Application Note CORR-1

Princeton Applied Research

Subject: Basics of Corrosion Measurements

POTENTIODYNAMIC POLARIZATION MEASUREMENTS

Introduction

Many corrosion phenomena can be explained in terms of electrochemical reactions. It follows then, that electrochemical techniques can be used to study these phenomena. Measurements of current-potential relations under carefully controlled conditions can yield information on corrosion rates, coatings and films, passivity, pitting tendencies and other important data.

Potentiodynamic anodic polarization is the characterization of a metal specimen by its current-potential relationship. The specimen potential is scanned slowly in the positive going direction and therefore acts as an anode such that it corrodes or forms an oxide coating. These measurements are used to determine corrosion characteristics of metal specimens in aqueous environments. A complete current-potential plot of a specimen can be measured in a few hours or, in some cases, a few minutes.

Investigations such as passivation tendencies and effects of inhibitors or oxidizers on specimens are easily performed with this technique. With this knowledge, the corrosion characteristics of different metals and alloys can be compared on a rational basis and compatible specimen-environment combinations secured for further long term testing.

Electrochemical Principles and Potentiodynamic Polarization Measurements

When a metal specimen is immersed in a corrosive medium, both reduction and oxidation processes occur on its surface. Typically, the specimen oxidizes (corrodes) and the medium (solvent) is reduced. In acidic media, hydrogen ions are reduced. The specimen must function as both anode and cathode and both anodic and cathodic currents occur on the specimen surface. Any corrosion processes that occur are usually a result of anodic currents.

When a specimen is in contact with a corrosive liquid and the specimen is not connected to any instrumentation – as it would be "in service" – the specimen assumes a potential (relative to a reference electrode) termed the corrosion potential, E_{CORR}. A specimen at E_{CORR} has both anodic and cathodic currents present on its surface. However, these currents are exactly equal in magnitude so there is no net current to be measured. The specimen is at equilibrium with the environment (even though it may be visibly corroding!). E_{CORR} can be defined as the potential at which the rate of oxidation is exactly equal to the rate of reduction.

It is important to stress that when a specimen is at E_{CORR} both polarities of current are present. If the specimen is polarized[1] slightly more positive than E_{CORR}, then the anodic current predominates at the expense of the cathodic current. As the specimen potential is driven further positive, the cathodic current component becomes negligible with respect to the anodic component. A mathematical relationship exists which relates anodic and cathodic currents to the magnitude of the polarization (Ref. 2 and 3), but a discussion of this relationship is beyond the scope of this application note. Obviously, if the specimen is polarized in the negative direction, the cathodic current predominates and the anodic component becomes negligible.

Experimentally, one measures polarization characteristics by plotting the current response as a function of the applied potential. Since the measured current can vary

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[1] This implies use of a voltage source to force the specimen to assume a potential other than the corrosion potential. The current measured in this case is a net current, representing the difference between anodic and cathodic currents.

over several orders of magnitude, usually the log current function is plotted vs. potential on a semi-log chart. This plot is termed a potentiodynamic polarization plot. Note that the use of a semi-log display prevents indication of polarity on such plots. Potentials negative of E_{CORR} give rise to cathodic currents, while potentials positive of E_{CORR} give rise to anodic currents.

Figure 1 shows the potentiodynamic anodic polarization plot of a sample of 430 stainless steel. The logarithm of the current is plotted (the abscissa) as a function of the applied potential (the ordinate). This plot is described in the following paragraphs.

Region A in Figure 1 is the *active* region, in which the metal specimen corrodes as the applied potential is made more positive. At B, further increase in the rate of corrosion (as measured by the current) ceases and the onset of *passivation* begins. The loss of chemical reactivity under certain environmental conditions, probably due to the formation of a film on the surface of the metal, is referred to as specimen passivation. This point is characterized by two coordinate values, the *primary passive potential* (E_{PP}) and the *critical current density* (i_C). In region C, the current decreases rapidly as the passivating film forms on the specimen. A small secondary peak is observed followed by region D, where there is little change in current as the potential is increased. The passivating film begins to break down in region E, the *transpassive* region.

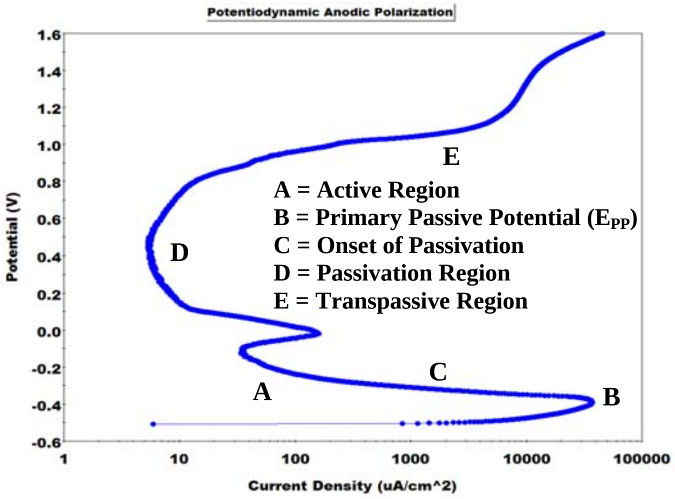

FIGURE 1: Standard potentiodynamic anodic polarization plot of 430 stainless steel.

A potentiodynamic anodic polarization plot such as Figure 1 can yield important information such as:

1. The ability of the material to spontaneously passivate in the particular medium.
2. The potential region over which the specimen remains passive.
3. The corrosion rate in the passive region.

The following discussion will deal with a class of metals that can exhibit active to passive behavior. Whether a specimen will or will not passivate depends on the form and intersection of the individual anodic and cathodic polarization plots. A diagrammatic presentation of these concepts in Figure 2 will be helpful.

Figures 2A, 2B and 2C are “theoretical” examples of an anodic polarization curve (labeled a), upon which are superimposed three “idealized” cathodic polarization curves (diagonals, labeled c). Each cathodic curve represents a single reduction process (such as hydrogen evolution) with different possible exchange current densities. These curves are theoretical in nature because it is not possible to independently measure the cathodic curve at potentials positive to the corrosion potential since the specimen has net anodic character in this region. Similarly, it is also not possible to independently measure anodic performance at potentials negative to E_{CORR}. In these figures, E_{CORR} corresponds to the intersection point(s) of the individual anodic and cathodic plots – point(s) at which the anodic current exactly equals the cathodic current. As previously stated, in the vicinity of E_{CORR} both currents are present in the specimen, but experimentally it is possible to measure only the net current. The net current has a single measurable polarity – either positive or negative. At E_{CORR} the net measured current is exactly zero.

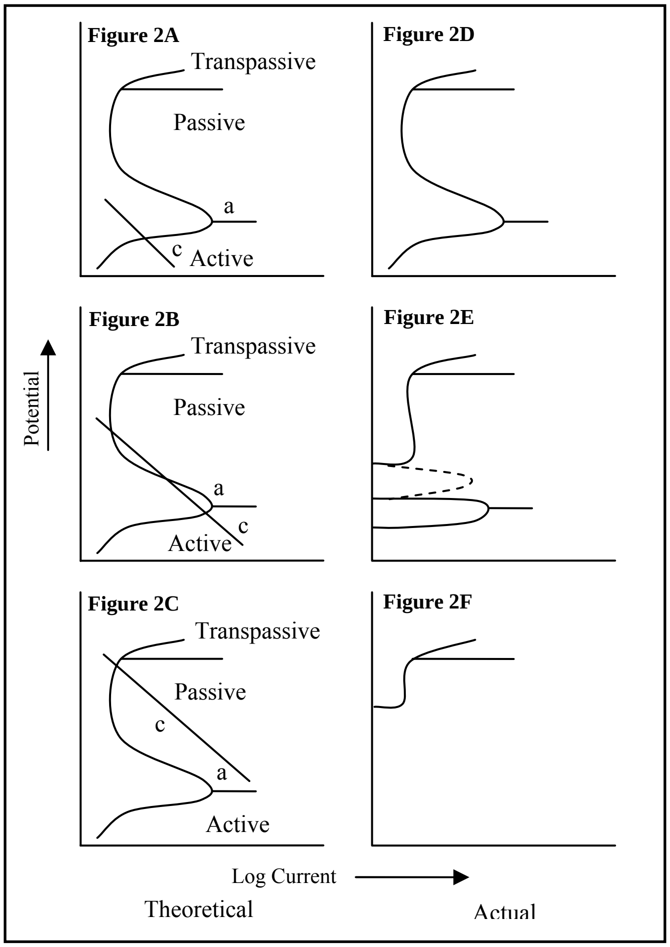

FIGURE 2: Theoretical and actual potentiodynamic polarization plots of active-passive metals.

Figures 2D, 2E and 2F correspond to the experimentally determined curves for Figure 2A, 2B and 2C, respectively. It is instructive to treat each pair separately.

If the cathodic curve intersects the anodic curve in the passive region only, as in Figure 2C, the material will passivate spontaneously. Such behavior is exhibited by stainless steels and titanium in acid solutions containing oxidizers. This situation is the most desirable from a materials construction point of view and easiest to facilitate if the critical anodic current density can be made small enough so as not to intersect the reduction polarization curve. Experimentally, Figure 2F does not exhibit the peak-shaped active to passive transition because the specimen has already been fully passivated.

If the cathodic curve intersects the anodic curve in the active region, as is in Figure 2A, the specimen will corrode rapidly even though it may be passivated under other experimental conditions. This behavior is observed for titanium in dilute, air-free sulfuric or hydrochloric acid. Figure 2D, the experimental counterpart to the theoretical Figure 2A, shows very similar shape to the anodic portion of 2A since the intersection of the polarization curves occurs low in Figure 2A and the anodic portion predominates. Obviously, Figure 1 for 430 stainless steel corresponds to the shape of Figure 2D except that 430 stainless exhibits a secondary peak in the passive region.

If the cathodic curve intersects the anodic curve as in Figure 2B, the specimen can exhibit either high corrosion rates or low corrosion rates. Such behavior is observed for chromium in air-free sulfuric acid or iron in dilute nitric acid. Figure 2B indicates intersections in the active, partially passive and passive regions. Measurements of the polarization curve of the specimen yields Figure 2E, in which "cathodic" current loops are observed after the peak-shaped active to passive transition has already occurred. Multiple loops can also be observed if the anodic and cathodic lines become superimposed in the partially passive region. In effect, the specimen doesn't know whether to behave as an anode or a cathode – or both. Metals that exhibit this behavior are undesirable since a surface believed to be passive can be rendered active by scratching the passive film or through some other mechanism. Once the surface becomes active it may not passivate again and corrosion can proceed to complete destruction of the material.

At this point, it is instructive to consider how the polarization curves can be manipulated to yield the desirable curve in Figure 2F, in which the specimen has spontaneously passivated. This can be achieved by arranging conditions such that the critical anodic current density, i_C, lies below the cathodic polarization curve. This in turn is done by:

1. Choosing alloying materials that have a small critical anodic current density.

2. Adding a sufficient quantity of oxidizer (Fe^{3+}, Cu^{2+}, CrO_4^{2-}, etc) so that a specimen exhibiting Figure 2D behavior is converted to Figure 2F behavior.

3. Taking advantage of velocity effects for metals in contact with flowing streams that corrode under diffusion control (see Ref. 2 for more details).

In summary, potentiodynamic polarization measurements are valuable in rapidly identifying desirable materials-environment combinations and in predicting how a material will behave when exposed to a particular environment. The technique quickly indicates the ability of the specimen to protect itself against aggressive attack from the liquid environment. However, it must be recognized that the procedures described in this note correspond to an artificial method for corroding the sample. This approach is similar to the use of elevated temperature studies to artificially accelerate a kinetically limited or aging process. Accordingly, these procedures can aid in predicting how a sample might behave over the long term but they should not be used to replace long term studies where other mechanisms may be operative.

POLARIZATION RESISTANCE

Introduction

The electrochemical technique of polarization resistance is used to measure absolute corrosion rates, usually expressed in milli-inches per year (mpy). Polarization resistance measurements can be made very rapidly, usually in less than ten minutes. Excellent correlation can often be made between corrosion rates obtained by polarization resistance and conventional weight loss determinations. Polarizations resistance is also referred to as “linear polarization”.

Polarization Resistance

A polarization resistance measurement is performed by scanning through a potential range that is very close to the corrosion potential, E_{CORR} (see Figure 3). The potential range is generally ± 25 mV about E_{CORR}. The resulting current is plotted versus potential, as shown in Figure 4. The corrosion current, i_{CORR}[2], is related to the slope of the plot through the following equation:

$$\Delta E/\Delta i \quad \frac{\beta_A \beta_C}{2.3\,(i_{CORR})\,(\beta_A + \beta_C)} \qquad \text{(Eq. 1)}$$

$\Delta E/\Delta i$ = slope of the polarization resistance plot, where ΔE is expressed in volts and Δi is expressed in µA. The slope has units of resistance, hence, polarization resistance.

$\beta_A \beta_C$ = anodic and cathodic Tafel constants (must be determined from a Tafel plot – see Section III). These constants have units of volts/decade of current.

i_{CORR} = corrosion current in µA.

Rearranging equation (1)

$$i_{CORR} = \frac{\beta_A \beta_C}{2.3(\beta_A + \beta_C)} \frac{\Delta i}{\Delta E} \qquad \text{(Eq. 2)}$$

The corrosion current can be related directly to the corrosion rate through the following equation:

$$\text{Corrosion Rate (mpy)} = \frac{0.13\ I_{CORR}(\text{E.W.})}{d} \qquad \text{(Eq. 3)}$$

E.W. = equivalent weight of the corroding species, g.

d = density of the corroding species, g/cm^2.

I_{CORR} = corrosion current density, µA/cm^2

See Section III of this application note for a derivation of equation (3). For a more complete discussion of corrosion potential and corrosion current, see Section I and III.

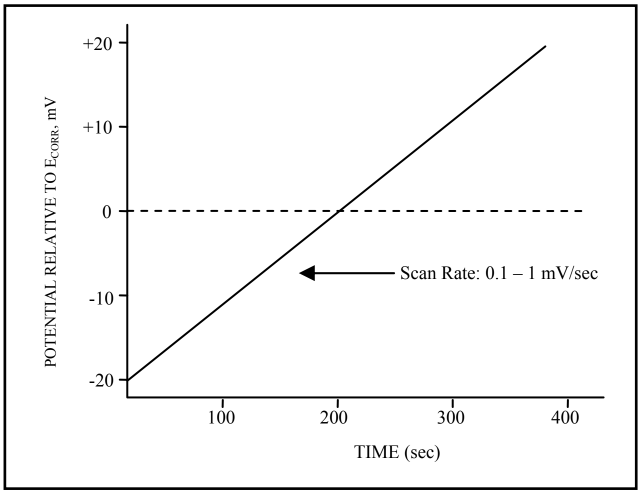

FIGURE 3: Excitation waveform for polarization resistance.

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[2] In this application note, “i” will be used to represent current, while “I” will denote current density.

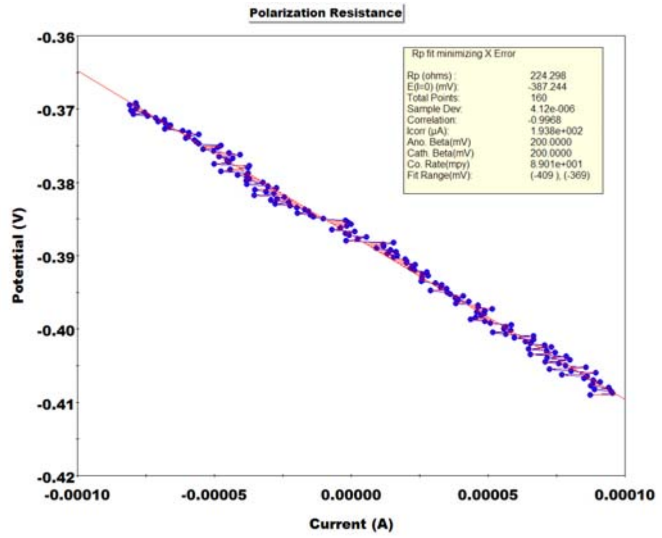

FIGURE 4: Experimentally measured polarization resistance.

Electrochemical Corrosion Theory and Polarization Resistance

Stern and Geary[15] have provided a firm theoretical background for polarization resistance measurements. The derivation is summarized in this section. For more detail, the original reference should be consulted.

In a corroding system, two co-existing electrochemical reactions are present

$$M^+ + e^- \leftrightarrow M \qquad \text{(Eq. 4)}$$

$$Z^+ + e^- \leftrightarrow Z \qquad \text{(Eq. 5)}$$

where M is the corroding metal and Z is usually a species in solution. The current-potential relationship of such a mixed-couple system is shown in Figure 5[16]. The equilibration potentials of the couples in equations (4) and (5) are labeled $E_{EQ,M}$ and $E_{EQ,Z}$, respectively. When the corrosion potential is sufficiently removed from $E_{EQ,M}$ and $E_{EQ,Z}$, the rate of reduction of M^+ becomes insignificant compared to the rate of oxidation of M, and the rate of oxidation of Z becomes insignificant with respect to the rate of reduction of Z^+. The corrosion potential is the potential at which the rate of oxidation of M (defined by current $i_{O,M}$) is equal to the rate of reduction of Z^+ (defined by current $i_{R,Z}$). The terms “rate” and “current” are used interchangeably since, according to equation (3), they are directly proportional. Since the net current is the difference between the oxidation and reduction currents, the current measured with an external device will be zero.

$$i_{MEAS} = i_{O,M} - i_{R,Z} = 0 \text{ at } E_{CORR} \qquad \text{(Eq. 6)}$$

and

$$i_{CORR} = i_{O,M} = i_{R,Z} \qquad \text{(Eq. 7)}$$

To calculate the corrosion rate, i_{CORR} must be determined.

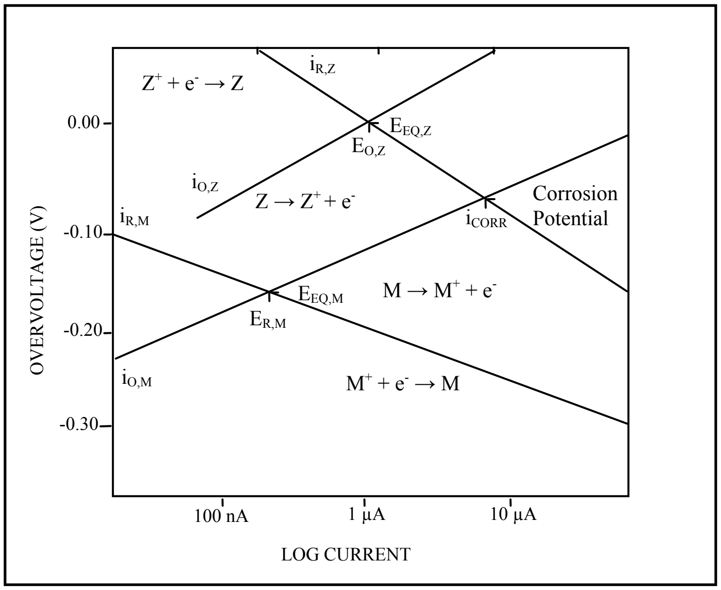

FIGURE 5: Potential-current relationship for a mixed-electrode system consisting of two electrochemical reactions.

When a potential is imposed on the metal specimen from an external voltage source, such as a potentiostat, a current will pass according to the following equation:

$$i_{MEAS} = i_{O,M} - i_{R,Z} \qquad \text{(Eq. 8)}$$

The anodic and cathodic currents obey the Tafel equation (see Section III):

$$\eta = \beta_A \log \frac{i_{O,M}}{i_{CORR}} \qquad \text{(Eq. 9)}$$

$$\eta = -\beta_C \log \frac{I_{R,Z}}{i_{CORR}} \qquad \text{(Eq. 10)}$$

η = overvoltage, the difference between the potential imposed on the specimen and the corrosion potential, $\eta = E_{APP} - E_{CORR}$.

Equations (9) and (10) may be rearranged to give:

$$\log \frac{i_{O,M}}{i_{CORR}} = \eta/\beta_A \qquad \text{(Eq. 11)}$$

$$\log \frac{I_{R,Z}}{i_{CORR}} = -\eta/\beta_C \qquad \text{(Eq. 12)}$$

Since log x = y is the same as $10^y = x$, equations (11) and (12) may be rewritten as:

$$10\ {-\eta/\beta_C} = \frac{i_{R,Z}}{i_{CORR}} \qquad \text{(Eq. 13)}$$

$$10\ \ \eta/\beta_A = \frac{I_{O,M}}{i_{CORR}} \qquad \text{(Eq. 14)}$$

Substitution of equation (13) and (14) into (8) yields:

$$i_{MEAS} = i_{CORR}\,(10^{\eta/\beta A} - 10^{-\eta/\beta C}) \qquad \text{(Eq. 15)}$$

10^x can be approximated by the following power series:

$$10^x = 1 + 2.3x + \frac{(2.3x)^2}{2!} + \ldots + \frac{(2.3x)^n}{n!} \qquad \text{(Eq. 16)}$$

If x in this series is small, the third and later terms of the series can be neglected without significant error. Substituting η/β_A and $-\eta/\beta_C$ for x gives:

$$10^{\ \eta/\beta A} = 1 + 2.3\ \eta/\beta_A \qquad \text{(Eq. 17)}$$

$$10^{\ -\eta/\beta C} = 1 - 2.3\ \eta/\beta_C \qquad \text{(Eq. 18)}$$

Substitution of equations (17) and (18) into equation (15) and simplifying yields:

$$i_{MEAS} = 2.3\ i_{CORR}\ \eta \frac{\beta_A + \beta_C}{\beta_A\beta_C} \qquad \text{(Eq. 19)}$$

Rearrangement to solve for polarization resistance gives:

$$\eta\ /i_{MEAS} = \frac{\beta_A\beta_C}{2.3\ i_{CORR}\ (\beta_A + \beta_C)} \qquad \text{(Eq. 20)}$$

which is identical to equation (1).

It is important to realize that equation (20) is valid only if the assumption regarding equation (16) is valid, i.e., η/β is small. This means that η must be small compared to β. A typical value of β is 100 mV/decade. The overvoltage in this case should be less than 10 mV.

Remarks

Polarization resistance is an extremely rapid procedure for determining corrosion rates. At a scan rate of 0.1 mV/sec, a potential range of 50 mV requires less than 10 minutes. The rapidity of the measurement also makes polarization resistance useful for less rigorous experiments, such as qualitative evaluation of inhibitors.

Since the applied potential is never far removed from the corrosion potential, the surface of the specimen is not materially affected by the experiment and the same specimen can often be used in other studies.

For the most accurate results, the Tafel constants, β_A and β_C, must be independently determined from a Tafel plot (see Section III). For a more rapid measurement, values of the Tafel constants may be assumed. Tafel constants are generally found to be in the range of 0.1 V/decade. Pourbaix[17] has found that if β_A and β_C are assumed to be 0.1 V/decade, the calculated corrosion rate will be correct within a factor of 2.2. In many cases, more accurate Tafel constants can be inferred from the literature for similar chemical systems.

Experimentally, polarization resistance data can exhibit significant curvature within 10-20 mV of the corrosion potential. This deviation from linearity is theoretically recognized. For further discussion on this phenomenon and procedures for calculating the corrosion current, see Ref. 18 through 23 and Ref. 33.

TAFEL PLOTS

Introduction

Electrochemical techniques of corrosion measurement are currently experiencing increasing popularity among corrosion engineers, due primarily to the rapidity with which these measurements can be made. Long term corrosion studies, such as weight loss determinations, may take days or weeks to complete, while an electrochemical experiment will require, at most, several hours. The speed of electrochemical measurements is especially useful for those metals or alloys that are highly corrosion resistant.

This section describes the use of Tafel Plots to measure corrosion rates. Tafel plots will be described in terms of electrochemical corrosion theory.

Tafel Plots

A Tafel plot is performed on a metal specimen by polarizing the specimen about 300 mV anodically (positive-going potential) and cathodically (negative-going potential) from the corrosion potential, E_{CORR}, as shown in Figure 6. The potential does not have to be scanned, but can be "stepped" in a staircase waveform if desired. The resulting current is plotted on a logarithmic scale as shown in Figure 7.

The corrosion current, i_{CORR}, is obtained from a Tafel plot by extrapolating the linear portion of the curve to E_{CORR}, as shown in Figure 7. The corrosion rate can be calculated from i_{CORR} by using equation 3.

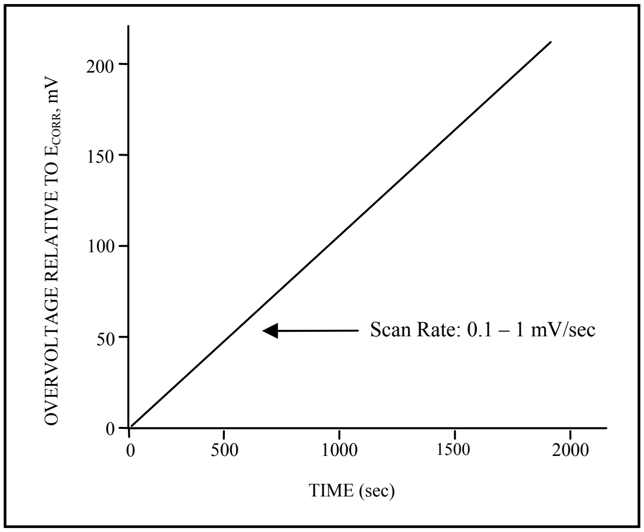

FIGURE 6: Excitation waveform for Tafel plots.

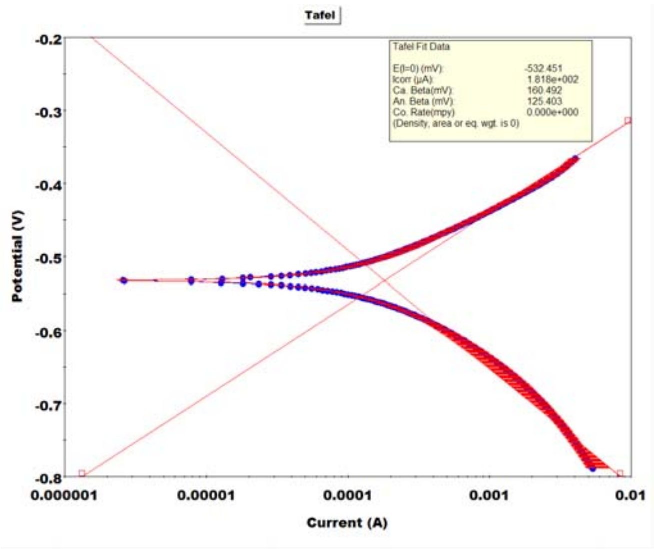

FIGURE 7: Experimentally measured Tafel plot.

The anodic or cathodic Tafel plots are described by the Tafel equation:

$$\eta = \beta \log \frac{i}{i_{CORR}} \qquad \text{(Eq. 21)}$$

η = overvoltage, the difference between the potential of the specimen and the corrosion potential.

β = Tafel constant

i_{CORR} = current at overvoltage η, µA.

Rearrangement of equation (21) gives:

$$\eta = \beta\,(\log I - \log i_{CORR}) \qquad \text{(Eq. 22)}$$

This equation has the form y = mx + b, so a plot of η vs. log i is a straight line with slope β. Notice from equation (22) that when η = 0 (E_{CORR}), log $i/i_{CORR} = 0$ or $i/i_{CORR} = 1$ or $i = i_{CORR}$.

Tafel constants, designated β_A and β_C, must be calculated for both the anodic and cathodic portions of the Tafel plot. The unit of the Tafel constant is either mV/decade or V/decade. A decade of current is one order of magnitude. A Tafel constant calculation is illustrated in Figure 7. Tafel constants are used to calculate corrosion rates from polarization resistance data (see Section II).

Calculation of Corrosion Rate from the Corrosion Current

According to Faraday's Law:

$$Q = \frac{nFW}{M} \qquad \text{(Eq. 23)}$$

Q = coulombs

n = number of electrons involved in the electrochemical reaction

F = Faraday constant, 96,487 coulombs

W = weight of the electroactive species

M = molecular weight

From equation (23):

$$W = QM/nF$$

Since equivalent weight = M/n:

$$W = \frac{Q \times E.W.}{F}$$

and since Q = it from Faraday's Law:

$$W = \frac{it\,(E.W.)}{F} \qquad \text{(Eq. 24)}$$

W/t is the corrosion rate (C.R.) in grams/second. It is convenient and traditional to express corrosion rate as milli-inches per year (mpy). These units provide an indication of penetration.

Dividing equation (24) by the electrode area and the density gives:

$$C.R.\ (cm/sec) = i\,(E.W.)/dFA$$

Convert seconds to years and centimeters to milli-inches. Convert the Faraday (amp-sec/eq) to microamps.

$$C.R.\ (mpy) = \frac{i\,(E.W.) \times 31.6 \times 10^6 \times}{dFA \times 2.5 \times 10^6}$$

Express the terms i/A as current density. Combining all the constants gives:

$$\text{Corrosion Rate (mpy)} = \frac{0.13\, I_{CORR}\,(E.W.)}{d} \qquad \text{(Eq. 25)}$$

I_{CORR} = corrosion current density, μA/cm^2

E.W. = equivalent weight of corroding species, g

d = density of corroding species, g/cm^3

Equation (25) is used to calculate the corrosion rate directly from I_{CORR}.

Electrochemical Corrosion Theory and Tafel Plots

According to the mixed potential theory[26], any electrochemical reaction can be divided into two or more oxidation and reduction reactions and there can be no accumulation of electrical charge during the reaction (to avoid confusion later, note that this electrochemical reaction is taking place in the absence of any externally applied potential). In a corroding system then, oxidation of the metal (corrosion) and reduction of some species in solution are taking place at the same rate and the net measurable current is zero.

$$i_{MEAS} = i_{RED} - i_{OX} = 0 \qquad \text{(Eq. 26)}$$

When a metal or alloy is placed in contact with a solution, the metal will assume a potential that is dependent upon the metal and the nature of the solution. This "open-circuit" potential, i.e., no external potential is applied to the cell, is referred to as the corrosion potential, E_{CORR}. E_{CORR} should be measured with a potentiometer.[3]

It is essential to the understanding of corrosion phenomena to realize that the oxidation current(s) and the reduction current(s) at the corrosion potential are equal and nonzero. Unfortunately, only the total current is measurable and the net current is zero, in accordance with equation (26).

The mechanism of corrosion is extremely complex in comparison to a homogeneous chemical system. Not only may several different elements be present, but several different compounds of each element may be present or may be formed during the corrosion process. There are also surface effects to consider. For this reason, corrosion rate measurements must be made rather

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[3] A potentiometer does not draw any current while making a voltage measurement.

non-specific with regard to the element in the metal or alloy. For example, rate measurement by weight loss determination requires no presumption of the actual identity of the corroding species.

Electrochemically, corrosion rate measurement is based on the determination of the oxidation current at the corrosion potential. The oxidation current is now called the corrosion current, i_{CORR}. Equation (21) may now be rewritten as:

$$i_{MEAS} = i_{CORR} - i_{RED} = 0 \text{ at } E_{CORR} \qquad \text{(Eq. 27)}$$

Current has units of coulombs per second. As shown in the last section, coulombs can be equated to the weight of electroactive material through Faraday's Law. The corrosion current then, is related directly to the corrosion rate. A Tafel plot is performed to experimentally determine i_{CORR}, from which the corrosion rate is calculated.

Stern-Geary Treatment

Much of modern corrosion techniques are based on theoretical analyses of the shape of polarization curves by Stern and Geary[15]. The following is a brief description of the derivation. For more details, the original papers should be consulted.

In a simple non-corroding system containing Z and Z^+ (such as copper electrode in contact with a Cu^{2+} solution) at equilibrium:

$$Z^+ + e^- \leftrightarrow Z$$

and

$$i_{R,Z} = i_{O,Z} = i_{EX} \qquad \text{(Eq. 28)}$$

$i_{R,Z}$ = current for reduction of Z^+

$i_{O,Z}$ = current for oxidation of Z

i_{EX} = the exchange current (analogous to i_{CORR} in a corroding system)

If a potential is imposed on the metal from an external voltage source and the reaction rate is controlled by a slow chemical step that requires activation energy:

$$i_{R,Z} = i_{EX}\, e^{-\eta/\beta'} \qquad \text{(Eq. 29)}$$

$$i_{O,Z} = i_{EX}\, e^{\eta/\beta''} \qquad \text{(Eq. 30)}$$

η = overvoltage, the difference between the potential imposed on the specimen and the corrosion potential, $\eta = E_{APP} - E_{CORR}$

β' and β'' = constants

Taking the log of equations (29) and (30) and solving for η yields:

$$\eta = -\beta_C \log \frac{i_{R,Z}}{i_{EX}} \qquad \text{(Eq. 31)}$$

$$\eta = \beta_A \log \frac{i_{O,Z}}{i_{EX}} \qquad \text{(Eq. 32)}$$

where $\beta_C = 2.3\beta'$ and $\beta_A = 2.3\beta''$.

Equations (31) and (32) are called Tafel equations after J. Tafel, who proposed an equation of similar form in 1904 to express hydrogen overvoltage as a function of current density.[27]

When the equilibrium of the reaction is disturbed by an externally applied potential, the forward and reverse rates change as shown in Figure 8. An exchange current of 1 µA and Tafel constants of 0.1 V were assumed. Figure 8 was constructed from equations (31) and (32). Experimentally, only the total current is measured. The total current is the difference between the rate of oxidation and the rate of reduction.

$$i_{MEAS} = i_{R,Z} - i_{O,Z} \qquad \text{(Eq. 33)}$$

In Figure 8, if a potential of -0.10 V is applied, the rate of reduction is 10 µA and the rate of oxidation is -0.1 µA. The measured current will therefore be 9.9 µA.

It is obvious from Figure 8 and equation (33) that as the difference between E_{APP} and E_{CORR} becomes more negative, i_{MEAS} approaches $i_{R,Z}$.

Substituting equation (14) into equation (12) gives:

$$\eta = -\beta_C \log \frac{i_{MEAS} + i_{O,Z}}{i_{EX}} \qquad \text{(Eq. 34)}$$

A plot of η vs. log of i_{MEAS} is shown in Figure 9. Deviation from linear Tafel behavior occurs at low current levels. Only when the oxidation current becomes insignificant with respect to the reduction current will a true Tafel relationship be obtained.

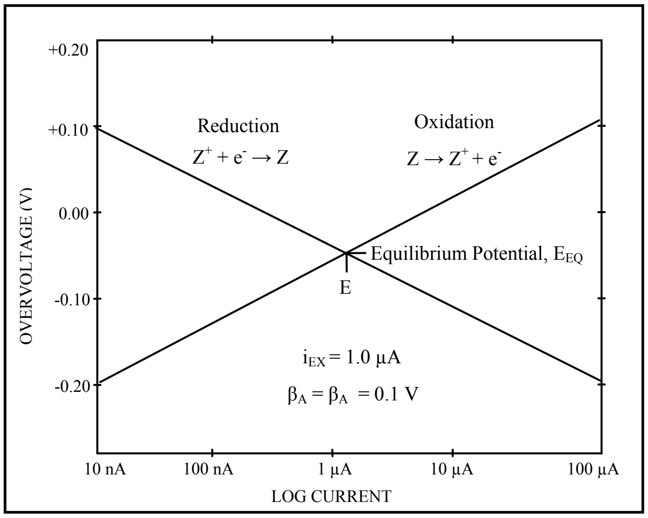

FIGURE 8: Response of a reduction-oxidation system to an externally applied potential.

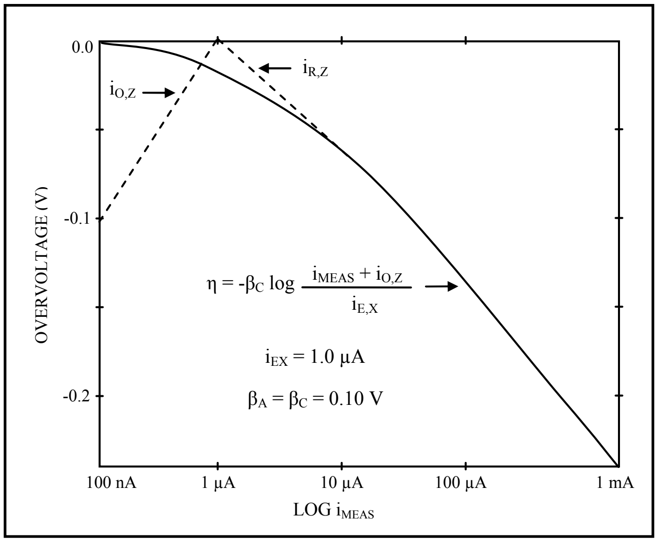

FIGURE 9: Measured current as a function of externally applied potential.

The relationships described thus far are dependent only on activation overvoltage. The measurement may be complicated by two interfering phenomena: concentration polarization and resistance drop effects.

Concentration polarization occurs when the reaction rate is so high that the electroactive species cannot reach or be removed from the electrode surface at a sufficiently rapid rate. The reaction rate becomes diffusion controlled. Figure 10 illustrates the effect of concentration polarization on the experiment. As η increases, the current becomes diffusion limited and the linear current range is truncated. The effect of concentration polarization is minimized by stirring the solution.

Resistance drops across the solution can also cause non-linear Tafel behavior at high currents.

$$E_{iR} = i_{MEAS}\,R_{SOLN}$$

R_{SOLN} is the uncompensated resistance of the solution, i.e., the resistance between the working electrode and the reference electrode bridge tube. It is dependent on the geometry of the electrodes. As i_{MEAS} increases, E_{iR} increases, causing an error in true potential at the working electrode.

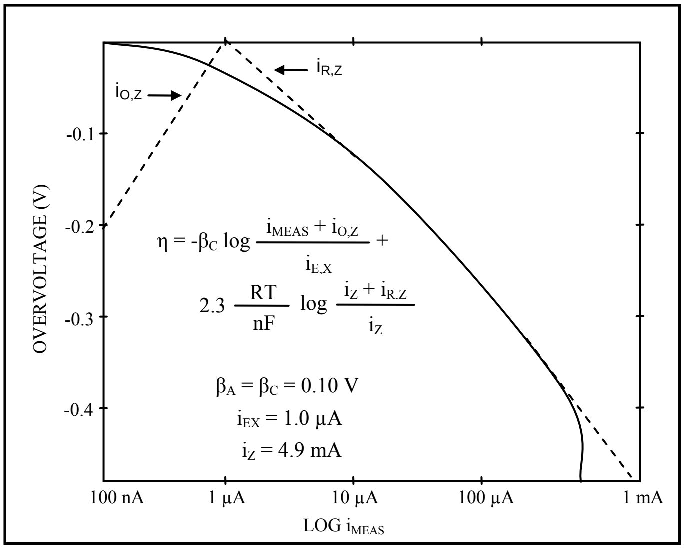

FIGURE 10: Effect of concentration polarization on measured current as a function of applied potential.

The effects of concentration polarization and resistance drops are most serious when $i_{E,X}$ (or i_{CORR}) is large and high currents are needed to verify Tafel behavior. As a general rule, linearity over two decades of current is desired. This may require current measurements in the region of 1000 i_{CORR}.

In a corroding system, the situation is more complicated. In addition to the reaction treated above,

$$Z^+ + e^- \leftrightarrow Z$$

the corroding metal must also be considered.

$$M^+ + e^- \leftrightarrow M$$

Each of these systems has its own equilibrium potential, exchange current and Tafel slope. At the corrosion potential:

$$i_{R,Z} + i_{R,M} = i_{O,Z} + i_{O,M} \qquad \text{(Eq. 35)}$$

Figure 5 illustrates the potential-current relationships for such a mixed-electrode system. In Figure 5, the Tafel constants for M are assigned a value of 0.06 V and i_{EX} for M is assigned a value of 0.1 µA. The equilibrium potential for M is arbitrarily assumed to be -0.160 V compared to the equilibrium potential of Z.

The corrosion rate by definition is $i_{O,M}$ - $i_{R,M}$. By rearrangement of equation (35) it may also be defined as $i_{R,Z} - i_{O,Z}$. When the corrosion potential of the mixed electrode system is sufficiently different from the equilibrium potentials of the individual reactions, then $i_{R,M}$ and $i_{O,Z}$ become insignificant in comparison to $i_{O,M}$ and $i_{R,Z}$, respectively. The corrosion rate, i_{CORR}, then becomes equal to $i_{O,M}$ or $i_{R,Z}$. The corrosion potential is closely approximated by the potential at which $i_{R,Z} = i_{O,M}$ as shown in Figure 5.

The overall effect of the mixed-electrode system, concentration polarization and resistance is shown in Figure 11. Tafel parameters are the same as in Figures 8 and 10. An uncompensated resistance of 10 Ω is assumed. The parameters used to calculate the curve in Figure 11 are completely arbitrary. Actual measurements may be better or worse. A high corrosion current in conjunction with a low diffusion-limited current and a high solution resistance may reduce the linear Tafel region to the extent that extrapolation to i_{CORR} is extremely difficult. In most cases, non-linear Tafel behavior can be minimized by stirring the solution and compensating instrumentally for iR effects.

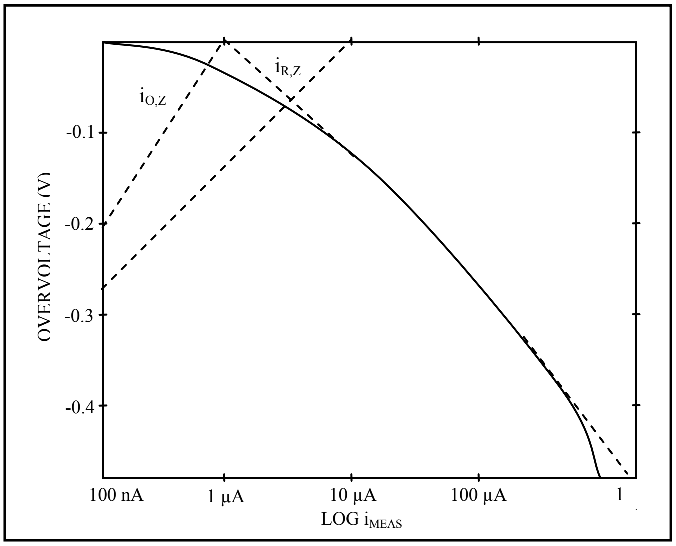

FIGURE 11: Effect of mixed-electrode system, concentration polarization and resistance effects on measured current as a function of applied potential.

Remarks

Tafel plots can provide a direct measure of the corrosion current, which can be related to corrosion rate. The technique is extremely rapid compared to weight loss measurements. The Tafel constants, β_A and β_C, obtained from Tafel plots can be used with Polarization Resistance data (Section II) to calculate corrosion rates.

The rapid determination of corrosion rates with Tafel plots can be advantageous for such studies as inhibitor evaluations, oxidizer effects and alloy comparisons.

However, several experimental disadvantages can be associated with Tafel plots. Although Tafel plots are fairly rapid, polarization resistance measurements (Section II) can be made even faster. At a scan rate of 0.1 mV/sec, a Tafel plot with a scan range of 250 mV requires about 45 minutes. An anodic and cathodic scan would require about 2 hours.

The relatively large potential range associated with the Tafel plot has the effect of changing the surface of the specimen, so that two specimens are required for a complete Tafel plot.

As described in Section III, concentration polarization and iR drops can combine to reduce the linear region to a point where extrapolation to i_{CORR} is difficult. A linear region over one current decade is generally considered to be the minimum for reliable measurement of i_{CORR}.

Experimentally, it can happen that the extrapolations of the anodic and cathodic linear Tafel regions do not intersect at E_{CORR}. The true value of the corrosion current will then be subject to interpretation. If this occurs, the interference must be drawn that there is an error in the measurement, since the rate of oxidation must equal the rate of reduction at E_{CORR}. In most cases, the error is probably in the anodic measurement. Since the metal specimen is corroding, the surface is changing and the mechanism of corrosion may not be completely described by the equations in Section III. The measured Tafel plot could then reflect the combination of several different Tafel slopes. If this behavior is observed, it is probably safest to measure i_{CORR} at the point where the cathodic Tafel extrapolation intersects E_{CORR}.

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Several additional references are included if additional information is required. Reference 24 is a collection of papers presented at a symposium on Electrochemical Techniques for Corrosion. It is highly recommended for a theoretical and practical background of electrochemical corrosion studies. Reference 33 gives the ASTM recommended practices for electrochemical corrosion measurements.

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