Chapter 9
Metal Corrosion

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9.1 Interaction of Metallic Biomaterials with the Human Body Environment

Degradation of metals by interaction with the environment is called corrosion. In most industrial corrosion situations, the damage to the object is of main concern, while the effect of the corrosion process on the environment is either negligible or of secondary importance. For devices inserted in the human body, on the other hand, both the degradation of the device and the effect of the interaction on the physiological system, local or systemic, are of equal importance. Corrosion degradation may result in a loss of mass, mechanical integrity, functionality, and, sometimes, esthetic quality, while the release of corrosion products and the flow of the corrosion currents may cause inflammation, allergic reactions, local necrosis, and many other health problems. Although the intensity of the interaction is an important parameter, an equally important factor is the identity of the corrosion products and their toxicity, carcinogenicity, allergenicity, and other potentially hazardous properties.

The corrosion interaction of electronic conductors, such as metals, with ionically conducting liquids, such as human fluids, is almost always an electrochemical process, involving a change from the metallically bonded solid to dissolved ions or ionically bonded products. There are also physical and chemical rather than electrochemical interactions with components of body fluids and tissues, but they do not fall into the generally accepted meaning of the term corrosion. The only notable exception in the area of biomaterials may be the release of mercury from dental amalgam fillings. Because of the high nobility of mercury but low bond strength, mercury dissolves much more easily in the atomic, non-ionized form.

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When a foreign object, such as a medical implant, is inserted in the tissues, it causes irritation not only because of the chemical or electrochemical interactions but also by its mere presence. The irritation induces foreign body reactions and tendency to remove the foreign body. The type of the physiological response depends on the size and shape of the object as well as the reactivity of the material. While particulates and fluids may be ingested by macrophages, larger objects are usually either extruded or walled off (encapsulated). Encapsulation first involves accumulation of epithelium cells, which may develop into a membrane and a fibrous capsule.

The presence of a membrane on metallic implants has an effect on the corrosion interaction, which has not been fully examined. There is evidence that the thickness of the membrane increases with increasing reactivity of the material, the reactivity being a combination of the intensity of the corrosion reactions and the toxicity of the released elements. On the other hand, the membrane slows down the transport of the corrosion products into surrounding tissues or fluids and also affects the chemistry of the environment at the metal surface and thus the corrosion process itself.

While the released metal ions in a sufficiently high concentration may be toxic enough to cause inflammation and necrosis of the cells and tissues, and accumulation of metal ions in various organs may be a health hazard, another common problem are allergic reactions, which require only a small amount of the released ions for a response of the immune system in susceptible individuals. Although allergic reactions are often described as dose independent, this term is inherently inaccurate, because one could always identify a quantity that would not provoke the reaction. However, the threshold dose is difficult to determine. One of the allergens among components of implant alloys, known for a high percentage of susceptible individuals, is nickel, which is contained in such common alloys as stainless steel and Ni-Ti ("nitinol") alloys.

For the most common materials for implants and dental restorations and appliances, the most important environmental variables from the corrosion viewpoint are the concentrations of chloride and hydrogen ions and dissolved oxygen. The chloride ion concentration varies in a relatively narrow range close to 0.1 mol/L for most body fluids, such as blood plasma, interstitial fluid, bile, and gastric juice, but is quite variable in urine (depending on the salt intake) and considerably lower in saliva. The hydrogen ion concentration (usually expressed as pH value) is close to neutral (pH 7) for plasma, interstitial fluid, bile, and saliva but more variable in urine (pH 4–8) and very low (acidic) in gastric juice (pH 1–3).[1] The dissolved oxygen concentration varies, but for most common implant conditions, the partial pressure of oxygen is about 40 mmHg (interstitial fluid, venous blood) or 100 mmHg (arterial blood). More detailed data on body fluid compositions can be found in various sources, such as Burke [2] and Lentner [3, 4].

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[1] The pH value is defined as a function of the activity of hydrogen ions $[H^+]$, pH = $-\log [H^+]$. Solution with pH < 7 have a higher concentration of H^+ than when neutral (pH 7) and are acidic; those with pH > 7 have the H^+ concentration lower than in neutral water and are alkaline.

9.2 Electrochemical Reactions on Metallic Biomaterials

Spontaneous electrochemical corrosion of metals is a process that lowers the free energy of the system. With the exception of a few very noble metals, most elements in the metallic condition and in natural environments are in a metastable state, and their energy can be lowered by conversion to an ionic form, thus reversing the process of producing the metal from the ore. During this conversion some of the metal atoms, which in the metallic state share their free electrons with all the other atoms in the given solid, are released from the solid, leave the free electrons in the solid, and become positive ions or cations. Since this would make the solid negatively charged and electrostatic attraction would make further release of positively charged cations difficult, continuation of the process requires another reaction that consumes the superfluous electrons. In the electrochemical terminology, the process of creating positive ions is called oxidation and that of consumption of electrons is called reduction.

The above conversion can be achieved by a chemical reaction of a metal with a nonconductive environment, such as a reactive gas, for instance, oxygen, a process called “dry oxidation.” Even this outwardly chemical reaction involves transfer of electrons, i.e., in principle, electrochemical reactions. In a conductive environment, however, true electrochemical corrosion occurs, which involves a flow of electricity through the environment between the sites of oxidation and reduction. The electronically conducting solid metal is called an electrode, and an ionically conductive liquid environment is an electrolyte. In the conductive human body fluids, electrochemical corrosion is the dominant form of interaction with metals.

The electrochemical degradation of metals caused by dissolution or formation of nonmetallic corrosion products is directly caused by the oxidation part of the process, while reduction plays an enabling role. The formation of cations by stripping the metal atom of some of its electrons does not by itself lowers the energy; as a matter of fact, some energy must be supplied, resulting in a positive energy change and an “energy barrier.” The energy drop, which allows the process to proceed spontaneously, is due to the interaction of the cations with molecules, called “ligands.” In aqueous environments, such as body fluids, water molecules almost exclusively serve the role of ligands. In the conventional writing of an oxidation reaction, such as

$$\mathrm{Ni} \rightarrow \mathrm{Ni}^{++} + 2\mathrm{e}^{-} \tag{9.1}$$

and in any associated calculation of energies, if (9.1) describes a reaction in an aqueous environment, it is assumed that the nickel cation, Ni^{++}, is in this “hydrated” form, i.e., surrounded by attached water molecules. If the reaction proceeds in the opposite direction, i.e., as reduction, the ligands must first be stripped from the cation before the ion can become a neutral atom. For both oxidation and reduction, the species involved must overcome an energy barrier called “activation energy” associated with the “activated state” in between the conditions as neutral atoms and hydrated ions.

It is of fundamental interest to know how strong is the tendency of different metals to form these hydrated cations, i.e., to dissolve in water. It is possible to express this tendency by showing the energy change involved in the reaction. However, since the charge of the ions also plays a role, because more highly charged positive ions are more strongly attracted to the negatively charged metal they have left, a more convenient way is to introduce a concept of electrode potential difference $\Delta\Phi$ at equilibrium, which is proportional to the energy change ΔG and inversely proportional to the ionic charge z

$$\Delta\Phi = -\Delta G / zF \tag{9.2}$$

where F is a constant, called Faraday,[2] which serves as a conversion between the energy units for ΔG [J/mol] and electric units for the potential [V]. The physical meaning of $\Delta\Phi$ is that at equilibrium it is such a difference between the potential of the hydrated metal ions in the electrolyte just outside the metal surface and the potential of the same ions within the metal surface that the electric work of moving the ions of charge z across this potential difference balances the energy change ΔG involved in the reaction. The negative sign in reaction (9.2) is due to the fact that the potential difference and the energy change are measured in opposite directions.

Since (9.2) is applicable to reactions written in either direction (oxidation or reduction), and since most available data for energies of reactions are relative to the energy involved in the reaction of hydrogen, an international convention has been accepted for expressing the fundamental dissolution tendency of elements using (9.2). According to this convention, the reactions are considered at equilibrium (i.e., proceeding at the same rate in both directions), are written as reduction, rather than oxidation, and the values of the energy change ΔG are relative to the energy change in the reaction

$$2H^+ + 2e^- = H_2 \tag{9.3}$$

The potential difference with respect to the potential of a standard reference reaction (9.3) is then called "the single electrode potential" for the given reaction, and a simple symbol, such as e, is used for this parameter. The true meaning of e is thus a tendency for a reaction to proceed spontaneously in the direction of reduction relative to the tendency of hydrogen ions to be reduced in reaction (9.3).

The ΔG values and thus also the values of e generally vary with temperature, pressure, and activity of the ions. When all the reactants and products are in the standard state[3] (ΔG^o), the potential (e^o) is called "the standard single electrode potential." A listing of such standard reduction potentials is called an electromotive or electrochemical series. Because of the way e is defined, the higher the tendency for dissolution, the more negative is the single electrode potential, while noble

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[2] $F = 96{,}485$ C/mole.

[3] For electrochemical reactions the standard state is defined by temperature 25 °C (298.16 K), pressure 101325 Pa (1 atm, 760 torr), and activity of ions equal to one.

elements, such as gold, have a positive value of e^o. Selected standard single electrode potentials for some elements common in implant and dental alloys are shown in Table 9.1. The potentials are listed on a standard hydrogen scale (SHE), i.e., with respect to the standard potential of the reference reaction (9.3), which is considered zero.[4]

It is important to keep in mind that standard single electrode potentials of elements show only the fundamental thermodynamic tendency to form hydrated cations and thus to dissolve in water under standard conditions and not necessarily the susceptibility to electrochemical corrosion. In many cases the corrosion susceptibility is more a function of the rate of the reactions, i.e., the kinetics, than of the thermodynamic "driving force." On the other hand, since thermodynamics predict what cannot happen more decisively than what will happen, a lack of thermodynamic tendency for dissolution is a safe indication than the metal will not corrode. The choice of noble metals, such as gold and platinum in dentistry and in some special cases of implants, is based on this consideration.

An important factor that must be considered in evaluation of the thermodynamic tendency (driving force) for a reaction is the difference between the actual and standard conditions. The effect of the temperature, pressure, and activities on the single

Table 9.1 Standard single electrode potentials for reduction reactions of hydrated ions of selected metals

Metal	Reaction	e^o (V, SHE)
Gold	$Au^{3+} + 3e^- = Au$	1.498
Platinum	$Pt^{2+} + 2e^- = Pt$	1.188
Palladium	$Pd^{2+} + 2e^- = Pd$	0.987
Silver	$Ag^+ + e^- = Ag$	0.799
Mercury	$Hg_2{}^{2+} + 2e^- = 2Hg$	0.788
Copper	$Cu^{2+} + 2e^- = Cu$	0.337
Tin	$Sn^{2+} + 2e^- = Sn$	−0.136
Molybdenum	$Mo^{3+} + 3e^- = Mo$	−0.200
Nickel	$Ni^{2+} + 2e^- = Ni$	−0.250
Cobalt	$Co^{2+} + 2e^- = Co$	−0.277
Iron	$Fe^{2+} + 2e^- = Fe$	−0.440
Chromium	$Cr^{3+} + 3e^- = Cr$	−0.744
Zirconium	$Zr^{4+} + 4e^- = Zr$	−1.539
Titanium	$Ti^{2+} + 2e^- = Ti$	−1.630

Based on data in Pourbaix (1974)

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[4] A standard hydrogen electrode (SHE) can be constructed using a platinized platinum electrode immersed in an acid of unit activity of H^+ ions (pH 0), saturated with hydrogen gas at 1 atm pressure, and maintained at 25 °C. More commonly other, more convenient secondary standard reference electrodes are used in experimental work, such as mercury/mercury chloride (calomel electrode), silver/silver chloride, and copper/copper sulfate couples in appropriate electrolytes, which have accurately known and stable potential differences from SHE. In any reporting of potential values, the potential scale used must be specified.

electrode potential of a reaction is given by the Nernst equation (9.4). For an electrochemical reaction at equilibrium $a\mathrm{A} + b\mathrm{B} + z\,\mathrm{e}^- = c\mathrm{C} + d\mathrm{D}$, where [A] and [B] are activities[5] of the oxidized reactants A and B, [C] and [D] are activities of the reduced products C and D, and a, b, c, and d are the numbers of the molecules in the reaction:

$$e = e^0 + \frac{RT}{zF}\ln\frac{[\mathrm{A}]^a \cdot [\mathrm{B}]^b}{[\mathrm{C}]^c \cdot [\mathrm{D}]^d} \tag{9.4}$$

where R is the universal gas constant, T is temperature (K), and z is the number of electrons.

In the human body, the pressure and temperature are not substantially different from those defining the standard state; the chemical species, especially the metallic ions dissolved in the liquids, however, usually are in concentrations (and activities) much lower than one. For a simple reaction showing equilibrium between a metal and its hydrated ions with a charge z, and for human body temperature (37 °C), the Nernst equation simplifies to

$$e = e^{\mathrm{o}} + (0.061/z)\log\left[\mathrm{Me}^{z+}\right] \tag{9.5}$$

where the activity of metal ions $[\mathrm{Me}^{z+}]$, for diluted solutions, is approximately equal to the concentration of the dissolved metal ions at the electrode.

Since the value of e is a measure of the thermodynamic tendency for dissolution in water, the importance of the metal ion concentration for dissolution of metals in the human body now can be appreciated. For example, although the standard single electrode potential for iron ($e_{\mathrm{Fe}} = -0.44\,\mathrm{V}$, SHE) is considerably lower than for cobalt ($e_{\mathrm{Co}} = -0.277\,\mathrm{V}$, SHE), making cobalt significantly more noble than iron, the difference is much smaller at the mean concentrations of the elements in blood plasma, where the concentration of iron normally is much higher than that of cobalt [4]. Also, although noble metals, such as gold, do not have any tendency to dissolve under standard conditions (and are found in nature in the metallic state), as the concentration of their ions approaches zero, even their single electrode potentials, according to (9.4), approach very high negative values, indicating an extremely high driving force for dissolution. The practical significance of this result is that there is no “zero dissolution,” even for the most noble metals. On the other hand, for very noble metals, such as Au and Pt, the tendency for dissolution quickly drops to zero at extremely low concentrations at the practical potentials that get established in the human body environment.

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[5] Activity of ions a is proportional to the concentration c [mol/L], $a = \gamma . c$, where γ is the “activity coefficient.” For dilute solutions γ is close to one, and activity may be replaced by concentration. For concentrated solutions, however, the difference between concentration and activity must be considered. For gaseous species partial pressure is used in place of activity in (9.4).

Another factor that may substantially affect the tendency for dissolution is the propensity of metal ions to form complexes with components of the environment. In the complicated human body fluids, there are many substances, inorganic and organic, that may form complexes with ions of metallic biomaterials. When a complex has a lower energy than a simple hydrated cation, ΔG in (9.2) is higher (for reduction), and the potential *e* becomes lower, indicating a higher tendency for dissolution than in pure water.

It is important to keep in mind that a single reaction at equilibrium, i.e., when the actual potential of the electrode *E* is equal to *e* of the reaction, does not produce any significant corrosion damage, because the oxidation part of the reaction is balanced by the reduction process of the same reaction, both occurring at the same rate. Even at equilibrium some of the ions entering the liquid may drift away and possibly cause allergic reaction, but the rate of such a release normally is too low to cause a noticeable loss of mass.

True corrosion occurs when the oxidation part of a reaction between metal and its ions significantly exceeds the rate of the same reaction going in the opposite direction, i.e., reduction. For oxidation or reduction to exceed the rate of the other process, the actual electrode potential *E* must deviate from the equilibrium potential *e*. In spontaneous electrochemical corrosion of a single electrode, this deviation is due to some other reaction occurring simultaneously. For a reaction to proceed in the oxidation direction, as shown in (9.1), another, different reaction must be available to consume the electrons liberated in the oxidation process and thus proceed in the direction of reduction. In the body fluids and many other aqueous electrolytes, the two dominant reactions that may serve this role are the reduction of hydrogen ions, shown in (9.2), and reduction of dissolved oxygen:[6]

$$O_2 + 4H^+ + 4e^- = 2H_2O \tag{9.6}$$

Both reactions involve as reactants only species always present in body fluids, hydrogen ions formed by dissociation of water molecules and dissolved oxygen, and thus are, in principle, capable of serving as reduction reactions for electrochemical corrosion.

When the equilibrium potentials of two or more possible reactions on the electronically conducting surface are different, this potential difference causes a flow of electric current *I*. This current may be the sum of many small current flowing between atomically close sites of the reactions or a current between quite distant areas of the electrode surface, depending on the conditions, as discussed later. Within the metal electrode, electrons carry the current, and the circuit is completed by ionic conduction in the electrolyte. The electric current per unit area (current density *i*) associated with an electrochemical reaction can be taken as a measure of the rate of that reaction, because it is proportional to the amount of the substances

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[6] Standard potential $e^o = 1.228$ V (SHE) [5].

reacted or produced. Faraday's law gives the conversion between the mass of the substance involved and the amount of electricity:

$$m = \frac{QA}{zF} = \frac{ItA}{zF} \tag{9.7}$$

where Q is the electric charge [C], A is atomic weight [mol^{-1}], z is the oxidation state change, F is the Faraday's constant, I is the electric current [A], and t is time [s].

The flow of the current causes each reaction to be "polarized," i.e., its potential changes from the equilibrium value. When an electrochemical reaction is polarized, the rates of oxidation and reduction are not the same. Polarization in the positive direction of the potential causes the oxidation rate to exceed the reduction rate, because to achieve a positive potential change, some electrons must be removed, lowering the force of attraction and thus making the loss of positive cations easier. A potential change in the negative direction results in the rate of reduction exceeding the rate of oxidation. (More accurately, the potential change increases or decreases the activation energy barrier for the transfer of charges between the metal and the electrolyte.)

For only two corrosion reactions on an electrode, the potential of each reaction shifts toward the potential of the other one. If there is no electric resistance in the current circuit, the two potentials become identical, and the sites are completely "short-circuited." This condition is closely approximated when the oxidation and reduction sites are atomically close. For oxidation and reduction sites macroscopically distant the resistance, usually in the electrolyte, may be sufficient to result in a substantial potential difference between the two reactions.

Regardless of whether the potentials of the two or more reactions are almost identical or different, they are always established in such a way that the total oxidation current is equal to the total reduction current to keep electric neutrality. For two simultaneous reactions, the reaction with the lower (less positive or more negative) equilibrium potential is polarized in the positive direction until the net oxidation current equals the net reduction current of the other reaction, which is polarized from a more positive (higher) potential in the negative direction. When the resistance in the current path is low and the two or more potentials are virtually equal, the common potential is called "mixed potential."

A very characteristic feature of the kinetics of electrochemical reactions is that the relationship between a potential change and the current flow is nonlinear. Fundamentally, for a simple electrochemical reaction involving an activation energy barrier, the oxidation current exponentially increases, and the reduction current exponentially decreases with a positive potential change. In the field of electrochemical corrosion, it is traditional to switch the variables and express the potential change ΔE as a function of the current densities in the form of the "Tafel equation":

$$\Delta E = E_2 - E_1 = \beta \ \log i_2 / i_1 \tag{9.8}$$

where β is a Tafel constant. The Tafel constant β is positive for oxidation and negative for reduction. The units of a Tafel constant are volts (or mV) per tenfold current density change (decade), and usual values range from about 30 to 200 mV/decade. In other words, for an electrochemical reaction controlled by the energy barrier (activation energy), the rate of the reaction increases or decreases by a factor of ten for each 30–200 mV of potential change.

When an electrochemical reaction is at equilibrium, the rates of oxidation and reduction currents are equal, and the value per unit area is called exchange current density i_o. A deviation of the potential from the equilibrium value e (single electrode potential) is called overpotential $\eta = E - e$. The Tafel equation as applied to the deviation from equilibrium then can be written as follows:

$$\eta = e - e_o = \beta \log i / i_o \tag{9.9}$$

The Tafel relationship can be conveniently shown in a semilogarithmic plot called a polarization diagram, where current density is plotted on a logarithmic scale and potential on a linear scale, as shown in Fig. 9.1. The variations of current densities for oxidation and reduction with the potential in such a diagram are straight lines, intersecting at e and i_o, where the reaction is at equilibrium and the absolute values of the current densities for oxidation and reduction are equal. The slopes of the lines are equal to the values of the Tafel constants, β_a for oxidation and β_c for reduction. The value of the exchange current density i_o depends on both the reaction and the material of the electrode and varies widely for different reactions and materials from about 10^{-14} A/cm^2 to about 10^{-2} A/cm^2.

For a corrosion process with different reactions providing the main oxidation and reduction currents, the balance of the oxidation and reduction currents at the mixed potential can be shown in a polarization diagram similar to the one for a single reaction. The lines intersecting at the mixed potential are those for total oxidation and total reduction currents, which are obtained by summing the currents of all the oxidation reaction and the currents of all the reduction reactions for all electrically

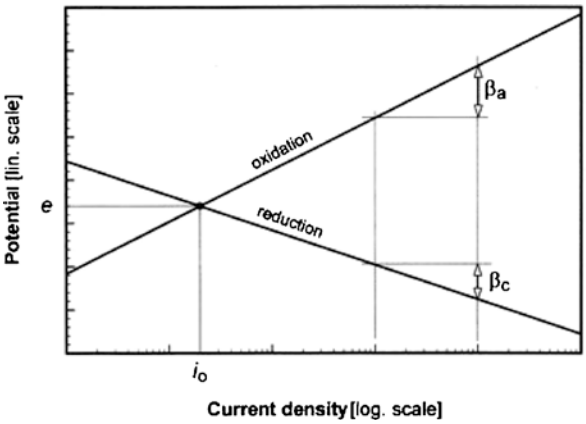

Fig. 9.1 Polarization diagram for an electrochemical reaction under activation energy control, showing the equilibrium potential e, exchange current density i_o, and Tafel slopes β_a and β_c

connected electrode surfaces exposed to the electrolyte. Because of the rapid exponential decrease of the reduction current with increasing (more positive or less negative) potential and similar decrease of the oxidation current with decreasing (less positive or more negative) potential, in many cases some of the currents are negligible at certain potentials and can be ignored. Figure 9.2 presents a polarization diagram, called Evans diagram, for corrosion of a metal where only oxidation of the metal (reaction with e_a and i_{oa}) and reduction of one species in the electrolyte, such as hydrogen ions or dissolved oxygen (reaction with e_c and i_{oc}), play significant roles. The mixed potential, at which the oxidation and reduction currents are equal, is called the corrosion potential E_{corr}, and the oxidation current density at this potential is the corrosion current density i_{corr}; the corrosion rate is proportional to i_{corr} according to Faraday's law (9.7).

The use of the corrosion current density i instead of current I in Fig. 9.2 suggests that both oxidation and reduction take place uniformly on the same electrode surface. Such a condition would occur exactly only for ideally pure metals and perfect surface conditions in an ideally homogeneous electrolyte. In such a case, although oxidation and reduction take place on atomically different sites at any instant, both reactions are distributed uniformly on a microscopic and macroscopic scale. In more common practical situations, the surface chemistry and conditions are more favorable for one or the other reaction on microscopically or macroscopically distinct areas, and the current density values in the Evans diagram are averages over the whole surface area of the electrode. For technically pure metals, for example, impurities may be preferential sites for reduction, and oxidation may occur at a higher rate on some surface irregularities. Even for heterogeneous alloys consisting of chemically different phases, it is common to plot average current density values because the total current can be directly measured, while individual current components for different phases would be difficult to determine. It is important to keep in mind, however, that actual current density may be considerably higher than average on very active but small areas of the surface.

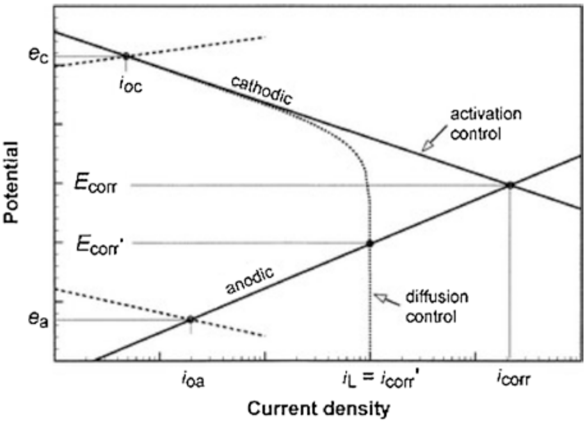

Fig. 9.2 Evans diagram for metal corrosion showing polarization curves for metal oxidation under activation energy control (anodic line) and reduction of some electrolyte species under activation and diffusion control (cathodic line)

When oxidation dominates on one of two dissimilar areas of the metal surface (or two dissimilar electrodes are electrically connected), while reduction dominates on the other, the former is called the anode, while the latter is the cathode.[7] In this case the electric current flows between two identifiable macroscopic surfaces, as opposed to many local currents flowing between many small sites on the surface, which may have only atomic dimensions. Because of the use of the terms anode and cathode for different electrodes, it is also common to use the terms anodic sites (where oxidation occurs) and cathodic sites (where reduction occurs), to call reactions proceeding in the direction of oxidation "anodic reactions," and those proceeding in the direction of reduction "cathodic reactions," and to use terms "anodic Tafel constant" and "cathodic Tafel constant" for the constants for oxidation and reduction, respectively.[8]

The straight, "Tafel" polarization lines shown in Fig. 9.2 represent the current-potential relationships controlled by the activation energy barriers. A metal or alloy corroding under the conditions of this control is said to be under "active corrosion condition," in "active state," or "actively corroding." Since the oxidation process generates metal ions, which have to be transported away from the electrode for the process to continue, and reduction requires a supply of species transported to the electrode, either process can become controlled by transport of the respective species in the electrolyte rather than by activation energy as the reaction rate increases. This condition occurs more likely for slower moving cathodic species, such as dissolved oxygen, than, for instance, hydrogen ions or hydrated metal ions. Diffusion is usually the most important transport mechanism for dissolved species at the electrode surface, and oxygen diffusion control of corrosion of metals with substantial thermodynamic dissolution tendency is quite common in aqueous environments containing dissolved air. When the cathodic reaction is completely diffusion limited, corrosion is under full cathodic control, the corrosion rate becomes potential independent and equal to the diffusional flow, and the maximum rate can be expressed as a limiting current density i_L. The effect of mass transport on the

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[7] Formally, the anode is defined as the electrode, at which the direction of the current is from the electrode into the electrolyte, while for the cathode the direction is from the electrolyte into the metal. Since the positive charges move from the metal into the electrolyte during oxidation while electrons flow through the metal to the cathode where they are consumed by the reduction reaction, this definition is in accord with the convention of current flowing in the direction opposite to the flow of electrons.

[8] The use of the terms "anodic" and "cathodic" can be confusing. Since polarization in the positive direction of the potential increases the rate of oxidation, this direction of the potential change is called "anodic direction," and "cathodic direction" is the potential change toward less positive or more negative values. Consequently, scanning the potential in the positive direction is "anodic polarization," and scanning in the negative direction is "cathodic polarization." On the other hand, when two electrodes have different potentials, the one with the more positive potential is "cathodic" or "more noble" with respect to the one with the less positive or more negative potential, and the other one is "anodic" or "less noble" or "more active." It is also important to keep in mind that the terms "higher potential" and "lower potential" always mean more positive (or less negative) and more negative (or less positive) values, respectively.

cathodic reaction is shown by the dotted line in Fig. 9.2. The illustrated condition shows corrosion under full cathodic diffusion control at E_{corr}' and $i_{\mathrm{corr}}' = i_{\mathrm{L}}$.

Figure 9.2 illustrates the types of interaction of oxidation and reduction processes common in corrosion of base metals that are in the state of activity, i.e., when products of oxidation are soluble or not protective. For biomaterials in the human body, this condition is uncommon, because it usually results in a relatively high corrosion rate, which is unacceptable for this type of application. The diagram in Fig. 9.2 is important, however, as an illustration of the fundamental principles of electrochemical interaction, allowing prediction of the effects of some variables. It shows, for instance, that an increase in the oxidation rate, perhaps as a result of a change in the surface condition of the metal while the cathodic kinetics remains the same, causes a shift of the oxidation line in the diagram to the right and thus an increase in i_{corr} and a shift of the corrosion potential toward a lower value.[9] An increase in the rate of reduction under activation energy control (a shift of the cathodic line to the right) also increases i_{corr} but shifts E_{corr} to a higher value. Under full cathodic diffusion control, an increase in i_{L} (perhaps due to an increase in the flow rate of the electrolyte) is associated with an increase in both i_{corr} and E_{corr}, while a change in the oxidation kinetics under cathodic diffusion control changes E_{corr} but i_{corr} remains constant at i_{L}. Thus an observed change in the corrosion potential may or may not indicate a change in the rate of corrosion, and a correct interpretation requires some knowledge of the type of kinetics involved.

The successful use of base metals, such as chromium, cobalt, nickel, titanium, niobium, and zirconium, in the human body is due to the phenomenon of passivity. In spite of some conflicting theories of the passivation process, there is little doubt that in a passive state the above metals in an aqueous electrolyte are covered with a thin and very protective film of a stable, poorly soluble oxide or hydroxide. The stability of oxides and hydroxides is typically a function of the pH. In water the oxides form electrochemically, and their existence is thus also potential dependent. A convenient illustration of a region of stability of an oxide as well as of other potential or pH dependent species is a potential-pH (*E*-pH) diagram, commonly called a Pourbaix diagram.[10] Figure 9.3 shows a simplified *E*-pH diagram for titanium, one of the metals of special significance for medical implants. A collection of *E*-pH diagrams for most metal/water systems can be found in an atlas [5].

Pourbaix diagrams are constructed based on the thermodynamic data for various chemical and electrochemical reactions possible in the given metal-electrolyte system. They can be interpreted as showing regions of thermodynamic stability of various species. If the stable specie is a non-ionized metal, the region is one of immunity, because under those pH and potential conditions the metal is thermodynamically stable and thus cannot corrode. Regions of stability of soluble species generally are regions of corrosion, because there is a thermodynamic tendency for dissolution. In

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[9] It is assumed that such a change would result in an increase in the effective exchange current density, while the anodic Tafel constant remained the same.

[10] Prof. Marcel Pourbaix of Belgium devoted his life to the construction and application of potential-pH diagrams.

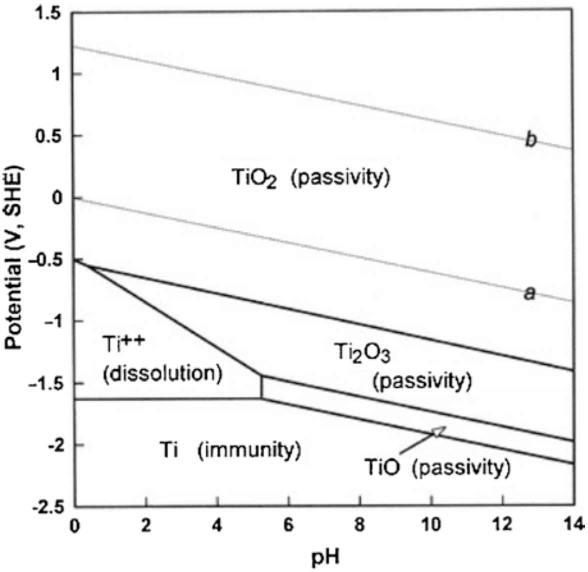

Fig. 9.3 Potential-pH (Pourbaix) diagram for the system titanium/water at 37 °C. Based on data in [5]

the regions of stability of an oxide (or hydroxide), passivity is possible, assuming that the oxide is poorly soluble and nonporous and thus protective.

Although a Pourbaix diagram thus provides a "map" of regions of immunity, corrosion, and passivity at various pH and potential conditions, it must be kept in mind that for a specific corrosion condition the pH of the electrolyte is probably more or less constant, and the above regions are reduced to ranges of potential values along a vertical line in the diagram. The actual corrosion condition is then the result of a combination of thermodynamic and kinetic factors that determine the actual corrosion potential, the diagram showing only the former and not the latter factors.

Traditionally, each Pourbaix diagram for metal-water systems also includes two lines, marked (a) and (b), representing the equilibria for reactions (9.3) and (9.5), respectively. Both reactions are pH dependent with the same slopes in the diagram, $e = e^{o} - 0.061$ pH at 37 °C. These two reactions, proceeding in the direction of reduction, are the two most important cathodic reactions for corrosion in aqueous electrolytes, such as body fluids. Since the corrosion potential must establish itself below the equilibrium potential of the cathodic reaction (so that the reaction proceeds in the direction of reduction), the lines (a) and (b) show the theoretical maxima for the corrosion potentials in oxygen-free water (line a) and oxygen-saturated water (line b).

When a metal without a surface oxide is exposed to water not containing its ions, there is a very high tendency for oxidation, and the potential rapidly increases from the very low value toward the potential of the available reaction providing reduction. If the mixed potential of the balance of oxidation and reduction stabilizes in the field of dissolution in the Pourbaix diagram, active corrosion occurs. If the potential reaches the field of a stable, protective oxide, the metal becomes passive.

The variations of the corrosion current density with potential again can be depicted in a polarization or Evans diagram. If the potential change along a vertical line in the E-pH diagram for the given pH value passes through the field of dissolution before reaching the field of passivity, the diagram shows a classical "textbook-type" anodic polarization curve for passivation, illustrated in Fig. 9.4. The anodic line, in principle starting from the equilibrium conditions, shows a segment of Tafel behavior through the field of dissolution (active region) where the current density for oxidation increases exponentially with the potential. It then reaches a peak current density called critical current density for passivation (i_{crp}) at the boundary between the regions of dissolution and stability of the oxide at the primary passivation potential E_{pp} and drops rapidly to the current density in the passive state (i_{p}). The current density remains more or less constant in the region of passivity. This type of polarization behavior is experimentally observed, for instance, for iron in acidic solutions and theoretically should also be observed for titanium (see Fig. 9.3).

Alternatively, and more commonly for metallic biomaterials with a high passivation tendency, as the potential increases, the metal passivates without any significant active dissolution, the potential-pH conditions moving from the region of immunity to passivity. The result is an experimental anodic polarization curve lacking the typical "passivation" peak but showing the potential-independent region of passivity with a low value of i_{p}. Moreover, since passivating metals have a high tendency for oxidation, they react easily with atmospheric oxygen, so that the surface usually becomes covered with an oxide film even before immersion in the electrolyte. This film may dissolve if the kinetics of the anodic and cathodic reactions maintain the E-pH condition in the region of dissolution. If, however, after immersion the potential quickly passes through the active region to passivity, the characteristics of the film may change, but active corrosion does not necessarily occur.

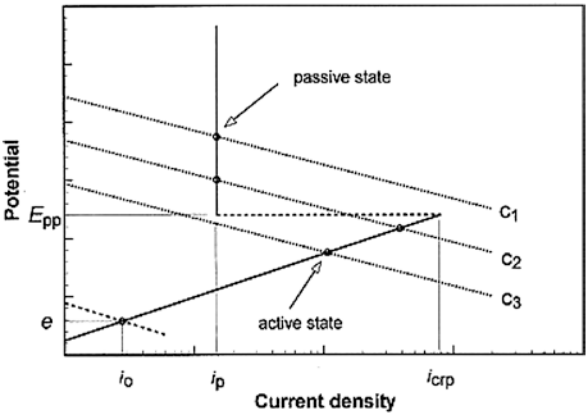

Fig. 9.4 Evans diagram for metal corrosion showing polarization curves for a passivating metal and activation energy controlled reduction of electrolyte species (lines c_1, c_2, and c_3)

Similarly to the behavior of an actively corroding electrode illustrated in Fig. 9.2, the corrosion potential for a passivating metal establishes itself at a value resulting in the equality of oxidation and reduction currents. This is shown in Fig. 9.4 as the intersection of the cathodic polarization line with the anodic line. When a true passivation peak exists, the reduction current must exceed the oxidation current at the primary passivation potential E_{pp} for spontaneous passivation to take place. For a theoretically uniform distribution of the current, this means $i_{red} > i_{crp}$ at E_{pp} for the electrode to exist in a state of stable passivity (line c_1 in Fig. 9.4). If $i_{red} < i_{crp}$ at E_{pp} (the cathodic polarization line intersects the anodic line in both the dissolution segment and the region of passivation, line c_2 in Fig. 9.4), the electrode is in a state of unstable passivity and may be either active or passive or even switch from one state to the other.[11]

In the region of passivity, the current density is very low (typically less than 1 μA/cm^2 for implant alloys in actual or substitute body fluids) and often approximately potential independent. Since the driving force for the oxidation reaction increases with increasing potential, the potential independence of i_p indicates that the passive film becomes more protective with increasing potential, mostly by increasing thickness. However, there are many cases where i_p varies with the potential in the passive region, either increasing or decreasing. Still, this potential dependence is always much weaker than the exponential variation for Tafel behavior in the active state. The oxide films, especially on solid solutions or other multicomponent phases, can be quite complex in structure and chemistry, and the changes in the properties also may be potential dependent.

The existence of measurable anodic current density in the passive state even under steady state conditions at a constant corrosion potential indicates that oxidation continues. The rate of oxidation equals the rate of chemical dissolution of the oxide, thus keeping the oxide thickness constant. Therefore, implants in passive condition continue to release metal ions, albeit at a low rate. Because of the variation of the solubility of the oxide with the pH of the solution, i_p shows a similar dependence.[12]

For some polyvalent metals (e.g., Cr), soluble species (CrO_4^{2-}) become thermodynamically stable as the valence changes at potentials above those for a stable oxide, (from three to six for Cr). This change results in another region of active dissolution, a phenomenon called transpassivity.[13]

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[11] In this case the cathodic line also intersects the anodic line in the segment of a current density drop from i_{crp} to i_p. Since this is a region of "negative resistance" (positive current decreasing with positive potential increase), this condition cannot be sustained.

[12] Most oxides providing passivity for metallic biomaterials exhibit increasing solubility with increasing acidity (decreasing pH) below neutral conditions and some also under alkaline conditions. While alkaline conditions are physiologically of little importance, the increase in solubility with increasing acidity plays a major role in localized forms of corrosion.

[13] Lately, the term "transpassivity" frequently has been applied to any increase in activity for passivating metals at potentials above the passive region, such as when localized breakdown of passivity occurs, resulting in pitting.

9.3 Forms of Corrosion of Metallic Biomaterials

The principles of electrochemical corrosion discussed in Sect. 9.2 apply universally in all cases of corrosion of metallic biomaterials. In the individual forms of corrosion, however, specific conditions may make the corrosion process much more complex, for instance, because of the interaction of areas of dissimilar electrochemical properties, localized variations in the solution chemistry, interaction with mechanical effects, etc. Following are the main forms of electrochemical corrosion relevant to biomaterials. In practical situations, several forms may occur at the same site, e.g., pitting combined with galvanic corrosion, crevice corrosion with wear corrosion, etc.

9.3.1 Uniform Dissolution

The corrosion process is most easily analyzed when the oxidation and reduction reactions take place uniformly on a homogeneous metal surface. Completely uniform corrosion, however, is an ideal condition that does not occur in practice. Ideally, oxidation and reduction would occur randomly on surface atoms that were identical in electrochemical properties so that the oxidation and reduction sites were interchangeable and allowed instantaneous and continuous redistribution. In reality, defects of the crystal structure (vacancies and interstitials, dislocations, impurities) and segregation of elements result in an inhomogeneous distribution of electrochemical activity on the surface even for very pure metals and solid solutions. In many cases, impurities precipitating as second phases play an important role as preferential sites for reduction, oxidation, or both. The conditions are even more complex for multiphase alloys, where some phases may be clearly anodic and other cathodic. In many cases averaging of the corrosion parameters over the nominal surface provides a reasonable picture of the electrochemical behavior at the corrosion potential or under polarization and yields useful values of corrosion parameters. However, surfaces of previously smooth metals usually show distinct roughness after active state corrosion. Uniform corrosion of single phase materials in passive state usually preserves smoothness of the surface, both because of the low corrosion rates and because the surface reaction is chemical dissolution of a relatively uniform film.

An aspect of uniform corrosion that usually receives little attention is selectivity of dissolution in alloys.[14] Electrochemically more active components of a solid

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[14] Selective leaching as a specific form of corrosion, often called by a generic term "dezincification" (leaching of zinc from brass), is a sometimes serious form of industrial corrosion, resulting in loss of mass and a porous layer on the surface of alloys containing elements of very different electrochemically activity. Such a severe degradation is normally not observed in much more corrosion-resistant biomedical alloys.

solution have a tendency to dissolve preferentially, resulting in their depletion in the surface layer and enrichment in more stable elements. The commonly observed increase in the corrosion potential with time is usually attributed to the growth of an oxide film or formation of other corrosion products, but selective dissolution also may contribute to the effect.

From the practical viewpoint, the most important corrosion parameter in uniform corrosion is the (nominally uniform) corrosion rate. For biomaterials the corrosion rate must be very low and is usually determined by sensitive electrochemical techniques as corrosion current density. Physiologically, on the other hand, the more important value is the release rate of specific elements in view of the diversity in toxicity and generally dissimilar human body tolerance for different elements. Although the corrosion current density can, in principle, be converted to the mass loss using Faraday's law (9.7), with the exception of pure metals, the determination is considerably less straightforward because the elements do not necessarily dissolve at relative rates equal to the atomic ratios in the alloy.

There are several methods of determination of the average corrosion current density, most of them based on calculation from the value of the polarization resistance R_p. The polarization resistance is defined as the slope of the polarization curve at zero current density, $R_\mathrm{p} = (\mathrm{d}E/\mathrm{d}i_\mathrm{n})_{\mathrm{in}=0}$, where i_n is the net current density, which is the difference between the anodic (oxidation) and cathodic (reduction) current densities.[15] The corrosion current density is then calculated using (9.10):

$$i_\mathrm{corr} = \frac{\beta_a \cdot \beta_c}{2.3R_p\left(\beta_a + \beta_c\right)} \tag{9.10}$$

9.3.2 Galvanic Corrosion

In galvanic corrosion the degradation is enhanced by a combination of two or more dissimilar metals that touch each other or are otherwise in electronic contact. "Galvanic interaction" also occurs between dissimilar phases in multiphase materials, but the term "galvanic corrosion" usually is used for structures consisting of two or more components made of different materials, such as ball and stem of a total hip implant.

Galvanic corrosion occurs when the corrosion potentials (E_corr) of the individual materials (electrodes), when not connected with each other, are different. When an electric connection is established, the potential difference causes a current to flow, and the current polarizes the individual electrodes toward a common "galvanic potential" (E_g). Electrodes with the lower individual potential ($E_\mathrm{corr} < E_\mathrm{g}$) are

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[15] The measured net current $I_\mathrm{n} = I_\mathrm{oxidation} - I_\mathrm{reduction}$ assuming both oxidation and reduction currents to be positive values. It is more common to take the reduction current as negative, in which case the net current is the sum of oxidation and reduction currents.

polarized in the positive direction (anodically), their oxidation rates exceed the reduction rates (they become anodes), and they are likely to corrode more than in the absence of the galvanic contact. Those with the higher individual potential ($E_{\mathrm{corr}} > E_{\mathrm{g}}$) are polarized in the negative direction, become cathodes, and may to some extent be protected.

The electrodes of the galvanic system would reach the same galvanic potential E_{g} only if the total resistance in the path of the current between them was zero. Since the current must flow not only through the metal contact but also through the ionically conducting solution, the resistance is not necessarily negligible, except near the interface between the contacting metals. The result is that there is often a significant variation in the potential from the interface to the more distant areas. For the anode(s) of the system, it means that the increase in the corrosion rate tends to be highest near the interface and decrease with a distance from it.

Overall, for the whole galvanic system, the oxidation current must still equal the reduction current, and the anodic current increase on the anode(s) must equal the cathodic current increase on the cathode(s). For electrodes of unequal area, this means a higher current density increase for a small electrode than for a large one. Thus a combination of a large cathode with a small anode is potentially more damaging than the opposite case.

The actual severity of galvanic corrosion also depends, however, on the polarization behavior of the electrodes, especially of the anode(s). The essential effect of galvanic interaction is an increase in the potential of the anode, and if this increase does not result in an increase in the oxidation rate, there is no galvanic corrosion. This is true for a passivating metal in the region of potential independence of the current density. Coupling with a more noble electrode may increase the corrosion potential, but if E_{corr} remains in the region of passivity, the dissolution rate increases little or not at all. Since the corrosion potential cannot exceed the equilibrium potential of the reduction reaction (or the highest one if several reactions participate), galvanic interaction has no detrimental effect if there is no current density increase on the anode at up to this potential.

A special case of galvanic interaction, called “oral galvanism,” may occur in the oral cavity if restorations or appliances made of dissimilar metals are in contact continuously or intermittently (during biting). The electric current circuit includes a path through the tissues, and the current flow may affect nerves, causing pain. The conditions for galvanic interaction are much more common for metals in the oral cavity than for implants because of the frequent use of both noble and base metals, as in a contact between a gold crown and a dental amalgam filling. Still, severe continuing galvanic corrosion is relatively rare because the galvanic effect rapidly diminishes when an electric resistance is placed in the current path, causing an *IR* (current times resistance) potential drop and thus reducing the potential increase on the anode. When two dissimilar restorations are placed in contact, the initial galvanic current may be high (and cause pain), but the corrosion reactions often result in the formation of nonmetallic corrosion products at the interface that increase the resistance. Intermittent contacts of upper and lower jaw restorations are more likely to cause high current spikes, but even there the oxide formation on the anode is likely in time to reduce the effect.

Galvanic interaction also may have beneficial effects. In industrial practice one type of corrosion protection is achieved by using a “sacrificial anode” made of a cheap base metal as “cathodic protection” (the protected part is made the cathode of the cell) to protect the more valuable structure. This type of protection is normally not applied to biomaterials because the intensive corrosion of the anode would be unacceptable within the human body. However, a mild galvanic interaction that increases slightly corrosion of one part and decreases dissolution of the other part may be beneficial if the elements dissolving from the protected part (cathode) are more harmful (such as Ni) than those from the anode (such as Ti). Galvanic effect may also be used to ensure stable passivity by increasing the corrosion potential well above the primary passivation potential (E_{pp}), but this must be done carefully to avoid the danger of passivity breakdown (see Sect. 9.3.4). Conversely, the danger of passivity breakdown may be lessened by coupling with a material with lower E_{corr} (anode of the galvanic cell), on the condition that this will not result in unacceptable corrosion of the anode or shift the potential of the cathode into the region of unstable passivity or activity.

9.3.3 Concentration Cell Corrosion

Similarly to galvanic corrosion, concentration cell corrosion involves a potential difference between macroscopically separate electrode areas causing a flow of the current and changes in the polarization of the areas. While in galvanic corrosion the potential difference results from a difference in the electrochemical properties of the electrode surfaces, in concentration cell corrosion there is a difference in the concentration of species in the electrolyte involved in the corrosion reactions on the electrode areas. The equilibrium potential of an electrochemical reaction is a function of the ionic concentration according to the Nernst equation (9.4), and a concentration difference generates a potential difference. Differences in concentration of both anions and cations can create a potential difference; since hydrogen ions, dissolved oxygen, and metal ions are the most important reactants or products of corrosion reactions in aqueous solutions, hydrogen ion, oxygen, and metal ion concentration cells are most common.

In a metal ion concentration cell, the electrode area exposed to a lower concentration of the ions has a higher tendency to dissolve and lower individual corrosion potential. When connected with the area of higher ionic concentration, it is polarized toward the higher potential of the other area, it becomes the anode, and its corrosion rate increases. Differences in the concentration of cathodic reactants, such as hydrogen ions or dissolved oxygen, on the other hand, do not result directly in a difference in the corrosion rate of the regions, because under short-circuit conditions the corrosion potential is the same, and thus both areas are polarized to the same potential, resulting in the same anodic overpotential for the same oxidation reaction. Such a concentration cell may cause corrosion acceleration of one of the areas indirectly, as a result of chemistry changes at the electrode surface. Both reduction of hydrogen ions and reduction of dissolved oxygen involve consumption of hydrogen ions, and the areas where these reactions are more intensive exhibit a pH increase. In the industrially important case of an oxygen concentration cell (situation called "differential aeration"), corrosion of steel is accelerated in the oxygen-depleted region next to the air-saturated region because of the passivation of the latter due to the pH increase, in spite of the fact that an oxygen concentration increase by itself normally results in a higher corrosion rate.

Although some concentration differences are common, concentration cell corrosion of metallic biomaterials on unshielded surfaces is rare and usually mild. As seen from the Nernst equation, a difference in metal ion concentrations by a factor of 2 and 10, for the most common divalent ions, results in potential differences of only about 10 and 30 mV, respectively. Moreover, similarly to galvanic corrosion, the strength of the interaction diminishes with distance because of the electric resistance in the current path, but unlike the galvanic situation at the interface between different solid phases, a sharp transition of one concentration to another within the electrolyte cannot be sustained. Body fluids are well buffered against large pH changes, but even for the larger pH variations due to post-surgery trauma, the concentration effect is rather mild for the common highly passivating alloys. Concentration cells exist in the oral cavity because of the exposure of restorations to both the oral and tissue fluids, but the corrosion effect is again relatively small. Concentration cells, however, play important roles in the forms of occluded cell corrosion, which are discussed next.

9.3.4 Pitting and Crevice Corrosion

Except for degradations combining corrosion with mechanical effects, pitting and crevice corrosion are the most destructive forms of corrosion of metallic biomaterials. Both are types of localized attack occurring in what is called "occluded corrosion cells," i.e., where solution at the site of the attack becomes different and much more aggressive than the solution outside those sites because of the restricted transport of ionic species in and out of the site. Both pitting and crevice corrosion are most common and severe for passivating metals exposed to solutions containing chloride ions, where small regions of actively corroding metal become anodes, surrounded by large cathode areas of slowly corroding passive surface.

The mechanism of corrosion in active pits and crevices is virtually the same, and the main difference between the two forms is in the initiation, pitting requiring a breakdown of the passive film to establish the occluded condition. In the absence of a mechanical action, such as scratching, the breakdown is usually electrochemical. Such a breakdown of passivity is potential dependent and occurs when the electrode potential exceeds a critical value, called breakdown potential (E_b) or pitting potential (E_{pit}). In spontaneous corrosion breakdown occurs when the corrosion potential, which, for passive metals, usually increases with time, reaches the breakdown potential. Thus a material with a lower breakdown potential is more susceptible to pitting initiation, assuming otherwise the same anodic and cathodic kinetics. Since the corrosion potential cannot exceed the equilibrium potential of the cathodic reaction, this latter potential can be considered the minimum value of E_b for immunity against pit initiation.

There are conflicting theories for the mechanism of the breakdown, but there is evidence that chloride ions are involved (other halogens and some other aggressive ions may play this role in some solutions), either by making the oxide film locally soluble, slowing down repassivation of breaks in the film, or some other mechanism. Pitting may also be initiated by surface impurities, such as sulfide inclusions in stainless steels. Once the metal becomes locally active, the corrosion reactions cause local changes in the electrolyte chemistry, which prevent repassivation. The most important of these changes is acidification, which results from a chemical reaction of metal ions with water, called hydrolysis. For example, for chromium the hydrolysis reaction may be as follows:

$$\mathrm{Cr}^{3+} + 3\mathrm{H_2O} = \mathrm{Cr}\left(\mathrm{OH}\right)_3 + 3\mathrm{H}^+ \tag{9.11}$$

The reaction consumes the dissolving metal ions, a solid corrosion product precipitates, and hydrogen ions are generated, thus causing the pH to drop. The high acidity generated by the hydrolysis reaction prevents repassivation because of the higher solubility of the oxide at lower pH. The precipitated solid is non-protective and may impede transport of ions from and to the active surface.

The hydrolysis reaction starts when the concentration of the metal reaches a critical value, which depends on pH and on the value of the solubility product K_s. For metals with poorly soluble oxides and hydroxides, which also form stable passive films, acidification thus starts generally earlier than for metals with less effective passivation. The pH drop continues, and metal ion concentration increases (because of higher oxide solubility at lower pH) until either a balance of transport in and out of the pit is reached or the metal concentration becomes high enough for precipitation of a salt. Values of pH as low as 1.5 have been found experimentally in active occluded corrosion cells.

Contributing to acidification is local depletion in dissolved oxygen, which normally consumes hydrogen ions (9.6), because oxygen diffuses slowly and cannot be replaced sufficiently quickly at the site of dissolution. On the other hand, negative chloride ions from outside the pit are attracted by the positive charge of the metal ions within the pit, further impeding passivation.

If the whole surface of the electrode became active, the corrosion potential would drop from the region of passivity to the region of activity. Since initiated pits are only a small fraction of a total area of the electrode and are surrounded by a large passive surface, the potential does not change that much, resulting in high anodic polarization for the active area within the pits and a very high corrosion current density, often three or more orders of magnitude higher than outside the pits. The consequence is a high rate of growth of the pits. The growth rate may decrease with time, however, as the resistance in the current path between the outside and the bottom of the pits increases and results in a potential drop, which reduces the anodic polarization of the active surface.

The maintenance of an active pit requires a dissolution rate generating enough ions to keep the pH continuously low by hydrolysis, while some hydrogen and metal ions escape from the pit and some oxygen diffuses inside. Since the dissolution rate in the active state is a function of the potential, lowering the potential decreases the dissolution rate, until eventually the active surface within the pit cannot be sustained and the surface repassivates. The potential value at which this happens has been called "protection potential" (E_{prot}) or "repassivation potential" (E_{rp}).

Crevice corrosion involves the same mechanism as pitting, except that the occlusion results from shielding of a part of the surface. Crevice corrosion cells are thus common where two metal parts or a metal and a nonmetal part are in contact that allows access of the electrolyte between them. For medical implants some common sites are between the head of a bone screw and a bone plate or between a ball and stem of a two-component hip implant. For a newly formed crevice, or a crevice newly exposed to the solution, there is a period of inactivity, during which the occluded cell conditions are getting established, i.e., depletion of dissolved oxygen, accumulation of metal ions by a slow dissolution of the oxide film, followed by metal ion hydrolysis, pH drop, accelerated dissolution of the oxide, and increasing concentration of chloride ions. The active surface within the crevice is coupled with the usually larger external passive surface and is thus anodically polarized, which results in a high corrosion rate. Similarly to pitting, lowering the potential below a critical value reduces the dissolution to a rate, at which the active corrosion conditions within the crevice are not sustained.

Crevice corrosion is generally more severe for narrower crevice gaps, because the transport restriction is more effective. On the other hand, since the important polarization effect of the external surface requires a current flow, a too narrow crevice or a crevice filled with corrosion products may involve a potential drop that reduces the crevice effect. For the same reason, dissolution is usually most severe inside but near the mouth of the crevice. The crevice corrosion rate may be increased or decreased by a galvanic interaction if the two contacting components are made of dissimilar materials, resulting in a potential change.

Ranking of the most common orthopedic implant alloys based on the values of the breakdown potential in vitro shows increasing corrosion resistance in the order Type 316 LVM stainless steel, Co-Cr alloys, and Ti alloys, which is in agreement with the clinical experience. In the area of dental restorative materials, high-copper dental amalgams, which do not exhibit breakdown of passivity in vitro, also show less corrosion than low-copper amalgams, which do.

9.3.5 Environment-Induced Cracking

When a metal part is subjected to a mechanical load in a corrosive environment, cracking may occur as a result of a combination of those conditions. If the load is mostly static, the failure is usually called stress corrosion cracking (SCC), while fluctuating loading may result in corrosion fatigue (CF). The term hydrogen-induced cracking (HIC) is used when the failure can be attributed to the entry of hydrogen atoms into the metal.

These forms of failure are of great industrial importance, and there are many conflicting theories and models of the mechanisms. While some researchers seek and favor a single mechanism for different alloy/environment combinations, others find evidence for different mechanisms in different systems. Dissolution models of SCC and CF attribute the crack extension to anodic dissolution of a strained metal at the crack tip, while mechanical models describe the process as a mechanical failure facilitated in various ways by the environment, such as by weakening of the atomic bonds at the crack tip due to adsorption of species from the electrolyte, formation of brittle films or other brittle phases, various effects of the electrolyte on dislocation generation, interaction and movements, etc. Hydrogen-induced cracking may be due to absorbed hydrogen affecting the metal lattice properties or dislocations or formation of brittle hydrides. An increase in the electrode potential (anodic polarization) often is observed to increase the rate of crack propagation, which is predicted by dissolution models but is also in accord with some mechanical models. When cracking is accelerated by cathodic polarization, which increases the supply of reduced hydrogen ions at the metal surface, it suggests that HIC is involved.

Stress corrosion cracking has been observed in specific metal/environment systems and is mostly confined to alloys, and most common metallic biomaterials are resistant to SCC. Stainless steels are well known to suffer from SCC in hot chloride solutions, but there is no conclusive evidence that SCC occurs for implant-grade stainless steel in body fluids at body temperature. Some titanium alloys are highly susceptible to SCC, but commercially pure Ti and implant Ti alloys, such as Ti-6Al-4 V, do not appear to be susceptible in body fluids. On the other hand, there is some concern regarding possible HIC of Ti and its alloys.

In contrast to SCC, corrosion fatigue is not confined to specific systems, and acceleration of fatigue crack propagation by corrosive environments is common. Moreover, since metal fatigue is highly sensitive to surface conditions, initiation of fatigue (and CF) failure may be facilitated by localized corrosion, such as pitting. Thus the corrosive environment may decrease the threshold stress intensity or the fatigue crack propagation rate or both.

9.3.6 Intergranular Corrosion

In intergranular corrosion the dissolution is confined to a narrow region along the grain boundaries, and the attack may not be clearly visible until failure occurs due to the loss of mechanical integrity. A severe susceptibility of the grain boundary regions may be due to the precipitation of corrosion susceptible phases or to depletion of elements providing corrosion protection along the boundaries due to precipitation of phases rich in those elements. The latter is the cause of intergranular corrosion of "sensitized" stainless steels (and some Ni-Cr alloys), sensitization being due to precipitation of chromium-rich carbides along grain boundaries, and may occur during heating into a specific temperature range, for instance, during welding. This dangerous form of corrosion of stainless steel may be avoided by proper heat treatment (dissolving existing carbides at high temperature and rapid cooling to prevent precipitation) or by alloying with other strong carbide forming elements, but in stainless steel for implants normally it is prevented by using steels with a very low carbon content.

9.3.7 Wear-Corrosion, Abrasion-Corrosion, Erosion-Corrosion, and Fretting

In these forms of corrosion, the mechanical action destroys the protective films, allowing active corrosion of the unprotected metal surface. If only part of the surface is active, the coupling of the active surface with neighboring passive areas intensifies corrosion. Wear-corrosion involves parts in a friction contact with relative movement, while abrasion-corrosion involves abrasive particles between the contacting surfaces, which may be the debris from the wear process. In erosion-corrosion the destruction of the surface film is due to the flow of a liquid, mostly one containing abrasive particles. Fretting is a special case of wear-corrosion, in which there are only small relative movements between contacting parts that are essentially in a static mutual relationship. Thus wear- and abrasion-corrosion may occur in articulating implants, such as on a metal ball of a hip joint in contact with the polyethylene cup, and fretting may take place between the ball and stem of multi-component hip implant. Wear- and abrasion-corrosion occur on the mastication surfaces of dental restorations. Erosion-corrosion may cause degradation of metallic heart valves.

Wear- and abrasion-corrosion and fretting are often electrochemically quite complex. The narrow gap between contacting surfaces creates crevice conditions, so that the destructive effect of friction and abrasion on the protective surface film is superimposed on the corrosion mechanism in the occluded cell. Galvanic interaction may be involved for contacting metal parts, resulting in either acceleration or mitigation of the attack. For intermittent wear and abrasion events, the repassivation ability of the metal is an important factor.

9.4 Corrosion Testing of Metallic Biomaterials

In corrosion research a large number of tests that can be used are often designed for the purpose of investigation of corrosion mechanism and determination of parameters for specific materials or classes of materials. Most corrosion tests are performed in the laboratory (in vitro); tests in animals or humans (in vivo) are mostly limited to examination of retrieved implants and dental restorations or surrounding tissues and only rarely to determine details of the corrosion behavior and parameters. The discussion here is limited to laboratory tests used for general evaluation of metallic implant and dental materials with the purpose of predicting their performance in the human body.

The choice and design of such laboratory corrosion tests are based on a number of scientific and practical considerations, including the following: (1) the type of corrosion in the human body environments is almost exclusively electrochemical; (2) metallic biomaterials are mostly highly corrosion resistant, resulting in very low corrosion rates requiring very sensitive testing techniques; (3) the chemistry of the human body fluids is relatively stable for specific application sites; and (4) the rate of release of metallic ions and their nature is an important factor in the suitability of materials for use in the human body. As a result of these considerations, the evaluation tests have the following general characteristics. First, electrochemical tests, which are highly sensitive, are used to determine the major parameters of the corrosion behavior, and immersion tests, which include solution analysis for metal ions, are used to determine qualitatively and quantitatively the released metal ions. Second, tests are performed using relatively simple solutions, omitting components of minor corrosion significance, but controlling the most important characteristics of the target environment. The conditions and procedures for the most common tests have been standardized [1].

Because of the simplification involved in the choice of the environment and some of the test conditions, such as short exposure time, laboratory corrosion tests of biomaterials are mostly ranking tests, predicting a relative rather than absolute performance. Their usefulness is based on the clinical experience with some traditional medical implant and dental restorative materials. If a tested material yields corrosion results similar or better than materials with proven, acceptable performance in the human body, there is reason to believe that the new material will perform equally well or better clinically. Eventually, this assumption must be confirmed in animal and human tests, but the laboratory tests are an important way of eliminating unsuitable materials before the clinical test phase is reached.

Most metallic biomaterials are passivating alloys, and electrochemical tests are capable of yielding a substantial number of parameters related to the passivation and passivation breakdown. For the purpose of predicting the corrosion performance, however, in vitro electrochemical corrosion tests focus mainly on the resistance to the loss of passivity. When active corrosion occurs locally on otherwise passive surface, it results in a severe corrosion attack, usually in the localized form of pitting or crevice corrosion. The fundamental electrochemical resistance to the localized loss of passivity is related to the passivity breakdown that occurs when the potential exceeds a critical value, the breakdown potential E_b. The breakdown potential is commonly determined using an electronic potentiostat[16] and subjecting the tested sample to increasingly higher potentials until a sharp increase in the anodic current signals initiation of active corrosion. This potential scanning technique is described, for instance, in the standard test method ASTM 2129, "Conducting Cyclic Potentiodynamic Polarization Measurements to Determine the Corrosion Susceptibility of Small Implant Devices." The same procedure can be used for testing laboratory specimens of any passivating biomaterial. The standard test solution according to ASTM 2129 is a phosphate-buffered saline at pH 7.2 and is used at 37 °C and saturated with pure nitrogen (deaerated). This solution is appropriate for testing of biomaterials that are to be exposed to blood or tissue (interstitial) fluids. The standard also describes a synthetic bile solution for testing of biliary implants, and the same procedure may be used with other body fluid substitutes. The results are somewhat dependent on the choice of the potential scanning speed, the most common values being 0.1667 or 1 mV/s.

The ASTM standard F2129 also describes the determination of the "protection" or "repassivation" potential E_{prot}, which is obtained by reversing the scan after the passivity breakdown occurs, and is defined as the potential at which the current density drops to the value previously observed during the forward scan. Although this determination is theoretically valid, the results must be treated with caution. The reversal of the solution chemistry changes that occur during initiation of pitting depends on the extent of the damage that occurs after the breakdown, and E_{prot} generally decreases with increasing current at scan reversal. Even at the same current value at reversal, however, E_{prot} also depends on the size and number of initiated pits, since many small pits repassivate more easily than few large ones. The observed value of E_{prot} also depends on the breakdown potential E_b, because pits initiated at a higher potential grow faster than those initiated at lower potentials. Still, cyclic polarization (potential scan with a scan reversal) is useful because the presence of a hysteresis loop, i.e., the current density returning to the pre-breakdown value at a potential $E_{prot} < E_b$, is evidence that the current increase was due to localized passivity breakdown rather than some oxidation process in the electrolyte or general reactivation.

Another way to determine the repassivation potential of alloy specimens (rather than actual devices) is described in ASTM F746, "Standard Test Method for Pitting or Crevice Corrosion of Metallic Surgical Implant Materials." A cylindrical specimen is equipped with a plastic collar creating an artificial crevice, breakdown of passivity is induced by application of a high potential, and the potential is lowered in steps until repassivation occurs. Localization of the attack inside the artificial

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[16] Electronic potentiostat is a device for controlling the potential of a tested electrode by flowing the necessary current through it. It is usually used with three-electrode corrosion test cells, in which the tested sample is a "working electrode," the potential of which is measured with respect to a reference electrode, and a relatively inert auxiliary "counter electrode" is used to complete the circuit for the current flow through the electrolyte.

crevice is intended to lessen the problem of differences in active cell size, but the exposure time may not be always sufficient for creation of crevice conditions.

Corrosion current density is an important parameter both with respect to the damage to the device and release of metal ions into the body, but its determination is often problematic. Typically i_{corr} is substantially time dependent, for passivating alloys mostly decreasing with time of exposure, and the test results thus vary with timing of the test. Since the directly measurable current at E_{corr} is zero, indirect methods, such as extrapolation of the Tafel lines to E_{corr} or calculation from polarization resistance, must be used. A standard test method for conducting potentiodynamic polarization resistance measurements is described in ASTM G59.

Most serious degradation of metallic implants often is due to a combination of corrosion with mechanical forces. Devices subjected to fluctuating loads, such as many orthopedic implants, may fail by corrosion fatigue. A standard practice for corrosion fatigue testing of metallic implant materials is described in ASTM F 1801. Modular devices, such as hip implants consisting of a separate femoral head and stem, may suffer fretting corrosion and are tested as per ASTM F 1875. Fretting corrosion also may occur at the contact between bone screws and plates, and the susceptibility to this degradation is tested as per ASTM F 897.

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