

# Chapter 2

## Fundamentals of Corrosion Kinetics

G.S. Frankel

### 2.1 Introduction

Corrosion, the environmental degradation of materials, is a complex process that depends on details of the environment and material, and is controlled by underlying thermodynamic and kinetic factors. The ultimate goal of a corrosion engineer is to predict and control the rate of corrosion. To do so requires a thorough understanding of the thermodynamic and kinetic fundamentals. This chapter will review the electrochemical kinetics important to the overall corrosion process, including activation controlled kinetics, mixed potential theory, and mass transport effects.

The chapter will begin with a description of the typical anodic and cathodic half reactions that comprise the corrosion phenomenon. This is followed by an introduction to the most fundamental type of electrochemical kinetics, activation controlled kinetics, which are applicable in situations where the rate is controlled by the charge transfer reaction. The Tafel equation describes many of the reactions involved in corrosion. With the basis of simple electrochemical kinetics, it is then possible to present mixed potential theory, which predicts corrosion potential and rate on the basis of the kinetics and thermodynamics of all of the reactions occurring on an electrode surface. The Evans diagram, a graphical representation of this situation, is introduced to, clarify the mixed potential condition. The rate of corrosion is often controlled by mass transport of species to the surface from the bulk solution, and the kinetics of mass transport are the next topic of discussion. The inhibition of corrosion, in which the kinetics of one or more of the corrosion reactions are altered by the presence of species added to the environment, will then be covered. Passivity, or the spontaneous formation of a thin protective surface film, can be viewed as a form of anodic inhibition and is introduced at the end of this chapter.

---

G.S. Frankel (✉)

Fontana Corrosion Center, The Ohio State University, Columbus, OH 432310, USA  
e-mail: frankel.10@osu.edu

## 2.2 Corrosion Reactions

Corrosion often involves oxidation of metal atoms to form ionic species with higher oxidation state and the liberation of electrons. For a generic metal M:



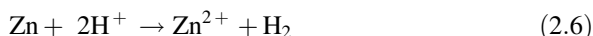
Examples of real metals:



These are called half-cell reactions because the electrons liberated by the oxidation reaction must be consumed by a reduction reaction occurring on the same electrode. A reduction reaction that is common in acids is hydrogen evolution:



The complete corrosion reaction for Zn in an acid would be the sum of the oxidation and reduction reactions:



The sites for the oxidation reactions are called anodes, and the sites for the reduction reactions are called cathodes. Anodes and cathodes can be spatially separated at fixed locations associated with heterogeneities on the electrode surface. Alternatively, the locations of the anodic and cathodic reactions can fluctuate randomly across the sample surface. The former case results in a localized form of corrosion, such as pitting, crevice corrosion, intergranular corrosion, or galvanic corrosion, and the latter case results in nominally uniform corrosion.

In most environments of interest to corrosion there is not a large concentration of metal ions acting as cathodic reactants (*i.e.* the reverse of reaction (1)). The important cathodic reactions in corrosion mechanisms involve water. There are two primary cathodic reactions, each of which takes a different form in acids or bases. The first is the hydrogen evolution reaction, in acids takes the form shown in Eq. 2.5. In neutral or basic solutions the hydrogen evolution reaction is:



Each of the half reactions given in Eqs. 2.1–2.7 will be in equilibrium at a specific potential called the reversible potential,  $E^{rev}$ . When all reactants and products are in their standard states with activity of unity, the potential reaches a

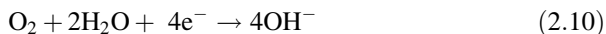
special value of reversible potential called the standard potential,  $E^0$ . The well-known electromotive force series is a list of half reactions ordered by their standard potentials. These standard potentials are derived from the free energies of formation of the species involved in the reactions.

For conditions under which the reactants and products are not in their standard states, which is the typical condition of corrosion,  $E^{\text{rev}} \neq E^0$ , and  $E^{\text{rev}}$  can be calculated from the Nernst equation. The Nernst equation for the hydrogen evolution reaction given in Eq. 2.5 at room temperature is:

$$\begin{aligned} E^{\text{rev}}(\text{H}^+/\text{H}_2) &= E^0(\text{H}^+/\text{H}_2) + (0.059/2) \log [\text{H}^+]^2 \\ &= 0.059 \log [\text{H}^+] \\ &= -0.059 \text{ pH} \end{aligned} \quad (2.8)$$

It can be easily shown that the Nernst Equation for the base form of the hydrogen evolution reaction, Eq. 2.7, is also  $E^{\text{rev}} = -0.059 \text{ pH}$ .

When dissolved oxygen gas is present in the aqueous solution, the following oxygen reduction reactions are possible, with Eq. 2.9 dominant in acids and Eq. 2.10 in neutral or basic solutions:



The Nernst equation for the acid form of the oxygen reduction reaction is:

$$\begin{aligned} E^{\text{rev}}(\text{O}_2/\text{H}_2\text{O}) &= E^0(\text{O}_2/\text{H}_2\text{O}) - (0.059/4) \log [\text{H}^+]^4 \\ &= 1.229 - 0.059 \text{ pH} \end{aligned} \quad (2.11)$$

As for the case of the hydrogen evolution reaction, the Nernst Equation for the base form of the oxygen reduction reaction is the same as that for the acid form. The base form of either the hydrogen evolution reaction or the oxygen reduction reaction is obtained from the acid form by adding a multiple of the water dissociation reaction:

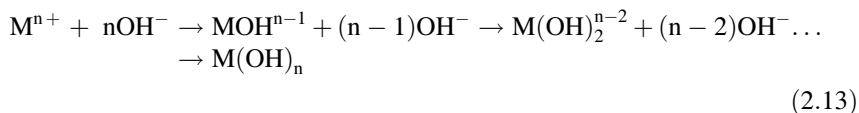


This chapter deals primarily with the corrosion of a fictitious metal M with no relevant microstructural heterogeneities. In reality, engineering alloys have complex microstructures and surface features that can have a large effect on the progression of the corrosion processes. It was described above, that metal corrosion takes place by a combination of an anodic half reaction such as given in Eqs. 2.1–2.4, and a cathodic half reaction such as in Eqs. 2.5, 2.7, 2.9, and 2.10. The locations of the local anodes and cathodes depend on the surface and microstructural details and determine the form of corrosion that results.

The corrosion reactions will tend to occur on the most reactive spots on a surface. An ordered list of increasing reactivity might be: crystal ledges, crystal kinks, emerging dislocations, high index grain faces, impurities, grain boundaries, inclusions and particles, second phases, crevices and cracks. For example, for a very pure metal that is single crystalline and well annealed with a well-prepared surface, the reactions might take place on crystalline ledges and kink sites. The form of corrosion might be etch pits at dislocations, grain boundary etching, or second phase attack, depending on what are the most susceptible sites present on the surface. Because most alloy surfaces have heterogeneities that provide reactive sites and surface films, it is rare for attack to be dominated at the less reactive sites like emergent dislocations.

The anodic and cathodic reactions will take place at separate sites, but those sites might be extremely close. For the current to pass from cathode to anode, there must be a potential difference. However, if the anodes and cathodes are extremely close, the potential difference will be extremely small. Nominally uniform corrosion will occur if the local anodic and cathodic sites continually move across the surface owing to small changes in surface reactivity as the corrosion process proceeds. If the location of the anodic reaction does not continually move, but stays at localized sites, the form of attack will be localized. For example, etch pits will form at dislocations if those sites remain the most active sites for dissolution. Extensive localized attack in the form of pits, crevices, intergranular corrosion or cracks can occur if the separation of the anodic and cathodic reactions is sustained.

The cathodic reactions involving water in Eqs. 2.5, 2.7, 2.9, and 2.10 all result in an increase in production of  $\text{OH}^-$  or the consumption of  $\text{H}^+$ . Therefore, the pH tends to increase in the region near a sustained cathode. In contrast, the pH tends to decrease in the region near a sustained anode, such as a pit or crevice owing to metal cation hydrolysis:



Hydrolysis will consume hydroxide ions, causing the pH to decrease. Complete hydrolysis of the cations to form hydroxide, the right most product in Eq. 2.13, does not generally occur. Each of the steps of the hydrolysis process will reach equilibrium, with different equilibrium constants for different cations. If cation hydrolysis were able to go to completion and complete mixing of the anode and cathode environments was possible, every hydroxide ion produced or  $\text{H}^+$  ion consumed by the cathodic reaction would be balanced by an equal consumption of hydroxide ion by hydrolysis and there would be no pH change. However, because of the lack of complete cation hydrolysis, the pH of a closed corroding system always increases.

For the case of localized corrosion, in which there is sustained spatial separation of the anodic and cathodic reactions, a gradient in chemistry as well as potential will

exist between the anode and cathodic sites. Migration of anions toward the anode will also occur owing to the potential gradient. Therefore, the local anode environment might be enriched with both chloride anions and  $H^+$  cations, forming a very aggressive solution. This will tend to prevent repassivation and sustain the localized corrosion.

### 2.3 Activation Controlled Kinetics

Consider a metallic electrode immersed in a corrosive aqueous environment. Anodic and cathodic reactions will occur spontaneously on the electrode surface, possibly resulting in corrosion of the electrode. The resulting potential of the electrode will be different from the reversible or equilibrium potentials of each of the reactions occurring on the surface. If the concentrations of the reactants and products at the electrode surface are the same as in the bulk solution, the difference in potential from the reversible potential for a given reaction is called activation overvoltage or charge transfer overvoltage,  $\eta$ . It stems from the fact that the rate of charge transfer at the electrode-electrolyte interface is not infinitely fast. Note that the concentration at the electrode surface equals the bulk concentration when the rate of mass transport is fast compared to the rate of charge transfer. This aspect will be discussed in more detail later.

For a reaction in which the rate is limited by activation overvoltage, the relationship between the rate of reaction, which can be expressed by a current density  $i$ , and the driving force for the reaction, or potential  $E$ , is given by the Butler-Volmer equation:

$$i = i_0 \exp \left[ \frac{\alpha n F (E - E_{\text{rev}})}{RT} \right] - i_0 \exp \left[ \frac{-(1 - \alpha) n F (E - E_{\text{rev}})}{RT} \right] \quad (2.14)$$

$$i = i_0 \exp \left[ \frac{\alpha n F \eta}{RT} \right] - i_0 \exp \left[ \frac{-(1 - \alpha) n F \eta}{RT} \right]$$

where  $F$  is the Faraday constant = 96,487 C/equivalent,  $n$  is the charge on the ion in equivalents/mol,  $R$  is the gas constant = 8.314 J/mol-K, and  $\alpha$  is the unitless charge transfer coefficient. The value of  $\alpha$  is usually close to 0.5, but must be between 0 and 1.

For a sufficiently large value of anodic polarization from the reversible potential (overpotential  $\eta_a > \sim 50$  mV), the first term on the right side of Eq. 2.14 dominates the second term. Therefore, at large overpotentials, the Butler-Volmer equation simplifies to:

$$i_{\text{net}} = i_0 \exp \left[ \frac{\alpha n F \eta_a}{RT} \right] \quad (2.15)$$

Rearranging, one gets the Tafel equation:

$$\eta_a = b_a \log(i/i_0) \quad (2.16)$$

where  $b_a = 2.3 RT/\alpha nF$  is the anodic Tafel slope. For  $\alpha = 0.5$  and  $n = 1$ ,  $b_a = 0.12$  V (or V/decade). A similar equation is found for cathodic activation polarization:

$$\eta_c = -b_c \log(|i|/i_0) \quad (2.17)$$

Corrosion conditions typically are far removed from the reversible potentials for any of the reactions. Therefore, Tafel kinetics are usually an accurate description of corrosion kinetics for conditions under which mass transport limitations are not important.

## 2.4 Mixed Potential Theory

Under conditions of importance in corrosion, the predominant cathodic reaction is typically one of the hydrogen or oxygen reactions described above. Furthermore, the electrode potential is usually far from the reversible potentials for any of the reactions occurring on the surface.

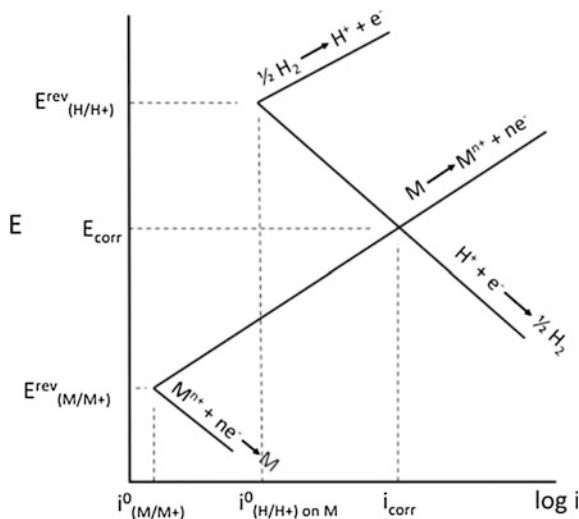
The principle of charge conservation dictates that, to avoid the accumulation of charge on a freely-immersed electrode, the sum of all of the oxidation currents must equal the sum of all of the reduction currents. Any electrode immersed in an environment will naturally have a potential, called the corrosion potential, that fulfills this requirement. Therefore, at the corrosion potential:

$$\Sigma I_a + \Sigma I_c = 0 \quad (2.18)$$

Note that reduction currents ( $I_c$ ) are negative. The corrosion potential is also called the open-circuit potential, free potential, or rest potential. The corrosion potential is a mixed potential indicating that its value depends on the rate of the anodic as well as the cathodic reactions. Furthermore, if the corrosion cell involves one dissolution reaction and one cathodic reaction, the corrosion potential will be between the reversible potentials of the two half reactions.

The situation can best be visualized using an Evans diagram, Fig. 2.1. In this figure, the Tafel lines for the anodic and cathodic branches of the hydrogen reaction are shown together with the Tafel lines for the dissolution and plating of a metal with reversible potential below that for the hydrogen reaction. These are the possible electrochemical reactions for an active metal in acid containing little dissolved metal ion, where the primary cathodic reaction is hydrogen evolution. In this figure,  $E_{M/M+}^{rev}$  and  $E_{H/H+}^{rev}$  represent the reversible potentials for the metal M dissolution and hydrogen evolution reactions, respectively;  $i_0, M/M+$  and  $i_0, H_2/H+$  represent the exchange current densities for metal dissolution and hydrogen evolution on M,

**Fig. 2.1** Schematic Evans diagram for the corrosion of metal M by an acid showing the application of mixed potential theory



respectively. The principle of charge conservation, Eq. 2.18 can be applied. Since the reactions are all occurring on a single electrode of given area, Eq. 2.18 can be written in terms of current density,  $i = I/A$ :

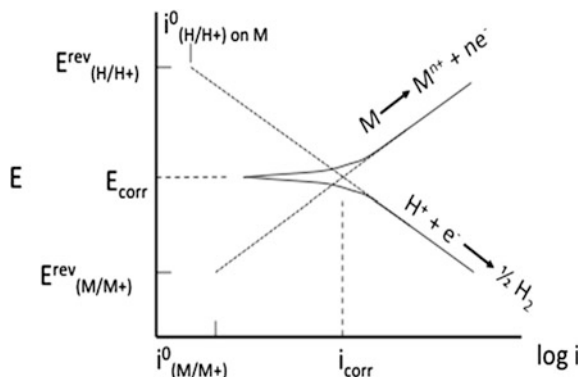
$$\Sigma i_a + \Sigma i_c = 0 \quad (2.19)$$

The total oxidation and reduction current densities will be equal at the point where the anodic line for the metal dissolution reaction intersects the cathodic line for hydrogen evolution. The potential at which these lines intersect is the corrosion potential. The rate of the anodic reaction at the corrosion potential is the corrosion rate (corrosion current density). It can be seen that the corrosion potential always takes a value between the reversible potentials for the two partial reactions.

The corrosion potential and current density can shift with time if the surface or solution changes and the Tafel lines representing the reactions change. Note that the electrode is not in equilibrium at the corrosion potential because net changes occur: metal is oxidized and water or other oxidants are reduced. The corrosion potential and current density are influenced by both *thermodynamics*, through the reversible potentials of the various reactions, and by *kinetics*, through the exchange current densities and the Tafel slopes of the reactions.

Polarization curves of metals in solution can be determined by potentiodynamic polarization. Using a potentiostat, a counter electrode, and a reference electrode, the potential of a sample is scanned or stepped in small increments over a range from about 250 mV below the corrosion potential to well above the corrosion potential. The potentiostat determines the current passed at the electrode surface as a function of the potential. The current density is easily calculated and is often plotted as a function of potential on a semi-log plot like that shown in Fig. 2.2. Such a plot is called a polarization curve. Note that the absolute value of the current is plotted, as

**Fig. 2.2** Schematic measured polarization curve for metal M in an acid showing  $E_{\text{corr}}$  and Tafel extrapolation for determination of  $i_{\text{corr}}$



the log of a negative number is undefined. The net measured current for the case of a metal corroding at a mixed potential in a solution containing an oxidizing agent will look like the curve presented in Fig. 2.2. Far from the corrosion potential, one of the reactions, either the cathodic or anodic reaction, occurs at a much greater rate, and so the relationship tends to follow the straight line representative of Tafel kinetics for the anodic reaction at high potentials and for the cathodic reaction at low potentials. At the corrosion potential,  $I_a = I_c$ , so the measured or net current equals zero, the log of which is  $-\infty$ . Therefore the potential at which the curve points to the left denotes the corrosion potential. Extrapolation to the corrosion potential of the linear regions of the semilogarithmic plot, or Tafel regions, gives the corrosion rate, Fig. 2.2. In the region close to the corrosion potential, the anodic and cathodic reactions occur at similar rates so the measured current, which is a sum of the two, deviates from the Tafel relationship.

The schematic polarization curve shown in Fig. 2.2 plots potential and current on the ordinate and abscissa axes, respectively. This is a common plotting format but is not intuitive because nowadays the measurements are typically performed by controlling the potential and measuring the current. This format has historical precedence because, before the advent of potentiostats, polarization measurements were made by controlling current and measuring potential. It is equally common to plot polarization curves with the independent variable, current, on the ordinate and the potential on the abscissa, as they should be based on the measurement. Experienced practitioners can transform such plots readily.

For a corroding system in which a single anodic reaction and a single cathodic reaction occur, such as illustrated in Fig. 2.2, the relationship of the net current as a function of potential will be:

$$i_{\text{net}} = i_{\text{corr}} \exp \left[ \frac{2.3(E - E_{\text{corr}})}{b_a} \right] - i_0 \exp \left[ \frac{2.3(E - E_{\text{corr}})}{b_c} \right] \quad (2.20)$$

where  $b_a$  and  $b_c$  are the anodic and cathodic Tafel slopes, respectively. The form of this relationship is similar to the Butler-Volmer equation, Eq. 2.14, which describes



the kinetics of a single half reaction at potentials above and below the reversible potential for that reaction. In contrast, this equation, which has no commonly-referred to name, describes the net current when two different half reactions occur on a single electrode surface. Non-linear least squares fitting of the  $i_{\text{net}}(E)$  data set to Eq. 2.20 by the analysis software provided by the potentiostat manufacturer is the most common means to evaluate corrosion data as it provides values for the constants in the equation,  $i_{\text{corr}}$ ,  $E_{\text{corr}}$ ,  $b_a$ , and  $b_c$ , in an automated fashion.

## 2.5 Mass Transport Controlled Kinetics

For conditions in which the surface concentration of a reactant is not the same as the bulk concentration, the equations describing the reaction kinetics must be altered. The oxygen reduction reaction, Eqs. 2.9 and 2.10, is an important reaction in corrosion that often meets this condition because the reactant, molecular oxygen, is consumed at the surface, which reduces its surface concentration. This then requires the transport of oxygen from the bulk through a layer adjacent to the surface. For this condition, the cathodic Tafel equation, which is similar to Eq. 2.15, must be altered to include the concentration of oxygen in the bulk and at the surface,  $c_b$  and  $c_s$ , respectively:

$$i = -i_0 \left( \frac{c_s}{c_b} \right) \exp \left[ - \left( \frac{(1 - \alpha)nF}{RT} \right) (E - E^{\text{rev}}) \right] \quad (2.21)$$

The equation shows that the rate of the charge transfer reaction at the interface depends not only on the applied potential but also on the concentration of reacting species prevailing at the electrode surface.

Consider now a metal sample being corroded by a generic oxidizing agent, B, which is being transported from the bulk and consumed at the surface. For neutral species such as oxygen, or charged species present in small amounts in the presence of a supporting electrolyte, the contribution of migration to transport is small. For the subsequent discussion it will be assumed that near the electrode surface there is a stagnant layer of electrolyte of thickness  $\delta$ , which is called the Nernst Diffusion layer or, somewhat loosely, the diffusion layer. Within the stagnant diffusion layer only diffusion contributes to the flux of the reacting species, whereas outside the diffusion layer no concentration gradients exist and convection is the only transport mechanism for the reacting species.

The reaction of species B at the surface will reduce its concentration and the transport of B from the bulk to the surface through the diffusion layer can be described by the electrochemical equivalent of Fick's first law:

$$i = \frac{-nFD_B(c_{B,b} - c_{B,s})}{\delta} \quad (2.22)$$

where  $i$  is the current density associated with the reduction of B,  $F$  is the Faraday constant, and  $D_B$  is the diffusion coefficient of B. The effect of convection on the electrode reaction can be understood from this equation by considering that increased convection decreases  $\delta$  and thus increases the flux of B and its reduction rate  $i$ .

Solving Eq. 2.22 for surface concentration of B gives

$$c_{B,s} = c_{B,b} + \frac{i\delta}{nFD_B} \quad (2.23)$$

Note that in this expression  $i$  is a negative quantity as it describes a reduction reaction so it is equivalent to write it as:

$$c_{B,s} = c_{B,b} - \frac{|i|\delta}{nFD_B} \quad (2.24)$$

The surface concentration of the reacting species therefore decreases with increasing current density.

As the cathodic current density increases, the surface concentration of the reacting species,  $c_{B,s}$ , decreases until reaching a value of  $c_{B,s} = 0$ . The current associated with this condition is the maximum possible reduction rate of B and is called the limiting current density  $i_{lim}$ .

$$i_{lim} = \frac{-nFD_B c_{B,b}}{\delta} \quad (2.25)$$

Dividing Eq. 2.22 by Eq. 2.25 yields:

$$\frac{i}{i_{lim}} = 1 - \frac{c_{B,s}}{c_{B,b}} \quad (2.26)$$

which can be rearranged to give:

$$\frac{c_{B,s}}{c_{B,b}} = 1 - \frac{i}{i_{lim}} \quad (2.27)$$

Substituting into Eq. 2.20 gives:

$$i = i_0 \left( 1 - \frac{i}{i_{lim}} \right) \exp \left[ \frac{-(1 - \alpha)nF}{RT} (E - E^{rev}) \right] \quad (2.28)$$

This can be rearranged to yield Eq. 2.29, which describes the current-potential relationship for a cathodic reaction controlled by combined charge transfer kinetics and mass transport.

$$i = \frac{i_0 \exp \left[ \frac{-(1-\alpha)nF}{RT} (E - E^{\text{rev}}) \right]}{1 - \frac{i_0}{i_{\text{lim}}} \exp \left[ \frac{-(1-\alpha)nF}{RT} (E - E^{\text{rev}}) \right]} \quad (2.29)$$

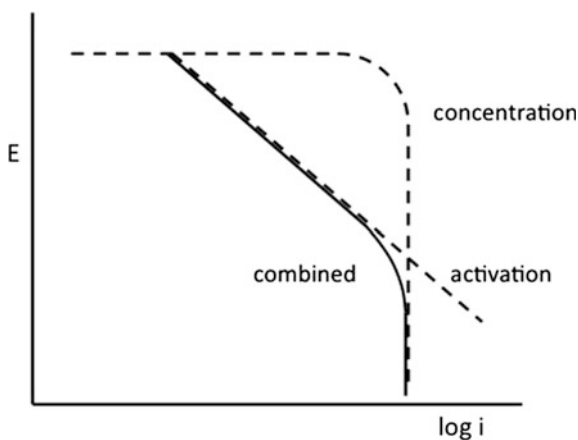
If  $i_{\text{lim}} \gg i_0 \exp \{[-(1-\alpha)nF/RT](E - E^{\text{rev}})\}$ , then the denominator of Eq. 2.29 goes to 1 and this equation becomes the Tafel equation. However, if  $i_{\text{lim}} \ll i_0 \exp \{[-(1-\alpha)nF/RT](E - E^{\text{rev}})\}$ , this equation becomes  $i = i_{\text{lim}}$  and the reaction rate is independent of potential.

Another way to look at the situation of combined influences of charge transfer overvoltage and mass transport is to rearrange Eq. 2.29 to get:

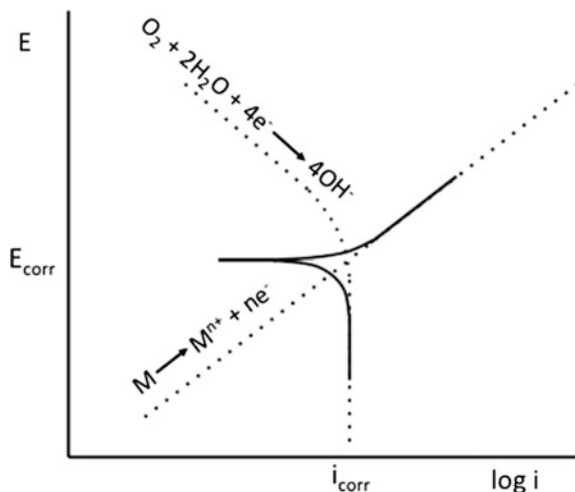
$$E - E^{\text{rev}} = \eta = -\frac{RT}{(1-\alpha)nF} \ln \frac{i}{i_0} - \frac{RT}{(1-\alpha)nF} \ln \left( 1 - \frac{i}{i_{\text{lim}}} \right) \quad (2.30)$$

The first term on the right hand side is the charge transfer or activation overvoltage and the second term is concentration overvoltage. The total overvoltage is seen to be a sum of the two. The concentration overvoltage goes to negative infinity as the current approaches the limiting current, Fig. 2.3. According to Eq. 2.25, the  $i_{\text{lim}}$  depends on diffusivity, diffusion layer thickness, and bulk concentration of the reacting species. Diffusion is a thermally activated process and the diffusion layer thickness depends on the solution velocity, so environment temperature and agitation will affect  $i_{\text{lim}}$ . The charge transfer (activation) and concentration overvoltages combine as shown in Fig. 2.3. This is the typical polarization behavior observed for a system under mixed charge transfer and transport control.

**Fig. 2.3** Representation of the combine effects of activation- and concentration-controlled kinetics



**Fig. 2.4** Schematic measured polarization curve for the corrosion of metal M in an environment where the rate of reaction is controlled by the diffusion limitation of  $O_2$  to the surface



Mass transport is of primary importance for the rate of corrosion in environments with limited cathodic reactant, for example in a neutral solution containing dissolved oxygen as reacting species. The maximum corrosion rate in such a situation is given by the limiting current density of the cathodic reactant to the surface,

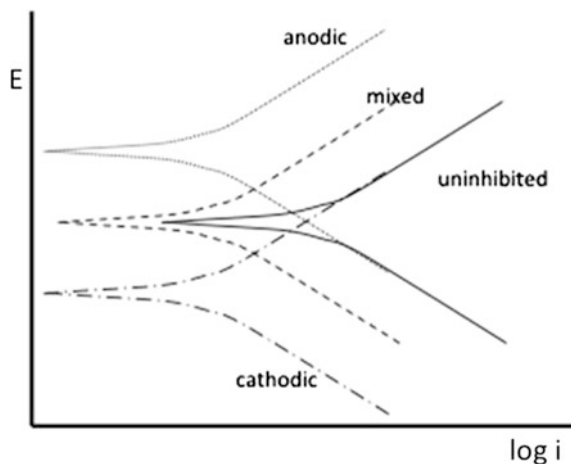
$$i_{\text{corr}} = i_{\text{lim}} \quad (2.31)$$

An example is corrosion of steel in an aerated neutral solution where the rate of oxygen reduction reaction is largely controlled by mass transport. An Evans diagram for this situation is given in Fig. 2.4. Similarly, the rate of corrosion of iron in dilute hydrochloric acid is limited by the rate of the mass transport of the proton to the iron surface.

## 2.6 Inhibition

Corrosion inhibitors are chemicals added to an environment to decrease the rate of corrosion of metals exposed to that environment. The most common applications of inhibitors are limited-size or closed systems such as acid pickling baths or closed-loop water cooling systems. Acidic pickling baths are used to chemically dissolve the iron oxide scale on steel, and organic inhibitors are added to adsorb onto the metal surface after dissolution of the scale and thereby block the electrochemical attack of the steel. Closed-loop water cooling systems used, for instance, to extract heat from engines are typically neutral or alkaline solutions to which inorganic molecules are added to promote oxide formation on contacting metal surfaces or to buffer the pH.

**Fig. 2.5** Schematic representation of the effects of *anodic, cathodic and mixed inhibition*



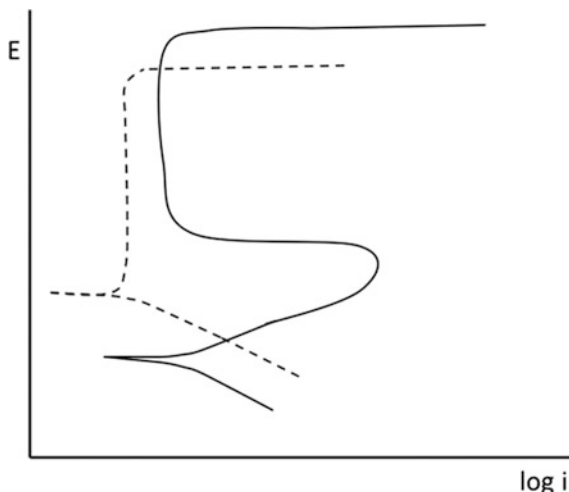
Inhibitors are also added as soluble pigments in protective organic coatings, or paint. The poly-electrolyte formed when the paint is saturated with water, protects the metal and can release inhibitive species into local environments such as delaminations or through-scratches so as to protect the exposed metal.

The effect of the inhibitor on the corrosion process can be understood and classified by comparing polarization curves in environments with and without the inhibitor added. Figure 2.5 shows schematic examples of the types of inhibition and their effects on the polarization curves. Inhibitors can be classified as an anodic, cathodic, or mixed inhibitor as shown in this figure. As the names imply, an anodic inhibitor reduces the rate of the anodic reaction while having less of an effect on the cathodic reaction, a cathodic inhibitor reduces the rate of the cathodic reaction while having less of an effect on the anodic reaction, and a mixed inhibitor reduces the rates of both reactions equally. The corrosion potential will often be different in a solution containing inhibitor compared to the value in an uninhibited solution, and the nature of the change will be different for the different classes of inhibitor.  $E_{\text{corr}}$  will increase for an anodic inhibitor, decrease for a cathodic inhibitor, and not change for a mixed inhibitor. As long as the corrosion rate is indeed reduced, the shift in  $E_{\text{corr}}$  can be used as a diagnostic for the type of inhibitor.

## 2.7 Passivity

In the field of corrosion passivity describes a state in which the corrosion rate of a metal substrate is very low because of the presence of a thin oxide or oxy-hydroxide layer on the surface that deactivates or passivates the metal. The best passive films, such as those that form on Al and other so-called valve metals like Ti, Zr, Nb, etc. are very thin, on the order of a few nm. Stainless steels have high corrosion

**Fig. 2.6** Schematic polarization curves for passive samples. *Solid line* is for a metal showing an active/passive transition and *dashed line* is for a spontaneously passive metal



resistance owing to the presence of a Cr-rich passive film on their surfaces. The highly corrosion resistant engineering alloys achieve that property by passive films.

Passivity can be considered a form of anodic inhibition because the rate of metal dissolution is greatly reduced by the passive film. As mentioned above, the inorganic corrosion inhibitors added to neutral environments such as cooling water systems act by improving the passivity of the metals in contact with them. Schematic polarization curves for passive materials are shown in Fig. 2.6. The solid line represents a metal exhibiting active-passive behaviour. As the potential increases above the corrosion potential, the current increases exponentially, as would be expected for an actively dissolving metal. However, at a potential called the Flade potential, the current trend reverses and can decrease by many orders of magnitude because of the formation of a passive film. In the passive region, the current density tends to have little dependence on potential. In comparison with an extrapolation of the current behaviour from the actively dissolving region, the current density in the passive region is decreased enormously. In certain conditions, current can increase again at a higher potential owing to the breakdown of the passive film by localized corrosion or by transpassive reactions such as oxygen evolution or Cr dissolution as chromate. For a case such as shown by this curve, passivity can only be achieved by applying an anodic potential, which is called anodic protection, or by the addition of oxidizing agents that would increase the corrosion potential to a value in the passive region as described next.

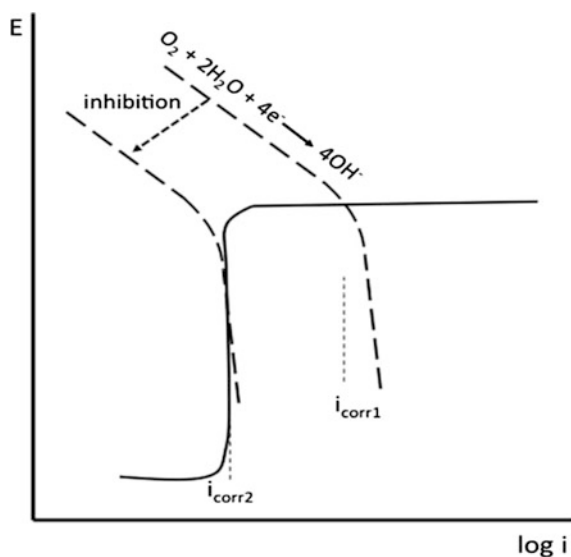
The dashed line in Fig. 2.6 shows the polarization curve for a spontaneously passive metal. For this material, the active-passive transition is at lower potentials and is not observed because it is dominated by the cathodic reaction in that potential region. The intersection of the curve for the cathodic reaction with the anodic polarization curve is in the passive region such that the material is spontaneously

passive at the open circuit potential. In this case,  $i_{\text{corr}}$  is limited by the anodic reaction and is equal to the passive current density.

The curves shown in Fig. 2.6 were arbitrarily drawn such that the spontaneously passive metal has lower values of corrosion current density, passive current density and breakdown potential, which is given by the potential at which there is a sharp increase in current. These values will depend on the material properties and environmental severity.

As shown in Fig. 2.6, the dissolution current increases rapidly with increasing potential after breakdown of the passive film. An example of such a system is the corrosion of high strength Al alloys in chloride-containing environments, which takes the form of pitting or intergranular corrosion when passive film breakdown occurs. The rate of corrosion in such a case is often controlled by the cathodic reaction, which is oxygen reduction in many natural aerated environments. Therefore, inhibition of oxygen reduction is an important strategy for limiting the extent of corrosion in natural environments. Inhibiting species can be added to the environment or to protective films to be released into a local environment as needed. Figure 2.7 shows how inhibition of the oxygen reduction reaction can greatly reduce the rate of corrosion for a material like a high strength Al alloy. For an uninhibited case, the dashed curve representing the kinetics of the oxygen reduction reaction intersects the curve representing the anodic behaviour of the Al alloy at a potential above the breakdown potential. In this case, the alloy will undergo localized corrosion at the open circuit potential. In contrast, inhibition moves the oxygen reduction curve to the left so that the intersection with the anodic curve occurs below the breakdown potential. In the inhibited case, localized corrosion is not spontaneous at the corrosion potential, and the corrosion rate is given by the passive current density.

**Fig. 2.7** Schematic representation of the effect of inhibition of the oxygen reduction reaction on the corrosion of a metal such as high strength Al alloy, which undergoes localized corrosion



## Recommended Reading

1. D.A. Jones, *Principles and Prevention of Corrosion*, 2nd edn. (Prentice Hall, 1996)
2. D. Landolt, *Corrosion and Surface Chemistry of Metals* (CRC Press, 2007)
3. E. McCafferty, *Introduction to Corrosion Science* (Springer, 2010)
4. M. Fontana, N. Greene, *Corrosion Engineering* (McGraw-Hill, New York, 1978)
5. F. Mansfeld (ed.), *Corrosion Mechanisms* (Marcel Dekkar, New York, 1987)
6. P. Marcus (ed.), *Corrosion Mechanisms in Theory and Practice*, 2nd edn. (Marcel Dekkar, New York, 2002)
7. J.O'M. Bockris, A.K.N. Reddy, *Modern Electrochemistry*, vol. 2 (Plenum Press, 1970)



Active Protective Coatings

New-Generation Coatings for Metals

Hughes, A.E.; Mol, J.M.C.; Zheludkevich, M.L.; Buchheit, R.G. (Eds.)

2016, VIII, 428 p. 170 illus., 70 illus. in color., Hardcover

ISBN: 978-94-017-7538-0