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Research Article

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Chemical and electron microbial influenced corrosion

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ABSTRACT

In microbiologically influenced corrosion (MIC) study, the electron acceptor of the cathode plays a decisive influence on corrosion characteristics. Some bacteria which can directly absorb electrons releasing from the anode reaction of the microbial dissolution of iron have been found in anaerobic biofilm studies, including some of the sulfate-reducing bacteria (SRB), methanogens and some other corrosion-reducing bacteria. These bacteria in biofilm are showing severe corrosion because of their different electron transfer mechanism. The corrosion mechanisms of these corrosion bacteria is called electron microbial influenced corrosion(EMIC), EMIC and its electronic transfer mechanisms distinct from those chemical microbial influenced corrosion(CMIC) mechanism bacteria that indirectly effects on the anode and cathode electrode reaction from nature. In recent years, EMIC mechanism has become a hot topic in the field of microbial corrosion. This paper describes the microbial membrane CMIC and EMIC and its electronic delivery mechanisms in detail, and gives some suggestions on corrosion studies.

Keywords: Biofilm; MIC; SRB; CMIC; EMIC; Electron transfer

INTRODUCTION

Abiotic corrosion of metals is generally the result of chemical and electrochemical reactions between metals and the environment they are around. Bacteria in biofilm are also closely related to corrosion. Many different terms have been used to describe corrosion caused or induced by microbes, including biocorrosion, microbial corrosion, and microbiologically influenced/induced corrosion (MIC). They have different connotations and MIC has been accepted widely. The term MIC is usually interpreted as to indicate an increase in corrosion activity due to the presence of bacteria which accelerate the rates of the anodic and/or cathodic corrosion reaction while leaving the corrosion mechanism more or less unchanged [1]. That is in other words that is to say that, redox reactions on metal surface are microbially mediated [2]. First article about the MIC could be traced back to 1891[3], but understanding deeply of MIC mechanism began to mature until the late 1980s [1]. Due to investigation of biocorrosion mechanisms involves multidisciplinary knowledge in several diverse research areas such as bio-electrochemistry, microbiology, corrosion engineering and chemical engineering, much confusion remains in MIC mechanism [4]. There is no universal mechanism of MIC.

According to Lewandowski and Beyenal[5], biofilms can influence the corrosion of metals (1) by metabolic reactions in the biofilm consuming oxygen, the cathodic reactant; (2) by controlling the mass transport of the corrosion reactants and products, therefore changing the kinetics of the corrosion process; (3) by generating corrosive substances; and (4) by generating substances that serve as auxiliary cathodic reactants. Above mechanisms showed MIC connected the action on the cathode or anode reaction directly or indirectly. In MIC, due to microbial metabolic process attendance corrosion reaction of cathode, electron acceptor in the system is particularly important.

In many corrosion systems, oxygen is removed by oxygen scavengers or flash rust, or exhausted by the upper aerobic biofilm. Thus, anaerobic corrosion is still threatening. Under anaerobic conditions, electrons must be accepted by the non-oxygen substance. Sulfate used by SRB as a typical electron acceptor. Some strains can also use sulfur, thiosulphate or CO_2 as an oxidizing agent [6]. Besides SRB, other bacteria such as acid-producing bacteria (APB) and methanogenic bacteria are also common corrosive bacteria. There are at least different two types of anaerobic corrosion in anaerobic metabolism [7]. In the study of anaerobic corrosion mechanism, a class of δ-proteobacteria belonging to a new marine SRB is isolated, using metallic iron (ie, no organic substrates, such as lactate) as the sole electron source for sulfate reduction [8]. This type of SRB is highly corrosive to metal substrate, its corrosion rates up to 0.7mm $Fe^0 \cdot yr^{-1}$, corresponding to corrosion density of $61\mu A \cdot cm^{-2}$ [9]. Like other microorganisms, SRB depends on oxidation-reduction reaction of lactate coupled the reduction of sulfate to provide energy for metabolism. If there is local absence of organic carbon because of the mass transfer resistance by the biofilm on the bottom, SRB can be switched to use as sulfate respiration Fe^0 as electron donor [10]. Such corrosion mechanism is called electric microbiologically influenced corrosion (EMIC) of SRB. D. Enning first proposed such concept of chemical microbiologically influenced corrosion (CMIC) and EMIC, and gives quantitative methods for the corrosion proportion of EMIC of SRB [8,11].

In some SRB corrosion process, the sulfide generated in their metabolism as a chemical aggressive compound mainly caused the following reaction:

$$Fe + H_2S \rightarrow FeS + H_2 (1)$$

In such way, SRB act indirectly through its metabolic end products. This mechanism is called CMIC. In the case of carbohydrate oxidation state, for example, the overall reaction can be expressed as:

$$3(HCOH)+2SO_4^{2-}+2Fe+H^+ \rightarrow 2FeS+3HCO_3^-+2H_2O \qquad (2)$$

SRB can also be involved more intimately in anaerobic iron corrosion by a mechanism that is fundamentally different from the above CMIC. SRB use iron as the only source of reducing equivalents for sulfate reduction [10].

$$3Fe^0+SO_4^{2-}+3HCO_3^-+H_2O \rightarrow FeS+FeCO_3+5HO^- (3)$$

The mode that direct electron uptake from iron by SRB is called EMIC [9].

2. MIC mechanism of SRB

SRB corrosion mechanisms can be divided into: Cathodic Depolarization by Hydrogenise (1934) , Iron Sulfides

(King's Mechanism) (1971), A Volatile Phosphorous Compound (1983), Anodic Depolarization (1984), Fe-Binding Exopolymers (1995), Sulfide and Hydrogen-Induced Stress Corrosion Cracking (SCC) (1995), Sulfide (1998), Three Stages Mechanism (Romero Mechanism) (2005), and Biocatalytic Cathodic Sulfate Reduction (BCSR) (2009). Except for the last one belongs to the EMIC, other are CMIC.

2.1. CMIC mechanism

Many mechanisms of MIC are established on the inherent attribute that SRB using H_2 as the electron donor, according to :

$$4H_2 + SO_4^{2-} + 2H^+ \rightarrow H_2S + 4\,H_2O. \qquad (4)$$

First, the initial electron donor is iron as anode, reaction is as follows:

$$Fe \rightarrow Fe^{2+} + 2e^- ,\ E_{SHE,298K} = -0.47 + 0.0296 lg(a_{Fe}{}^{2+}) \qquad (5)$$

Then, H^+ of water reductioned to H_2 by reaction (2):

$$2H^+ + 2e^- \rightarrow H_2 ,\ E_{SHE,298K} = 0.00 - 0.0296 lg(a_{H2}) - 0.0592pH \qquad (6)$$

Overall reaction of (1) and (2) is

$$Fe + 2\,H^+ \rightarrow Fe^{2+} + H_2 \qquad (7)$$

The first mechanism of CMIC is the cathode depolarization theory. Existence of microorganisms such as SRB could consume H_2. So, partial pressure of H_2 decreased and iron could be dissolved continuously due to depolarization. Then H_2S, produced from metabolites of SRB, combined with Fe^{2+} released from the iron. The total reaction is as follows:

$$4Fe + SO_4^{2-} + 3HCO_3^- + 5H^+ \rightarrow FeS + 3FeCO_3 + 4H_2O \qquad (8)$$

The second mechanism of CMIC is H^+ reduced to H_2, this process stimulated by the iron sulfide with catalytic activity on the iron electrode. Therefore, SRB absorbed H_2 from FeS but not from the metal surface.

2.2. EMIC of SRB

Based on biocatalysis cathodic sulfate reduction theory (BCSR), MIC takes place since the sulfate reduction at the cathode will consume the electrons released by iron dissolution at the anode with the help of biocatalyst and the interface of biofilm and the metal are a place for both anodic and cathodic sites [12]. It assumes that a corrosive SRB biofilm is formed on an iron surface causing the following cathode reactions to go forward due to biocatalysis.

Cathode reaction: $SO_4^{2-} + 8H^+ + 8e^- \rightarrow HS^- + OH^- + 3H_2O.$ (9)

The reaction rate in the absence of bio-enzyme of biofilm is very low. Control factor is biofilm catalysis controlling the rate of half reaction of sulfate reduction from sulfate to sulfide[13].

Because the reaction between iron and water to generate H_2 is extremely slow [8], and the electrical conductivity of

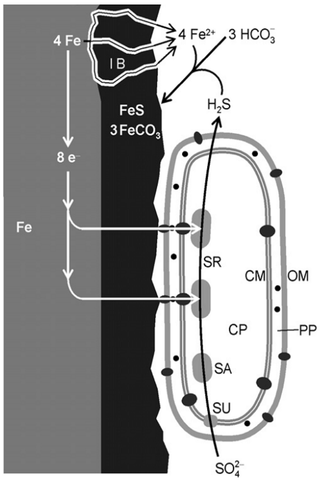
FeS rust, so corrosion rate is very high when metallic iron used as the sole electrons source to reduce sulfate. The process could not be explained by the H_2.Therefore, the EMIC mechanism was formed——bacteria which attached on the surface of metallic iron directly absorb electronic by reaction (5):

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

$$E_{SHE;\ average;\ 298K} = 0.30 + 0.0074\ \lg\ (a_{SO4}{}^{2-}/a_{H2S}) - 0.074\ pH \qquad (10)$$

EMIC is the reaction coupled with the iron dissolution reaction (5). The overall reaction is same as (8).

EMIC mechanism of corrosivity SRB is shown in Fig 2 [8]. The stoichiometric reaction of CMIC and EMIC mechanisms of SRB is show in Fig 3 [8].



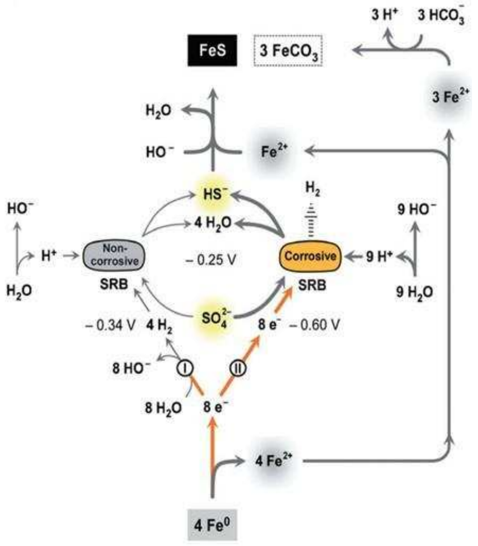


Fig 2 SRB corrosion mechanism

Fig 3 SRB stoichiometry comparison chart of the schematics of EMIC reaction of CMIC and EMIC mechanism

3. Electron Transfer Mechanism

3.1. Direct electron transfer (DET) and mediator electron transfer (MET)

The bacteria attached in the biofilms, not suspended in the water, are associated with microbial corrosion. For EMIC, the electrons released by iron oxidation must be transported to the periplasm to complete the oxidizing substances' reduction. Different from the ion, electron cannot transmit in the water. Planktonic bacteria cannot obtain electrons from metal surface through the water medium, which cannot directly cause EMIC. The microbial fuel cell (MFC) researchers do a lot of work about maximum power output produced by biofilms and form some electron transfer mechanisms. The mechanisms include two sides, that is direct electron transfer (DET) and mediator electron transfer (MET). This is the essential difference between EMIC and CMIC mechanisms: DET corresponds EMIC, MET corresponds CMIC.

Direct electron transfer depends on the film containing the electron transfer proteins such as C type pigment, ferrous hemoglobin and pili (known as nanometer wire), transferring the electrons into the cell periplasm. In the case of electron transfer protein, cytoderm must contact with the conductive surface directly. That means only a single cell layer lead corrosion. Pili plays a role in the electron transfer process and multi-layers of the cell cause corrosion. Sherar et al [14] noted that when SRB become the dominant bacteria in biofilm at the condition of no organic carbon solution, SRB form many pili which connect cytoderm to the iron surface. This indicates that cells are stimulated by the lack of carbon and produce pili, so as to the electron transferring released by Fe^0 oxidation.

The MET depends on electronic media with oxidation-reduction active as electros mediators. Many mediators were found in the MFC research, most of compounds concerning membrane connecting and electron transferring come from Proteobacteria [13]. Experimental investigation has found that electronic media can promote the biological corrosion [14]. Involving the CMIC about methanogen and hydrogen consumption SRB, molecular hydrogen can be used as the electron carrier, which is the theoretical source of cathode depolarization process. Methanogens and SRB in hydrogenase positive can use hydrogen as the energy source. In the traditional chemical corrosion, H_2 is found as corrosion products. Proton H^+ adsorbs electron released by iron oxidation, then form H_2. The oxidation of H_2 releases electrons, electrons were used by reduction reaction, and then the protons were generated again.

3.2. Electron transfer mechanism of XRB

Gu et al proposed a biological corrosion mechanism model [15] based on the famous bio-catalytic cathode sulfate reduction (BCSR) theory. This model introduces standardized parameter “biofilm aggressive" so as to ignore the details about anode and cathode electron transfer. Therefore, in the EMIC of SRB, all forms of electron transfer mechanisms can be applied to the model, rather than the cathodic polarization theory. In the BCSR theory, there is no real physics meaning concept of cathode. The cathodic reaction only involves biological catalysis SRB reduction reaction occurring in the SRB periplasm. In order to explain the EMIC of the nitrate / nitrite reduction electrogenic bacteria, this theory has been expanded to a biological catalysis cathode nitrate reduction (BCNR) theory [7].

All microorganisms involved in EMIC anaerobic respiration can be summarized as "XRB". In the “XRB”, X represents an oxidant, such as sulfate, nitrate/nitrite, and CO_2; B represents microorganisms, including bacteria, archaea and eukaryotes [7]. XRB corrosion is caused by the XRB using Fe^0 as energy. Experiments have shown that Fe^0 can be used as the sole energy source of SRB, NRB and methanogenic bacteria [8]. Xu and Gu found that culturing D. vulgaris biofilm under the same initial conditions was more aggressive for the carbon steel because of lacking organic carbon bio-film [10]. XRB have a common feature, they are all anaerobic respiration bacteria that is to say they use an external electron acceptor. The reduction reaction of oxidizing substances in the periplasm needs hydrogenase. That means EMIC is meaningful, as it relates to the microbial catalyst. Electric production biofilm (the bio-film that uses H_2 as electron carrier) is necessary. Because the Fe^0 is insoluble, electrons released by extracellular iron oxidation must depend on complicated electron transport chain to go into periplasm, involving the reduction reaction of sulfate, nitrate/nitrite and CO_2 from beginning to the end.

CONCLUSION

Although MIC has been studied and reported for many years, the mechanism of microbiological corrosion is still insufficient. The energy sharing in biofilm population is particularly important, especially for EMIC mechanism. It must be noted that the secretion of non-corrosive microbial electron mediator plays a role in promoting EMIC of corrosive bacteria. The development of chemical and electrochemical methods can ensure the detection of the electron mediator. The knowledge of microbial membrane electron transfer is essential.

It is not surprising that methanogens as one of biofilm bacteria appear in the petrochemical industry frequently, since the release of H_2 in iron corrosion is their source of energy. H_2 as an electron carrier is the electronic transmission intermediary in biofilm microbial populations. In addition to H_2, the format can also be used as the electron mediator of some microbes which contain microbial of organic carbon degradation, methane-producing bacteria and SRB that make use of H_2. It frequently observed that microbial biological membrane populations that provided electronics on the anode behaved better than pure microbial membrane populations to the anode. In the studies of biological corrosion, the more serious threat may come from the biofilm biodiversity, because the microbial populations can remove the electronics on the metal surface more effectively.

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