratum to react with sulfide ions (Syrett, 1977). Because most metal sulfides are cathodic to the base metal, turbulence or any other form of agitation that causes part of the sulfide film to slough, can create a surface of localized cathodic and anodic sites.

Hamilton (2003) reviewed the literature on SRB MIC and provided a unifying theory. Accordingly, in the case of SRB influenced corrosion, he proposed that sulfate is the terminal electron acceptor (TEA) in the biological reaction (anaerobic respiration), but that oxygen is the terminal TEA in the corrosion reaction. In situations where oxygen intermittently reaches the metal/electrolyte interface the metal sulfide may act as a catalyst for the reduction of oxygen (Hamilton, 2003; Hardy and Bown, 1984). Lee et al. (2005) reported much higher corrosion rates, by up to a factor of three as recorded by linear polarization resistance measurements, when carbon steel exposed to SRB was cycled between oxygenated and deoxygenated (<0.2 ppm O_2) seawater than corrosion rates observed under either continuous condition. Sherar et al. (2013) also reported that the introduction of air to anaerobically grown iron sulfide layers increased corrosion rates by an order of magnitude, resulting in oxide deposition beneath the FeS film and eventual blistering of the latter. In natural environments the relationship between SRB influenced corrosion and DO can be more complicated than sequential extremes alternating between oxygenated and deoxygenated (<0.2 ppm O_2) events (Lee et al., 2005). Instead, there can be a continuum of DO concentrations from anoxic niches in biofilms to an oxygenated bulk electrolyte.

In summary, the CDP hypothesis is incorrect, as it is not consistent with the known electrochemical mechanism of hydrogen evolution on steel substrates and reports that corrosion rates for hydrogenase⁺ and hydrogenase⁻ SRB are identical. A more plausible explanation for the observed positive shift in OCP in the presence of SRB is the development of conductive iron sulfide films, which are catalytic for the reduction of protons. Furthermore, as most metal sulfide films are cathodic to the base metal, any damage to the film that exposes the substratum will lead to rapid galvanic corrosion of the metal. Finally, there is evidence that metal sulfides may act as catalysts for the reduction of oxygen, such that any cycling between localized oxygenated and deoxygenated environments can cause corrosion rates to increase by as much as an order of magnitude.

2.2. Direct extracellular electron transfer

Organisms conserve energy by coupling the oxidation of a reduced species to the reduction of a more oxidized species. The difference in redox potential between electron donor and acceptor is proportional to the maximum amount of energy that could be metabolically derived from such reactions. (Fig. 1). Compared to higher organisms, microbes exhibit extraordinary metabolic diversity and are known to survive by exploiting a range of electron donors and acceptors including those in the solid phase. The feasibility of such respiratory processes is often assessed in terms of bioenergetics, which requires that the ΔG° for a reaction be negative, i.e. exergonic. In the context of corrosion, biological reactions with a positive ΔG° (i.e. endergonic), would not be, by definition, as quantitatively important as those from which the cell gains energy (Zhang et al., 2015).

Several authors have attributed direct electron transfer from carbon

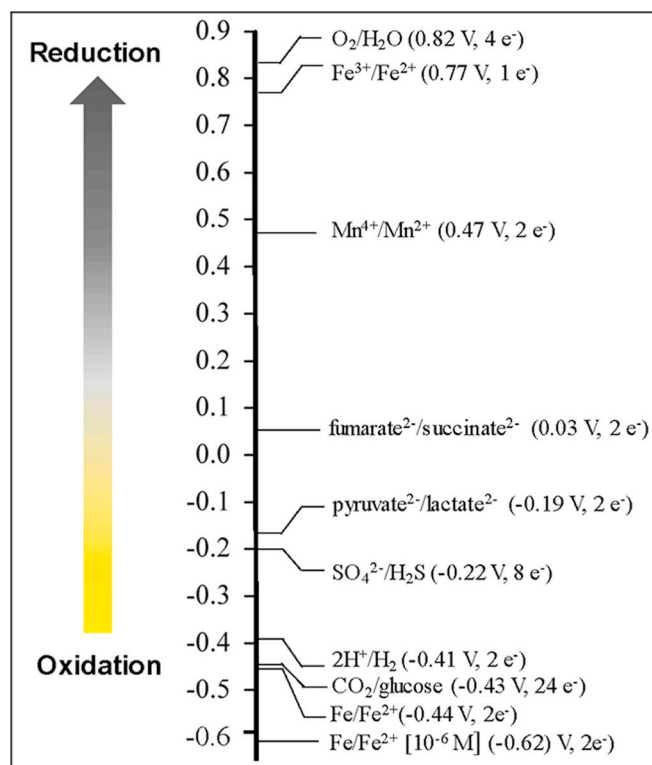


Fig. 1. The electron tower concept is useful to illustrate energy yielding redox reactions in biology. Theoretically, any reaction at the bottom of the electron tower can be coupled to a reaction at the top. The amount of energy (ΔG) available from a given reaction is proportional to the difference in the reduction potential of the redox couples in question (Adapted from Hinks et al., 2017).

steel to SRB, methanogens, and other bacteria, e.g., *Shewanella* spp., as a mechanism for MIC (Venzlaff et al., 2013; Xu and Gu, 2014; Kato, 2016; Li et al., 2018; Jia et al., 2018; Philips et al., 2018). Many environments in which MIC occurs are oligotrophic. In the absence of alternative, thermodynamically favorable (i.e. reduced) electron donors, some microorganisms can reportedly use elemental iron (Fe^0) as an electron donor to produce metabolic energy (Philips et al., 2018).

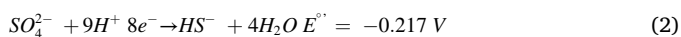
According to this type of cathodic reaction, elemental metals provide the reducing power for microbial respiration. Electrons would, therefore, be required to transit the cell envelope where they reduce a biological electron carrier (e.g. FAD) and later a TEA in either the cytoplasm, the periplasm or even outside the cell. The cell envelope is the protective outer portion of the cell which, for bacteria, includes either a single or a double lipid membrane and a carbohydrate cell wall. The periplasm is the space between the two cell membranes when they are both present or between the membrane and the cell wall when only one membrane is present. The cytoplasm refers to the interior of the cell.

In the case of SRB, sulfate is the TEA in a respiratory process that must have an overall negative ΔG° if the organism is to conserve energy. Direct electron transfer between aqueous species typically occurs over the sub-nanometer scale but cannot occur over distances greater than 2 nm (Gray and Winkler, 2005). Biological membranes are 3–4 nm thick (Zhou et al., 2019). Therefore, for electrons to traverse the cell envelope, multiple electron carriers must be arranged in a manner that facilitates such exchanges. All respiratory processes require efficient electronic transitions over such distances. In aerobic respiration, which is the most energetic form of respiration, oxygen is the TEA, giving rise to the maximum potential difference (i.e., 1.23 V) that exists between biological electron donors (e.g. -430 mV against SHE for the glucose/ CO_2 redox couple) and the TEA (around 820 mV against SHE). However, anaerobic respiration, by definition, requires the microbe to use electron

acceptors that have a lower redox potential and therefore yield less energy. The oxidation of glucose to CO_2 yields $-2870 \text{ kJ mol}^{-1}$ yet some anaerobes can exist by exploiting reactions yielding only 4.5 kJ mol^{-1} (Hinks et al., 2017). Knowing that some anaerobes are able to exist on small energetic yields, it is feasible that microbes could accommodate the energetic losses that arise from a series of electronic transitions that would allow electrons to be transported over larger spatial ranges than those involved in typical membrane-bound electron transport chains. Each electronic transition necessarily engenders an overpotential that will result in an energetic loss. Extending extracellular electron transfer (EET) over a few nm (in either the cathodic or anodic direction) comes at a metabolic cost to organisms exploiting such niches. An upper limit to the possible number of such transitions will exist before the ΔG° of the reaction is insufficient to sustain life. The extent to which such energy losses may occur during EET is currently not well described. The lower free energy requirement to support life is reportedly around -20 kJ mol^{-1} and may be as low as -17 kJ mol^{-1} for some sulfate reducers (Müller, 2015; Delattre et al., 2020). Under standard biological conditions, the redox potential of an $\text{Fe}^{2+}/\text{Fe}^0$ couple is given by the Nernst equation:

$$4\text{Fe} \rightarrow \text{Fe}^{2+} + 8e^- \quad E^\circ = -0.44 \text{ V} + (0.0295 \text{ V}) \text{Log} [\text{Fe}^{2+}] \quad (1)$$

Assuming a ferrous concentration of 10^{-6} M to mark the onset of corrosion (as used in Pourbaix diagrams, albeit a somewhat arbitrary value), yields a potential of -0.617 V vs SHE. Notwithstanding the fact that Equation (1) refers to pure iron in a simple aqueous environment, which will not be the real situation, it is still clear that from a purely thermodynamic perspective, iron could be a very good biological electron donor that can be coupled to the reduction of, for example, sulfate as follows:



The potential difference between reactions (1) and (2) is 0.23 V and thus will yield a negative ΔG° and therefore metabolic energy making it an feasible biological niche (Zhang et al., 2015).

The mechanisms by which electrons transit the cell envelope in the cathodic direction remain unresolved, but two assumptions can be gleaned from mechanisms described for anodic electron transfer in microbes.

- 1) Direct extracellular electron transfer (DEET) – direct transfer involves contact between the cell and the electron donor either via the cell envelope or via proposed conductive filaments, i.e., pili.
- 2) Mediated extracellular electron transfer (MEET) – electrons are shuttled between donors and acceptors through reversible redox reactions mediated by mobile, extracellular electron carriers.

The most plausible electron transport mechanism in SRB-mediated MIC is MEET, where mediators act as shuttles between the metallic substratum and the cell envelope. In anodic MEET reactions, lipophilic redox mediators transit cell membranes and undergo reduction by a biological redox carrier in the periplasm (or even at the outer surface of the cell envelope by outer membrane cytochromes). The redox carrier subsequently leaves the cell and is oxidized at the anode. In theory, this process could be reversed for cathodic MEET reactions, whereby such mediators are reduced at the iron surface and later oxidized by a microbe as an electron source. Evidence for the role of MEET in the corrosion of stainless steel exists for pure cultures of SRB (Zhang et al., 2015). Common mediators include flavins, produced by organisms such as *Shewanella* spp. and phenazines, produced by pseudomonads. Phenazines have a midpoint redox potential of around $+65 \text{ mV}$ vs SHE and for flavin mononucleotide the midpoint redox potential is -145 mV for the dominant MEET process observed in *Shewanella oneidensis* MR1 (Okamoto et al., 2014; Roller et al., 1984). To be energetically favorable, the midpoint redox potential for putative cathodic redox mediators would

likely be substantially more negative than phenazines and preferably closer to that of reduced electron donors such as H_2 at -420 mV vs SHE. At least one study describes a microbe obtaining reducing power directly from an electrode and suggested that the process occurred through an unknown mediator with a midpoint redox potential under standard biological conditions of around -400 mV vs SHE (Aulenta et al., 2009). However, Huang et al. (2018) implicated phenazine production in *Pseudomonas aeruginosa* as the key component mediating electron extraction from stainless steel for pseudomonads (Huang et al., 2018).

However, strong conviction exists amongst bioelectrochemists that microbes can access cathodic current ‘directly’ from metal surfaces to gain energy without the need for mobile redox shuttles. Recent studies support such a possibility, implicating DEET in corrosion (Rowe et al., 2018; Hua et al., 2019). As described above, the major problem with descriptions of DEET as a mechanism for MIC is the terminology - direct electron transfer means different things to biologists and electrochemists. Any concept of a ‘direct’ biological electron transfer mechanism necessarily includes multiple electron carriers, e.g., NAD^+ , quinoids and cytochromes, each of which may contain more than one reactive center (Hinks et al., 2017; Jiang et al., 2019). Therefore, by definition, DEET can never be ‘direct’ in an electrochemical sense and the term DEET is used here merely to encompass the idea that there are no mobile extracellular-electron carriers mediating a particular bio-electrochemical reaction and that electron transport occurs via direct contact of the cell or biological charge carriers with the surface that is donating or accepting the electrons, i.e., it describes only the first or the final electron transfer.

Additional arguments against claims of cathodic DEET arise because many reports of such phenomena have failed to experimentally account for alternative electron donors such as H_2 or organic carbon in addition to the metal surface. A recent report appears to show cathodic DEET by a methanogen from a graphite electrode while discounting the effect of H_2 based on controls that showed both the absence of H_2 generation by the electrode over an extended period and that hydrogenotrophic methanogens did not grow in the system (Yee et al., 2019; Rowe et al., 2018). A recent study by Philips et al. (2018) reports a *Shewanella* isolate purportedly using Fe^0 as the sole source of electrons and fumarate as the electron acceptor. The authors discounted the role of mediators by using a defined medium absent of YE and by cyclic voltammetry which showed that no mediators had been exogenously produced. The authors were not able to completely rule out the role of hydrogen in reducing fumarate to succinate, but this eventuality did not stoichiometrically account for all of the succinate observed in the system. A recent study with *Geobacter* strain ACL unequivocally discounted both H_2 and formate as electron donors in Fe^0 oxidation while providing convincing evidence for the role of outer membrane proteins OmcA and OmcZ in corroding iron (Tang et al., 2019). The redox carriers responsible for cathodic DEET have not been characterised. Explanations include: 1) the reversibility of well-known cytochrome pathways involved in anodic electron transfer; 2) membrane-bound carriers such as cuproredoxins and pyroquinolones (Holmes et al., 2017); and 3) long-range transport via conductive fibers (pili) referred to as nanowires. Until the role of such structures is definitively revealed, cathodic DEET will continue to be the subject of debate.

Although conductive pili or nanowires have been proposed as mechanisms for long range extracellular electron transfer (Reguera et al., 2005; Bjerg et al., 2018), their role is controversial. The proposed mechanisms for electron transport along the length of a pilus include the following: electron hopping, analogous to the process which occurs in membrane-bound cytochromes, or a type of ‘metallic’ conductivity which occurs in pi-conjugated organic polymers. The two mechanisms are referred to as incoherent and coherent electron transport, respectively (Polizzi et al., 2012). Incoherent electron transport occurs in cytochromes. There is no biological precedent for coherent electron transport. A spirited debate about which of these mechanisms account for postulated long-range electron transfer is ongoing (Malvankar et al.,

2011, 2012, 2015; Strycharz-Glaven and Tender, 2012; Lovley and Malvankar, 2015), however, from an electrochemical perspective, neither mechanism is wholly satisfactory and a convincing description of the energetics of this process and the identification of precise structural redox centers remains elusive (Blackwood, 2018).

Ding et al. (2016) performed concurrent electrical and electrochemical measurements of living *Shewanella* and demonstrated that the apparent conductive current from these microbes arises from electrochemical faradic charge transfer at the cell/electrode interface, stating that no non-faradic electron pathway exists across the biofilm (Ding et al., 2016). These authors went as far as to say that results and the interpretations made in earlier experimental and theoretical studies should be revisited. Although the work of Ding et al. (2016) rules out electronic conductivity via a network of pili, they did not measure the electronic conductivities of individual pili (Wang et al., 2019; El-Naggar et al., 2010), so their findings do not rule out the possibility of electron transport along individual pili that link the microorganisms directly to a metallic substratum.

Polizzi et al. (2012) conducted a theoretical analysis of possible mechanisms for electrical conductivity in pili reported by El-Naggar et al. (2010) but were unable to provide a unified explanation. Polizzi et al. (2012) ruled out delocalization, as seen in the pi-conjugation of conducting polymers (i.e., rational electron transport), but felt that an irrational or hopping mechanism was possible, provided that the sample preparation method used by El-Naggar et al. (2010) had reduced the re-organization energy per hop by a factor of 1000 of that expected for a biological system. Polizzi et al. (2012) left open the possibility of a combination of hopping and delocalization, which they did not analyze. The combination seems a logical mechanism for the stacked heme arrangement of the reactive centers of cytochromes more recently reported by Wang et al. (2019).

Overall, it seems possible that pili can conduct electrons via some form of hopping mechanism, but the conductivities for individual pili reported by Wang et al. (ca. 3 S/m) (2019) are below the ionic conductivity of seawater (ca. 5 S/m). Furthermore, only those pili in direct contact with the metallic substratum, as opposed to contact with insulating corrosion products, will be able to participate in any electron transfer between the metal and the organism. Therefore, per unit volume, the conductance through the electrolyte can be expected to be orders of magnitude greater than that through the pili. As a result, when compared to ionic transport via redox mediators, any electronic transport through pili is unlikely to make a significant contribution to charge transfer processes that occur in MIC.

3. Iron and manganese oxidizing bacteria: under deposit corrosion and ennoblement

FeOB and MnOB are often cited individually and collectively as “corrosive” microorganisms. FeOB and MnOB colonize substrata, e.g., glass, titanium, and rock, and produce macroscopic deposits. FeOB oxidize soluble ferrous (Fe^{+2}) to insoluble ferric (Fe^{+3}) and MnOB oxidize soluble manganous (Mn^{+2}) to insoluble manganic (Mn^{+4}), which can lead to the deposition of oxides on solid surfaces. There is no evidence that FeOB or MnOB directly remove metal, e.g., there is no evidence that FeOB oxidize Fe^0 to Fe^{+2} . Both soluble ions and FeOB and MnOB can be present in the same waters. Microbial oxidation of Fe^{+2} is typically restricted to redox boundaries between aerobic and anaerobic zones (e.g., $50 \mu\text{M O}_2$) where abiotic oxidation of Fe^{+2} is limited. In contrast, Mn^{+2} is stable in fully oxygenated water and, in the absence of strong oxidizing agents, biological oxidation dominates Mn^{+2} oxidation in most natural environments.

Corrosion by FeOB has been reported in aerobic, freshwaters containing 15–600 ppm chloride (Cl^-) for a narrow range of vulnerable stainless steel alloys, e.g. 304, 316 and their low carbon counterparts (304L and 316L (Lee and Little, 2019). The mechanism typically cited for FeOB influenced corrosion is under-deposit corrosion or differential

aeration cells. It follows that only those materials that are susceptible to under deposit corrosion and/or crevice corrosion will suffer MIC due to FeOB. In an oxygenated environment, the area under the accumulated iron oxides is deprived of oxygen, causing the formation of a relatively small anode compared to the large surrounding oxygenated cathode. Within the developing pit, metal ion hydrolysis reactions create acidic conditions and attract charge-neutralizing counterions, e.g., chloride or sulfate, resulting in a fixed self-sustaining pit. The pH of pit solutions depends on specific hydrolysis reactions of the alloying elements (Shreir et al., 1994).

Mathiesen and Frantsen (2008) challenged the above model for FeOB influenced corrosion. They concluded that the failures due to FeOB, always associated with voluminous tubercles, could not be due to oxygen concentration cells alone. Emerson (2018) suggested that FeOB produced complex 3-dimensional biofilms that aided in the colonization of steel surfaces by other microbes directly involved in MIC, e.g., SRB. Laboratory experiments demonstrated some synergy in MIC between SRB and FeOB in artificial media (Zhang et al., 2007; Xu et al., 2007). Investigators have not demonstrated SRB or sulfur compounds in association with FeOB or MnOB in field studies. In addition, pit solutions in 304 and 316 stainless steels are highly acidic ($\text{pH} < 2$) and may not be conducive environments for SRB growth (Shreir et al., 1994).

Case histories of MnOB influenced corrosion of include variations of 304 and 316, martensitic alloy EN1.4313 (UNS S41500) stainless steels and copper (Dickinson and Wiatr, 2013; Linhardt, 2010). The significance of MnOB influenced corrosion is growing as water conservation and recurrent draught conditions throughout the world increase manganese and aggressive anion concentrations in natural water supplies. The mechanism for pitting corrosion in the presence of MnOB differs from that attributed to FeOB in several important aspects. In addition to under deposit corrosion, MnO_2 electrochemically couples to underlying metal, forming galvanic cells that can lead to aggressive pitting corrosion in some alloys. Unlike iron oxides, Mn^{+4} oxides are strong oxidizing agents. Microbial deposition of manganese dioxide (MnO_2) provides an alternative cathodic reaction as it can be reduced to MnOOH or Mn^{+2} ions (akin to manganese batteries), which causes a shift of the corrosion potential (E_{corr}) in the positive direction, i.e., ennoblement. The MnOB subsequently re-oxidize the $\text{Mn}^{+2,+3}$ back to MnO_2 (i.e. recharge the battery) (Fig. 2), which explains why the amount of Mn^{+2} ions required in the bulk solution can be as little as 6 ppb (Mathiesen and Frantsen, 2008).

Ennoblement increases the likelihood that stable pitting will occur in association with surface deposits on vulnerable alloys. Positive shifts in E_{corr} caused by MnO_2 typically range from +400 to +500 mV in neutral oxygenated water and exceed the critical pitting potentials of susceptible alloys in typical industrial waters. Alloys with pitting potential beyond this range are not susceptible to MnOB influenced corrosion. For example, Kuosmanen et al. (2005) reported that manganese-containing

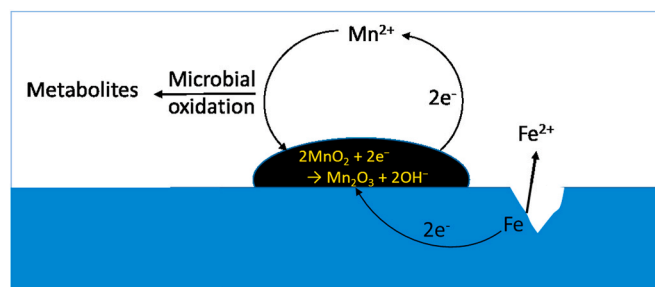


Fig. 2. Schematic of possible corrosion mechanism by MnOB. Microbial oxidation of Mn^{+2} ions results in the deposition of MnO_2 , the reduction of which acts as an alternative cathodic reaction for the corrosion reaction; compare the zinc - manganese battery system. Note that the MnO_2 and the corroding substrate must be in direct electrical contact.

deposits were a major fouling problem in titanium heat exchangers operating with Baltic seawater. They did not indicate any corrosion problems with this corrosion-resistant alloy (Kuosmanen et al., 2005). Ennoblement has not been reported for Fe⁺³ deposits.

4. Summary opinions

The cross-disciplinary approach of ascribing electrochemical observations to specific microbiological reactions over a wide range of electrolytes and exposure conditions has resulted in misleading generalizations and confusion. Any discussion of MIC mechanisms must include environmental considerations, (e.g., DO, electrolyte composition, flow) and material vulnerabilities. Mechanisms must include the possibility of microbial interactions within communities.

For example, FeOB and MnOB are typically associated with corrosion of crevice corrosion prone alloys. Under-deposit corrosion is typically cited as the mechanism for their involvement. The collective association of the two groups obscures differences in the mechanisms by which the microorganisms influence corrosion. Deposits of MnO₂ can cause galvanic corrosion and stable pit formation in vulnerable alloys. More recently investigators have suggested that in the case FeOB, pitting may require the activities of other microorganisms.

Despite the intuitive plausibility and having been repeated many times, the CDP hypothesis for SRB influenced corrosion, based on removal of adsorbed H₂, does not explain SRB influenced MIC. Other proposed mechanisms, including direct electron uptake and under-deposit corrosion are topics of active research and debate.

Use of the term “direct electron transfer” has caused some confusion in MIC literature. All known EET mechanisms rely on multiple electron carriers. The biological distinction as to whether the mediator is located on or inside the cell wall or is mobile in the environment is not important electrochemically. In electrochemical terms “direct electron transfer” refers to any transfer of electrons between an electrode and the redox species in a single step, i.e. no intermediate species are involved. While evidence for cathodic DEET using elemental metals as the electron source is emerging, the role of DEET in MIC is still unclear. All demonstrations of “direct electron transfer” have required precise, controlled experimental conditions, i.e., anaerobic, nutrient starved, Fe⁰ as the sole electron donor and specific microorganisms. To date, the role of microorganisms as catalysts for electron transfer and the influence of metabolic rates have received insufficient attention.

Communication regarding precise MIC mechanisms is mired in scientific and semantic uncertainty. History has shown that microbes are important in many processes that were once thought to be purely physical phenomena. Progress in understanding MIC mechanisms requires an interdisciplinary effort, integrating knowledge and methods from electrochemistry and microbiology into a real synthesis of approaches to first understand and then address important questions. For example, the distinction between mediated and direct electron transfer is inconsequential to electrochemists but of great microbiological significance.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

- Aulenta, F., Canosa, A., Reale, P., Rossetti, S., Panero, S., Majone, M., 2009. Microbial reductive dechlorination of trichloroethene to ethene with electrodes serving as electron donors without the external addition of redox mediators. *Biotechnol. Bioeng.* 103, 85–91.
- Bjerg, J.T., Boschker, H.T., Larsen, S., Berry, D., Schmid, M., Millo, D., Tataru, P., Meysman, F.J., Wagner, M., Nielsen, L.P., 2018. Long-distance electron transport in individual, living cable bacteria. *Proc. Natl. Acad. Sci. Unit. States Am.* 115, 5786–5791.
- Blackwood, D., 2001. An Investigation into the Anaerobic Corrosion Behaviour of Stainless Steel Surfaces under Simulated Radioactive Waste Repository Conditions Using the Guillotine and Shear Electrode Technique. *Aet/R/Env 0225*, 2001 available at www.nda.gov.uk/documents/biblio.
- Blackwood, D.J., 2018. An electrochemist perspective of microbiologically influenced corrosion. *Corros. Mater. Degrad* 1, 59–76.
- Costello, J., 1974. Cathodic depolarization by sulphate-reducing bacteria. *South Afr. J. Sci.* 70, 202–204.
- Delattre, H., Chen, J., Wade, M.J., Soyer, O.S., 2020. Thermodynamic modelling of synthetic communities predicts minimum free energy requirements for sulfate reduction and methanogenesis. *J. R. Soc. Interface* 17, 20200053.
- Dickinson, W.H., Wiatr, C., 2013. Manganese-related corrosion and fouling in water systems. *The Analyst* 20.
- Ding, M., Shiu, H.-Y., Li, S.-L., Lee, C.K., Wang, G., Wu, H., Weiss, N.O., Young, T.D., Weiss, P.S., Wong, G.C.L., Nealon, K.H., Huang, Y., Duan, X., 2016. Nanoelectronic investigation reveals the electrochemical basis of electrical conductivity in *Shewanella* and *Geobacter*. *ACS Nano* 10, 9919–9926.
- Dinh, H.T., Kuever, J., Mußmann, M., Hassel, A.W., Stratmann, M., Widdel, F., 2004. Iron corrosion by novel anaerobic microorganisms. *Nature* 427, 829.
- El-Naggar, M.Y., Wanger, G., Leung, K.M., Yuzvinsky, T.D., Southam, G., Yang, J., Lau, W.M., Nealon, K.H., Gorby, Y.A., 2010. Electrical transport along bacterial nanowires from *Shewanella oneidensis* Mr-1. *Proc. Natl. Acad. Sci. Unit. States Am.* 107, 18127–18131.
- Emerson, D., 2018. The role of iron-oxidizing bacteria in biocorrosion: a review. *Biofouling* 34, 989–1000.
- Enning, D., Garrelfs, J., 2014. Corrosion of iron by sulfate-reducing bacteria: new views of an old problem. *Appl. Environ. Microbiol.* 80, 1226–1236.
- Frankenthal, R., Milner, P., 1986. Hydrogen evolution kinetics on a high-carbon steel and on tin in seawater. *Corrosion* 42, 51–53.
- Gray, H.B., Winkler, J.R., 2005. Long-range electron transfer. *Proc. Natl. Acad. Sci. Unit. States Am.* 102, 3534–3539.
- Hamilton, W.A., 2003. Microbially influenced corrosion as a model system for the study of metal microbe interactions: a unifying electron transfer hypothesis. *Biofouling* 19, 65–76.
- Hardy, J.A., 1983. Utilisation of cathodic hydrogen by sulphate-reducing bacteria. *Br. Corrosion J.* 18, 190–193.
- Hardy, J.A., Bown, J.L., 1984. The corrosion of mild steel by biogenic sulfide films exposed to air. *Corrosion* 40, 650–654.
- Hinks, J., Zhou, M., Dolfing, J., 2017. Microbial electron transport in the deep subsurface. In: Chénard, C., Lauro, F.M. (Eds.), *Microbial Ecology of Extreme Environments*. Springer.
- Holmes, D.E., Shrestha, P.M., Walker, D.J., Dang, Y., Nevin, K.P., Woodard, T.L., Lovley, D.R., 2017. Metatranscriptomic evidence for direct interspecies electron transfer between *Geobacter* and *Methanoxithrix* species in methanogenic rice paddy soils. *Appl. Environ. Microbiol.* 83 e00223-17.
- Hua, T., Li, S., Li, F., Zhou, Q., Ondon, B.S., 2019. Microbial electrolysis cell as an emerging versatile technology: a review on its potential application, advance and challenge. *J. Chem. Technol. Biotechnol.* 94, 1697–1711.
- Huang, Y., Zhou, E., Jiang, C., Jia, R., Liu, S., Xu, D., Gu, T., Wang, F., 2018. Endogenous phenazine-1-carboxamide encoding gene Phzh regulated the extracellular electron transfer in biocorrosion of stainless steel by marine *Pseudomonas aeruginosa*. *Electrochem. Commun.* 94, 9–13.
- Hubert, C., Nemati, M., Jenneman, G., Voordouw, G., 2005. Corrosion risk associated with microbial souring control using nitrate or nitrite. *Appl. Microbiol. Biotechnol.* 68, 272–282.
- Hungate, R.E., 1969. Chapter iv A roll tube method for cultivation of strict anaerobes. In: Norris, J.R., Ribbons, D.W. (Eds.), *Methods in Microbiology*. Academic Press.
- Imo, E.O., Ihejirika, C.E., Orji, J.C., Nweke, C.O., Adieze, I.E., 2016. Mechanisms of microbial corrosion: review. *J. Chem. Biol. Phys. Sci.* 6.
- Javaherdashti, R., 2017. Microbiologically influenced corrosion (MIC). In: Springer.
- Javed, M., Neil, W., Mcadam, G., Wade, S., 2017. Effect of sulphate-reducing bacteria on the microbiologically influenced corrosion of ten different metals using constant test conditions. *Int. Biodeterior. Biodegrad.* 125, 73–85.

- Jia, R., Tan, J.L., Jin, P., Blackwood, D.J., Xu, D., Gu, T., 2018. Effects of biogenic H₂S on the microbiologically influenced corrosion of C1018 carbon steel by sulfate reducing *Desulfovibrio vulgaris* biofilm. *Corrosion Sci.* 130, 1–11.
- Jiang, X., Burger, B., Gajdos, F., Bortolotti, C., Futera, Z., Breuer, M., Blumberger, J., 2019. Kinetics of trifurcated electron flow in the decaheme bacterial proteins Mtrc and Mtrf. *Proc. Natl. Acad. Sci. Unit. States Am.* 116, 3425–3430.
- Jigletsova, S., Rodin, V., Kholodenko, V., Zhirkova, N., Alexandrova, N., 2004. Influence of nutrient medium composition on the direction of microbiologically induced corrosion. Paper 04575 NACE International.
- Jo, J., Cortez, K.L., Cornell, W.C., Price-Whelan, A., Dietrich, L.E.P., 2017. An orphan cbh3-type cytochrome oxidase subunit supports *Pseudomonas aeruginosa* biofilm growth and virulence. *eLife* 6, e30205.
- Kahyarain, A., Nesic, S., 2019. H₂S corrosion of mild steel: a quantitative analysis of the mechanism of the cathodic reaction. *Electrochim. Acta* 297, 676–684.
- Kakooei, S., Ismail, M.C., Ariwahjoedi, B., 2012. Mechanisms of microbiologically influenced corrosion: a review. *World Appl. Sci. J.* 17, 524.
- Kato, S., 2016. Microbial extracellular electron transfer and its relevance to iron corrosion. *Microb. Biotechnol.* 9, 141–148.
- King, R.A., Miller, J.D.A., Smith, J.S., 1973. Corrosion of mild steel by iron sulphides. *Br. Corrosion J.* 8, 137–141.
- Kuosmanen, T., Peltola, M., Raulio, M., Pullainen, M., Laurila, T., Selin, J.-F., Huopalaainen, H. & Salkinoja-Salonen, M. Effect of polarization on manganese biofouling of heat exchanger surfaces. In: Müller-Steinhagen, H., Malayeri, M. R. & Watkinson, A. P., eds. 6th International Conference on Heat Exchanger Fouling and Cleaning - Challenges and Opportunities, 05-10 June 2005 Kloster Irsee, Germany. Pp. 283-288.
- Lee, J.S., Little, B.J., 2019. A mechanistic approach to understanding microbiologically influenced corrosion by metal-depositing bacteria. *Corrosion* 75 (1), 6–11.
- Lee, J.S., Ray, R.I., Little, B.J., Lemieux, E.J., 2005. Evaluation of deoxygenation as a corrosion control measure for ballast tanks. *Corrosion* 61, 1173–1188.
- Li, Y., Xu, D., Chen, C., Li, X., Jia, R., Zhang, D., Sand, W., Wang, F., Gu, T., 2018. Anaerobic microbiologically influenced corrosion mechanisms interpreted using bioenergetics and bioelectrochemistry: a review. *J. Mater. Sci. Technol.* 34, 1713–1718.
- Linhardt, P., 2010. Twenty years of experience with corrosion failures caused by manganese oxidizing microorganisms. *Mater. Corros.* 61, 1034–1039.
- Lovley, D.R., Malvankar, N.S., 2015. Seeing is believing: novel imaging techniques help clarify microbial nanowire structure and function. *Environ. Microbiol.* 17, 2209–2215.
- Macdonald, D.D., 1999. Passivity—the key to our metals-based civilization. *Pure Appl. Chem.* 71, 951–978.
- Malvankar, N.S., Tuominen, M.T., Lovley, D.R., 2012. Comment on “On Electrical Conductivity of Microbial Nanowires and Biofilms” by S.M. Strycharz-Glaven, R.M. Snider, A. Guiseppe-Elie and L.M. Tender. *Energy Environ. Sci.*, 2011, 4, vol. 5. *Energy & Environmental Science*, pp. 6247–6249, 4366.
- Malvankar, N.S., Vargas, M., Nevin, K., Tremblay, P.-L., Evans-Lutterodt, K., Nykpanchuk, D., Martz, E., Tuominen, M.T., Lovley, D.R., 2015. Structural basis for metallic-like conductivity in microbial nanowires. *mBio* 6.
- Malvankar, N.S., Vargas, M., Nevin, K.P., Franks, A.E., Leang, C., Kim, B.-C., Inoue, K., Mester, T., Covalla, S.F., Johnson, J.P., Rotello, V.M., Tuominen, M.T., Lovley, D.R., 2011. Tunable metallic-like conductivity in microbial nanowire networks. *Nat Nano* 6, 573–579.
- Mathiesen, T., Frantsen, J.E., 2008. Unusual Corrosion Failures of Stainless Steel in Low Chloride Waters, vol. 2008. NACE International, Houston, TX. Paper 08174 NACE International.
- McNeil, M.B., Odom, A., 1994. Thermodynamic prediction of microbiologically influenced corrosion (MIC) by sulfate-reducing bacteria (SRB). In: *Microbiologically Influenced Corrosion Testing*. ASTM International.
- Mehanna, M., Basséguy, R., Délia, M.-L., Bergel, A., 2010. *Geobacter sulfurreducens* can protect 3041 stainless steel against pitting in conditions of low electron acceptor concentrations. *Electrochem. Commun.* 12, 724–728.
- Mori, K., Tsurumaru, H., Harayama, S., 2010. Iron corrosion activity of anaerobic hydrogen-consuming microorganisms isolated from oil facilities. *J. Biosci. Bioeng.* 110, 426–430.
- Müller, V., 2015. Microbial life at the thermodynamic limit: how much energy is required to sustain life? *Environmental Microbiology Reports* 7, 31–32.
- Okamoto, A., Nakamura, R., Neelson, K.H., Hashimoto, K., 2014. Bound flavin model suggests similar electron-transfer mechanisms in *Shewanella* and *Geobacter*. *Chemelectrochem* 1, 1808–1812.
- Philips, J., Van Den Driessche, N., De Paepe, K., PrévotEAU, A., Gralnick, J.A., Arends, J. B.A., Rabaey, K., 2018. A novel *Shewanella* isolate enhances corrosion by using metallic iron as the electron donor with fumarate as the electron acceptor. *Appl. Environ. Microbiol.* 84 e01154-18.
- Polizzi, N.F., Skourtis, S.S., Beratan, D.N., 2012. Physical constraints on charge transport through bacterial nanowires. *Faraday Discuss* 155, 43–61.
- Procópio, L., 2019. The role of biofilms in the corrosion of steel in marine environments. *World J. Microbiol. Biotechnol.* 35, 73.
- Reguera, G., McCarthy, K.D., Mehta, T., Nicoll, J.S., Tuominen, M.T., Lovley, D.R., 2005. Extracellular electron transfer via microbial nanowires. *Nature* 435, 1098.
- Roller, S.D., Bennetto, H.P., Delaney, G.M., Mason, J.R., Stirling, J.L., Thurston, C.F., 1984. Electron-transfer coupling in microbial fuel cells: 1. comparison of redox-mediator reduction rates and respiratory rates of bacteria. *J. Chem. Technol. Biotechnol.* 34, 3–12.
- Rowe, A.R., Rajeev, P., Jain, A., Pirbadian, S., Okamoto, A., Gralnick, J.A., El-Naggar, M. Y., Neelson, K.H., 2018. Tracking electron uptake from a cathode into *Shewanella* cells: implications for energy acquisition from solid-substrate electron donors. *mBio* 9, e02203–e02217.
- Sherar, B.W.A., Keech, P.G., Shoesmith, D.W., 2013. The effect of aerobic corrosion on anaerobically-formed sulfide layers on carbon steel in dilute near-neutral pH saline solutions. *Corrosion Sci.* 77, 257–264.
- Shreir, L.L., Jarman, R., Burstein, G., 1994. *Corrosion: Corrosion Control*. Butterworth-Heinemann.
- Spruit, C., Wanklyn, J., 1951. Iron/sulphide ratios in corrosion by sulphate-reducing bacteria. *Nature* 168, 951.
- Strycharz-Glaven, S.M., Tender, L.M., 2012. Reply to the ‘comment on “on electrical conductivity of microbial nanowires and biofilms” by N.S. Malvankar, M.T. Tuominen and D.R. Lovley. *Energy Environ. Sci.*, 2012 5, 6250–6255. <https://doi.org/10.1039/c2ee02613a>. *Energy & Environmental Science*, 5.
- Syrett, B.C., 1977. Accelerated corrosion of copper in flowing pure water contaminated with oxygen and sulfide. *Corrosion* 33, 257–262.
- Tang, H.-Y., Holmes, D.E., Ueki, T., Palacios, P.A., Lovley, D.R., 2019. Iron corrosion via direct metal-microbe electron transfer. *mBio* 10, e00303–e00319.
- Tanner, R.S., 2007. *Cultivation of bacteria and fungi*. In: *Manual of Environmental Microbiology*, third ed. American Society of Microbiology.
- Venzlaff, H., Enning, D., Srinivasan, J., Mayrhofer, K.J., Hassel, A.W., Widdel, F., Stratmann, M., 2013. Accelerated cathodic reaction in microbial corrosion of iron due to direct electron uptake by sulfate-reducing bacteria. *Corrosion Sci.* 66, 88–96.
- Von Wolzogen Kühr, C.A.H., Van Der Flugt, L.S., 1964. Graphitization of Cast Iron as an Electrochemical Process in Anaerobic Soils. Defense Technical Information Center, Fort Belvoir, Va.
- Wang, F., Gu, Y., O’Brien, J.P., Sophia, M.Y., Yalcin, S.E., Srikanth, V., Shen, C., Vu, D., Ing, N.L., Hochbaum, A.I., 2019. Structure of microbial nanowires reveals stacked hemes that transport electrons over micrometers. *Cell* 177, 361–369 e10.
- Webster, B.J., Newman, R.C., 1994. Producing Rapid Sulfate-Reducing Bacteria (SRB)-Influenced Corrosion in the Laboratory. In: Kearns, J.R., Little, B.J. (Eds.). *ASTM International*, West Conshohocken, Pa.
- Xu, C., Zhang, Y., Cheng, G., Zhu, W., 2007. Localized corrosion behavior of 316L stainless steel in the presence of sulfate-reducing and iron-oxidizing bacteria. *Mater. Sci. Eng. A* 443, 235–241.
- Xu, D., Gu, T., 2014. Carbon source starvation triggered more aggressive corrosion against carbon steel by the *Desulfovibrio vulgaris* biofilm. *Int. Biodeterior. Biodegrad.* 91, 74–81.
- Yee, M.O., Snoeyenbos-West, O.L., Thamdrup, B., Ottosen, L.D.M., Rotaru, A.-E., 2019. Extracellular electron uptake by two *Methanosarcina* species. *Frontiers in Energy Research* 7.
- Zhang, P., Xu, D., Li, Y., Yang, K., Gu, T., 2015. Electron mediators accelerate the microbiologically influenced corrosion of 304 stainless steel by the *Desulfovibrio vulgaris* biofilm. *Bioelectrochemistry* 101, 14–21.
- Zhang, Y.H., Xu, C.M., Cheng, G.X., Zhu, W.S., 2007. Pitting initiation of 316L stainless steel in the media of sulfate-reducing and iron-oxidizing bacteria. *Inorg. Mater.* 43, 614–621.
- Zhou, C., Chia, G.W.N., Ho, J.C.S., Moreland, A.S., Seviour, T., Liedberg, B., Parikh, A.N., Kjelleberg, S., Hinks, J., Bazan, G.C., 2019. A chain-elongated oligophenylenevinylene electrolyte increases microbial membrane stability. *Adv. Mater.* 31 (18) <https://doi.org/10.1002/adma.20180821>.