A Review: Basics of Electrochemical-Thermodynamics for FeS Scale Formation

Noora Al-Qahtani[1], Jiahui Qi[2], Aboubakr M. Abdullah[3], Nicholas J. Laycock[4], Mary P. Ryan[5]
[1,2,5]Department of Materials, Imperial College London, Exhibition Road, London, SW1 7AZ, UK
[1,3]Center for Advanced Materials, Qatar University, P. O. Box 2713, Doha-Qatar
[4]Qatar Shell Research and Technology Centre, Doha-Qatar
([1]noora.alqahtani@qu.edu.qa)

Abstract- A selection of hypotheses and investigative instruments for the thermodynamic and kinetics explanation of acidic corrosion will be summarized here. The relationship between thermodynamics and kinetics, a choice of electrochemical measurement techniques, and the application of electrochemistry in steel surface treatments are explained. Thermodynamics requires knowledge of the energy alterations participating in the electrochemical effects of corrosion. These energy alterations offer the driving force and monitor a spontaneous way of a chemical response. Consequently, thermodynamics might demonstrate how requirements can be modified to make corrosion difficult.

Keywords- *Electrochemical, Thermodynamic, FeS, Scale Formation*

I. INTRODUCTION

Alloy corrosion is performed through electrochemical responses in the interface among the alloy and medium (electrolyte). Deterioration obviously appears at a rate specified through equilibrium along with counteracting electrochemical reactions. The 1st reaction is metal oxidation and the discharging of electrons inside the alloys, i.e., anodic reaction. Besides the 2nd reaction, which is the reduction of species (habitually O_2 or H^+) and rejecting electrons from the alloys, which means a cathodic reaction [1–3]. For more clarification, a piece of metal exposed to an electrolyte by chemical or electrochemical reaction through its atmosphere. At the anode side, iron ions (Fe^{2+}) are freed through the oxidation process, and on the cathode side, OH^- ions are released *via* a reduction process on the surface of the metal [4,5]. When corrosion occurs, for instance, at the anode reconsider Equation 1, this reaction implicates the decrease of hydrogen ions to hydrogen gas along with Equation 2. This is called a hydrogen evolution reaction and happens across a wide variation of metals and acids.

Oxidation or Anodic Reaction: Iron

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2\,e^- \tag{1}$$

Reduction or Cathodic Reactions: Hydrogen

$$2\,H^+_{(aq)} + 2\,e^- \rightarrow H_{2\,(g)} \tag{2}$$

Examining the Equation 1 illustrates that the anodic reaction can happen through corrosion and may be inscribed in the universal formula in Equation 3.

General anodic reaction:

$$M_{(S)} \rightarrow M^{n+}_{(aq)} + ne^- \tag{3}$$

M is the corroding metal, and the consequence is metal oxidation to the ion with a valency charge of $n+$ and then the release of n electrons. The value of n is obviously contingent nature on of the metal. Hence, corrosion reactions contain at least one reaction of each (oxidation and reduction). Those electrons made at the metal are wholly consumed by various species in solution. Electrochemical equilibrium is recognized among the M and the mixture; the value of oxidation of the metallic is similar to the rate of reduction of specific species. The noticeable net current is zero. Nevertheless, a potential is produced because of the reactions. This potential is a function of the qualities and attributes of the alloys and the medium of the solution, and it is stated as the corrosion potential, E_{corr} [6].

The mechanisms of corrosion are considered through creating an electrochemical cell, as presented in Figure 1. In this cell, both reactions (oxidation and reduction) typically occur at individual electrodes in the cell, which build an electrical potential variation amongst them. The cell potential of an open circuit is a scale of the tendency of an alloy to deteriorate. Therefore, when the two "electrodes" are in electrical connection, an electrical path is established in which current drifts across the electrical relationship between the probes and a subsequent ion current flows *via* the solution among the electrodes. This flow is a quantification of the corrosion happening at the anode [7,8].
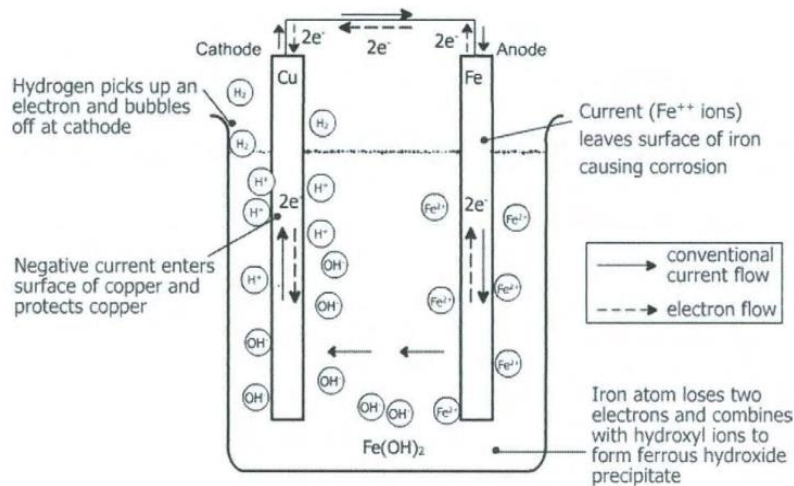
Figure 1. Schematic of the experimental cell, adapted from [5].

II. THERMODYNAMICS AND POTENTIAL

A. Relationship between Free Enthalapy (Gibbs Free Energy) And the Cell Potential

The driving force for any reaction under a constant temperature and pressure can be assessed by the Gibbs free energy (ΔG). It can be definite as follows; "When a scheme is moved to one state from another at fixed pressure and temperature, it is exposed to an alteration of free enthalpy or Gibbs free energy specified by [9,10]; "ΔG" = - (maximum work available from the system through the state transition) when this work is given a positive sign."

All fundamental aspects in this section are from [5,6,16–25,7,26–35,8,36–38,9,11–15]. Consider the response of corrosion again, as was demonstrated in section 2. There is a variation of free energy, ΔG, connected to any chemical effect. Once the reaction results have lesser energy than the reactants, ΔG is negative in the natural reaction. Consequently, the significance of the sign of ΔG can be realized as follows in Table 1.

TABLE I.   THE SPONTANEITY OF THE REACTION OF FREE ENERGY

ΔG	Meaning of the sign in the system
$\Delta G < 0$	Perform the effort and distributes energy. Therefore, the chemical reaction: spontaneous and irreversible. i.e., the response is thermodynamically favored.
$\Delta G = 0$	It is at equilibrium. Hence, the chemical reaction: reversible, and neither the forward nor the reverse reaction prevails.
$\Delta G > 0$	Energy must be given to the system to progress. Hence, the chemical reaction: non-spontaneous, and it proceeds in the opposite path. i.e., the reaction is thermodynamically unfavored.

In an electrochemical reaction, the electrical energy accessible, corresponds to the product of the cell potential and the amount of electricity involved.

$$E = I \times V \times t$$
$$= V \times Q$$
$$= E \times Q \rightarrow \text{This is equivalent to the network completed by the cell.}$$

Where:

- E is the energy transferred in (joules, J)
- I is the current in (amperes, A)
- V is the potential differences in (volts, V)
- t is the time in (seconds, s)
- Q is the charge in (coulombs, C)

From Faraday's law, Q is one Faraday (F) for individual gram equivalent of the reactants.

$Q=nF$

Where:

- n is the number of moles of electrons (or equivalents) replaced in an electrochemical reaction,
- F is Faraday's constant = (96,485 C/mol (g.Equiv.) $^{-1}$. The gram equal is the number of moles divided by the number of electrons elaborate in the response
- E is electromotive force (emf) of the cell or the cell potential or standard potential of the reaction (volts).

The alteration in free energy can result from a measurement of the electrochemical potential (cell potential) E at equilibrium. The maximum amount of work complete or (electrical energy) which can be distributed by an electrochemical cell in an assumed state which is nFE that is equal to the change in Gibbs free energy:

$$\Delta G = -nF\Delta E \tag{4}$$

Where:

- ΔG is free energy change (joules)
- ΔE is the potential difference of the reaction (volts).

The half-cell reaction in Equation 1 and Equation 2, have free-energy changes analogues to ΔG and subsequent potentials e_a and e_c. The numerical sum of these potentials is equivalent to $\Delta E = e_c - e_a$. The e_a and e_c (anodic and cathodic) have been variously considered half-cell, single probe, or redox potentials (reduction/oxidation) for consequent half-cell reaction.

Assuming the reaction arises in a corrosion scheme at constant temperature T and pressure P. The difference of Gibbs free energy (also known as free enthalpy) is the central point for any thermodynamic examination of reaction of corrosion. From the Gibbs–Helmholtz equation:

$$G(P,T)=H-TS \tag{5}$$

Where:

- H is enthalpy (joules)
- T is the temperature (Kelvin)
- S is entropy ((joules per Kelvin)

Substituting $H = U + PV$ from the First Law of Thermodynamics

$$F = PV - TS \tag{6}$$

Where:

- F is Helmholtz free energy, (joules)
- U is the internal energy, (joules)
- V is the volume, (m3)

Differentiating:

$$dG = dU + PdV + VdP - TdS - SdT \tag{7}$$

Nonetheless for a reversible process (rev), $dU = q_{rev} - PdV$ at constant P and $q_{rev} = TdS$ at constant T, So,

$$dG = TdS - PdV + PdV + VdP - TdS - SdT \tag{8}$$

Corresponding to the 2nd law of thermodynamics, Equation 4. can be stated as the difference among two equilibrium states:

$$dG = VdP - SdT, \text{ where } G = f(T, P) \tag{9}$$

At constant P, the dP disappears, and this becomes: $\frac{dG}{dT} = -S$ and at constant T, the dT vanishes and $dG = VdP$.

The system can be exposed to both mechanical work (PV) and electrical work (W). Thus, the dG in Equation 10 can be expressed as:

$$dG = -SdT + VdP - dW \tag{10}$$

As stated by the law negative sign for dW in Equation 11 requires that the work be performed by the system. For processes taking place at constant P and T, can be stated as:

$$-dG_{T,P} = dW \tag{11}$$

The decline in dG in Equation 11 is equivalent to the W and because the electrical work is stated as $W = nFE$, where $dW = nFdE$

$$dG_{T,P} = -nFdE \tag{12}$$

Thru the corrosion progression, the amount of the oxidizing and reducing kind alteration, therefore the properties of thermodynamic of the scheme must be contingent on the composition in addition to on T and P. The nG, "i.e., Gibbs free-energy" is a function of the number of moles of the condensed and corroded species contributing in the reaction over the subsequent equation:

$$d(nG) = (nV)dP - (nS)dT + \sum_i \left[\frac{\delta(nG)}{\delta n_i}\right]_{P,Tn_i} dn_i \tag{13}$$

The derivative of nG in Equation 13 concerning the mole's number of the species take part in the corrosion response is well-defined as the chemical potential, μ_i.

$$\mu_i = \left[\frac{\delta(nG)}{\delta n_i}\right]_{P,Tn_i} \tag{14}$$

The overall equation for $d(nG)$ stated in relationships of the chemical potential, μ_i is:

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i \, dn_i \tag{15}$$

This Equation 15 is utilized as a basis to figure the assembly of corrosion mixture thermodynamics. Such as for one mole, $n=1$ of participating interacting species, it can be established in the formula in which n_i is changed by a mole fraction x_i.

$$dG = VdP - SdT + \sum_i \mu_i \, dx_i \tag{16}$$

At fixed T and P, the equation 16 becomes:

$$d(nG)_{T,P} = \sum \left[\frac{\delta(nG)}{\delta n_i}\right]_{P,Tn_i} = \sum \mu_i \, dn_i \tag{17}$$

After integration

$$G_{T,P} = \sum \mu_i n_i \tag{18}$$

Equation 12 and equation 18 can be established for the electrochemical process as:

$$\Delta G_{T,P} = -nFdE = \sum \mu_i dn_i \text{ or } nFE = -\sum \mu_i n_i \tag{19}$$

are at unit action. Leaving from unit activity can be established by the Nernst equation, which is derived by supposing that the reaction incomes isothermally and reversibly in a deterioration system.

$$[v_A]A + [v_B]B + \cdots \overset{\pm nF}{\longleftrightarrow} [v_C]C + [v_D]D + \cdots \ldots \ldots \pm Q \tag{20}$$
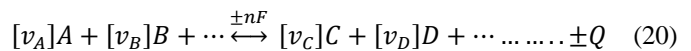
Along with Equation 12, the reversible potential of the corrosion scheme $E_{T,P}$ is definite as:

$$E_{T,P} = -\frac{\Delta G_{T,P}}{nF} \tag{21}$$

The overall equation for $d(nG)$ is uttered in relation to the chemical potential, μ_i, and each dn_i might be swapped by the product $v_i a\varepsilon$.

Where:

- a is characterizes the activity of the reactants,
- ε is the reaction coordinate and symbolizes the range of the corrosion reaction
- v_i is the stoichiometric number

For the species with a chemical potential μ_i, at constant P and T and unit activity, Equation 12 becomes:

$$d(nG) = \sum_i \mu_i \, dv_i d\varepsilon \tag{22}$$

For the reason that nG is a state function, the right-hand side of the Equation 12 signifies a precise difference expression, and it directed that:

$$\sum_i \mu v_i = \left[\frac{\delta(nG)}{\delta n_i}\right]_{P,Tn_i} \tag{23}$$

The amount $\sum \mu v_i$ characterizes the rate of the variation of the overall Gibbs free energy for electrochemical approach, besides the extent of the response ε at fixed P and T. This measure is zero at the balance state. Therefore, giving to Equation 18,

$$\Delta G = \sum \mu_i v_i \tag{24}$$

Since the chemical potential is a fractional characteristic of the Gibbs free-energy, its rate can be considered from the equation:

$$\mu_i = \mu_i^o + RT \ln(a_i) \tag{25}$$

Where:

- μ_i^o is the standard chemical potential, and
- a_i is the activity of the species in the corrosion reaction.

Instead of Equation 24, one may write:

$$\Delta G = \sum \mu_i^o v_i + RT \sum v_i \ln(a_i)$$
$$= \sum \mu_i^o v_i + RT \sum v_i \ln \frac{a_C^{n_C}.a_D^{n_D}}{a_A^{n_A}.a_B^{n_B}} \tag{26}$$

Supposing that the reactants and the products are in their ordinary states, the actions of the kind participating in the response are equivalent to unity. Under these circumstances, the Gibbs free-energy ΔG is identical to the ordinary Gibbs free-energy $\Delta G^{o,}$ and the absolute rate is equivalent to the usual logarithm of the equilibrium fixed K.

$$\Delta G = \Delta G^o = \sum \mu_i^o v_i + RT\ln K \tag{27}$$

Since ΔG_i^o is a property of pure kind "i" in their ordinary state and at fixed P, its value is contingent only on T. Actually, ΔG^o appears the quantity $\sum v_i G_i^o$. Hence, this function is the variance amid the Gibbs free energies of the products and reactants and is contingent on their stoichiometric coefficients. It is distinct from the equilibrium structure or P, and it is static for any agreed deterioration reaction when the T is recognized. The Gibbs free-energy alteration is definite according to Equation 24 and Equation 27 as:

$$\Delta G = RT \ln K + RT\ln \prod a_i^{v_i} \tag{28}$$

where Π indicates, the product completed all species.

$$E_{cell} = -\frac{RT}{nF} \ln K - \frac{RT}{nF} \ln \frac{a_C^{n_C}.a_D^{n_D}}{a_A^{n_A}.a_B^{n_B}} \tag{29}$$

The logarithmic look in the 2nd term on the right side of Equation 29, when $a_i=1$, is equivalent to zero, and:

$$E^o = -\frac{RT}{nF} \ln K \tag{30}$$

The potential in Equation 30 is well-defined as E^o and is termed the standard electromotive force of a deterioration scheme. Giving to Equation 29, for any balance corrosion system, the (emf) E is the sum of the standard electromotive force, E^o, and the actions of the products and the reactants take part in the reaction:

$$E_{cell} = E^o - \frac{RT}{nF} \ln \frac{a_C^{n_C}.a_D^{n_D}}{a_A^{n_A}.a_B^{n_B}} \tag{31}$$

which is equal to:

$$E_{cell} = E^o - 2.303 \frac{RT}{nF} \log \frac{a_C^{n_C}.a_D^{n_D}}{a_A^{n_A}.a_B^{n_B}} \tag{32}$$

or

$$E_{cell} = E^o + 2.303 \frac{RT}{nF} \log \frac{a_C^{n_C}.a_D^{n_D}}{a_A^{n_A}.a_B^{n_B}} \tag{33}$$

Equations 32 and Equations 33 are well-recognized procedures of the Nernst equation. The values of $b_o = 2.303 \frac{RT}{F}$ in Equations 31 are linear functions of T.

B. The Development of the Potential Change, Kinetic and Thermodynamic (Nernst's) Equation Ideas

The Nernst equation was called after Walther Nernst, who formed an identical useful relationship among the energy and the cell potential to the focus of sharing ions and other chemical types. Equation 34 can be derived from the equation linking free energy changes to the reaction quotient ($Q_{reaction}$) [4,24,39,40].

$$\Delta G = \Delta G^0 + RT \ln Q_{reaction} \tag{34}$$

where $Q_{reaction}$ is defined in Equation 36 for an overall equation of the procedure:

$$aA + bB + ... \rightarrow mM + nN + ... \tag{35}$$

A, B, M, and N in Equation 35 are capital letters characterize, correspondingly, the reactants and products of an assumed response although the small letters signify the coefficients compulsory to balance the reaction.

$$Q_{reaction} = \frac{a_M^m.a_N^n}{a_A^a.a_B^b} \tag{36}$$

At equilibrium, $\Delta G = 0$ and $Q_{reaction}$ resembles the equilibrium constant (K_{eq}) defined previous Equation 34.

In the situation of an electrochemical reaction, exchange of the relations $\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$ into the terms of a reaction free energy and division of both sides by $-nF$ provides the Nernst code for a probe reaction designated in Equation 37.

$$E = E^o - \frac{RT}{nF} RT \ln Q_{reaction} \tag{37}$$

Merging constants at 25 °C (298.15 K) provides the easier arrangement of the Nernst equation for an electrode response at this T:

$$E = E^o - \frac{0.059}{n} \log Q_{reaction} \tag{38}$$

In equation 37, the electrode potential (E) might be the real potential change crossways a cell comprising this probe as a half cell and a standard hydrogen probe as the other half-cell. Otherwise, the relationship in $E_{cell} = E_{cathode} - E_{anode}$ can be applied to syndicate two Nernst equations consistent to two half-cell reactions interested in the Nernst equation for a cell response:

$$E_{cell} = E_c^0 - E_a^0 \frac{0.059}{n} \log Q_{reaction} \tag{39}$$

$Q_{reaction}$ = product of activities of reactants/ product of activities of products

Roughly of the species that join in these probe reactions are clean solid mixtures and pure liquid composites. In dilute acidic solutions, water can be considered as a pure fluid. For pure solid composites or pure fluid composites, actions are constant, and their amount is measured to be unity. The activities of vapors are typically reserved as their partial P, and the activities (a_i) of solutes for instance ions are the produce of the molar amount and the activity coefficient of each chemical species (i):

$$a_i = \gamma_i[i]_i \approx [i] \tag{40}$$

The activity coefficient (γ_i) in Equation 40 can be a compound role extremely reliant on a multitude of variables regularly hard even to estimate. Hence, it is frequently convenient to disregard (γ_i) and usage of the concentration term [i] as an estimate of a_i.

III. CORROSION KINETICS

Chemical kinetics is an investigation of the charges of such reactions. Corrosion in sour systems is ruled mainly by electrochemical reactions, as deliberated in Section 2. A sympathetic of the fundamental laws of electrochemical response, kinetics is accordingly vital to grow extra corrosion-resistant alloys and to advance approaches of defense in contradiction of corrosion. This section commonly surveys the treatment of Stern and Geary' and later Fontana and Greene, who prearranged the basics into a sound educational framework. All fundamental aspects are discussed in detail in this part are from [5,6,16–25,7,26–35,8,36–38,9,11–15].

A. Faraday's Law of Electrolysis

The traditional electrochemical work shows by Michael Faraday in the nineteenth century generated two laws distributed in 1833 and 1834 after him. The two laws can be underneath [36,41]. If the current generated by one of the anodic reactions uttered earlier were recognized, it might be likely to alter this current to a corresponding mass loss or corrosion diffusion rate with a precious relation discovered by Michael Faraday, a nineteenth-century pioneer in electrochemistry.

Faraday's observed laws of electrolysis relate the current of an electrochemical reaction to the number of moles of the element being reacted, and the number of moles of electrons involved [4].

Faraday's first law of electrolysis states that: ' When a current is passing through a solution, the mass of a substance involved in reaction at the electrode is directly proportional to the quantity of electricity (charge) passed through the solution' [42].

The Faraday's second law states that: 'The masses of different substances produced by the passage of 1 Faraday (96,487 .Coulombs) are directly proportional to their equivalent weights' [42].

These two Laws specify that the amount of material involved in a chemical reaction can be related to the electrical current. Therefore, from knowledge of current magnitude and duration, the weight of products shaped through an electrolytic process can be calculated, i.e., the mass of main products shaped at an electrode by electrolysis is straight proportional to the quantity of electricity passed. Accordingly:

m α It or m = Zit (41)

where:

- I is current in amperes

- t is time in seconds

- m is mass of the primary product in grams

- Z is constant of proportionality (electrochemical equivalent M/nF , where M = molecular weight and n= number of electrons involved). It is the mass of a substance liberated by one ampere-second of a current (1 coulomb).

The masses of diverse main products by equivalent quantities of electricity are proportional to the fraction of molar mass to the figure of electrons intricate with a specific reaction:

$$m_1 \propto \frac{M_1}{n_1} \propto Z_1 \tag{42}$$

$$m_2 \propto \frac{M_2}{n_2} \propto Z_2 \tag{43}$$

where:

- m_1, m_2 is masses of primary product in grams

- M_1, M_2 is molar masses (g.mol^{-1})

- n_1, n_2 is number of electrons

- Z_1, Z_2 is electrochemical equivalent.

Merging the first law and the second law, and substituting for Z, from Equation 43 into Equation 41

$$m = k \frac{M}{n} It \tag{44}$$

or

$$m = \frac{1}{F} \cdot \frac{M}{n} It \qquad (45)$$

where:

- F is Faraday's constant,

- It is the amount of electricity compulsory to deposit the ratio of mass to the valency of any substance and stated in coulombs per mole (C (g equiv.)$^{-1}$).

- It has a value of 96485 coulombs per gram equivalent. This is occasionally written as 96485 coulombs per mole of electrons.

Faraday's Law is used to calculate the corrosion rate of any species of material in "weight lost (or gained) per ampere of current flow per unit time.

The corrosion rate has magnitudes of mass x reciprocal of the period (g.y^{-1} or Kg.s^{-1}). In standings of loss of weight of metallic with a period, from Equation 45, we get:

$$\frac{dw}{dt} = \frac{MI}{nF} \qquad I = current \qquad (46)$$

The rate of corrosion is proportional to the current passed and to the molar mass. Dividing Equation 45 by the exposed area of the metal in the alloy, we get

$$\frac{w}{At} = \frac{MI}{nFA} \qquad (47)$$

But $i_{corr} = \frac{I_{corr}}{A}$

where:

- i_{corr} is corrosion current density, (μA/cm^2)

- I_{corr} is total anodic current, (μA)

- A is exposed specimen area, (cm^2)

, then $\frac{w}{At} = \frac{M i_{corr}}{nF}$

$$Corrosion\ rate, r = \frac{m}{At} = \frac{M i_{corr}}{nF} \qquad (48)$$

The above equation has been effectively used to calculate the corrosion rates. Equation 48 yields a relative mass loss per unit area per unit time (e.g., mg/dm^2 /day), Other functional units are millimeters per year (mm y^{-1}) and mils per year (mpy) and current density (e.g., μA/cm²). The proportionality constant contains *a/nF* and any conversion influences for units. Current density rather than current is comparative to rate of corrosion since the similar current focused into a minor surface area consequence in a more corrosion rate. The rate of corrosion is in inverse proportional to the area for the identical dissolving current.

Penetration unit time can be gained by dividing Equation 48 by density of the alloy. The subsequent equation can be used conveniently:

$$Corrosion\ rate, r = C \frac{M i_{corr}}{n\rho} \qquad (49)$$

where:

- p is density (g/cm^3)

- i_{corr} is corrosion current density, (μA/cm^2)

- M is atomic weight (g /mol)

- n is the number of electrons involved

- C is constant which includes F and any other conversion factor for units,

The above Equation 48 demonstrates the correspondence amid penetration rate and current density for a metal. The same agreement among the penetration rate and current density for metal can be well-known. Nevertheless, it would need the purpose of corresponding weight for the alloy. For pure elements, the equal weight is specified by:

$$EW = \frac{W}{n} \qquad (50)$$

where:

- W is the atomic weight of the element, and

- n is the number of electrons essential to oxidize an atom of the element in the corrosion process, that is, the valence of the element.

To gauge the alloy correspondent weight, the subsequent approach may be used. Deliberate a unit mass of alloy oxidized. The electron equivalent for of an alloy, Q

$$Q = \sum \left[\frac{n_i f_i}{W_i} \right] \qquad (51)$$

where:

- f_i is the mass fraction of the ith element in the alloy,

- W_i is the atomic weight of the ith element in the alloy, and

- n_i is the valence of the ith element of the alloy.

Thus, the next is the connection which is used to regulate the equivalent weight (*M/n*) of an alloy:

$$Equivalent\ weight = \frac{1}{\sum \left[\frac{f_i}{n_i / M_i} \right]} \qquad (52)$$

where:

- f_i is the mean fraction of an element presents in the alloy

- n_i is electron exchanged

- M_i is the atomic mass.

B. Corrosion Kinetics

Thermodynamics provides a sign of the direction of electrode response, whereas electrode kinetics gives the rate of such reactions. The reactions of concern are mostly corrosion reactions; therefore, it is additionally suitable to call the kinetics of such reaction's corrosion kinetics. To recognize the concept of sour corrosion, it is crucial to progress a comprehensive, consideration of the kinetics of the reactions happening on an electrode surface in interaction with an acidic electrolyte. Procedures that are used to explore the rate of a reaction include the determination of the concentration of reactant residual in products after a specified time. In sour corrosion, it is very significant to escalate the nature of

irreversible reactions which arise on the electrode surface through corrosion.

1) Exchange Current Density

We focus on the response for the oxidation/reduction of hydrogen:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2\,(g)} \tag{53}$$

This reaction is under the equilibrium condition at the ordinary half-cell potential $e^0(H^+/H_2)$, which means that the forward reaction rate (left to right) r_f and the reverse reaction rate (right to the left) r_r have similar magnitude. The rate of reaction in the forward route, r_f is given by

$$r_f = K_1\, exp - \left(\frac{\Delta G^*_A}{RT}\right) \tag{54}$$

where:

- K_1 is the constant contingent on temperature, time, and activity.

- ΔG^* is the free energy of activation of the reaction.

The rate of the reverse process is:

$$r_r = K_2\, exp\left(\frac{\Delta G^*_C}{RT}\right) \tag{55}$$

However, if the scheme is at equilibrium $r_f = r_r$. Associating the two progressions forward (anodic) and reverse (cathodic), it became

$$\frac{K_2}{K_1} = \exp - \left(\frac{\Delta G^*_A - \Delta G^*_C}{RT}\right) = \exp\left(\frac{zEF}{RT}\right) \tag{56}$$

Accordingly, the individually reversible process has a distinguishing potential, named electrode potential. When the reaction irreversible, $i_f \leftrightarrows i_r = \cdot$, no net current flows, $i_f = i_r = i_o$ (exchange) is termed the exchange current density.

The exchange current i_o is a central characteristic of electrode behavior that can be defined as the rate of oxidation or reduction at an equilibrium electrode stated in standings of current. The term exchange current is a misnomer; as there is no net current flow, there is no net transfer of charge, as presented above.

Each reversible electrode reaction has its individual exchange current density. The association among exchange reaction rate and current density can be derived from Faraday's law described previously:

$$r_f = r_r = \frac{Mi_o}{nF} \tag{57}$$

where:

- r_f is the rate of oxidation

- r_r is the rate of reduction expressed in terms of current density (i_o).

It is a suitable technique for finding r_f or r_r at equilibrium. In this circumstance i_o, the exchange current density is equal to the reversible rate at equilibrium. Simply, whereas the standard half-cell potential e^o is the general thermodynamic factor, i_o is the basic kinetic factor of an electrochemical reaction.

Therefore, the net current is zero at equilibrium, and this suggests that the totality of these two currents is zero, $i_a + i_c = 0$. Since i_c is, by agreement, permanently positive, it follows that, when no external voltage or current is useful to the system, the exchange current is as given by $i_a = -i_c = i_o$. There is no hypothetical technique of correctly defining the exchange current for any specific system. This must be determined experimentally. The next figure displays that the exchange current density for the hydrogen reaction is contingent powerfully on the electrode material, whereas the standard half-cell potential remains the same. Figure 2 illustrates the half-cell electrode potential for the hydrogen reaction plotted against i_o. Two shreds of essential evidence are highlighted from this figure. Initially, the surface on which the reaction arises does not affect the electrode potential. Additionally, the i_0, in contrast, is enormously exaggerated by the surface. That is, "ΔG" the thermodynamic energy alteration is not influenced by surface, nevertheless, the reaction kinetics, as quantified by i, are extremely vulnerable to surface properties.
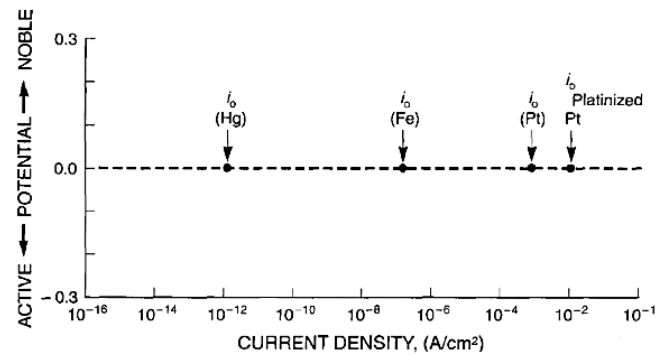

Figure 2. Effect of reaction surface on electrode potential and exchange current density for the hydrogen reaction, adapted from [26].

For the classification of electrochemical processes, it is desirable to normalize the value of the current by the surface area of the electrode and use the current density, repeatedly stated as i, i.e., $i = I/A$. The scale of exchange current density is a function of the succeeding core variables:

- Electrode composition: exchange current density is contingent upon the structure of the electrode and the solution. For redox reactions, the exchange current density would rely on the composition of the components of the equilibrium reaction.

- Surface roughness: exchange current density is typically articulated in relation to the projected or symmetrical surface area and is contingent upon the roughness of the surface.

- Soluble species value: The exchange current is likewise a complex function of the concentration of the reactants and the products complicated in the exact reaction pronounced by the exchange current. This function is predominantly

reliant on the shape of the charge transfer barrier β across the electrochemical interface.

- Impurities at the surface: it is adsorbed on the electrode surface regularly mark its exchange current density. Exchange current density for the H^+/H_2 system is evidently reduced by the occurrence of trace impurities like arsenic, sulfur, and antimony.

C. Electrochemical Polarization

For every electrochemical reaction, there is an equilibrium electrode potential, E_{eq} for which the equilibrium state of the response at the phase-boundary amid a metallic and an electrolyte is realised. The direction of this reaction is contingent exclusively on the rate at the electrode, E of the metal, in relation to the value of the equilibrium potential. All fundamental aspects are discussed in detail in this part are from [5,6,16–25,7,26–35,8,36–38,9,11–15]

- $E > E_{eq}$, the reaction can only proceed in the direction of oxidation.

- $E < E_{eq}$, the reaction can only proceed in the direction of a reduction.

Any deviation from the steady-state, which may be achieved by polarizing the metal or bringing it into contact with another metal, would inevitably lead to the deceleration of the rate of one reaction and the acceleration of the other. Such change from the equilibrium state due to the passage of current is known as polarization or sometimes overvoltage or overpotential, and the electrode is supposed to show irreversibility. An electrode is said to show irreversibility. Polarization of the separate anodic and cathodic processes is known as anodic polarization and the cathodic polarization, respectively. Positive polarization always makes anodes more positive and cathodes more negative than their equilibrium potentials. The degree of polarization is frequently measured in terms of overvoltage, abbreviated as η. The amount by which the potential of a working electrode deviates from its equilibrium potential can be expressed by the overpotential, η which is distinct by:

$$\eta = E - E_{eq} \tag{58}$$

The departure of the potential of an electrode from equilibrium (or reversible) value when external current flows arise from 3 causes:

- activation overvoltage η_A, due to the activation energy barrier between reactants and products.

- concentration overvoltage η_{con} due to the concentration gradient between the bulk" and surface of the electrode; and

- resistance overvoltage η_R representing a voltage drop of the system caused by ohmic resistance.

Therefore, the total overvoltage in an actual system is given by the summation:

$$\eta = \eta_A + \eta_{Con} + \eta_R \tag{59}$$

Hence, in corrosion studies, it is highly desirable to be able to determine the exact effect of these contributions on the total overvoltage. There are two different types of polarization (occasionally likewise recognized as overpotential), i.e., activation and concentration polarization.

1) Activation Polarization

In this instance, a stage in the half cell reaction monitoring the rate of an electron (charge) flow, such as the hydrogen evolution reaction:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2\,(g)} \tag{60}$$
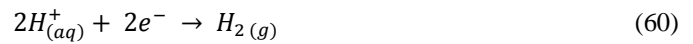
Produces at a metallic surface in 3 main stages. In the primary stage, H^+ responds with an electron from the metal to procedure an adsorbed hydrogen atom at the surface.

$$H^+_{(aq)} + e^- \rightarrow H_{(ads)} \tag{61}$$

In the second stage the reaction of two adsorbed hydrogen atoms form a hydrogen molecule.

$$H_{(ads)} + H_{(ads)} \rightarrow H_{2\,(g)} \tag{62}$$

In the third stage, sufficient adsorbed hydrogen molecules join and nucleate a hydrogen bubble on the surface. Any of these stages can be the sate limiting step and so cause the activation polarization. The activation polarization can be considered using the current densities, that signify the reaction rates. For cathodic η_c and anodic η_a polarization one can transcribe:

$$\eta_a = \beta_a log \frac{i_a}{i_o} \tag{63}$$

or

$$\eta_c = \beta_c log \frac{i_c}{i_o} \tag{64}$$

β is zero, both equations decrease to $i = i_o$, and for polarization potentials less than the equilibrium half-cell potential, reduction or forward response is preferable. Overpotential is a term applied often for polarization, for anodic overpotential, η_a, is positive, and β_a, necessity likewise is positive, consequently. Correspondingly, for cathodic polarization, β_c, is negative because η_c is negative. β_a and β_c are recognized as the Tafel constant for the half-cell-reaction. The anodic, i_a, and cathodic, i_c, current densities flow in opposite directions. The Tafel relations pronounced by equations Equation 63 and 64 have commonly been detected by testing for activation polarization.

In both Equations, 63 and 64 designate that a scheme of overpotential, η_{cat} against $log\ i$ is direct for both anodic and cathodic polarization, as revealed in Figure 3. The slopes are specified by the Tafel constants, which are presumed as ± 0.1 V per decade of current. For zero η, either of Equation 63 and Equation 64 reduced to $i = i_o$. Under the reversible half-cell electrode potential, the reduction or forward reaction is preferable:

$$2\,H^+_{(aq)} + 2e^- \rightarrow H_{2\,(g)} \tag{65}$$

is favored, while above the same potential, the oxidation or reverse reaction is favored,

$$H_{2\,(g)} \rightarrow 2H^+_{(aq)} + 2\,e^- \qquad (66)$$
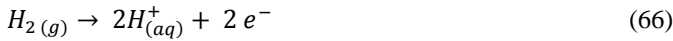
The rate, as gauged by i_a, or i_c, rises by one direction of degree for an overpotential alteration of + 0.1 V for anodic polarization and - 0.1 V for cathodic polarization, individually, spending the expected values of β. The absolute standards of the β Tafel constants are typically between 0.03 to 0.2 V and might not be equivalent for anodic and cathodic reactions, as shown in Figure 3. However, 0.1 and - 0.1 V are reasonable estimates for $β_a$ and $β_c$, respectively, for many purposes.
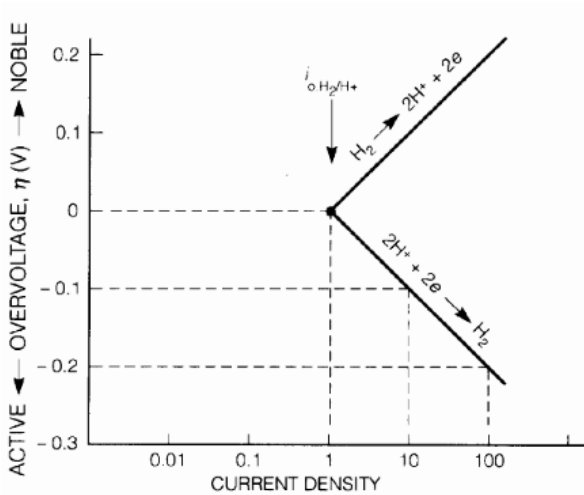
Figure 3.   Activation overpotential showing Tafel behavior, adapted from [5].

The hypothetical derivation of the Tafel relations as Equation 63, stated clearly in Figure 3, is as surveys. Considering reaction in Equation 65 as an instance, the half-cell electrode potential, $e^o(H^+/H_2)$, is recognized when the response is at equilibrium. The rate of discharge of H^+ (forward) precisely balances the rate of ionization of H_2 (reverse). The occurrence of overpotential proposes the existence of energy barriers (activation energies), ΔG^*_f and ΔG^*_r agreeing to the forward and reverse reactions, individually, as revealed schematically in Figure 4. The activation energy change is associated with half-cell electrode potential by the countenance:

$$\Delta G^*_f - \Delta G^*_r = \Delta G_{\frac{H^+}{H_2}} = -nFe_{\frac{H^+}{H_2}}$$

The Maxwell distribution rule provides the energy distribution of countering species and progress to terms for forwarding r_f, and reverse r_r, reaction rates as a function of the particular activation energies:

$$r_f = K_f\,exp\left[\frac{\Delta G^*_f}{RT}\right] \quad and \quad r_r = K_r\,exp\left[-\frac{\Delta G^*_f}{RT}\right]$$

where:

- K_f and K_r, are the reaction rate constants for the forward and reverse reactions, respectively.

At equilibrium,

$$r_f = r_r = \frac{Mi_o}{nF} \qquad (67)$$

Thus,

$$i_o = K'_r\,exp\left(-\frac{\Delta G^*_r}{RT}\right) = K'_f\,exp\left(\frac{\Delta G^*_f}{RT}\right)$$

This obviously establishes that exchange current density is a function of the activation energies.

While a cathodic overpotential, $η_c$, is utilized on the electrode, the discharge reaction rate is minimized, and that of the ionization is augmented. This is accomplished by reducing the activation energy for the discharge response by a quantity, $αnFη_c$, and growing that for the ionization reaction by a quantity, $(1-α)nFη_c$, as designated by the dashed mark in Figure 4. The factors α and $(1-α)$ are the fractions of $η_c$ possessed by the discharge and ionization (forward and reverse) reactions, correspondingly.

The cathodic discharge response rate in standings of current density converts:

$$i_c = K'_f\,exp\left(-\frac{\Delta G^*_f - αnFη_c}{RT}\right)$$

and the anodic ionization reaction rate develops

$$i_a = K'_r\,exp\left(-\frac{\Delta G^*_f - (1-α)nFη_c}{RT}\right)$$

Noting the definition of the exchange current density, $i_o=-i_c$ at $η=0$, and potential-dependence of the current density rearranging, we have the Butler-Volmer equation for the complete process. To sum up, the net current density below the two conditions, when $i_f \gg i_r$ and $i_r \gg i_f$ is given by

$$i_{net} = i_a - i_c = i_o\left\{exp\left(\frac{αnFη_a}{RT}\right) - exp\left(\frac{(1-α)nFη_c}{RT}\right)\right\} \qquad (68)$$

which is the universal arrangement of current against a potential relationship. The previous equation is named the Butler–Volmer equation and is a fundamental equation of electrode kinetics.

where:

- The initial term in { } in Butler-Volmer defines the forward (metal dissolution, anodic) reaction,

- another term in { } defines the backward (metal deposition, cathodic) reaction,

- R, is gas constant.

- T, is the absolute temperature.

- n, is the number of charges transferred (valency).

- F, is the Faraday constant.

- $α$, is the symmetry coefficient and
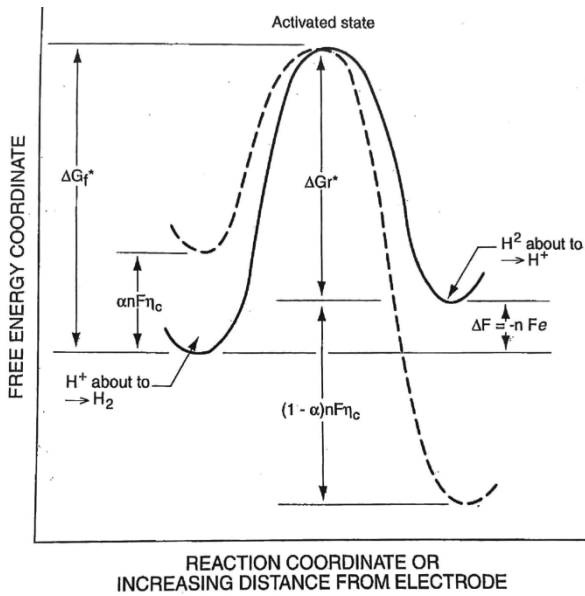
- i_o, is the exchange current

Figure 4. Activation energy model for activation overpotential. Equilibrium (———); polarized state (-----), adapted from [24]

Consider the departure of the anodic and cathodic reactions from the equilibrium potential at huge sufficient voltages, around > 0.12 volt. Below the above circumstances, one of the two standings (partial current) becomes insignificant, only one response would succeed, and the other might become unimportant.

Consider the anodic polarization (η_c> 0) individual at voltages greater than 0.1 volts. The current $i_{net,a}$ may be equivalent to the anodic partial current density, and i_c might be negligible (the reverse cathodic reaction). Underneath these circumstances, the right-hand expression of equation 68 would be removed, nevertheless, for the anodic reaction.

$$i_{\text{net,a}} = i_o exp\left(\frac{\alpha nF\eta_a}{RT}\right) \tag{69}$$

that connects the partial anodic current density to the over-potential. By analogous influences, at a great, plentiful cathodic polarization [η_c(negative)], the anodic partial current develops negligible, and the current density is:

$$i_{net,c} = i_o exp\left(-\frac{(1-\alpha)nF\eta_c}{RT}\right) \tag{70}$$

those demonstrations which the anodic or cathodic current densities differ around as the exponential of the over-voltage.

The terms derived above for $i_{net,a}$ and $i_{net,c}$ can be established in the expression of (η), the over-voltage. Taking logarithms of Equations 69 and Equations 70, which is identical to

$$ln\ i_a - ln\ i_o = \left(\frac{\alpha nF\eta_a}{RT}\right) \rightarrow \left(when\ i \gg i_f\right)$$
$$\eta_a = \frac{-ln\ i_o + ln\ i_a}{\frac{\alpha nF}{RT}}$$

$$\eta_a = \left(-\frac{RT}{\alpha nF}\right) ln\left(\frac{i_a}{i_o}\right)$$

$$\eta_a = \left(-\frac{RT}{\alpha nF}\right) ln i_o + \left(\frac{RT}{\alpha nF}\right) \ln(i_a)$$

For over-potential: $\eta = (>0)$

$$\eta_a = \left(-\frac{RT}{\alpha nF}\right) ln i_o + \left(\frac{RT}{\alpha nF}\right) \ln(i_a)$$

$$\eta_a = \left(\frac{RT}{\alpha nF}\right) ln\left(\frac{i_a}{i_o}\right) \tag{71}$$

Likewise, for cathodic polarization, on taking logarithms,

$$ln\ i_c - ln\ i_o = -\left(\frac{(1-\alpha)nF\eta_c}{RT}\right)$$

$$\eta_c = \frac{ln\ i_o - ln\ i_c}{\frac{(1-\alpha)nF}{RT}}$$

$$\eta_c = \left(\frac{RT}{(1-\alpha)nF}\right) ln\left(\frac{i_c}{i_o}\right)$$

$$\eta_c = \left(\frac{RT}{(1-\alpha)nF}\right) ln i_o + \left(\frac{RT}{(1-\alpha)nF}\right) \ln(i_c)$$

For over-potential: ($\eta < 0$):

$$\eta_c = \left(\frac{RT}{(1-\alpha)nF}\right) ln i_o = \left(\frac{RT}{(1-\alpha)nF}\right) \ln(i_c)$$

$$\eta_c = \left(\frac{RT}{(1-\alpha)nF}\right) ln\left(\frac{i_c}{i_o}\right) \tag{72}$$

where:

- $\eta = (E - E_{rev})$
- $\eta_a > 0$, anodic polarization
- $\eta_c < 0$, cathodic polarization.

The experimental equations progressed by Tafel are very equivalent to Equations 71 and Equations 72, where the Tafel constant, b_a and b_c in Equations 96 by Equations 71 and Equations 70 by Equations 72 are:

$$b_a = \frac{2.3RT}{(1-\alpha)nF} \text{ and } b_c = \frac{2.3RT}{(1-\alpha)nF} \tag{73}$$

The matter is additional described next Section.

2) Tafel Equation

The comparative amid the over-voltage (η) and the reaction rate is enormously significant. Contemplate anodic polarization only, at extraordinary anodic over- density voltage, $i_r \gg i_f$, i_c is insignificant and the current $i_{net,a}$ becomes equivalent to the anodic partial current density

$$\eta_a = \left(\frac{RT}{\alpha nF}\right) ln\left(\frac{i_a}{i_o}\right) \tag{74}$$

Instead, at great, plentiful cathodic polarization (η negative) one of the exponential standings of the Butler-Volmer equation will be negligible as compared to the other, the anodic partial current becomes negligible, therefore:

$$i_{net,c} = i_o exp\left(-\frac{(1-\alpha)nF\eta_c}{RT}\right)$$

$$\eta_c = \left(\frac{RT}{(1-\alpha)nF}\right)ln i_c - \left(\frac{RT}{(1-\alpha)nF}\right)ln\,i_o \qquad (75)$$

Equations 74 and Equations 75 are Tafel equations. The above terminologies can be transcribed in a more general formula of equation (Tafel equation)

$$\eta = a + b\,\log I \qquad (76)$$

where:

- a and b are constants and

- b is the Tafel slope.

The subsequent are the experiential relationships among the current I and over-voltage η for the anodic and cathodic over-voltage as exposed:

$$\eta_a = b_a log\frac{i_a}{i_o} \qquad (77)$$

$$\eta_c = b_c log\frac{i_c}{i_o} \qquad (78)$$

So, for a constant in Anodic:

- a is $\left(-\frac{RT}{\alpha nF}\right)log\,i_o$

- b is the slope $\left(\frac{RT}{\alpha nF}\right)$

It is extra suitable to express these in the formula of the log to the base of 10:

- $a = -\left(\frac{2.3RT}{\alpha nF}\right)log\,i_o$

- $b = \left(\frac{2.3RT}{\alpha nF}\right)$

So, for the constant in Cathodic:

- a is $\left(-\frac{RT}{(1-\alpha)nF}\right)log\,i_o \rightarrow a = \left(\frac{2.3RT}{(1-\alpha)nF}\right)log\,i_o$

- b is the slope $\left(\frac{RT}{(1-\alpha)nF}\right) \rightarrow \left(-\frac{2.3RT}{(1-\alpha)nF}\right)$

Comparison of the anodic and cathodic Tafel constants demonstrates that when $\alpha = 0.5$, $a_c = -a_a$; $-b_c = b_a$

The Tafel equation is commonly written as:

$$\eta_A = \pm b.\,log\frac{i_c}{i_o} \qquad (79)$$

where:

- η_A is the activation polarization

- b is the constant, being positive for anodic and negative for cathodic reactions

- i_o is the exchange density.

- i is the net rate of reaction

Another special case of the Butler-Volmer equation, Equation 79 arises when the overpotential is extremely small $\eta \ll \left(\frac{RT}{\alpha nF}\right)$; under this condition, one can consider the value of $F\eta/RT$ to be small. Under such situations, the partial current densities are negligible.

$$i = i_a - i_c = i_o\left\{exp\left(\frac{\alpha nF\eta}{RT}\right) - exp\left(\frac{(1-\alpha)nF\eta}{RT}\right)\right\}$$

can be stated into a sequence

$$e^x = 1 + x + \frac{x^2}{2^1} + \frac{x^3}{3^1} + \frac{x^{2n}}{n^1} \rightarrow e^x = 1 + n$$

$$i = i_o\left\{exp\left(\frac{\alpha nF\eta}{RT}\right) - exp\left(\frac{(1-\alpha)nF\eta}{RT}\right)\right\}$$

$$i = i_o\left\{+\frac{\alpha nF\eta}{RT} - \frac{(1-\alpha)nF\eta}{RT}\right\} \qquad (80)$$

$$i_a = \frac{i_o nF\eta}{RT} \quad and \quad i_c = \frac{i_o nF\eta}{RT}$$

Accordingly, the overvoltage is proportional to current density. Thus, polarization resistance can be distinct as:

$$R_p = \left(\frac{dn}{di}\right)_{i\to 0} = \frac{RT}{i_o nF}$$

A small field estimated, $\eta < 0.002$, the hyperbolic sine function, approaches to a linear function therefore that based on the relations, which is the lesser field estimate for the Butler–Volmer equation:
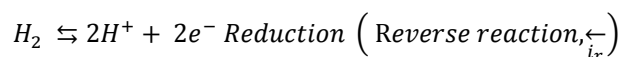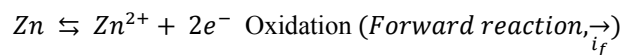
$$sinh\,x = \frac{(e^x - e^{-x})}{2} \quad and \quad sinh\,x = x\;when\;x \to 0\;to$$

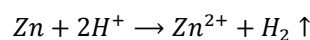$$i_{net} = 2\,i_o sinh = \frac{nF\eta}{RT} = \frac{i_o nF\eta}{RT}$$

The ratio of the overpotential to the current in the above equation is named the charge- transfer resistance. This equation adds more physical sense to the exchange current density, i_o, and can be viewed as a parameter to estimate the resistance of an electrochemical (corrosion) reaction. A high value of the exchange current density implies a high reaction rate, while a low exchange current density value designates sluggish corrosion kinetics. Based on low-field approximation, a simple procedure for the evaluation of corrosion currents and corrosion rates was developed, and then Stern and Geary [20,43] and Stern [44] developed an experimental procedure for measuring the corrosion rates known as the linear polarization technique. This technique will be deliberated in detail later.

3) Mixed Potential Theory

Multiple reactions happen in a corrosion cell that has an electrolyte, anode, cathode, and a metallic path. For example, when zinc rusts in dilute acid, the subsequent reactions arise:

$$Zn \leftrightarrows Zn^{2+} + 2e^- \;\; \text{Oxidation}\; (Forward\; reaction, \underset{i_f}{\rightarrow})$$

$$H_2 \leftrightarrows 2H^+ + 2e^- \;\; Reduction\left(\text{R}everse\; reaction, \underset{i_r}{\leftarrow}\right)$$

The total reaction is:

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2 \uparrow$$

Consequently, the metal establishes a multielectrode, as at least two diverse reactions occur on its surface instantaneously, one oxidation and one reduction. The mixed potential concept partially stated previously is applied with benefit to guessing

the rate of corrosion of metals and alloys in an assumed situation. It has two straightforward assumptions:

- Electrochemical reactions are collected from two or more partial anodic and cathodic reactions.

- There cannot be any accumulation of charges

Charge conservation is obligatory to concern the equations derived for polarization potentials. This means that the totality of anodic oxidation currents must equivalent the sum of cathodic reduction currents.

IV. ELECTROCHEMICAL TEST TECHNIQUES

The electrochemical corrosion method is believed to be a rapid and effective technique that indicates the transient corrosion process, so it can be utilized for determining the corrosion rate on-site. The utilization of the polarization curve is hugely restricted on account of its destructive nature. Nevertheless, it has to be highlighted since, from the outline of the experimental curve, it could be possible to get crucial information on the kinetics of the corrosion reactions [45]. This commonly applied technique of electrochemical measurement allows determination of the [18,21,42].

- E_{corr} steady-state corrosion potential.

- Variation of E_{corr} with time.

- E - I relationship through polarization at constant current density (galvanostatic), the potential being flexible.

- E - I relationship thru polarization at a constant potential (potentiostatic), the current being the variable.

A. Basic Electrochemical Instrumentation

Electrochemical tests are the most common and fast method for the detection of corrosion and corrosion rates. To perform an electrochemical experiment an electrochemical cell is required and a device for the polarization of the metal, a potentiostat. Numerous assessment cells for polarization measurements are available commercially. Polarization cells can have numerous arrangements depending on test condition, whether examining thin coupons testing sheet materials, or testing inside autoclaves. The electrochemical cell contains three electrodes located in the electrolyte solution. These electrodes are the working electrode, the counter electrode, and reference. The voltage between the working electrode and the reference electrode is measured by the potentiostat, and the current between the working electrode and the counter electrode is measured. Figure 5 is a diagram of the system. The main features of a cell are [11,21,41,46–48]:

1- The working electrode (WE) is the metal of interest for the test. This is the main electrode whose CR is being measured. Care must be taken that this electrode is appropriately equipped and attached (without any crevice). Commonly, the working electrode is not the actual metal structure being studied. Instead, a small sample is used to represent the structure.

2- The counter electrode (CE) is auxiliary and typically composed of inert materials, e.g., platinum or graphite, and it supplies the current to the working electrode. Usually, two auxiliary electrodes or one big piece of one auxiliary electrode are applied, and it is shaped in a similar method as that of the WE. For in field probes, it is generally another piece of the working electrode material. The current that flows into the solution *via* the working electrode leaves the solution *via* the auxiliary electrode.

3- The reference electrode (RE) is used in measuring the working electrode potential, and it has a constant electrochemical potential as long as no current flows through it. It has a highly reproducible potential. The most common laboratory reference electrodes are the saturated calomel electrode (SCE) and the silver/silver chloride (Ag/AgCl) electrodes as displayed in Table 2.

4- Electrolyte, which is the elementary condition of any electrochemical measurement, is practically conducting (low resistivity) electrolyte, which means electrically conductive. It is regularly a liquid having ions that combine in an electric field.

5- The potentiostat is the tool that preserves the potential of the WE, and it must have an appropriate variety of potential and current to maintain the set value.
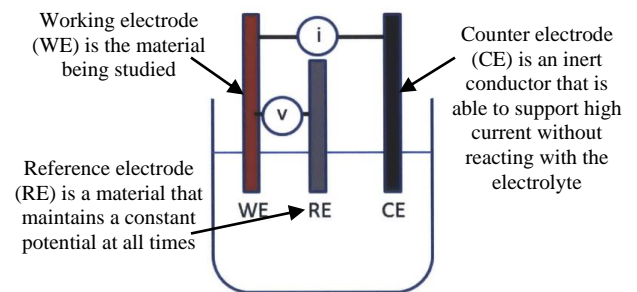

Figure 5. A diagram of a typical three-electrode cell, adapted from [49].

TABLE II. EQUILIBRIUM POTENTIAL OF THE MAIN REFERENCE ELECTRODES USED IN CORROSION, THESE DATA ADAPTED AND REPRODUCED FROM [48].

Name	Potential (V) *vs.* SHE at 25 °C.			Potential (V) *vs.* SHE at 60 °C.
Hydrogen	0			0.0216
Silver chloride	0.1 M KCl- 0.2881	1.0 M KCl - 0.2224	Seawater- 0.250	0.1880
Calomel	0.1 M KCl- 0.3337	1.0 M KCl- 0.280	Saturated - 0.241	0.2463
Mercurous sulfate	0.6151			0.6035
Mercuric oxide	0.926			0.9360
Copper sulfate	Saturated- 0.318			0.3812

B. Types of Polarization Test Methods

1) Open Circuit Potential (OCP)

OCP is also called the free corrosion potential or electrode potential or the equilibrium potential, the resting potential, or the corrosion potential in which no net current runs over the external circuit of the cell. In all experiments of electrochemical corrosion, the first step taken is to measure OCP (E_{ocp} or E_{corr}). It is a measurement of voltage between the WE (metal) and a RE with a high-impedance voltmeter or potentiostat Figure 6. In this setup, the instrument is configured to measure voltage and source 0A [50]. Observing an OCP over time can deliver data about the corrosion system and in which state it is (steady, transition, passive, and active states) [51]. Consequently, a knowledge of E_{corr} is valuable in establishing whether a reaction can happen spontaneously, although unfortunately there is a lack of information about the rate of the corrosion reactions [40,42]. The results of E_{OCP} are as follows: an increase of potential in a positive direction is indicative of the formation of a passive film, and a steady potential specifies that the film remains intact and protective. A potential drop suggests breaks in the film, dissolution of the layer, or no film formation [52–55].

2) Polarization Resistance (Linear Polarization Resistance -LPR)

Based on theory concerning the kinetics of electrochemical reactions there is a linear correlation between the polarization resistance E and the corrosion rate near open-circuit conditions [56]. LPR is an accelerated electrochemical method that is applied to quantify the corrosion rate in the research laboratory and in the field by investigating the linear relationship amid a small applied potential and the resulting current, such a

correlation is shown in Figure 7, which was established by Stern.
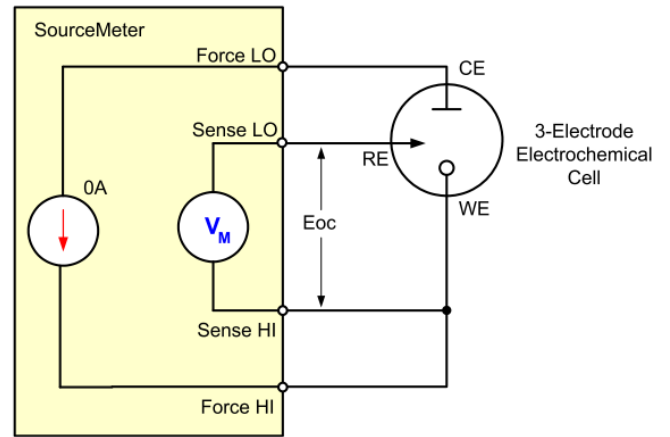

Figure 6.   Using an Electrochemistry Lab System to measure the open circuit potential of an electrochemical cell, adapted from [50].

For a scheme in which electrode reaction contains a slow reaction at the electrode surface, the reaction rate is restricted by activation overvoltage; the relationship amid the rate of reaction, or net current density i, and the driving force for the reaction, or potential E, is specified by the Butler-Volmer equation. This equation relates i, for a single electrode process, such as Equation 81 to E by the formulation Equation 82.
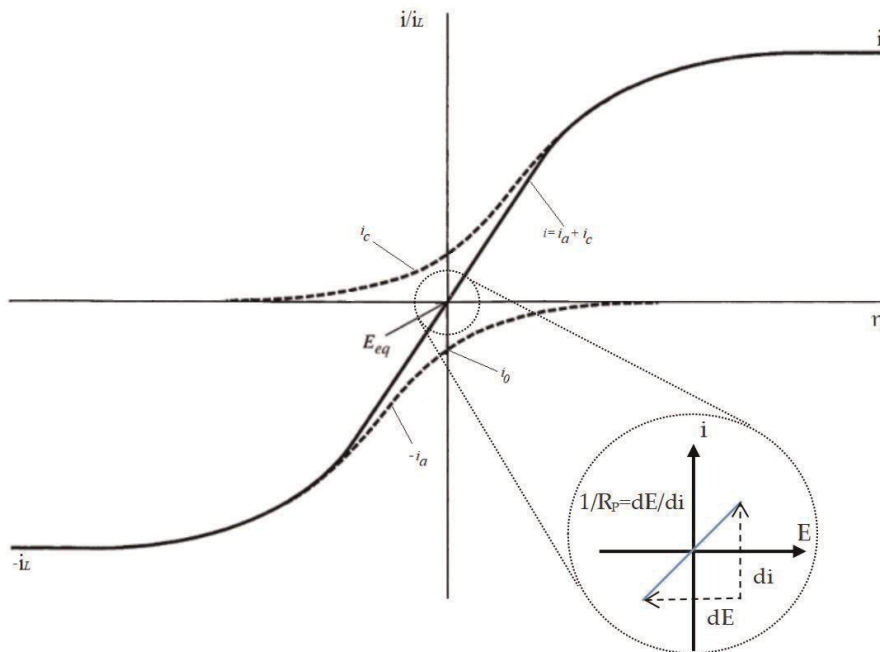

Figure 7.   Scheme representative linear potential-current relationship, where i: Current density; η: overpotential curves for the system at T= 25°C, α = 0.5, $i_{l,a}$ = $i_{l,c}$ = i_l. Partial current densities: i_a, i_c (dashed line), i_l limit current density (horizontal line), and R_P the polarization resistance (circle), adapted from [56].

$$Fe_{(s)} \rightarrow Fe_{(aq)}^{2+} + 2\,e^- \tag{81}$$

$$i = i_o \left[exp\left(\frac{\alpha nF\eta}{RT}\right) - exp\left(\frac{(1-\alpha)nF\eta}{RT}\right) \right]$$

$$i = i_o \left[exp\left(\frac{\alpha nF(E-E_{res})}{RT}\right) - exp\left(\frac{(1-\alpha)nF(E-E_{res})}{RT}\right) \right] \tag{82}$$

where:

- η is the overpotential,

- i_o is the exchange current density (rate of either the forward or reverse half-cell reaction) at the equilibrium potential E_{res},

- α is the transfer coefficient (usually close to 0.5, but must be between 0 and 1), and

- n is the number of electrons transferred.

It is well recognized that the electrochemistry of decomposing metals includes two or more half-cell reactions. Assume there is a simple corrosion system, for example, an iron metal which is a corroding WE submerged in a sulfuric acid media, as well as Equation 83, the subsequent half-cell reaction Equation 84 similarly happens:

$$H_{(aq)}^+ + e^- \rightarrow H_{ads} \tag{83}$$

$$i = i_o \left[exp\left(\frac{\alpha nF\eta}{RT}\right) - exp\left(\frac{(1-\alpha)nF\eta}{RT}\right) \right]$$

$$i = i_o \left[exp\left(\frac{\alpha nF(E-E_{ocp})}{RT}\right) - exp\left(\frac{(1-\alpha)nF(E-E_{ocp})}{RT}\right) \right] \tag{84}$$

From Figure 7, the linear connection among the polarization resistance and the corrosion rate can be simply explained graphically. In the diminutive area near the corrosion potential, E_{corr}, only an identical trivial perturbation potential, normally lower than $\pm$ 30 mV (naturally $\pm$ 10 mV), is employed above or below the corrosion potential, elastic a linear relationship amid the overpotential ($\eta = E - E_{corr}$) or the polarization from the corrosion potential and the current.

Polarization resistance (R_p) of a rusting metal is defined using Ohm's rule as the slope of a potential (E) against the current density ($log\ i$) graph at the corrosion potential (E_{corr}). Polarization measurements are made using a variety of potentials close to the corrosion potential (E_{corr}) and then calculating the resulting current. Along with Ohm's law ($R = \Delta E/\Delta i$), the ratio of the applied potential to the generated corrosion current (I_{corr}) is defined as the polarization resistance (R_p) [56]. The slope of that linearized curve (i-E) is distinct as the polarization resistance, R_P, that is scientifically interpreted as:

$$R_P = \left(\frac{\partial \eta}{\partial i}\right)_{E-E_{corr}=0}$$

where:

- i is the current density corresponding to a particular value of E.

The corrosion current, I_{corr}, can be considered when the overpotential nears zero and is associated to R_P as follows:

$$I_{corr} = \frac{B}{R_p}$$

$$I_{corr} = \frac{b_a b_c}{2.23(b_a+b_c)} \cdot \frac{1}{R_p} \tag{85}$$

where:

- b_a and b_c are the anodic and cathodic Tafel slopes or Tafel parameters.

The corrosion current density, I_{corr}, can thus be calculated from Equation 85 if R_P, ba, and bc are identified. ASTM standard (G 102 – 89) defines an experimental process essential to make polarization resistance measurement.

3) Tafel Extrapolation Method

The presence of a direct relationship between E and $log\ I$ has been confirmed when the electrode is polarized at suitably large potentials, and distant from the corrosion potential both in anodic and cathodic directions, as can be realised in the polarization curvature showed in Figure 8. The portions in which such relationships prevail are termed Tafel portions or Tafel regions.

$$I = i_{corr} \left[exp\left(\frac{2.303\eta}{b_a}\right) - exp\left(-\frac{2.303\eta}{b_c}\right) \right]$$

$$I = i_{corr} \left[exp\left(\frac{2.303(E-E_{corr})}{b_a}\right) - exp\left(-\frac{2.303(E-E_{corr})}{b_c}\right) \right]$$

where:

- E_{corr} is the corrosion potential,

- E is the applied potential,

- η is the overpotential (the difference between E and E_{corr}),

- I is the current,

- I_{corr} is the corrosion current, and
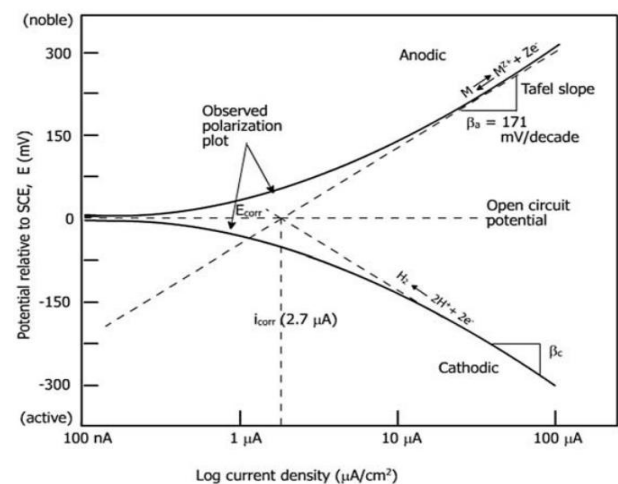
- b_a and b_c are the Tafel constants

Figure 8. Electrode kinetics as expressed by the Butler-Volmer equation, plotted in a semilogarithmic scale or Tafel plot showing that the corrosion current density can be obtained from the intercept, adapted from [56].

Generalizing from the Tafel portions of either anodic or cathodic or both, a connection spot is gained at E_{corr}, from which I_{corr} is readily accessible from the $log\ I$ axis. So, it is likely to get directly the corrosion current, I_{corr}, and the Tafel parameters (i.e., ba and bc) from this technique. At suitably greater values of η (100 mV ≤ η ≤ 500 mV), in the anodic direction (i.e., $η = η_a$) or similarly, at suitably larger values of η, in the cathodic direction (i.e., $η = ηc$):

$$\eta_a = b_a log \frac{I}{I_{corr}} \ and \ \eta_c = b_c log \frac{I}{I_{corr}}$$

So, the investigational relationship amid the current, I, and the overpotential, η, throughout an electrocatalytic examination of the reduction reaction of hydrogen (i.e., protons to form molecular hydrogen) on a number of electrode metals:

$$\eta = \pm a + b.log I$$

where the overpotential η is distinct as the change amid the potential of the working electrode E and the equilibrium potential. Tafel extrapolation regions can be achieved either by the potentiodynamic technique or by the stepwise potentiostatic polarization technique.

4) Potentiodynamic Polarization (PDP)

PDP is an electrochemical method that correlates the thermodynamic information (potential) parameter to the kinetics of a reaction (current). The statistics and information are useful for defining corrosion rates, passivity, and pitting susceptibility, besides information on the kinetics of the cathodic reactions of the electrochemical system can be gained. It is possibly the most common polarization testing technique used to gain information about the nature of anodic/cathodic processes [57]. It is a method where the potential of the electrode is altered at a set rate. It is applied for measuring the corrosion current and identifying specific corrosion reactions, such as pitting and crevice corrosion [58]. In this procedure, the potential is maintained at a given value, which can be altered slowly at a fixed rate to measure potential alongside current. The basics of analysis are shown in Figure 9, the corrosion active region, the onset of passivation, the critical current density, the primary passive potential, the current in the affected region, and the voltage span of the passive region. The data were obtained by recording the current as the applied potential increased continuously at a predetermined sweep rate [7]. The outcome is typically plotted as current density as a function of the potential, where current is plotted as *log/i/*.
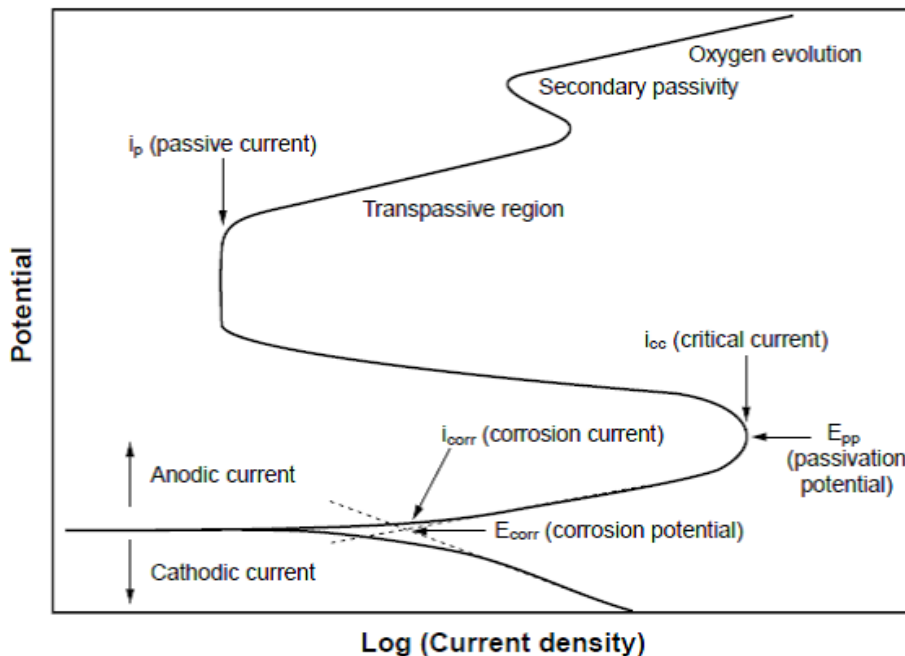

Figure 9. Hypothetical polarization diagram for an active/ passive/active system with anodic and cathodic branches, adapted from [7].

The polarization curve provides data on the kinetics of the corrosion reactions, active, passive, transpassive, and transitions have taken place. The measured corrosion current allows corrosion rates to be calculated. Extrapolation of anodic and cathodic Tafel slopes back to the (E_{corr}) corrosion potential is displayed. The joint point corresponds to corrosion current density (I_{corr}), or corrosion rate, and Tafel constants (b_a and b_c), which are considered from slopes of the anodic and cathodic branches. The Tafel technique is generally operated to measure CR, a faster experimental method compared with the traditional weight-loss assessment, and the CR obtained for Tafel is typically the same as those measured by the weight loss [59]. The measurement of the sum of cathodic and anodic current can be performed from PDP. To assess those

measurements, a theoretical anodic and cathodic current is useful to the straight regions of the measured current. This theoretical current can be obtained from the Tafel equation and, as in Figure 10, shows theory and a Tafel extrapolation fitted to measured data

$$I = I_o exp^{\frac{2.303}{b}(E-E_{ocp})} \qquad (86)$$

where:

- I is the current resulting from the reaction

- I_o is a reaction dependent constant called the Exchange current

- E is the electrode potential

- E_{OCP} is the equilibrium potential

- b is the reaction's Tafel Constant

If the Tafel equation for the anodic current is combined with the Tafel equation for the cathodic current, the Butler-Volmer equation is obtained:

$$I = I_{corr}\left[exp^{\frac{2.303}{ba}(E-E_{ocp})} - exp^{\frac{-2.303}{bc}(E-E_{ocp})}\right] \qquad (87)$$

where:

- I is the measured cell current, (the sum of the cathodic and anodic current)

- I_{corr} is the corrosion current in amps

- E is the electrode potential

- E_{OCP} is the equilibrium potential

- b_a is the anodic Tafel Constant in volts/decade

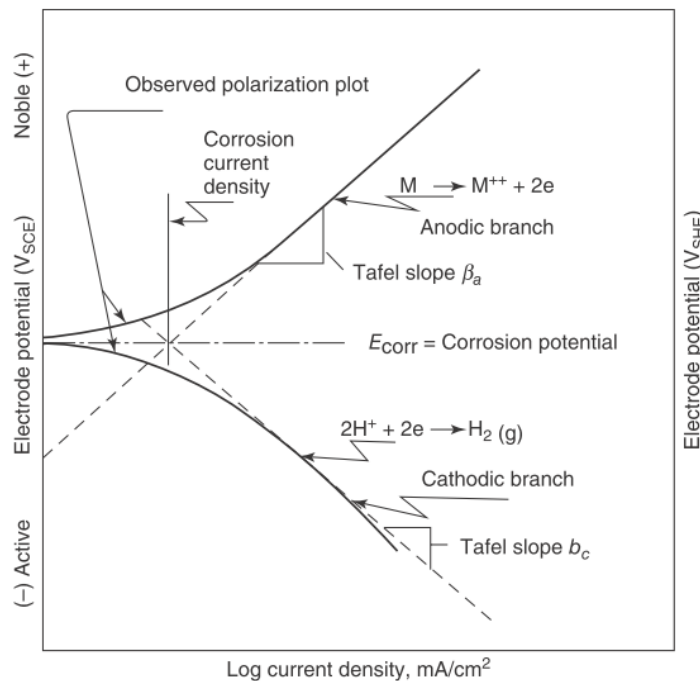- b_c is the cathodic Tafel Constant in volts/decade

Figure 10. Hypothetical cathodic and anodic Tafel polarization diagram, adapted from [21].

V. BENEFITS AND LIMITATIONS OF ELECTROCHEMICAL PROCEDURES

The core advantages of electrochemical methods contain the understanding to small corrosion rates, quick investigational period, and appropriately- recognized theoretical knowledge. Throughout electrochemical experimentations, samples are polarized to speeding up the corrosion, and the measurement is carried out in just a few minutes or hours. The electrochemical measurements are utilized both in the research lab and in the oilfield. Normally applied electrochemical polarization systems contain polarization resistance approaches, Tafel extrapolation procedures, potentiodynamic methods. After the fundamental aspects, each technique has benefits, and limitations for observing corrosion are obtainable in Table 3.

TABLE III.   FEATURES OF DIFFERENT ELECTROCHEMICAL POLARIZATION PROCEDURES, THESE DATA ADAPTED AND REPRODUCED FROM [11,21,41,46–48].

Polarization technique	Polarization resistance	Tafel extrapolation	Potentiodynamic polarization
Normal measurement	Implementation of ± 30 mV (naturally ± ten mV) about corrosion potential	Implementation of an overpotential of + 500 mV both in anodic and cathodic paths, from corrosion potential	Implementation of overpotential from corrosion potential towards the noble path to a potential on which current is five mA, somewhere the potential is overturned and examined till corrosion potential is attained
Information obtained	I_{corr}	I_{corr} Tafel slopes	Critical pitting potential passive current transpassive region
Appropriate standards ASTM	ASTM G3 ASTM G5 ASTM G59 ASTM G102	ASTM G5 ASTM G102	ASTM G5 ASTM G61 ASTM G102
Advantages and Disadvantages	I_{corr} is evaluated quickly, normally in just a few minutes, and thus this method could be utilized as an online observing method.	The test sample geometric shapes makes rigorous monitor to acquire a uniform current	It offers an easy, straightforward approach to decide Tafel constants
	Just very small quantities of potential are used (below ± 30 mV, usually under ± 10 mV); so the corrosion rate is not adversely changed because of measurements	The sample is responsible to be destroyed through high current	It offers a speedy approach to ascertain sensitivity to the start of pit initiation
	This method can be applied for measuring minimal corrosion rates (below 0.1 mil/yr (2.5µm/yr)). Measurements may be taken frequently.	The Tafel region is frequently obscured through concentration polarization and by the presence of more than one activation polarization procedure	This method does not give information about pit proliferation. The method could be applied only as the qualitative procedure. As sensitive equipment is necessary to carry out the test, it can no longer be regularly employed for all alloys

VI.   CONCLUSION

The major conclusion to be pulled from this review is that there is an electrochemical activity among the metal and the natural environment. Therefore the electrochemical procedures perform the main role in the understanding of the process of corrosion potential.

Generally, the length of the experiment and the kind of scientific techniques have also been identified. Because there are different types of exploring corrosion processes and analyzing the measurements that can be obtained, each of these methods has provided the essential information for an assumed corroding system. It is a very important thought for scheming the experimental procedures assumed in the corrosion study as electrochemical approaches are efficient and cost-effective for corrosion observing.

REFERENCES

[1] Lee K. A mechanistic modeling of CO2 corrosion of mild steel in the presence of H2S. Ohio University, 2004.

[2] FH-Schmalkalden. Principles of Corrosion. 1982. https://doi.org/10.1016/b978-0-408-01175-4.50007-6.

[3] Gardner S. Haynes and Robert Baboian. LABORATORY CORROSION AND TEST STANDARDS. ASTM Publication Code Number (PCN) 04-866000-27,1916 Race Street, Philadelphia, PA 19103; 1985.

[4] Roberge PR. Corrosion Engineering - Practices and Principles. 2008.

[5] Ahmad Z. Principles of Corrosion Engineering and Corrosion Control. n.d.

[6] U S-YC. A Study of The Effect of Some Inhibitors on The Corrosion Rates of Austenitic Stainless Steels in Sulfuric Acid. New Jersey Institute of Technology, 1989. https://doi.org/10.3141/2100-07.

[7] Popov BN. Basics of Corrosion Measurements. Corrosion Engineering, vol. 2, 2015, p. 181–237. https://doi.org/10.1016/b978-0-444-62722-3.00005-7.

[8] Hobbs LW. Electrochemical Corrosion Gibbs Free Energy, Anodic Corrosion & the EMF Series. 2006.

[9] BAGOTSKY VS. Fundamentals of electrochemistry. 2008. https://doi.org/10.1007/978-3-540-77508-9_8.

[10] BN P. THERMODYNAMICS OF CORROSION PROCESSES. Corrosion Engineering : Principles and Solved Problems, 2020, p. 58–60.

[11] BAGOTSKY VS. FUNDAMENTALS OF ELECTROCHEMISTRY. vol. 2. Elsevier Ltd; 2006. https://doi.org/10.1016/j.corsci.2010.09.011.

[12] Küter A. Management of Reinforcement Corrosion a thermodynamic Approach. 2009.

[13] Zamri Mfmba. The Study of Corrosion Rate for Carbon Steel Pipe in Alkaline Concrete Solution. Universiti Malaysia Pahang, 2008.

[14] Pessu Fo. Investigation of Pitting Corrosion of Carbon Steel in Sweet and Sour Oilfield Corrosion Conditions: A Parametric Study. The University of Leeds, 2015.

[15] Hinds G. THE ELECTROCHEMISTRY OF CORROSION. vol. 24. 1968. https://doi.org/10.5006/0010-9312-24.1.1.

[16] Aspects G, Corrosion OF, Corrosion C. GENERAL AND THEORETICAL ASPECTS OF CORROSION. n.d.

[17] Deinard LH, Stathis NJ, Rasenberger ME. Gamry Instruments Software Tutorials and Primers. 2000. https://doi.org/10.1002/0471238961.2018010404050914.a01.

[18] Revie RW and HHU. CORROSION AND CORROSION CONTROL An Introduction to Corrosion Science and Engineering. vol. 288. A JOHN WILEY & SONS, INC., PUBLICATION; 1984. https://doi.org/10.1136/bmj.288.6417.643.

[19] Lower SK. ELECTROCHEMISTRY. MODULE Biochemistry, Simon Fraser University; 1994, p. 40.

[20] GEARY SAAL. Electrochemical polarization. Journal of the Franklin Institute 1902;153:259–68. https://doi.org/10.1149/1.2428496.

[21] Frankel GS, Rohwerder M. Electrochemical Techniques for Corrosion. Encyclopedia of Electrochemistry, 2003. https://doi.org/10.1002/9783527610426.bard040007.

[22] Stern M. Electrochemical Polarization: I . A Theoretical Analysis of the Shape of Polarization Curves. Journal of The Electrochemical Society 1957;104:751. https://doi.org/10.1149/1.2428473.

[23] Swain, G.W. and Schultz MP. Corrosion Basics: An Introduction. 1984.

[24] Bushman JB. Calculation of Corrosion Rate from Corrosion Current (Faraday ' s Law) by. 2002.

[25] Electrochemical Kinetics of Corrosion and Passivity The basis of a rate expression for an electrochemical process is Faraday's law: n.d.

[26] K. A. Natarajan. Polarization Techniques – Corrosion Rate Determination. 2003.

[27] Measurements E. Standard Practice for Calculation of Corrosion Rates and Related Information. American Society for Testing and Materials Licensed by Information Handling Services 1999;89:1–7. https://doi.org/10.1520/G0102-89R10.

[28] Chilingar, George V. RM and GDA-Q. The Fundamentals of Corrosion and Scaling for Petroleum and Environmental Engineers. Houston, Texas: Gulf Publishing Company; 2008.

[29] Ramesh Divakar,Srinvasa G. Seshadri and MS. Electrochemical Techniques for Corrosion Rate Determination in Ceramics. Journal of the American Ceramic Society 1973;72:780–4.

[30] Enos DG and LLS. The Potentiodynamic Polarization Scan. Charlottesville: 2014.

[31] Sherar B. The Effect of the Environment on the Corrosion Products and Corrosion Rates on Gas Transmission Pipelines. University of Western Ontario, 2011.

[32] Berradja A. Electrochemical Techniques for Corrosion and Tribocorrosion Monitoring: Methods for the Assessment of Corrosion Rates. IntechOpen, vol. i, 2019, p. 13. https://doi.org/http://dx.doi.org/10.5772/57353.

[33] Ajayi FO. Mitigating corrosion risks in oil and gas equipment by elefctrochemical protection: Top of the line corrosion. University of Manchester, 2015.

[34] Fernández-Solis CD, Ashokanand Vimalanandan Abdulrahman Altin Jesus S. Mondragón-Ochoa KK, Keil P, Erbe A. Fundamentals of Electrochemistry, Corrosion and Corrosion Protection. vol. 917. 2016. https://doi.org/10.1007/978-3-319-24502-7.

[35] Kelly RG, Scully JR, Shoesmith DW, Buchheit RG. Electrochemical Techniques in Corrosion Science and Engineering. New York • Basel: Marcel Dekker, Inc.; 2002. https://doi.org/10.1201/9780203909133.ch8.

[36] Obuka Nnaemeka, O.N.C. Ikwu, Okechukwu GRO, E. Chukwumuanya. Review of Corrosion Kinetics and Thermodynamics of Co2 and H2S Corrosion Effects and Associated Prediction/Evaluation on Oil and Gas Pipeline System. International Journal of Scientific & Technology Research 2012;1:156–62.

[37] Popov BN. Corrosion Engineering: Principles and Solved Problems. 2015. https://doi.org/10.1016/C2012-0-03070-0.

[38] Pourbaix M. Thermodynamics and corrosion. Corrosion Science 1990;30. https://doi.org/10.1016/0010-938X(90)90205-J.

[39] Chen Z. The Open-Circuit Potential of a Polarizable and Reactive Electrode 2008;6:1–15. https://doi.org/10.1149/1.2900649.

[40] Zaki Ahmad. Principles of Corrosion Engineering and Corrosion Control. Elsevier Science & Technology Books; 2006.

[41] Lean Fong Khaw Lee. Potentiodynamic Polarization Studies of Aluminium Alloys in Synthetic Flue Gas Condensate. 1986.

[42] Vedalakshmi R, Thangavel K. Reliability of Electrochemical Techniques to Predict the Corrosion Rate of Steel in Concrete Structures. Arabian Journal for Science and Engineering 2011;36:769–83. https://doi.org/10.1007/s13369-011-0082-4.

[43] Revie RW and HHU. CORROSION AND CORROSION CONTROL: An Introduction to Corrosion Science and Engineering. 2008.

[44] Zou Y, Wang J, Zheng YY. Electrochemical techniques for determining corrosion rate of rusted steel in seawater. Corrosion Science 2011;53:208–16. https://doi.org/10.1016/j.corsci.2010.09.011.

[45] Bakrachevska E. Analysis of Corrosion Resistance Property of Cold Bended 316L and 6Mo Stainless Steel Pipes. 2010.

[46] DeLuccia J, Berman D. Electrochemical Corrosion Testing 1981:15–6. https://doi.org/10.1520/STP727-EB.

[47] Ingo G, Padeletti G, Caro T De, Ricucci C. Microchemical investigation of ancient silver and gold plated objects: coating techniques and degradation mechanisms. ΑΡΓΥΡΟΠit ΟΥΛΟΥ ΤΕΛΟS 2008:9–13.

[48] Li KKH. Microbially influenced corrosion in sour environments. 2014.

[49] Note A. Keithley Instrumentation for Electrochemical Test Methods and Applications n.d.

[50] LARSSON M. Electrochemical analysis of Zinc for biodegradable applications. 2012.

[51] Process C, Anodic S, Components CC, Potential OC, Potential OC, Potential C, et al. Getting Started with Electrochemical Corrosion Measurement. 2011.

[52] Kabir KB, Mahmud I. Study of Erosion-Corrosion of Stainless Steel, Brass and Aluminum by Open Circuit Potential Measurements. Journal of Chemical Engineering 2011;25:13–7. https://doi.org/10.3329/jce.v25i0.7234.

[53] Fayyad EM, Almaadeed MA, Jones A, Abdullah AM. Evaluation Techniques for the Corrosion Resistance of Self- Healing Coatings. Int J Electrochem Sci 2014;9:4989–5011.

[54] Lang PR, Liu Y. Soft Matter at Aqueous Interfaces. vol. 917. 2016. https://doi.org/10.1007/978-3-319-24502-7.

[55] Alkordy FM. Evaluation of Organic Protective Coatings as Corrosion Prevention for The Interior of Subsea Pipelines in Sour Gas Service. FLORIDA INTERNATIONAL UNIVERSITY, 2015.

[56] Genescá J, Mendoza J, Duran R, Garcia E. Conventional Dc Electrochemical Techniques in Corrosion Testing. XV International Corrosion Congress 2002.

[57] J. Genesca, J. Mendoza RD and EG. CONVENTIONAL DC ELECTROCHEMICAL TECHNIQUES IN CORROSION TESTING 2016.

[58] Prof. K. A. Natarajan. Polarization Techniques – Corrosion Rate Determination. NPTEL Web Course 2003:1–8.