

# Chapter 1

## A Short Journey to the Realm of Corrosion

**Abstract** In this chapter, we will review some important, basic concepts of corrosion. This chapter and the next chapter about technical treatment of corrosion will make the necessary electrochemical corrosion understanding of MIC.

**Keywords** Standard definition of corrosion · Anodic/cathodic reaction · Thermodynamics of corrosion · Kinetics of corrosion · Pourbaix diagram · Polarisation diagram

### 1.1 Introduction

The main idea of this chapter is to deal with the principles and basics of corrosion, to an extent that will be necessary for understanding microbial corrosion, or whatever you call it!<sup>1</sup>

### 1.2 Definition of Corrosion

Corrosion, according to ISO 8044 standard, is defined as<sup>2</sup> “Physicochemical interaction (usually of an electrochemical nature) between a metal and its environment which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part”. In a sense, corrosion can be viewed as “the chemical reversion of a refined metal to its most stable energy state”.<sup>3</sup> During extractive processes to obtain metals out of their ores or mineral compounds, reductive processes are applied. In these processes, by giving more electrons to

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<sup>1</sup>See Chap. 4 for alternative names.

<sup>2</sup>Mattson E (1989) Basic corrosion technology for scientists and Engineers, Chap 3. Ellis Horwood Publishers.

<sup>3</sup>Videla HA (1996) Manual of biocorrosion, Chap. 4. CRC Press, Inc.

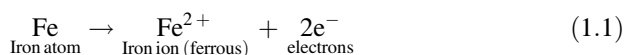
metallic compounds in the ore, thermodynamically stable metal in the ore is brought into thermodynamically instable state by reducing processes of extractive metallurgy. In other words, by investing energy to convert the ore to metal, chemical bonds are broken; oxygen, water and other anions are removed and the pure metal is arranged in an ordered lattice whose formation requires certain amount of excess energy, different for each metal, to be stored. It is the dissipation of this stored energy that drives the corrosion reaction. As a result, metals always are expected to reach a stable energy level by giving off additional electrons they have received during extractive metallurgical processes. This builds up the thermodynamic basis of oxidation, or more generally termed, corrosion, in metals.

The main components of electrochemical corrosion are the Anode (where anodic reactions occur), the Cathode (where cathodic reactions of receiving electrons from the anodic reactions happen) and the aqueous solution, or Electrolyte, which contains positively and negatively charged ions and is a conductor.

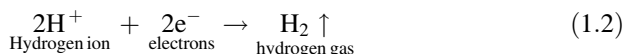
As all of the corrosive processes related to micro-organisms occur electrochemically, i.e. in aqueous environments, this chapter will just focus on the mechanisms of this type of corrosion and will not explain other types of corrosion such as high temperature corrosion.

### 1.3 Electrochemical Corrosion: A Brief Introduction

Definitions of the anode and the cathode are among basic definitions in electrochemical corrosion. The area of the metal surface that corrodes/the metal dissolves and goes into solution, is called the anode. The cathode is the area of the metal surface that does not dissolve. In the literature of electrochemistry, reduction and oxidation reactions are defined as when metals lose electrons (i.e. oxidation) or gain electrons (reduction):



Reaction (1.1) is an example of an oxidation reaction, the oxidation of iron. As it is seen, this reaction gives off electron into the solution. Such reactions are also called anodic reactions.



Reaction (1.2) is an example of a reduction reaction. Reduction reactions are also called cathodic reactions. So, alternatively, one can define corrosion as anodic reactions that are occurring at the anode. Thus, three main components of any electrochemical corrosive reaction are the anode, the cathode and the solution in which corrosion occurs. This solution is called the electrolyte and always water is an integral part of it. One may show these components as three corners of an “electrochemical triangle”:

The “electrochemical triangle” implies that for *corrosion to happen, all the three components must be available and interactive*. It follows that any method to be implemented to solve a corrosion problem must try to remove at least one of the sides of the triangle. This point will be discussed in more detail later (Fig. 1.1).

Some important points about corrosion are:

- As it is evident from definitions of anodic and cathodic reactions, there is exchange of electrons either as liberated (anodic reaction) or gained (cathodic reaction). This means that one can actually talk about flow of electrons, or, the current. On the other hand, if a certain area “A” of the anode loses (or, as cathode, gains) “n” electrons, it follows that an area of “2A” will give (or, again as cathode, will gain) “2n” electrons. So, it is possible to talk about current density instead of current. Defining the current density as total current (in Ampere) passing through an electrolyte per unit area of an electrode, it is shown as  $A/m^2$ . A very important point is that, by applying Faraday’s laws and noticing that as for many metals of engineering interest the ratio of the relative molar mass (equivalent weight) to the density is roughly constant, then:

$$A/m^2 = mm/yr$$

The relation states that the corrosion rate of metal, expressed in millimetre per year (mm/yr) is numerically equal to the current density expressed in Ampere per unit area ( $A/m^2$ ).<sup>4</sup>

- Most of the time, there is only one anodic reaction. For instance, in the “Galvanic cells” where there are two dissimilar metals such as iron and copper, the anodic reaction is always dissolution of the metal with higher tendency to corrode. However, there could be more than one cathodic reaction. Some of important cathodic reactions are as follows:

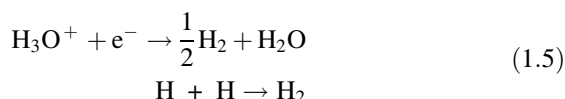
1. Reduction of oxygen in neutral/alkaline solutions:



2. Reduction of hydrogen that in anaerobic (oxygen-free) or acid electrolytes switches to



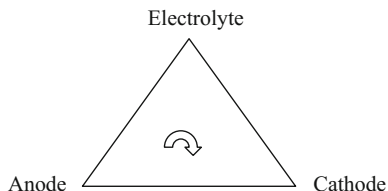
Or




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<sup>4</sup>West JM (1986) Basic corrosion and oxidation, Chap. 6. Ellis Horwood Publishers.

**Fig. 1.1** main components of an electrochemical triangle



This much slower reaction (except in acid conditions) explains why corrosion is hardly seen in anaerobic environments (except with passive/active metals such as stainless steels and in the presence of the micro-organisms) (see footnote 3).

### 1.3.1 When Corrosion Happens?

It will be of interest to anticipate under what conditions corrosion can actually occur. Every electrochemical reaction has a specific voltage that can be used with respect to a reference point or standard called “reference potential” to compare the voltages. In this way, one is able to say which reaction is more “noble” (not easy to take place) and which one is more “active” (thermodynamically easier to happen). Reference reactions are defined as to have the following characteristics:

- All of the substances taking part in the electrode reactions must have unit activity (activity = 1).
- Temperature must be 25 °C.
- Hydrogen pressure in the reference electrode must be one atmosphere.

By ranking and rating the electrode reactions according to the values of the standard potential, the *electrochemical series* is obtained. With respect to hydrogen voltage (accepted as zero), the potential required for reduction of  $\text{Cu}^{2+}$  to Cu is +0.34 volts and the potential of reduction of  $\text{Fe}^{+2}$  to Fe is -0.41 volts on the standard hydrogen electrode (SHE) scale. As reduction of copper ion to copper requires less energy (in terms of potential) than reduction of ferrous, then  $\text{Cu}^{2+}$  to Cu takes place easier and sooner. The net effect is cathodic reaction of copper and ANODIC reaction of iron to ferrous resulting in corrosion of iron in copper sulphate solution, in other words, galvanic corrosion of iron by copper cathode ( $\text{Fe} + \text{CuSO}_4 \rightarrow \text{FeSO}_4 + \text{Cu}$ ).

Although using the electrochemical series seem to be very useful, it does have very serious limitations such as (see footnote 2):

- Electrochemical series applies only to oxide-free metal surfaces and at the activities (concentrations), for which the standard potentials are valid. However, in actual practice, oxide films often cover the metal surfaces.

- The activities can deviate considerably from 1, especially when the metal ions are associated with other constituents in the so-called complex ions. It is not always possible to maintain standard temperatures and pressures.

Such conditions can result in the measured potentials having a completely different order than that given in the electrochemical series. That is why metals are exposed to a given electrolyte, say, seawater, and then arranged according to the measured electrode potential. What is then produced is called a *galvanic series* in a given environment at a given temperature. The potentials, however, are only valid for the electrolyte in which the measurements have been made. In seawater at 25 °C, stainless steel (18/8) in the passive state has a potential of 0.19 V (measured with respect to hydrogen scale) which will make it more noble to galvanised steel that has a voltage value of  $-0.81$  V (also with respect to hydrogen scale).

### 1.3.2 Corrosion Forecast

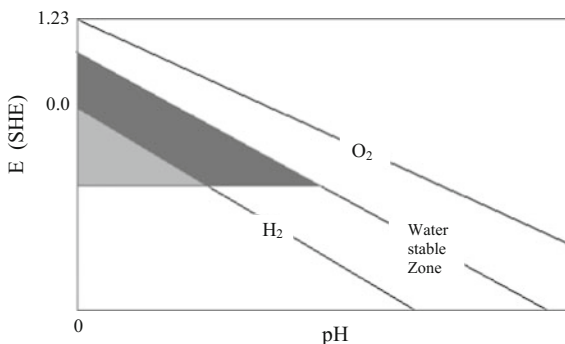
Pourbaix diagrams:

Thermodynamically, one may forecast or predict if certain reactions can occur, however, this does not mean that the reaction in question *will* occur. Thermodynamics can tell us about the “tendency” of corrosion to happen and it is by use of Pourbaix diagrams that one can thermodynamically predict if certain reactions will occur.

Pourbaix diagrams use potential (in Volts) versus pH. A more simplified Pourbaix diagram is seen from Fig. 1.2.

As it is seen from Fig. 1.2, two lines designated by  $O_2$  and  $H_2$ , upper and lower, define the domains for oxygen and hydrogen stability: above the upper line water is oxidised to  $O_2$ , so oxygen is evolved above the upper line. Below the lower line, water decomposes to  $H_2$  and thus, hydrogen will be liberated below the hydrogen line. Hence, the domain with dark colour represents where corrosion occurs solely

**Fig. 1.2** A simplified Pourbaix diagram



by oxygen reduction and the domain with lighter colour represents where hydrogen evolution can also take place.

These diagrams can be used to follow the consequences of environmental changes upon corrosion behaviour. Pourbaix diagrams are useful guides as to “what should occur” but what determines “what actually does occur in practice” are the rates of the processes and reactions. To understand kinetics of corrosion, or in other words, to understand how fast corrosion takes place, one may use another tool that is known as polarisation curves. To understand polarisation curves, it is necessary to understand the two components of them, that is, anodic and cathodic polarisations.

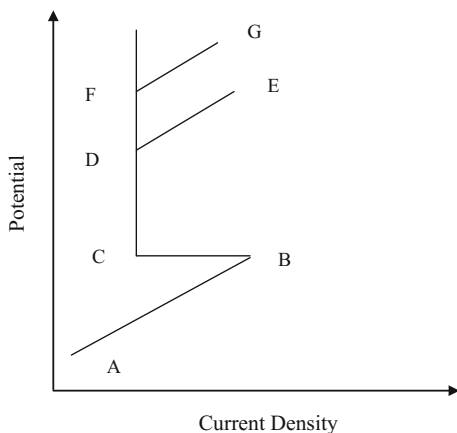
### 1.3.2.1 Anodic Polarisation (Anodic Polarisation Reaction)

An example of such polarisation curves is given in Fig. 1.3:

Such curves are observed (a) in solutions with very low pH (sufficiently acidic) and (b) if the metal is capable of forming films. In this type of curves, three regions can be differentiated

- The first region is where anodic current, and hence, the dissolution rate, will increase as the anode potential is made more positive (high dissolution)..... (A → B)
- The second region is where film formation and passivation of the metal beneath happen. Formation of the film will act as a barrier to further dissolution so that the current (i.e., corrosion rate) will fall.....(B → C)
- The third region is where the rise in potential (passive state) occurs.....(C → D)
- At very high potentials (point D) three possibilities, depending on the conductivity of the corrosion products film, can occur:

**Fig. 1.3** A typical anodic polarisation curve



- (a) If the film has a good electrical conductivity, it may be oxidised to soluble species and thus dissolution starts again along ( $D \rightarrow E$ ), where the metal transfers into the “trans-passive” state. This behaviour may be observed where continued dissolution of the passive film on chromium,  $\text{Cr}_2\text{O}_3$  [Cr(III)], to chromate,  $\text{CrO}_4^{2-}$  [Cr(VI)], takes place.
- (b) An alternative is if the film is a good electronic conductor, oxygen evolution may occur along ( $F \rightarrow G$ ).  
However, if the film is a poor electronic conductor, then high anodic potentials may be reached along ( $F \rightarrow H$ ) with a constant, high current density. This may facilitate “anodising” which is commercially used as a process for protecting aluminium.

It must be said that the presence of ions such as chloride ions, may prevent or delay passivation. Furthermore, passive films—especially in stainless steels—will tend to break down in the presence of such ions.

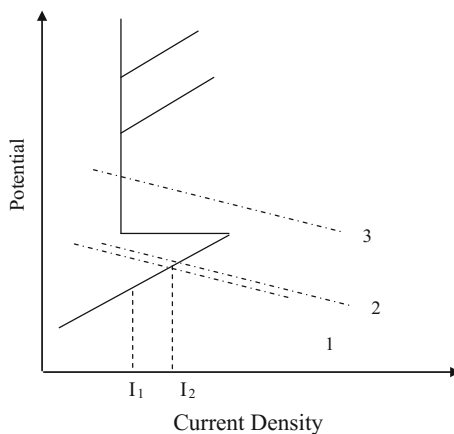
### 1.3.2.2 Cathodic Polarisation (Cathodic Polarisation Reaction)

Examples of such polarisation curves are shown in Fig. 1.4 as dashed lines:

In Fig. 1.4, the cathodic reaction designated as 2 has a larger corrosion rate than cathodic reaction 1 ( $I_2 > I_1$ ). With a cathodic reaction such as 3, passivation of the metal is reached. As mentioned earlier, there are a number of cathodic reactions such as hydrogen and/or oxygen evolution reactions, reduction of ions such as  $\text{Fe}^{3+}$  or  $\text{MnO}_4^-$  or molecular species such as nitric acid. In reality, the cathodic curves are not as straight lines as shown in Fig. 1.4. For example, the shape of the reduction curve of oxygen is rather “curvy” mainly due to the limited solubility of oxygen in aqueous solutions.

When a metal is exposed to an aqueous solution containing ions of that metal, on the surface of the metal, both *oxidation* (changing the metal atoms into the metal

**Fig. 1.4** Cathodic polarisation where the *dashed lines* 1, 2 and 3 represent different cathodic reactions that, according to their potentials, can occur



ions, or, *anodic reaction*) and *reduction* (changing the metal ions into the metal atom, or, *cathodic reaction*) can occur. When current is applied to the electrode surface, the electrode potential is changed and it is said that the electrode has been *polarised* and the change in electrode potential is called *polarisation*. *Overpotential* is the difference between the electrode potential of the electrode with applied current and the equilibrium potential for the electrode reaction in question. *Depolarisation* is then defined as the removal of factors diminishing the rate of an electrochemical reaction, for example, cathodic reaction.

## 1.4 Summary and Conclusions

In this chapter, we very briefly touched on some important theoretical elements of electrochemical corrosion such as how corrosion can be forecast (by using Pourbaix diagrams) and how fast it can happen (by using anodic and cathodic polarisation curves).

Pros and cons of the application of the polarisation methods in studies related to microbial corrosion will be addressed later (Chap. 6). In the next chapter, the implementation of theoretical electrochemistry will be discussed to show how and why some techniques such as inhibitor addition or coating application work in practice.

## References

- Mattson E (1989) Basic corrosion technology for scientists and engineers, Chap 3. Ellis Horwood Publishers  
Videla HA (1996) Manual of biocorrosion, Chap 4. CRC Press, Inc  
West JM (1986) Basic corrosion and oxidation, Chap. 6. Ellis Horwood Publishers

## Further Reading

- Fontana MG (1987) Corrosion engineering (3rd edn.). McGraw-Hill International Editions  
Scully JC (1983) The fundamentals of corrosion (2nd edn.). Pergamon Press  
Shreir LL, Jarman RA, Burstein GT (eds) (1995) Corrosion (3rd edn.). Butterworth-Heinemann Ltd.