## **Chapter 3**

# KINETICS OF ACTIVATION POLARIZATION

### 3.1 INTRODUCTION

Electrochemical reaction kinetics is essential in determining the rate of corrosion of a metal M exposed to a corrosive medium (electrolyte). On the other hand, thermodynamics predicts the possibility of corrosion, but it does not provide information on how slow or fast corrosion occurs. The kinetics of a reaction on a electrode surface depends on the electrode potential. Thus, a reaction rate strongly depends on the rate of electron flow to or from a metal-electrolyte interface. If the electrochemical system (electrode and electrolyte) is at equilibrium, then the net rate of reaction is zero. In comparison, reaction rates are governed by chemical kinetics, while corrosion rates are primarily governed by electrochemical kinetics.

Electrochemical kinetics of a corroding metal can be characterized by determining at least three polarization parameters, such as corrosion current density  $(i_{corr})$ , corrosion potential  $(E_{corr})$ , and Tafel slopes  $(\beta_a \text{ and/or } \beta_c)$ . Then the corrosion behavior can be disclosed by a polarization curve  $(E \ vs. \log i)$ . Evaluation of these parameters leads to the determination of the polarization resistance  $(R_p)$  and the corrosion rate as  $i_{corr}$ , which is often converted into **Faradaic corrosion rate**  $C_R$  having units of mm/y. This is an accelerated electrochemical process for determining  $C_R$  that has an advantage over the  $C_R$ determined by weight loss since the latter is a time consuming process, which may lead to unsatisfactory results when  $C_R$  changes with time [13]. Instead, a polarization curve is readily obtained and it can offer a practical method for characterizing electrochemical kinetics parameters.

### **3.2 ENERGY DISTRIBUTION**

For a polarized electrode under steady-state current flow, the generalized reaction given by eq. (1.2) can be used to derive the Butler-Volmer equation, which involves energy barriers known as activation energies. Only the activation energy change is used for the forward  $(\Delta G_f)$  (reduction) and reverse  $(\Delta G_r)$ (oxidation) reactions. For example, the hydrogen reaction,  $2H^+ + 2e^- = H_2$  at equilibrium requires that the rate of discharge of  $H^+$  ions in the forward direction (reduction) must be exactly equal to the rate of ionization of  $H_2$  molecule in the reverse direction (oxidation). However, if deviation from the equilibrium state occurs, an overpotential develops and consequently, the electrochemical cell polarizes and the activation energies become dependent on the exchange current density  $(i_o)$ . These energies are depicted in Figure 3.1 in which the activation state is at the maximum point (saddle point). This figure represents the Boltzmann or Maxwell-Boltzmann distribution law for the energy distribution of the reacting species (ions) [4,7]. This schematic energy distribution is for reversible electrodes. If these are polarized by an overpotential under steady-state conditions, the rate of reactions are not equal,  $R_f \neq R_r$ .



Figure 3.1 Schematic activation free energy distribution.

In general, the electrochemical and chemical rates of reactions due to either anodic or cathodic overpotentials can be predicted using both Faraday and Arrhenius equations, respectively

$$R_F = \frac{iA_{w,j}}{zF} \tag{3.1}$$

$$R_A = \gamma_a \exp\left(-\frac{\Delta G^*}{RT}\right) \tag{3.2}$$

where i = Applied current density  $(A/cm^2)$   $A_{w,j}$  = Atomic weight of species j (g/mol)  $A_{w,alloy} = \sum f_j A_{w,j}/z_j$  in units of g/mol z = Oxidation state or valence number  $z_j$  = Valence number of element j  $f_j$  = Weight fraction of element j  $\gamma_a$  = Chemical reaction constant  $\Delta G^*$  = Activation energy or free energy change (J/mol)

At equilibrium, Faraday's and Arrhenius' rate equations become equal  $(R_F = R_A)$ and consequently, the current density becomes

$$i = \gamma_o \exp\left(-\frac{\Delta G^*}{RT}\right) \tag{3.3}$$

Here, the term  $\gamma_o = zF\gamma_a/A_w$  may be defined as the electrochemical rate constant having unit of current density  $(A/cm^2)$ . For a reversible electrode at equilibrium, the current density in eq. (3.3) becomes the exchange current density; that is,  $i = i_o$ . In addition, Table 3.1 gives typical experimental values for  $i_o$ .

Table 5.1 Exchange current density data at 25°C [4].				
Electrode	Electrolyte	Reaction	$i_o (A/cm^2)$	
Al	$2N H_2SO_4$	$2H^+ + 2e^- = H_2$	$1x10^{-10}$	
Au	$1N \ HCl$	$2H^+ + 2e^- = H_2$	$1x10^{-6}$	
Cu	$0.1N \ HCl$	$2H^+ + 2e^- = H_2$	$2x10^{-7}$	
Fe	$2N H_2SO_4$	$2H^+ + 2e^- = H_2$	$1x10^{-6}$	
Ni	$1N \ HCl$	$2H^+ + 2e^- = H_2$	$4x10^{-6}$	
Ni	$05N NiSO_4$	$Ni = Ni^{+2} + 2e^{-}$	$1x10^{-6}$	
Pb	$1N \ HCl$	$2H^+ + 2e^- = H_2$	$2x10^{-13}$	
Pt	$1N \ HCl$	$2H^+ + 2e^- = H_2$	$1x10^{-3}$	
Pt	0.1N NaOH	$O_2 + 4H^+ + 4e^- = 2H_2O$	$4x10^{-13}$	
Pd	06N HCl	$2H^+ + 2e^- = H_2$	$2x10^{-4}$	
Sn	1N HCl	$2H^+ + 2e^- = H_2$	$1x10^{-8}$	

Table 3.1 Exchange current density data at  $25^{\circ}C$  [4].

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On the other hand, if an electrode is polarized by an overpotential under steady-state conditions, then the rates of reactions are not equal  $(R_F \neq R_A)$  and consequently, the forward (cathodic) and reverse (anodic) current density components must be defined in terms of the free energy change  $\Delta G^*$  deduced from Figure 3.1. Hence,

$$i_f = k'_f \exp\left[-\frac{\Delta G^*_f}{RT}\right]$$
 (Cathodic) (3.4)

$$i_r = k'_r \exp\left[-\frac{\Delta G^*_r}{RT}\right]$$
 (Anodic) (3.5)

where  $\Delta G_f^* = \Delta G_f - \alpha z F \eta_c$   $\Delta G_r^* = \Delta G_r + (1 - \alpha) z F \eta_a$  $\alpha =$  Symmetry coefficient

For a cathodic case, the net current and the overpotential are  $i = i_f - i_r$  and  $\eta_c$ , respectively. Substituting eqs. (3.4) and (3.5) into this expression yields the net current density in a general form

$$i = k'_{f} \exp\left(-\frac{\Delta G_{f}}{RT}\right) \exp\left(\frac{\alpha z F \eta}{RT}\right)$$

$$-k'_{r} \exp\left(-\frac{\Delta G_{r}}{RT}\right) \exp\left[-\frac{(1-\alpha) z F \eta}{RT}\right]$$
(3.6)

from which the exchange current density is deduced as

$$i_o = k'_f \exp\left(-\frac{\Delta G_f}{RT}\right) = k'_r \exp\left(-\frac{\Delta G_r}{RT}\right)$$
(3.7)

Substituting eq. (3.7) into (3.6) for one-step reaction yields the well-known **Butler-Volmer equation** for polarizing an electrode from the open-circuit potential  $E_o$  under steady-state conditions

$$i = i_o \left\{ \exp\left[\frac{\alpha z F \eta}{RT}\right]_f - \exp\left[-\frac{(1-\alpha) z F \eta}{RT}\right]_r \right\}$$
(3.8)  
= E - E.

where  $\eta = E - E_o$ E = Applied potential

It is clear that overpotential depends on the applied current density; therefore,  $\eta = f(i)$ . In addition, the exchange current density  $(i_o)$  can be defined as the rate of oxidation and reduction reactions at equilibrium. Specifically,  $i_o$  is the current density at which the rate of oxidation and rate of reduction are equal in a state of equilibrium. Thus,  $i_o$  is just the reversible reaction rate at equilibrium and it is a kinetic parameter, whereas  $\Delta G$  is a thermodynamic parameter. In fact,  $i_o$  is very sensitive to electrode surface condition and it is temperaturedependent as indicated by eq. (3.8). Thus, one can generalize the Arrhenius equation, eq. (3.2), for a series of electrochemical reactions as follows [47]

$$i_{o,T,l} = i_{o,T_o,l} \exp\left[-\frac{\Delta G^*}{RT} \left(\frac{1}{T} - \frac{1}{T_o}\right)\right]$$
(3.9)

where  $i_{o,T,k}$  = Exchange current density at temperature T $i_{o,T_o,k}$  = Reference exchange current density at temperature  $T_o$ l = 1,2,3,4,... = Number of reactions.

This expression, eq. (3.8), is the general non-linear rate equation in terms of current density that most electrochemical cells obey under charge-transfer control. Thus,  $\eta = \eta_a = (E - E^o) > 0$  and  $\eta = \eta_c = (E - E^o) < 0$  are the anodic and cathodic overpotentials, respectively, which represent a deviation from the half-cell potential  $E^o$ , and E is the applied potential. In summary, the applied anodic current density is  $i = i_a - i_o$  at  $\eta_a > 0$  and the cathodic current density is  $i = i_c - i_o$  at  $\eta_c < 0$ . At equilibrium conditions, the potential is  $E = E^o$  and  $\eta = 0$ , and eq. (3.8) yields  $i_a = i_c = i_o$ . This implies that the rates of metal dissolution (oxidation) and deposition (reduction) are equal. However, a deviation from equilibrium of the half-cells is the normal case in real situations.

Furthermore, if one is interested in determining the total ionic molar flux Jdue to the mass transfer of a species j, then i = zFJ and

$$J = \frac{i_o}{zF} \left\{ \exp\left[\frac{\alpha z F \eta}{RT}\right]_f - \exp\left[-\frac{(1-\alpha) z F \eta}{RT}\right]_r \right\}$$
(3.10)

This ionic molar flux will be defined in details in Chapter 4. The reaction rate in terms of current density *i* given by eq. (3.8) is valid for one-step reaction. Hence, the controlling reaction may be part of a series of reaction steps, but the slowest reaction step is the rate-controlling. For any reaction, eq. (3.8) can be approximated by letting  $x = \alpha z F \eta / RT$  and  $y = (1 - \alpha) z F \eta / RT$ . Expanding the exponential functions according to Taylor's series yields

$$\exp(x) = \sum_{k=0}^{\infty} \frac{x^k}{k!} \simeq 1 + x \tag{3.11}$$

$$\exp(-y) = \sum_{k=0}^{\infty} \frac{(-y)^k}{k!} \simeq 1 - y$$
 (3.12)

Thus, eq. (3.8) can be expressed as a linear approximation when the overpotential is small in magnitude

$$i \simeq i_o \left[ (1 + \alpha z F \eta/RT) - (1 - (1 - \alpha) z F \eta/RT) \right]$$
(3.13)

$$i \simeq i_o \left(\frac{zF\eta}{RT}\right)$$
 (3.14)

Eq. (3.13) and (3.14) can be used for small values of overpotential like  $\eta < 0.01 \text{ V}$  [7]. However, one can take a different approach to approximate the current density by considering the following inequality

$$\exp\left[\frac{\alpha z F \eta}{RT}\right]_{f} >> \exp\left[-\frac{(1-\alpha) z F \eta}{RT}\right]_{r}$$
(3.15)

If this is the case, then eq. (3.8) yield

$$i = i_o \exp\left(\frac{\alpha z F \eta}{RT}\right) \tag{3.16}$$

Solving eq. (3.16) for the overpotential yields the Tafel equation

$$\eta = a + b \log\left(i\right) \tag{3.17}$$

where

$$a = -\frac{2.303RT}{\alpha zF} \log(i_o) \tag{3.18}$$

$$b = \frac{2.303RT}{\alpha zF} \tag{3.19}$$

In fact, eq. (3.17) yields a linear behavior when  $\eta = f[\log(i)]$  for either an anodic polarization or cathodic polarization analysis. With regard to reaction rates, let  $R_f$  and Rr be the forward (reduction) and reverse (oxidation) reaction rates, respectively and let  $K = K_f/K_r$  be the equilibrium constant. Thus,

$$\ln\left(K\right) = \ln\left(K_f\right) - \ln\left(K_r\right) \tag{a}$$

and from eq. (3.2),

$$\ln(K_f) = \ln(R_f) + \frac{\Delta G_f}{RT}$$
 (b)

$$\ln (Kr) = \ln (R_r) + \frac{\Delta G_r}{RT}$$
 (c)

Substituting eqs. (b) and (c) into (a) yields

$$\ln\left(K\right) = \ln\left(R_f\right) + \frac{A_f}{RT} + \ln\left(R_r\right) - \frac{A_r}{RT}$$
(d)

Differentiating eq. (d) with respect to the temperature T gives

$$\frac{d\ln\left(K\right)}{dT} = \frac{\Delta G_r}{RT^2} - \frac{\Delta G_f}{RT^2} = \frac{\Delta G^*}{RT^2}$$
(f)

Rearranging eq. (f) yields the activation energy [5]

$$\Delta G^* = RT^2 \cdot \frac{d\ln\left(K\right)}{dT} \tag{3.20}$$

In addition, Faraday's law of electrolysis describes the quantitative relationship for determining the rate of charge transfer in terms of current. Thus, the quantity of charge transferred (Q) at a time t is Q = It, and the quantity of moles for zF charge transfer is N = Q/zF. Now, the Faraday's weight loss or gain can be deduced by multiplying the number of moles, eq. (3.12b), by the atomic weight of metal M

$$W = NA_w = \frac{ItA_w}{zF} \tag{3.21}$$

**Example 3.1** Two identical zinc rods are exposed to HCl-base electrolyte. One rod is immersed at 25°C for 2 hours, while the other rod is at 50°C for 1 hour. Calculate the time of exposure of a third identical rod immersed the electrolyte at 30 °C.

#### Solution:

The zinc oxidation reaction is  $Zn \longrightarrow Zn^{+2} + 2e^-$  which requires an chemical activation energy to proceed in the written direction. The zinc rods are not polarized through an external circuit. Thus, the Arrhenius equation, eq. (3.2), yields

$$R_1 = 1/t_1 = \gamma_a \exp\left(-\frac{\Delta G^*}{RT_1}\right)$$
 (a)

$$R_2 = 1/t_2 = \gamma_a \exp\left(-\frac{\Delta G^*}{RT_2}\right)$$
 (b)

Dividing these equations gives

$$\frac{t_2}{t_1} = \exp\left[-\frac{\Delta G^*}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$
(c)

Then, at  $T_1 = 25 \,^{\circ}\text{C} = 298 \,\text{K}$  and  $t_1 = 2 \,\text{h}$  with  $R = 8.314510 \,\text{J}\,\text{mol}^{-1} \,\text{K}^{-1}$ and at  $T_2 = 50 \,^{\circ}\text{C} = 323 \,\text{K}$  and  $t_2 = 1 \,\text{h}$  the reaction rates are

$$R_1 = 1/t_1 = 0.50 \text{ h}^{-1}$$
  

$$R_2 = 1/t_2 = 1.00 \text{ h}^{-1}$$

Then, the activation energy becomes

$$\Delta G^* = -R\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \ln\left(\frac{t_2}{t_1}\right) \tag{d}$$

$$\Delta G^* = -8.314510 \,\mathrm{J}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}\,\left(\frac{1}{298\,\mathrm{K}} - \frac{1}{323\,\mathrm{K}}\right)^{-1}\ln\left(\frac{1\,\mathrm{h}}{2\,\mathrm{h}}\right)$$
$$\Delta G^* = 22,189.16\,\mathrm{J}\,/\,\mathrm{mol}$$

Substituting this energy into eq. (a) and solving for  $\gamma_a$  yields

$$\gamma_{a} = \frac{1}{2 h} \exp \left[ \frac{22,189.16 \text{ J/mol}}{(8.314510 \text{ J mol}^{-1} \text{ K}^{-1}) (298 \text{ K})} \right]$$
(e)  
$$\gamma_{a} = 3,875.05 \text{ h}^{-1}$$

@,  $T_3 = 30 \,^{\circ}\text{C} = 303 \,\text{K}$ , the time and rate of reaction are, respectively

$$R_3 = 1/t_3 = \gamma_a \exp\left(-\frac{A_e}{RT_3}\right) \tag{f}$$

$$t_3 = \frac{1}{\gamma_a} \exp\left(+\frac{A_e}{RT_3}\right) \tag{g}$$

$$t_{3} = \frac{1}{3,875.05 \,\mathrm{h^{-1}}} \exp\left[\frac{22,189.10 \,\mathrm{J/Mol}}{(8.314510 \,\mathrm{J\,mol^{-1}\,K^{-1}}) (303 \,\mathrm{K})}\right]$$
  

$$t_{3} = 1.73 \,\mathrm{h}$$
  

$$R_{3} = 1/t_{3} = 0.58 \,\mathrm{h^{-1}}$$

For comparison purposes, the reaction rates are

 $R_1 < R_3 < R_2$ 

**Example 3.2** Given the following data for a hypothetical metal undergoing chemical oxidation in a aqueous solution, a) plot the data (Arrhenius plot) and determine the activation energy from the plot and b) calculate the chemical rate at 308°C.

$T(\mathbf{K})$	$R_A (x10^{-2} h^{-1})$
298	50.01
300	50.26
305	50.88
310	51.48
315	52.08

#### Solution:

a) Using eq. (3.2) to curve fit the given data yields the resultant curve fitting equation

$$\ln (R_A) = 4.3046 \times 10^{-2} h^{-1} - (219.20 h^{-1} K^{-1})/T$$
$$R_A = 1.044 \exp \left(-\frac{219.20}{T}\right)$$

where  $\ln(\gamma_a) = 4.3046 \times 10^{-2} h^{-1}$  and the slope =  $219.20h^{-1}K^{-1}$ . The required Arrhenius plot is shown below.



b) If T = 308K, then  $\ln(R_A) = -0.66863$  and  $R_A \simeq 0.51 \ h^{-1}$ 

**Example 3.3** Determine the atomic weight of 82Mg - 10Al - 8Zn alloy.

#### Solution:

The state of oxidation and the atomic weight of each element are

$$\begin{array}{rcl} z_{Mg} &=& +2 & A_{w,Mg} = 24.31 \ g/mol & f_{Mg} = 0.82 \\ z_{Al} &=& +3 & A_{w,Al} = 26.98 \ g/mol & f_{Al} = 0.10 \\ z_{Zn} &=& +2 & A_{w,Zn} = 65.37 \ g/mol & f_{Zn} = 0.08 \end{array}$$

The atomic weight of the alloy is

$$A_{w,alloy} = \sum \frac{f_i A_{w,j}}{z_i}$$

$$A_{w,alloy} = \frac{f_{Mg} A_{w,Mg} + f_{Al} A_{w,Al} + f_{Zn} A_{w,Zn}}{z_{Mg} + z_{Al} + z_{Zn}}$$

$$A_{w,alloy} = 13.48 \ g/mol$$

### **3.3 POLARIZATION**

This section partially treats the copious literature for supporting the mathematical models for characterizing the kinetics of charge transfer mechanism involved in an electrochemical system. Thus, electrode reactions are assumed to induce deviations from equilibrium due to the passage of an electrical current through an electrochemical cell causing a change in the working electrode (*WE*) potential. This electrochemical phenomenon is referred to as polarization. In this process, the deviation from equilibrium causes an electrical potential difference between the polarized and the equilibrium (unpolarized) electrode potential known as overpotential ( $\eta$ ) [1].

Figure 3.2 shows a partial polarization diagram and related kinetic parameters. For instance, both Evans and Stern diagrams are superimposed in order for the reader to understand the significance of the electrochemical behavior of a polarized metal (M) electrode in a hydrogen-containing electrolyte.



Figure 3.2 Schematic polarization curve showing Tafel extrapolation.

From Figure 3.2,  $E_{o,H}$  and  $E_{o,M}$  are the open-circuit potentials for hydrogen and metal M, respectively,  $i_{o,H}$   $i_{o,M}$  are the exchange current densities, and  $i_L$ is the limiting current density.

For a reversible electrode, Evans diagram allows the determination of the corrosion point where both the hydrogen cathodic and the metal anodic line intercept. On the other hand, the irreversible electrochemical behavior denoted by the cathodic and anodic Stern diagram is also used for determining the corrosion point by simply extrapolating the linear portions of both curves until the

intercept as indicated in Figure 3.2. The latter diagram is a very common in electrochemical studies of pure metals and their alloys. Therefore, both Evans and Stern polarization diagrams provide the corrosion potential ( $E_{corr}$ ) and the corrosion current density ( $i_{corr}$ ). The other parameters illustrated in Figure 3.2 will become relevant as the electrochemical analysis advances in this chapter. With respect to the Stern diagram, this represents a polarization behavior that can be determined experimentally using potentiostatic and potentiodynamic methods, and it will be referred to as a polarization curve. Thus, a polarization curve is the result of polarizing from the corrosion potential anodically or cathodically and it is a very common experimental output in electrochemical studies on corroding electrodes.

Evaluation of corrosion behavior is normally done through a function that depends on kinetic parameters depicted in Figure 3.2. Hence, the current density function for polarizing an electrode irreversibly from the corrosion potential is similar to eq. (3.8). Hence,

$$i = i_{corr} \left\{ \exp\left[\frac{\alpha z F \eta}{RT}\right]_{f} - \exp\left[-\frac{(1-\alpha) z F \eta}{RT}\right]_{r} \right\}$$
(3.22)

where  $\eta = E - E_{corr}$ 

E = Applied potential (V)

 $\beta_a$  = Anodic polarization constant (Tafel anodic slope) (V)

 $\beta_{e}$  = Cathodic polarization constant (Tafel cathodic slope) (V)

Moreover, anodic polarization caused by an anodic overpotential  $\eta_a = (E - E_{corr}) > 0$  is referred to as an electrochemical process in which a metal surface oxidizes (corrodes) by losing electrons. Consequently, the metal surface is positively charged due to the loss of electrons. This electrochemical polarization is quantified by  $\eta_a$ . On the other hand, cathodic polarization requires that electrons be supplied to the metal surface at an negative overpotential,  $\eta_e = (E - E_{corr}) < 0$ , which implies that  $E < E_{corr}$ .

### **3.4 ACTIVATION POLARIZATION**

In general, the activation polarization is basically an electrochemical phenomenon related to a charge-transfer mechanism, in which a particular reaction step controls the rate of electron flow from a metal surface undergoing oxidation. This is the case in which the rate of electron flow is controlled by the slowest step in the half-cell reactions [1-4].

Despite that eq. (3.22) is a generalized expression, it represents a measure of anodic polarization for corrosion studies and indicates that  $\eta_a = 0$  for an unpolarized and  $\eta_a \neq 0$  for a polarized electrode surface. For the latter case, the reaction rate for activation polarization depends on the charge-transfer overpotential as in metal oxidation due to electrons loss, the diffusion overpotential as in mass transport of ions, the reaction overpotential due to rate determining chemical reaction mechanism, the crystallization overpotential as in metal

deposition in which atoms are incorporated into the electrode crystal surface lattice, and the Ohmic overpotential due to a resistance at the electrode/terminal junctions [2].

In general, the anodic metal undergoes a succession of reaction steps prior to dissolve in the electrolyte. This succession is hypothetically shown by the following idealized metal oxidation reactions during activation polarization

$$M_{lattice} \longrightarrow M_{surface}^{+z} \longrightarrow M_{solution}^{+z}$$
 (3.23)

This succession indicates that the metal M looses +z electrons on its surface and eventually the metal cation  $M^{+z}$  goes into solution. If the metal is silver undergoing oxidation, then the cation is just  $Ag^+$ . For iron, the succession may be  $Fe \rightarrow F^+ \rightarrow Fe^{+2} \rightarrow Fe^{+3}$ .

For hydrogen evolution, Fontana's idealized model [1] for activation polarization is depicted in Figure 3.3 can be used to explain the succession of the reaction steps that may take place after the hydrogen cations are adsorbed (attached) on the electrode surface. Hence, the possible reaction steps are

$$H^+ + e^- \longrightarrow H$$
 (Atomic hydrogen) (3.24a)

$$H + H \longrightarrow H_2$$
 (Hydrogen molecule) (3.24b)

$$H_2 + H_2 \longrightarrow 2H_2 \quad (\text{Gas bubble}) \quad (3.24c)$$

Thus, only one step in eq. (3.23) and one in eq. (3.24) controls the charge transfer for activation polarization. For instance, the formation of hydrogen gas bubbles on the metal electrode surface is the last step in the succession of reactions and eventually, the bubbles move to the surface of the electrolyte where they burst.



Figure 3.3 Activation polarization model after Fontana [1]

According to the model in Figure 3.3, the metal oxidation process can be represented by the following redox **stoichiometric reaction**  $M + 2H^+ = M^{+z} + H_2$ . On the other hand, if this reaction is reversed, then the metal  $M^{+z}$  cations in solution, specifically at the electrode/electrolyte interface, are deposited (plated) on the metal electrode. This is possible since electrons in the solution are supplied to the electrode surface. Thus, cathodic polarization occurs giving a negative overpotential,  $\eta_e < 0$ . In any event, anodic and cathodic reaction rates are assumed to be sufficiently slow.

### 3.5 POLARIZATION METHODS

The polarization resistance  $(R_p)$  of a metal/electrolyte system and the pitting or breakdown potential  $(E_b)$  can be determined using at least two-electrode system. Subsequently, the rate of metal dissolution or corrosion rate is calculated using a function of the form  $i_{corr} = f(\beta, R_p) > i_o$ . The methods are

- Linear Polarization (LP) as schematically shown in Figure 3.4 covers both anodic and cathodic portions of the potential *E* versus current density *i* curve for determining *R*<sub>p</sub>.
- Tafel Extrapolation technique (TE) (Figure 3.2) takes into account the linear parts of the anodic and cathodic curves for determining  $R_p$ .
- Electrochemical Impedance Spectroscopy (EIS) as schematically shown in Figure 3.10 requires an alternating current (AC) and the output is a Nyquist plot for charge-transfer or diffusion control process, which can be used to determine  $R_p$ , which in turn, is inversely proportional to the corrosion current density  $i_{corr}$ .

Standard or recommended experimental procedures for measurements of  $R_p$  can be found in the American Society for Testing Materials ASTM G-59 and ASTM G-106 testing methods, and ASTM G-5 is for anodic potentiodynamic studies, are included in the annual Book of ASTM Standards Vol. 03.02.

#### 3.5.1 LINEAR POLARIZATION

First of all, using eq. (3.8) under anodic and cathodic polarization individually, the Tafel slopes are derived by letting  $\exp\left[\frac{\alpha z F \eta}{RT}\right]_f >> \exp\left[-\frac{(1-\alpha)z F \eta}{RT}\right]$  for an anodic polarization analysis, where  $i_a >> |i_c|$  and  $\eta_a >> \eta_c$ . On the other hand,  $\exp\left[\frac{\alpha z F \eta}{RT}\right]_f << \exp\left[-\frac{(1-\alpha)z F \eta}{RT}\right]$  is for characterizing cathodic polarization when  $|i_c| >> i_a$  and  $\eta_c >> \eta_a$ . Under these conditions, eq. (3.8) reduces to

$$i_{a} = i_{o} \exp\left[\frac{\alpha z F \eta_{a}}{RT}\right] \qquad (\text{for } i_{a} >> i_{c}, \eta_{a} >> \eta_{c}) \qquad (3.25a)$$

$$i_c = -i_o \exp\left[-\frac{(1-\alpha)zF\eta_c}{RT}\right] \quad \text{(for } i_c >> i_a, \eta_c >> \eta_a\text{)} \quad (3.25b)$$

Solving eqs. (3.25) for the overpotential yields

$$\eta_a = \beta_a \log\left(\frac{i_a}{i_o}\right)$$
 (3.26a)

$$\eta_c = -\beta_c \log\left(rac{i_c}{i_o}
ight)$$
 (3.26b)

where  $\beta_a$  and  $\beta_c$  are known as Tafel slopes of the anodic and cathodic reactions, respectively. These slopes are defined by

$$\beta_a = \frac{2.303RT}{\alpha zF} = \frac{(1-\alpha)\beta_c}{\alpha}$$
 (3.27a)

$$\beta_c = \frac{2.303RT}{(1-\alpha)zF} = \frac{\alpha\beta_a}{(1-\alpha)}$$
(3.27b)

Additionally, if  $\alpha = 0.5$ , then  $\beta_a = \beta_c$ . Figure 3.4 shows a theoretical polarization curve for conducting polarization resistance measurements.



Figure 3.4 Schematic linear polarization curve.

The linear polarization is confined to a small magnitude of the overpotentials  $\eta_a$  and  $\eta_c$ , respectively, using linear coordinates. This technique allows the determination of  $i_{corr}$  using a potential range of  $\pm 10$  mV from the  $E_{corr}$  [3]. Prior to determining  $i_{corr}$ , the polarization resistance  $R_p$  is estimated from the linear slope of the curve (Figure 3.4) as

$$R_p = \frac{\Delta E}{\Delta i} = \frac{\eta}{\Delta i} \tag{3.28}$$

The corresponding corrosion current density depends on kinetic parameters since  $i_{corr} = f(\beta, R_p)$ . Thus, the simple linear relation that defines the corrosion current density is of the form

$$i_{corr} = \frac{\beta}{R_p} \tag{3.29}$$

where  $\beta = f(\beta_a, \beta_c)$ , and  $\beta_a$  and  $\beta_c$  are taken as positive kinetic parameters for determining  $i_{corr}$  of a corroding or oxidizing metallic material. Notice that eq. (3.29) predicts that the corrosion current density is very sensitive to changes in the polarization resistance. In fact, the magnitude of the polarization resistance is mainly controlled by the corrosion current density [1,46]. Hence,

$$\beta = \frac{\beta_a \beta_c}{2.303 \left(\beta_a + \beta_c\right)} \tag{3.30}$$

This constant  $\beta$  will be derived in the next section. In fact, this method requires knowledge of the Tafel anodic  $\beta_a$  and cathodic  $\beta_c$  slopes in order to calculate  $\beta$ , and subsequently predict  $i_{corr}$  using eq. (3.29). This  $i_{corr}$  expression is simple, but essential in corrosion measurements since  $i_{corr}$  can be converted to corrosion rate in units of mm/y, which are more convenient for engineering purposes after  $\beta$  and  $R_p$  are determined. finally, the values of these slopes are  $\beta_a < 1$  volt and  $\beta_c < 1$  volt, and  $\beta < 1$  volt.

#### 3.5.2 TAFEL EXTRAPOLATION

This method involves the determination of the Tafel slopes  $\beta_a$  and  $\beta_c$  as well as  $E_{corr}$  and  $i_{corr}$  from a single polarization curve as shown in Figure 3.2. This curve is known as the Stern diagram (non-linear polarization) based on eq. (3.22). The Evans diagram (linear polarization) is also included in order to show that both diagrams have a common  $E_{corr} \cdot i_{corr}$  point. This figure illustrates a hypothetical electrochemical behavior of a metal M immersed in an electrolyte containing one type of oxidizer, such as  $H^+$  ions.

For electrochemical systems containing several oxidizers, determining the corrosion point is more complex using the Evans diagram, but the Stern diagram would provided a similar polarization curve as shown in Figure 3.2, from which both  $E_{corr}$  and  $i_{corr}$  are easily determined by extrapolating the Tafel anodic and cathodic linear parts until they intersect as straight lines. Also included in Figure 3.2 are the exchange current densities,  $i_{o,H}$  and  $i_{o,M}$ , and their

counterpart potentials,  $E_{o,H}$  and  $E_{o,M}$ , for hydrogen evolution and metal oxidation, respectively. These potentials,  $E_{o,H}$  and  $E_{o,M}$ , are known as open-circuit potentials. Furthermore, the limiting current density  $i_L$  for cathodic polarization is included as an additional information one can extract from a cathodic polarization curve. The latter term will be dealt with in Chapter 5.

Further analysis of Figure 3.2 yields the following summary:

- The solid curve can be obtained statically or dynamically.
- This non-linear curve is divided into two parts. If  $E > E_{corr}$ , the upper curve represents an anodic polarization behavior for oxidation of the metal M. On the contrary, if  $E < E_{corr}$  the lower curve is a cathodic polarization for hydrogen reduction as molecular gas (hydrogen evolution). Both polarization cases deviate from the electrochemical equilibrium potential  $(E_{corr})$  due to the generation of anodic and cathodic overpotentials, which are arbitrarily shown in Figure 3.2 as  $\eta_a$  and  $\eta_c$ , respectively.
- Both anodic and cathodic polarization curves exhibit small linear parts known as Tafel lines, which are used for determining the Tafel slopes  $\beta_a$  and  $\beta_c$ . These slopes can be determined using either the Evans or Stern diagram.
- Extrapolating the Tafel or Evans straight lines until they intersect define the  $E_{corr} \cdot i_{corr}$  point.
- The disadvantage in using the Evans diagram is that the exchange current density  $(i_o)$ , the open-circuit potential  $E_o$  (no external circuit is applied), and the Tafel slopes for the metal and hydrogen have to be known quantities prior to determining the  $E_{corr} \cdot i_{corr}$  point.
- The advantage of the Stern diagram over the Evans diagram is that it can easily be obtained using the potentiodynamic polarization technique at a constant potential sweep (scan rate) and no prior knowledge of the above kinetics parameter is necessary for determining the  $E_{corr} \cdot i_{corr}$  point. The resultant curve is known as a potentiodynamic polarization curve.
- In conclusion,  $E_{corr}$  and  $i_{corr}$  can be determined from an Evans diagram for an **unpolarized metal** since  $i_{corr} = i_a = -i_c$  at  $E = E_{coor}$ . On the other hand, if the metal is **polarized**, then the Stern diagram can be used for determining  $E_{corr}$ ,  $i_{corr}$ ,  $\beta_a$ , and  $\beta_c$ . In addition,  $E_{corr}$  is a reversible potential also known as a mixed potential. Further analysis of the polarization phenomenon requires use of the Ohm's law. Hence, the cell and the inner potentials are defined by, respectively

 $\phi_s$ 

$$E = E_{corr} - \eta_a - \eta_c - \phi_s = IR_x \tag{3.31}$$

$$= IR_s \tag{3.32}$$

where I = Current(A)

 $R_x$  = External resistance (Ohm = V / A)  $R_s$  = Solution resistance (Ohm = V / A)  $\phi_s$  = Internal potential (V)

Solving eq. (3.31) for *I* yields

$$I = \frac{E_{corr} - \eta_a - \eta_c - IR_s}{R_x} \tag{3.33}$$

The current in eq. (3.33) strongly depends on the magnitude of the external resistance. A slight decrease in  $R_x$  increases the current *I*. Hence, if  $R_x \rightarrow 0$ , then  $I \rightarrow \infty$  and  $I \rightarrow 0$  when  $R_x \rightarrow \infty$ . In addition,  $IR_x \rightarrow 0$  as  $E \rightarrow 0$ .

With regard to eq. (3.32),  $\phi_s$  can be neglected due to its small contribution to the cell potential. However, the electrolyte conductivity is of significance in determining the governing current expression. For instance, when  $IR_x >> IR_s$ the electrolyte has a high conductivity and if  $IR_x << IR_s$  the electrolyte has a low conductivity. Hence, from eq. (3.33) the governing current expressions are

$$I = \frac{E_{corr} - \eta_a - \eta_c}{R_x} \quad \text{for } IR_x >> IR_s \quad (3.34a)$$

$$I = \frac{E_{corr} - \eta_a - \eta_c}{R_s} \quad \text{for } IR_s >> IR_x \quad (3.34b)$$

Nowadays, sophisticated instrumentation, such as a potentiostat/galvanostat is commercially available for conducting electrochemical experiments for characterizing the electrochemical behavior a metal or an alloy in a few minutes. Nevertheless, a polarization diagram or curve is a **potential control** technique. This curve can experimentally be obtained statically or dynamically. The latter approach requires a linear potential scan rate to be applied over a desired potential range in order to measure the current response.

On the other hand, a galvanostat can be used as the **current control** source for determining the potential response on a electrode surface. However, the potential control approach is common for characterizing electrochemical behavior of metallic materials. The potential can be applied uniformly or in a stepwise manner using a waveform. The former case generates a steady-state current response, while the latter provides a transient current response.

Further interpretation of the polarization curves can be extended using Pourbaix graphical work depicted in Figure 3.5 for pure iron (*Fe*). The resultant plots represent the functions E = f(i) and E vs.f[log(i)] for an electrolyte containing  $C_{Fe^{+2}} = 0.01 \ g/l = 1.79x10^{-4} \ mol/l = 1.49x10^{-7} \ mol/cm^3$  at pH = 0. Additionally, the reactions depicted in Figure 3.5 and some related kinetic parameters are listed in Table 3.2 for convenience. One important observation is that both anodic and cathodic Tafel slopes,  $\beta_a$  and  $\beta_c$ , respectively are equal numerically and consequently, Figure 3.5b has an inflection point at( $i_{corr}, E_{corr}$ ). This electrochemical situation is mathematically predicted and discussed in the next section using a current density function for a mixed-potential system.



Figure 3.5 Corrosion of iron (0.01 g/l) with hydrogen evolution at pH = 0 [46].

Table 3.2	Kinetic para	meters for	Iron $(0.0)$	(1g/l)
and hydro	gen reactions	at $pH = 0$	0 [46].	

and hjarogon reactions at pri o [10].				
Parameters	$Fe = Fe^{+2} + 2e^{-1}$	$2H^+ + 2e^- = H_2$		
$E^o (V_{SHE})$	-0.50	0		
$i_o (A/cm^2)$	$3.16x10^{-5}$	$1.41x10^{-6}$		
$\beta_a (V)$	+0.328	+0.123		
$\beta_c (V)$	-0.328	-0.123		

In fact, Figure 3.5 compares both linear and extrapolation results for iron. The interpretation of this figure is based on complete activation control in the absence of diffusion and external current [46]. Thus, it can be deduced from this figure that

- the net current density  $(i_{net} = i_a i_c)$  is zero at equilibrium, but the corrosion current density is  $i_{corr} = 0.1622 \ mA/cm^2$  at the corrosion potential,  $E_{corr} = -0.25 \ V_{SHE}$ .
- The polarization curves are reversible in nature; however, if irreversibility occurs, the heavy line in Figure 3.5a would follow the vertical axis at a potential range  $E_{o,c} \leq E \leq E_{o,a}$  when  $i_{net} = 0$ .
- The open-circuit potentials,  $E_{o,H}$  and  $E_{o,Fe}$ , can be estimated using the Nernst equation.

One important fact is that the solution must be continuously stirred to keep a uniform concentration of the species in solution; otherwise, the concentration at the electrodes become uneven and the open-circuit potential  $E_{c,Fe}$  increases during oxidation and  $E_{c,H}$  decreases during reduction. At equilibrium, the overpotential becomes  $\eta = E - E_o = 0$  since the applied potential and the applied current density are  $E = E_o$ , and  $i = i_o$ , respectively. However, if  $i > i_{o,Fe}$ , the iron reaction is irreversible because it corrodes by liberating electrons.

Combining the Pourbaix diagram and the polarization curves for iron in water at pH = 7 yields interesting information on the electrochemical state as shown in Figure 3.6, which includes the hydrogen and oxygen lines for comparison [46]. Observe the correspondence of potential between both diagrams. For instance, the potential at point A, indicates that corrosion occurs along line CP, but at point B the potential suggests that passivation occurs and iron is protected anodically. Point P is a transitional potential at the critical current density. Any slight change in potential iron passivates at  $E > E_p$  or corrodes at  $E < E_p$ . Also, If  $E < E_c$  Pourbaix predicts immunity, but the polarization curve indicates that corrosion is possible.

Furthermore, the advantage of the Pourbaix diagram as shown in Figure 3.6a is that it predicts the electrochemical state for immunity, corrosion, and passivation, and it is related to the polarization curve shown in Figure 3.6b. However, only the polarization curve predicts the corrosion rate through the current density  $i_{corr}$  for metal oxidation and the passivation rate through the passive current density for metallic cation reduction to form an oxide protective film on the electrode surface. The passivation phenomenon is discussed in details in Chapter 6.



Figure 3.6 Comparison of Pourbaix diagram and polarization curve for iron in water at pH = 7 and P = 101 kPa [46].

### **3.6 CORROSION RATE**

During corrosion (oxidation) process, both anodic and cathodic reaction rates are coupled together on the electrode surface at a specific current density known as  $i_{corr}$ . This is an electrochemical phenomenon which dictates that both reactions must occur on different sites on the metal/electrolyte interface. For a uniform process under steady state conditions, the current densities at equilibrium are related as  $i_a = -i_c = i_{corr}$  @  $E_{corr}$ . Assume that corrosion is uniform and there is no oxide film deposited on the metal electrode surface; otherwise, complications would arise making matters very complex. The objective at this point is to determine both  $E_{corr}$  and  $i_{corr}$  either using the Tafel Extrapolation or Linear Polarization techniques. It is important to point out that  $i_{corr}$  cannot be measured at  $E_{corr}$  since  $i_a = -i_c$  and current will not flow through an external current-measuring device [3].

When polarizing from the corrosion potential with respect to anodic or cathodic current density, the overpotential expressions given by eqs. (3.26a) and (3.26b) become

$$\eta_a = \beta_a \log\left(\frac{i_a}{i_{corr}}\right)$$
 (3.35a)

$$\eta_c = -\beta_c \log\left(\frac{i_c}{i_{corr}}\right)$$
 (3.35b)

Recall that  $\eta_a = \Delta E = (E - E_{corr}) > 0$  and  $\eta_a = \Delta E = (E - E_{corr}) < 0$  now represent the potential changes from the steady-state corrosion potential  $E_{corr}$ . Solving eqs. (3.35a) and (3.35b) for the anodic and cathodic current densities yields, respectively

$$i_a = i_{corr} \exp\left[\frac{2.303 \left(E - E_{corr}\right)}{\beta_a}\right]$$
(3.36)

$$i_c = i_{corr} \exp\left[-\frac{2.303 \left(E - E_{corr}\right)}{\beta_c}\right]$$
(3.37)

Assuming that the applied current density is  $i = i_a - i_c$  and substituting eqs. (3.36) and (3.37) into this expression yields the **Butler-Volmer equation** that quantifies the kinetics of the electrochemical corrosion

$$i = i_{corr} \left\{ \exp\left[\frac{2.303 \left(E - E_{corr}\right)}{\beta_a}\right] - \exp\left[-\frac{2.303 \left(E - E_{corr}\right)}{\beta_c}\right] \right\}$$
(3.38)

This expression resembles eq. (3.22), but it is a convenient expression at this point since the inverse polarization resistance is easily obtainable by deriving eq. (3.38) with respect to the applied potential *E*. Thus,

$$\left(\frac{di}{dE}\right) = 2.303i_{corr} \left\{ \begin{array}{c} \beta_a^{-1} \exp\left[2.303\left(E - E_{corr}\right)/\beta_a\right] \\ -\beta_c^{-1} \exp\left[-2.303\left(E - E_{corr}\right)/\beta_c\right] \end{array} \right\}$$
(3.39)

Further,

$$\left(\frac{d^2i}{dE^2}\right) = 5.3038i_{corr} \left\{ \begin{array}{c} \beta_a^{-2} \exp\left[2.303\left(E - E_{corr}\right)/\beta_a\right] \\ -\beta_c^{-2} \exp\left[-2.303\left(E - E_{corr}\right)/\beta_c\right] \end{array} \right\}$$
(3.40)

Let's set some conditions for eq. (3.40) such that

$$\left(\frac{d^2i}{dE^2}\right) \Rightarrow \begin{cases} <0 & \text{for } E = E \max > E_{corr} \\ =0 & \text{for an inflation point: } E = E_{corr} \\ >0 & \text{for } E = E_{\min} < E_{corr} \end{cases}$$
3.41

Evaluating eq. (3.40) at the inflation point yields

$$\left(\frac{d^2i}{dE^2}\right)_{E=E_{corr}} = 5.3038i_{corr} \left(\beta_a^{-2} - \beta_c^{-2}\right)$$
(3.42)

which clearly indicates that the inflection point is achieved if and only if  $\beta_a = \beta_c$ . This condition was pointed out by Oldham and Mansfield [13] as the mathematical proof for the  $E_{corr} \cdot i_{corr}$  point depicted in Figure 3.2.

Additionally, evaluating eq. (3.39) at  $E = E_{corr}$  yields the polarization resistance

$$\left(\frac{di}{dE}\right)_{E=E_{corr}} = 2.303i_{corr}\left(\frac{\beta_a + \beta_c}{\beta_a \beta_c}\right)$$
(3.43)

$$R_p = \left(\frac{di}{dE}\right)_{E=E_{corr}}^{-1}$$
(3.44)

Thus,

$$R_{p} = \frac{\beta_{a}\beta_{c}}{2.303i_{corr}\left(\beta_{a} + \beta_{c}\right)} = \frac{\beta}{i_{corr}}$$
(3.45)

Here,  $\beta$  is the proportionality constant defined by (3.30). Notice that  $R_p$  is inversely proportional to  $i_{corr}$  as indicated by eq. (3.45) and depicted in Figure 3.7a, but it can be linearized as shown in Figure 3.7b. Thus,

$$\log (R_p) = \log (\beta) - \log (i_{corr})$$
(3.46)

In general, a corroding metal is equivalent to a short-circuit cell or energyproducing system, in which energy dissipation occurs during the production of a corrosion product [3].



Figure 3.7 Non-linear and linear  $R_p$  plots.

Thus, metal oxidation is equivalent to metal corrosion. Now, dividing Faraday's rate of reaction, eq. (3.1), by the metal density  $\rho$  defines the corrosion rate (rate of metal dissolution) as

$$C_R = \frac{R_F}{\rho} \tag{3.47}$$

$$C_R = \frac{i_{corr} A_w}{z F \rho} \tag{3.48}$$

In addition, corrosion rate can be represent by the rate of weight loss [1] or rate of penetration [4], but eq. (3.48) is a mathematical model convenient for determining the metal dissolution in terms penetration per year in units of mm/y. These are common units to the engineers or designers.

**Example 3.4** Calculate the corrosion rate  $C_{\rm R}$  in units of mm/y, and the electrochemical rate constant in  $\mu g/cm^2.s$ , and  $mol/cm^2s$  for a low carbon steel plate (1cmx1cmx4cm) immersed in sea water. Given data:  $I = 110 \ \mu A$  (current),  $\rho = 7.87g/cm^3$  and  $A_w = 55.85 \ g/mol$ .

#### Solution:

Since the carbon steel is basically iron (Fe), the oxidation reaction involved in this problem is  $Fe \longrightarrow Fe^{+2} + 2e^{-}$  with z = 2 and F = 96,500  $A \cdot s/mol$ , and the exposed area is A = 1cmx1cm = 1  $cm^2$ . Then, the current density is  $i = I/A = 110x10^{-6}$  amps/1 cm<sup>2</sup>. Using eq. (3.48), the corrosion rate is

$$C_R = \frac{iA_w}{zF\rho} = \frac{(110x10^{-6} \ A/cm^2) \ (55.85 \ g/mol)}{(2) \ (96, 500 \ A \cdot s/mol) \ (7.87 \ g/cm^3)}$$
  
$$C_R = 4.04x10^{-9} \ cm/s = 1.28 \ mm/y$$

From eq. (3.1), the electrochemical rate constant is

$$R_F = \frac{iA_w}{zF} = \frac{(110 \ \mu A/cm^2) \ (55.85 \ g/mol)}{(2) \ (96, 500 \ A \cdot s/mol)}$$
$$R_F = 0.0318 \ \mu g/cm^2 s$$

Eliminating the atomic weight in eq. (3.1) yields

$$R_F = \frac{i}{zF} = \frac{(110 \ \mu A/cm^2)}{(2) \ (96, 500 \ A \cdot s/mol)}$$
$$R_F = 5.70x 10^{-10} \ mol/ \ (cm^2 \cdot s)$$

**Example 3.5** Assume that the rates of oxidation of  $\mathbb{Z}n$  and reduction of  $H^+$  are controlled by activation polarization. Use the data given below to a) plot the appropriate polarization curves and determine  $E_{corr}$  and  $i_{corr}$  from the plot. Calculate b) both  $E_{corr}$  and  $i_{corr}$  c) the corrosion rate  $C_R$  in mm/y, and the polarization resistance Rp in ohm  $\cdot cm^2$ . Data:

$Zn = Zn + 2e^{-} \Longrightarrow$	$E_{Zn} = -0.80 \mathrm{V}$	$i_{o,Zn} = 10^{-7} \ A/cm^2$
	$\beta_a = 0.10  \mathrm{V}$	$ ho=7.14{ m g}/{cm^3}$
	$A_w = 65.37\mathrm{g}/mol$	
$2H^+ + 2e^- = H_2 \Longrightarrow$	$E_H = 0.10 \mathrm{V}$	$i_{o,H} = 10^{-10} \ A/cm^2$
	$\beta_c = 0.10 \mathrm{V}$	

#### Solution:

a) E vs.  $\log(i)$  plot

1) Plot  $(i_{o,H}, E_H) = (\log 10^{-10} \ A/cm^2, 0.10 \text{ V})$ 

and  $(i_{o,Zn}; E_{o,Zn}) = (\log 10^{-7} \ A/cm^2, -0.80 \ V)$ 

2) Draw the hydrogen reduction and zinc oxidation lines with  $\beta_c$  and  $\beta_a$  slopes, respectively

3) The intercepting point defines the corrosion point as  $(i_{corr}, E_{corr}) = (10^{-4} \ A/cm^2, -0.50 \ V)$  for the unpolarized Zn metal. In addition,  $i_{corr} = i_a = i_c$  at  $E = E_{corr}$  and  $E_{o,Zn}$  and  $E_{o,H}$  are the open-circuit potentials, which can be determined using the Nernst equation, eq. (2.32).



Example 3.5

b) Using eqs. (3.26a) and (3.26b) with  $i_a = i_c = i_{corr}$ ,  $\eta_a = E - E_{o,Zn}$  and  $\eta_c = E - E_{o,H}$  yields

$$E = E_{o,Zn} + \beta_a \log \left( i_{corr} / i_{o,Zn} \right)$$
 (a)

$$E = E_{o,H} - \beta_c \log \left( i_{corr} / i_{o,H} \right)$$
 (b)

Equating eqs. (c) and (d) and solving for  $i_{corr}$  yields the corrosion current density

$$\log i_{corr} = \frac{1}{\beta_a + \beta_c} [E_{o,H} - E_{o,Zn} + \beta_a \log i_{o,Zn} + \beta_c \log i_{o,H}] \quad (c)$$

$$\log i_{corr} = \frac{0.1 + 0.8 + 0.1 \log 10^{-7} + 0.1 \log 10^{-10}}{0.2} = -4$$

$$i_{corr} = 10^{-4} A/cm^2$$

Letting  $E = E_{corr}$  and using eg. (a) or (b) gives  $E_{corr} = -0.50 V$ 

c) From eg. (3.48)

$$C_R = \frac{i_{corr} A_w}{zF\rho} = \frac{(10x10^{-4} \ A/cm^2) \ (65.37 \ g/mol)}{(2) \ (96, 500 \ A \cdot s/mol) \ (7.14 \ g/cm^3)}$$
$$C_R = 1.50 \ mm/y$$

d) From eq. (3.30),

$$\beta = \frac{\beta_a \beta_c}{2.303 (\beta_a + \beta_c)}$$
  
$$\beta = \frac{(0.10 \text{ V}) (0.10 \text{ V})}{2.303 (0.10 \text{ V} + 0.10 \text{ V})} = 0.0217 \text{ V}$$

and from eq. (3.45),

$$R_p = \frac{\beta}{i_{corr}} = \frac{0.0217 \text{ V}}{10^{-4} \text{ A/cm}^2}$$
$$R_p = 217 \text{ ohm} \cdot \text{cm}^2$$

**Example 3.6** A copper surface area,  $A = 100 \text{ cm}^2$ , is exposed to an acid solution. After 24 hours, the loss of copper due to corrosion (oxidation) is  $15x10^{-3}$  grams. Calculate a) the current density *i* in  $\mu A/cm^2$ , b) the corrosion rate  $C_R$  in mm/y, and c) the number of reactions per unit time. Use the data:  $A_w = 63.54 \text{ g/mol}, \rho = 8.96 \text{ g/cm}^3, q_e = 1.6022x10^{-19} \text{ C/reaction}.$ 

#### Solution:

*First of all, the corrosion process of copper can be represented by the following anodic reaction:* 

$$Cu \longrightarrow Cu^{+2} + 2e^{-}$$

where the valence is Z = +2. Thus,

a) According to Faraday's law the current density is

$$i = \frac{I}{A_s} = \frac{zFm}{A_s tA_w}$$
(3.49a)  

$$i = \frac{(2) (96,500 \ A.s/mol) (15x10^{-3} \ g)}{(100 \ cm^2) (24x3600 \ s) (63.54 \ g/mol)}$$
  

$$i = 5.27 \ \mu A/cm^2$$

b) From eq. (3.48),

$$C_R = \frac{iA_w}{zF\rho}$$

$$C_R = \frac{(5.27x10^{-6} \ A/cm^2) \ (63.54 \ g/mol)}{(2) \ (96, 500 \ A.s/mol) \ (8.96 \ g/cm^3)}$$

$$C_R = 0.06 \ mm/y$$

c) Recall that 1 C = A.s so that  $q_e = 1.6022x10^{-19}$  A.s/reactions. Thus, the number of reactions per time in seconds is

$$r = \frac{I}{Zq_e} = \frac{iA}{Zq_e}$$
(3.49b)  

$$r = \frac{(5.27x10^{-6} \ A/cm^2) (100 \ cm^2)}{(2) (1.6022x10^{-19} \ A.s/reactions)}$$
  

$$r = 1.64x10^{15} \ reactions/s$$

**Example 3.7** An electrochemical cell shown below was used as a concentration cell in order to measure the current due to the difference in ionic concentration between the anodic half-cell and the cathodic-half cell. Determine the corrosion rate in terms of electrons/second and the number of anodic reactions/second if the measured current is  $3.23x10^{-7} \mu A = 3.23x10^{-7}C/s$ .



Example 3.7 Ionic concentration cell.

#### Solution:

The oxidation of copper (corrosion) is due to the following anodic reaction:

 $Cu \longrightarrow Cu^{+2} + 2e^{-}$ 

and the reduction of copper (electroplating) is due to cathodic reaction

 $Cu^{+2} + 2e^{-} \longrightarrow Cu$ 

Clearly, the oxidation state is Z = 2. Thus, the corrosion rates are

$$r = \frac{I}{q_e}$$

$$r = \frac{3.23x10^{-7}C/s}{(1.6022x10^{-19} C/electrons)}$$

$$r = \approx 2x10^{12} \ electrons/s$$
(3.50a)

Also,

$$r = \frac{I}{Zq_e}$$
(3.50b)
$$r = \frac{3.23x10^{-7}C/s}{(2 \frac{electrons}{reactions})(1.6022x10^{-19} C/electrons)}$$

$$r = 10^{12} reactions/s$$

#### 3.7 IMPEDANCE SPECTROSCOPY

The electrochemical impedance spectroscopy (EIS) method is very useful in characterizing an electrode corrosion behavior. The electrode characterization includes the determination of the polarization resistance  $(R_p)$ , corrosion rate  $(C_R)$ , and electrochemical mechanism [1,4,6,19-28]. The usefulness of this method permits the analysis of the alternating current (AC) impedance data, which is based on modeling a corrosion process by an electrical circuit. Several review papers address the electrochemical impedance technique based on the AC circuit theory [22-24,29-30].

The EIS technique is based on a transient response of an equivalent circuit for an electrode/solution interface. The response can be analyzed by transfer functions due to an applied small-amplitude potential excitation at varying signals or sweep rates. In turn, the potential excitation yields current response and vice verse. In impedance methods, a sine-wave perturbation of small amplitude is employed on a corroding system being modeled as an equivalent circuit (Figure 3.8) for determining the corrosion mechanism and the polarization resistance. Thus, a complex transfer function takes the form

$$T = \frac{Output}{Input} \tag{a}$$

The transfer functions depend on the angular frequency and are expressed as impedance  $Z(\omega)$  and admittance  $Y(\omega)$ . It should be emphasized that  $Z(\omega)$  is the frequency-dependent proportionality factor of the transfer function between the potential excitation and the current response. Thus, for a sinusoidal current

perturbation, the transfer function is the system impedance  $[Z(\omega)]$  and for a sinusoidal potential perturbation, the transfer function is the system admittance  $[Y(\omega)]$ . Hence,

$$Z(\omega) = \frac{E(t)}{I(t)} = Z'(\omega) + jZ''(\omega)$$
(3.51a)

$$Y(\omega) = \frac{I(t)}{E(t)} = Y'(\omega) + jY''(\omega)$$
(3.51b)

where E(t)= Time-dependent potential (V) I(t) = Time-dependent current (A)  $\omega = 2\pi f$  = Angular frequency (Hz) f = Signal frequency (Hz)  $Z'(\omega), Y'(\omega)$  = Real parts  $Z''(\omega), Y''(\omega)$  = Imaginary parts t = Time (s)  $j = \sqrt{-1}$  = Imaginary operator  $j^2 = -1$ 

In addition, Ohm's law can be viewed in two different current imposition cases as per ASTM G-106 standard testing method. Hence,

$$E = IR \qquad For DC, f = 0 Hz \qquad (3.52)$$

$$E = I[Z(\omega)] \quad For \ AC, \ f \neq 0 \ Hz \tag{3.53}$$

Here,  $|Z(\omega)|$  is the magnitude of the impedance containing elements of an equivalent circuit, such as capacitors and inductors. Capacitors oppose or impede the current flow. In modeling an electrochemical system as an electrochemical circuit, a potential waveform is applied across the circuit and a current response to the frequency signal generates impedance data. Thus, the impedance data is related to a phase shift angle and a variation in potential and current amplitudes. This technique is a straightforward approach for analyzing the corrosion behavior of a metal [24]. Figure 3.8 shows two schematic electrochemical circuit models. For a charge-transfer control (Figure 3.8a), only the solution resistance ( $R_s$ ), polarization resistance ( $R_p$ ), and the capacitor ( $C_{dl}$ ) are needed in a simple circuit. On the other hand, if the electrochemical system is diffusion-control (Figure 3.8b), a diffusion impedance ( $Z_D$ ) is incorporated in the circuit.



Figure 3.8 Schematic electrochemical circuits.

The potential excitation and its current response are schematically shown in Figure 3.9 as sinusoidal excitations. The electrochemical impedance spectroscopy method is conducted according to the ASTM G-106 standard practice, in which a range of small-amplitude sinusoidal potential perturbation is applied to the electrode/solution interface at discrete frequencies. These frequencies cause an out of phase current response with respect to the applied sinusoidal potential waveform.

If a sinusoidal potential excitation is applied to the electrode/solution interface, the potential, current and impedance can be predicted as per Barn and Faulkner mathematical models [6]. Thus,

$$E(t) = I(t) Z(\omega) = E_o \sin(\omega t)$$
(3.54)

$$I(t) = I_o \sin(\omega t + \theta) \tag{3.55}$$

where  $E_o$ ,  $I_o$ = Constants

 $\theta$  = Phase shift angle between E(t) and I(t) $\omega = 2\pi f$  and 10  $Hz \le f \le 100 Hz$  (intermediate)



Figure 3.9 Schematic sinusoidal potential excitation.

The magnitude of  $Z(\omega)$  and  $Y(\omega)$  are

$$|Z(\omega)| = \sqrt{\left[Z(\omega)'\right]^2 + \left[Z(\omega)''\right]^2}$$
(3.56)

$$|Y(\omega)| = \sqrt{\left[Y(\omega)'\right]^2 + \left[Y(\omega)''\right]^2}$$
(3.57)

and the phase shift angle is defined as

$$\theta = \tan^{-1} \left[ Z\left(\omega\right)'' / Z\left(\omega\right) \right]$$
(3.58)

The fundamental characteristic of an AC signal in a simple electrochemical circuit (Figure 3.8a) is described by the impedance of the form [22,24]

$$Z\left(\omega\right) = \left[R_s + \frac{R_p}{1 - \omega^2 C^2 R_p^2}\right] - j \left[\frac{\omega C R_p^2}{1 - \omega^2 C^2 R_p^2}\right]$$
(3.59)

where C is the interfacial capacitance of a electrical double-layer at the electrode surface  $(Farad/cm^2)$ .

For low and high frequency amplitudes, eq. (3.59) yields

$$Z(\omega)_{o} = R_{s} + R_{p} \quad @ \omega = 0 \tag{3.60}$$

$$Z(\omega)_{\infty} = R_s \qquad @ \omega = \infty \qquad (3.61)$$

Combining eqs. (3.60) and (3.61) yields the polarization resistance as

$$R_{p} = Z(\omega)_{o} - R_{s} = Z(\omega)_{o} - Z(\omega)_{\infty}$$
(3.62)

which is the sought output in electrochemical impedance measurements. Equating eqs. (3.45a) and (3.62) yields the corrosion current density in terms of impedance

$$i_{corr} = \frac{\beta}{\left[Z\left(\omega\right)_{o} - Z\left(\omega\right)_{\infty}\right]}$$
(3.63)

Upon using Faraday's law, eq. (3.63) becomes

$$C_{R} = \frac{\beta A_{w}}{\left[Z\left(\omega\right)_{o} - Z\left(\omega\right)_{\infty}\right] ZF\rho}$$
(3.64)

Further analysis of eq. (3.59), together with eq. (3.52), yields the impedance equation of a circle [22]. Hence,

$$Y(\omega) = \frac{1}{Z(\omega)} = Y'(\omega) + jY''(\omega)$$
(3.65)

$$Y'(\omega) = \frac{R_s + R_p + (\omega C R_s R_p)^2}{(R_s + R_p)^2 + (\omega C R_s R_p)^2}$$
(3.66a)

$$Y''(\omega) = \frac{\omega C R_p^2}{(R_s + R_p)^2 + (\omega C R_s R_p)^2}$$
(3.66b)

and

$$Z'(\omega) = \frac{Y'(\omega)}{[Y'(\omega)]^2 + [Y''(\omega)]^2}$$
(3.67a)

$$Z''(\omega) = \frac{Y''(\omega)}{[Y'(\omega)]^2 + [Y''(\omega)]^2}$$
(3.67b)

Then, the equation of a circle for charge-control mechanism becomes [22]

$$\left[Z'(\omega) - \left(R_s + \frac{1}{2}R_p\right)\right]^2 + \left[Z''(\omega)\right]^2 = \left[\frac{1}{2}R_p\right]^2$$
(3.68)

The locus of eq. (3.68) is schematically shown in Figure 3.10 with a radius of  $R_p/2$ . This figure is known as the **Nyquist plot**, from which the maximum phase shift angle and polarization resistance become

$$\tan{(\theta)} \simeq \frac{|Z(\omega)|}{R_p/2} \quad (\nabla abc)$$
(3.69)

$$R_{p} \simeq \frac{2|Z(\omega)|}{\tan{(\theta)}}$$
(3.70)



Figure 3.10 Ideal Nyquist plot of impedance for the electrochemical circuit shown in Figure 3.10a. Charge-control mechanism.

Figure 3.11 shows Nyquist plots of a AISI 1030 steel immersed in phosphoric acid  $(H_3PO_4)$  containing butanol and thiosemicarbonate (TSC) at room temperature. These data is for a charge-control mechanism with and without the

TSC inhibitor [26]. Notice from this Figure 3.11 that the Nyquist impedance semicircles increase with increasing content of the TSC inhibitor. This implies that the polarization resistance  $(R_p)$  also increases with additions of this inhibitor, which in turn, decreases the corrosion rate  $(C_R)$  as indicated in Table 3.3.



Figure 3.11 Experimental Nyquist plots for AISI 1030 steel in  $35\% H_3PO_4 + 6\%$  butanol + TSC inhibitor at room temperature [26].

In addition, the double-layer capacitance  $(C_{dl})$  can be calculated using the following expression [31]

$$C_{dl} = 1/[\omega R_p] \tag{3.71}$$

Table 3.3 gives relevant experimental data extracted from the complex Nyquist plot elucidated in Figure 3.11.

TSC $(x10^{-4} M)$	$R_p (Ohm \ cm^2)$	$C_{dl} \left( \mu F/cm^2 \right)$	$C_R (mm/y)$
0	4.80	130.80	63.25
0.10	14.50	121.00	20.85
0.50	31.30	77.49	9.65
1.00	33.50	74.08	9.02
5.00	77.90	45.45	3.89
10.00	119.50	39.11	2.52

Table 3.3 Electrochemical impedance data for AISI 1030 steel [26].

On the other hand, Figure 3.12 shows schematic **Bode plots** for the circuit in Figure 3.8a with three polarization resistance values. This type of plots show the effect of angular frequency on the impedance and phase shift angle.



Figure 3.12 Hypothetical Bode plots using the equivalent circuit shown in Figure 3.10a. a) Impedance magnitude and b) phase angle [24].

When an electrochemical process is controlled by diffusion or film adsorption, the electrochemical system can be modeled using the ideal circuit shown in Figure 3.8b. In this case, a diffusion impedance  $(Z_D)$  is included in the circuit series and it is known as **Warburg impedance**. Notice that  $Z_D$  and  $R_p$  are connected in series. An ideal Nyquist-Warburg plot is shown in Figure 3.13



Figure 3.13 Schematic Nyquist-Warburg plot for diffusion control.

The interpretation of Figure 3.13 indicates that the 45° portion of the line corresponds to a low angular frequency range. In this case, the kinetics of the electrochemical system is limited by a diffusion-control process (concentration polarization). Also, extrapolating the semicircle (dashed curve) to intercept the real impedance axis  $Z(\omega)'$  graphically defines the polarization resistance  $R_p$ . A particular case for using  $Z_D$  is when diffusion through a surface film is the rate-controlling of carbon steel immersed in concentrated sulfuric acid ( $H_2SO_4$ ). Thus, iron (Fe) oxidizes and forms a  $FeSO_4$  film [25].

Figure 3.14 shows an experimental Nyquist-Warburg plot for a precipitation hardening (aged) 2195 Al-Li alloy. Notice that the semicircle is depressed due to a diffusion process, which is confirmed by the 45° line. The polarization resistance for this alloy is  $R_p = 140$  ohm in an aerated solution containing 3.5% NaCl at 21.5°C.

The diffusion impedance expression due the formation of a thin oxide film is define by [31-32]



Figure 3.14 Nyquist-Warburg plot for Wledalite 2195 Al-Li alloy.

where  $\sigma_w$  = Warburg impedance coefficient =  $RT/(zFAC_x\sqrt{2D})$ ,  $\delta$  = Thickness of the diffusion layer,  $C_x$  =Concentration of the specie in the diffusion layer and A = Exposed area.

For the 45° Warburg line in Figure 3.13,  $Z_D(\omega)$  becomes

$$Z_D(\omega) = \sigma_w \omega^{-1/2} \left( 1 - \frac{D}{\omega} \sqrt{\frac{\pi \delta_x}{4}} \right)$$
(3.74)

since  $\delta \left(\frac{j\omega}{D}\right)^{1/2} = \pi/4$  and from which  $j = (D/\omega) \sqrt{(\pi \delta_x)/4}$ .

Furthermore, the impedance of a depressed Nyquist plot due to surface roughness, dielectric inhomogeneities and diffusion is defined as the Cole-Cole impedance formula [33-36]. Hence,

$$Z(\omega) = \frac{R_p}{1 + (jR_pC_x)^n} \quad \text{for } 0 < n < 1$$
 (3.75)

### 3.8 CHARACTERIZATION OF ELECTROLYTES

Assume that an electrolyte solution contains positively and negatively charged ions (particles) with valence equals to  $z^+$  and  $z^-$ , respectively. If the solution has different type of ions, the number of cations  $(z^+)$  and anions  $(z^-)$  are, respectively

$$N^+ = \sum N_j^+ = \sum y_j^+ N_A$$
 (3.76a)

$$N^{-} = \sum N_{j}^{-} = \sum y_{j}^{-} N_{A}$$
 (3.76b)

where j = Represents species or ions of different valance  $y_i^+, y_j^- =$  Number of moles

Let an applied electrical field disturb the thermodynamical equilibrium so that the ions migrate a distance x from their initial position toward the electrode of opposite charge due to exerted electric forces on them as the charge carriers. Hence, an electrical mobility  $B_j$  generates in the solution. Consequently, the distance traveled by ions to the opposite charged electrode (Figure 3.15) is [5]

$$x_j^+ = v_j^+ dt \tag{3.77a}$$

$$v_j^- = v_j^- dt \tag{3.77b}$$

where  $v_j^+$  = Velocity of cations (*cm/s*)  $v_j^-$  = Velocity of anions (*cm/s*) dt = Infinitesimal change of time (*s*)

The number of ions that travel distance  $x_j$  is

$$N^+ = \sum \frac{N_j^+ x_j^+}{L}$$
 (3.78a)

$$N^{-} = \sum \frac{N_{j}^{-} x_{j}^{-}}{L}$$
 (3.78b)

where L = Distance between electrodes (Figure 3.15).

Recall that electrical conduction is a mass transport phenomenon, in which electrons and ions carry the electric charge due to their particular mobility within the electrically charged system. Hence, the charge (Q) that passes through the cross-section of the electrolyte solution (conductor) at time dt is related to the rate of flow of charge referred to as the current (I). It should be mentioned that the electrons carry the current through the wires and electrodes, while the ions carry the current through the solution.



Figure 3.15 Schematic cell showing the ionic travel distance.

This phenomenon implies that electrochemical reactions occur at the electrodesolution interface by transferring electrons from or to the electrode. For instance, if  $Cu^+ + 2e^- \Longrightarrow Cu$  occurs, this means that one mole of Cu is deposited on the electrode surface while 2 moles of electrons flow through the circuit. This situation resembles an electrolysis process in which the cation valence is  $z_{Cu}^+ = 2$ electrons. Nevertheless, if the current is kept constant, the charge (q) that flows through the circuit is

$$dq = Idt \tag{3.79}$$

The total charge crossing a plane parallel to the electrodes in time dt [5]

$$\frac{dq^{+}}{dt} = \frac{z_{j}^{+}q_{e}v_{j}^{+}N_{j}^{+}}{L}$$
(3.80a)

$$\frac{dq^{-}}{dt} = \frac{|z_{j}^{-}| q_{e} v_{j}^{-} N_{j}^{-}}{L}$$
(3.80b)

where  $q_e$  = Electron charge =  $1.602x10^{-19}$  C.

In addition, the current I and density (i) are

$$I = \frac{dq}{dt} \tag{3.81}$$

$$i = \frac{1}{A} \frac{dq}{dt}$$
(3.82)

Combining eq. (3.80) and (3.82) yields

$$i^+ = \sum \frac{z_j^+ q_e v_j^+ N_j^+}{V}$$
 (3.83a)

$$i^{-} = \sum \frac{|z_{j}^{-}| q_{e} v_{j}^{-} N_{j}^{-}}{V}$$
 (3.83b)

where V = AL = Volume of the solution  $(cm^3)$ .

The concentration (activity) of ions is

$$C_j^+ = \frac{1}{V} \sum y_j^+ \qquad (3.84a)$$

$$C_j^- = \frac{1}{V} \sum y_j^- \tag{3.84b}$$

Combining eqs. (3.10a), (3.76), (3.84) and (3.83) yields

$$i^+ = \sum z_j^+ F v_j^+ C_j^+$$
 (3.85a)

$$i^- = \sum z_j^- F v_j^- C_j^-$$
 (3.85b)

The total current density becomes  $i = i^+ + i^-$  as in electrolysis. Hence,

$$i = \sum z_j^+ F v_j^+ C_j^+ + \sum |z_j^-| F v_j^- C_j^-$$
(3.86)

The ionic velocity  $v_j$  for migration toward the electrode is small when compared with the random velocity  $v_r$  based on the translational kinetic energy in the absence of an electrical field [5]. This is mathematically shown below

$$\frac{3}{2}kT = \frac{1}{2}mv_{r,j}$$
 (3.87)

From eqs. (3.85) and (3.87),

$$v_{r,j}^+ = \sqrt{\frac{3kT}{m_j^+}} >> v_j^+ = \frac{i^+}{z_j^+ F v_j^+ C_j^+}$$
 (3.88a)

$$v_{r,j}^{-} = \sqrt{\frac{3kT}{m_j^+}} >> v_j^{-} = \frac{i^-}{z_j^- F v_j^- C_j^-}$$
 (3.88b)

where  $m_i^+$  = Mass of cations (species).

In addition, electroneutrality is achieved when the rate of charge for cations and anions balance and this is represented by  $dq^+/dt = dq^-/dt$ . However, the "quality "of the electrolyte to act as an aqueous electrical conductor can be characterized by its conductivity parameter  $K_c$ . For a one-dimensional analysis,  $K_c$  is

$$K_{c} = i/F_{x} = 1/\rho_{c}$$
(3.89)  
where  $K_{c}$  = Conductivity  $(ohm^{-1} \cdot cm^{-1})$   
 $\rho_{c}$  = Resistivity  $(ohm \cdot cm)$   
 $F_{x} = -d\phi/L \approx -\Delta\phi/L$  = Electrical force gradient  $(V/cm)$   
 $\phi$  = Electrical potential at a point in the electrolyte solution  $(V)$ 

Furthermore, the effectiveness of ion migration can be characterized by the ionic mobility  $(B_j)$  in the solution when an electrical force field acts on the ions. This implies that the ionic mobility is related to the electrolyte conductivity. This can be assessed by substituting eq. (3.86) into (3.89)

$$K_{c} = \frac{1}{F_{x}} \left( \sum z_{j}^{+} F v_{j}^{+} C_{j}^{+} + \sum |z_{j}^{-}| F v_{j}^{-} C_{j}^{-} \right)$$
(3.90)

$$K_{c} = \sum z_{j}^{+} F B_{j}^{+} C_{j}^{+} + \sum |z_{j}^{-}| F B_{j}^{-} C_{j}^{-}$$
(3.91)

since the ionic or electrical mobility is defined as

$$B_j = v_j / F_x \tag{3.92}$$

which has units of  $cm^2/(V \cdot s) = mol \cdot cm^2/(J \cdot s)$ . Normally, an electrochemical process is analyzed using a particular metal ion  $M^{+z}$  in solution. Assuming that this is the case, eq. (3.91) can be treated in a general form. Hence,

$$K_c = z_j F B_j C_j \tag{3.93}$$

Then,  $B_j$  and i become

$$B_j = \frac{K_c}{zFC_j} \tag{3.94}$$

$$i = zFv_jC_j \tag{3.95}$$

From this crude approximation, one can determine the diffusion coefficient or diffusivity of the metal cation  $M^{+z}$  as follows. Multiply both sides of eq. (3.94) by the Boltzmann constant k and the absolute temperature T so that

$$kTB_j = kT\frac{K_c}{zFC_j} \tag{3.96}$$

Notice that  $kTB_j$  is the Nernst-Einstein diffusion coefficient *D*, which is the rate of swept area of cations [45]. Hence, the Nernst-Einstein equation is

$$D = kTB_j \tag{3.97}$$

and

$$D = kT\left(\frac{K_c}{zFC_j}\right) \tag{3.98}$$

The subject of diffusion is well documented [37-45] and it is a manifestation of continues atom or ion motion at random from position to a neighboring position in the atomic structure of solids (S), liquids (L), and gases (G). Thus, the diffusivity is related to the atomic jump frequency and jump distance. However,  $D_L > D_s$  at a constant or the same temperature and diffusion in liquids differ from diffusion in solids since the geometry of atomic arrangement in liquids is not complete understood.

In addition, electrolytes and n-type semiconductors conduct current by transport of ions and electron, respectively. Both ions and electrons are the charge carriers for both sources. With regard to an electrolyte under the influence of an electrical field, it can be expected that ions drift through the bulk aqueous medium at a lower velocity than the electron velocity. However, the nature of the ions and their concentration influence both electrolyte conductivity  $K_c$  and ionic mobility  $B_i$  as predicted by eqs. (3.93) or (3.94). If a relatively low steady potential (voltage) is applied to electrodes, virtually current ceases to flow after the electrical double-layer capacitor  $C_{dl}$  is positively charged on the negative electrode surface and negatively charged on the opposite side at a distance  $\delta$ from the electrode surface. The charged double-layer acts as an electrical capacitor, which breaks down as the applied potential is increased beyond a critical potential for current flow to resume motion across the electrode-electrolyte interface. In this case, metal oxidation occurs at the positive electrode, while reduction occurs at the negative electrode. Consequently, current flow causes energy dissipation as heat in the electrolyte since the ions must overcome frictional forces during their motion through the medium [42].

### **3.9 ELECTROLYTE CONDUCTIVITY**

The influence of an electrical field on an electrolyte can also be characterized by measurements of the electrolyte electrical conductivity. In fact, electrolytes conduct current by the bulk ionic mass transport and charge carrier across the ionic

double-layer at the electrode surface. Consequently,  $K_c$  in eq. (3.96) strongly depends on the ionic concentration, temperature, and ionic mobilities. The application of an external potential along with an alternating current (AC) mode of frequency f causes current flow through the bulk electrolyte and charges the ionic double-layer (Figure 2.7) as a capacitor. If current flows, then dissipation of electrical energy arises as heat in the bulk electrolyte and electrical energy is stored in the double layer capacitor. The dissipation of energy is attributed to the frictional forces during ionic mobility caused by the inner potential ( $\phi$ ). Thus,  $\phi$  is the driving force for Faradaic processes (e.g. reduction and oxidation reactions) and electrolyte Ohmic resistance [42].

The Wheatstone bridge shown in Figure 3.16 can be used to determine the electrolyte resistance  $(R_s)$ . This is a classical technique reviewed by Braunstein -Robbins [42] who provided clear details on the current topic. Moreover, only one Wheatstone bridge case is briefly described hereafter.



Figure 3.16 Wheatstone bridge with a series RC circuit [42].

The  $K_c$  expression given by eq. (3.89) is redefined as [43]

$$K_c = \frac{L}{A_e} \frac{1}{R_s} = \frac{\lambda}{R_s}$$
(3.99)

where  $\lambda = L/A_e$  = Cell constant (cm<sup>-1</sup>)

L = Distance between electrodes (cm)

 $A_e$  = Cross-sectional area of the electrolytic conducting path ( $cm^2$ ).

According to Braunstein-Robbins [42], the Kholrausch method [43] can be used for evaluating  $K_c$ . In this method, the electrodes are electrolytically coated with colloidal platinum black in order to

- increase the electrode surface area
- reduce the polarization resistance that may develop and
- adsorb any gases produced during the cycle of the alternating current.

On the other hand, AC is used in order to avoid changes of electrolyte resistance due to changes in concentration of the electrolyte and buildup of electrolysis products at the electrode surfaces [5]. Subsequently,  $\mathbf{R}_s$  is measured at potential frequency (f) by adjusting the resistance  $\mathbf{R}_x$  so that the current and potential are in-phase, which require a variable external conductance ( $C_x$ ). Also included in the Wheatstone bridge is the double-layer capacitor (C). Let's use two different balance conditions.

1) If the capacitance  $C_x$  and C are excluded, then for a pure resistance case the potential across points  $\mathbf{B}_1\mathbf{D}_1$  is  $E_{B_1D_1} = 0$  and the potential balance according to Ohm's law is

$$I_1 R_1 = I_x R_x \tag{a}$$

$$I_1 R_2 = I_x R_s \tag{b}$$

Eliminating  $I_1$  from eqs. (a) and (b) yields

$$R_s = R_x R_2 / R_1 \tag{c}$$

Then, eq. (3.99) becomes

$$K_{c} = \frac{L}{A} \frac{1}{R_{s}} = \frac{\lambda R_{1}}{R_{x} R_{2}}$$
(3.100)

2) If the capacitance  $C_x$  and C are included, then the circuit is not a pure resistance case and the potential drop across points  $\mathbf{B_1D_1}$  is defined in terms of impedance. Hence,

$$Z(\omega)_{s} = Z'(\omega)_{s} + jZ''(\omega)_{s} = R_{s} - j\left(\frac{1}{\omega C}\right)$$
(3.101)

$$Z(\omega)_{x} = Z'(\omega)_{x} + jZ''(\omega)_{x} = R_{x} - j\left(\frac{1}{\omega C_{x}}\right)$$
(3.102)

This implies that  $Z(\omega)_s = Z(\omega)_x$ ,  $C = C_x$ , and  $R_s = R_x$ . Inserting  $Z'(\omega)_x$  and  $Z''(\omega)_x$  into eq. (3.56) gives

$$|Z(\omega)_x| = \sqrt{R_x^2 + 1/(\omega C_x)^2}$$
 (3.103)

Inserting eq. (3.103) into eq. (3.53) yields

$$E_x = I_x \sqrt{R_x^2 + 1/(\omega C_x)^2}$$
 (3.104)

For an AC case with  $f \neq 0$  Hz, eq. (3.99) becomes

$$K_c = \frac{\lambda}{|Z(\omega)_x|} \tag{3.105}$$

$$K_{c} = \lambda \left[ R_{x}^{2} + 1/\left(\omega C_{x}\right)^{2} \right]^{-1/2}$$
(3.106)

The potential expression given by eq. (3.104) can also be derive using complex function [42]. Hence,

$$E = E_o e^{(j\omega t)} \tag{3.107}$$

$$I = I_o e^{j\omega t} \tag{3.108}$$

The charge (q) stored in the double-layer capacitor  $(C_x)$  is related to the potential drop  $(E_c)$  across the capacitor as indicated below

$$q = C_x E_c \tag{3.109}$$

$$E_c = E - IR_x \tag{3.110}$$

Combining eqs. (3.109), (3.110) and (3.81) yields

$$I = C_x \frac{dE}{dt} - R_x C_x \frac{dI}{dt}$$
(3.111)

Now, using the complex functions defined by eqs. (3.107) and (3.108) on (3.111) gives

$$I_o e^{j\omega t} = j\omega C_x e^{j\omega t} - j\omega R_x C_x e^{j\omega t}$$
(a)

Thus,

$$E_{o} = I_{o} \left[ R_{x} - j \left( \frac{1}{\omega C_{x}} \right) \right] = I_{o} Z \left( \omega \right)$$
 (b)

Letting  $E_x = |E_o|$ ,  $I_x = |I_o|$ , and  $Z(\omega)_x = |Z(\omega)| = \sqrt{R_x^2 + 1/(\omega C_x)^2}$  yields the applied potential

$$E_x = I_x \sqrt{R_x^2 + 1/(\omega C_x)^2}$$
 (3.104)

#### 3.10 SUMMARY

In determining the rate of corrosion of a metal M, one needs to know the kinetic parameters prior to computing it. Thus, the current density function  $i = f(\eta, i_{corr}, \beta_a, \beta_c)$  allows the evaluation of the corrosion behavior under activation polarization at steady-state conditions. In order for polarization to occur on a metal surface, an overpotential  $\eta \neq 0$  must develop in the electrochemical system and it is defined by the Tafel equation. Three electrochemical methods were described for determining  $i_{corr}$ . For instance, the linear polarization method is applied at a small potential range of  $\Delta E \pm 10 \ mV$  from the  $E_{corr}$ value. This method provides result for  $i_{corr}$ ,  $R_p$ ,  $\beta_a$ , and  $\beta_c$ . On the other hand, the extrapolation method generates anodic and cathodic curves near the corrosion potential. These curves normally a small part of linearization from which the Tafel slopes are determined and extrapolation of the linear lines converge at  $E_{corr}$  where  $i_{corr}$  is defined. The third method deals with impedance spectroscopy measurements (ISM). It is based on a transient current response to a potential excitation. This method allows the determination of the impedance  $Z(\omega)$  as a measurement of the polarization resistance  $(R_p)$  and generates impedance data for modeling a corrosion process based on an electrochemical circuit containing resistances and capacitors. This impedance technique is based on AC circuit theory. The output of the impedance technique is a Nyquist plot for charge-transfer or Nyquist-Warburg plot for diffusion control.

Finally, mathematical models based on diffusion describe the generation of current density in a electrolyte solution in terms of ionic mobility and conductive capacity of the electrolyte. Hence, the Nernst-Einstein equation for diffusivity was determined.

#### 3.11 **PROBLEMS/QUESTIONS**

**3.1** What are the three conditions for galvanic corrosion to occur?

3.2 If the state of equilibrium of an electrochemical cell is disturbed by an applied current density  $i_x$ , then  $i_a = -i_c = i_{corr}$  no longer holds. Let  $i_x$  be a cathodic current density and the slope of the corresponding polarization curve be  $dE/d\log(i_x)$ , which increases approaching the Tafel constant  $\beta_c$ . Determine a) the value of  $i_x$  when  $i_c = 10^{-3} A/cm^2$  and  $i_a = 10^{-9} A/cm^2$  and b) the value of  $\beta_c$  when  $i_{corr} = 10^{-5} A/cm^2$  and  $\eta = -0.20 V$ . [Solutions: a)  $i_x = 10^{-3} A/cm^2$  and b)  $\beta_c = 0.10 V$ ].

**3.3** According to the Stockholm Convention Cell  $Fe|Fe^{+2}||H^+, H_2|Pt$ , the corrosion potential of iron (*Fe*) is  $-0.70 V_{SCE}$  at pH = 4.4 and  $25^{\circ}C$  in a deaerated (no oxygen is involved) acid solution. Calculate a) the corrosion rate in mm/y when

$$\begin{split} i_{o,H} &= 10^{-6} \ A/cm^2 & \beta_c = -0.10 \ V_{SHE} \\ i_{o,Fe} &= 10^{-8} \ A/cm^2 & E_{Fe} = -0.50 \ V_{SHE} \end{split}$$

b) the Tafel anodic slope  $\beta_a$  and c) draw the kinetic diagram *E vs.* log *i* [Solutions: a)  $C_R = 1.16 \ mm/y$ , b)  $\beta_a = 0.010 \ V_{SHE}$ ].

3.4	Let the foll	owing anodic	and cathodic	reactions	be, respe	ectively
M =	$M^{+2} + 2e^{-1}$	$E_M = -$	-0.941 V <sub>SCE</sub>	$i_{o,M} =$	$10^{-2} \mu$	$1/cm^2$
$2H^+$	$+2e^{-}=H_{2}$	$E_H = -$	$0.200 V_{SHE}$	$i_{o,H} = 0$	$0.10 \ \mu A/$	$cm^2$

where  $i_{corr} = 10^2 \ \mu A/cm^2$  and  $E_{corr} = -0.741 \ V_{SCE}$ . a) Construct the corresponding kinetic diagram and b) determine both  $\beta_a$  and  $\beta_c$  from the diagram and from the definition of overpotential equations. [Solutions: b)  $\beta_a = 0.05 \ V_{SHE}$  and  $\beta_c = 0.10 \ V_{SHE}$ ].

3.5 A steel tank is hot dipped in a deaerated acid solution of  $5x10^{-4}$  mol/cm<sup>3</sup> molality zinc chloride  $(ZnCl_2)$  so that a 0.15-mm zinc coating is deposited on the steel surface. This process produces a galvanized steel tank. Calculate the time it takes for the zinc coating to corrode completely at a pH = 4. Data:  $E_{Zn} = -0.8 V$ ,  $i_{o,Zn} = 10 \ \mu A/cm^2$ ,  $i_{o,H} = 10^{-3} \ \mu A/cm^2$ ,  $\beta_a = 0.08 V$ ,  $\beta_c = 0.12 V$ ,  $T = 25^{\circ}C$ . [Solution:  $t \simeq 0.40$  years].

**3.6** Calculate the activity and the corrosion rate of iron (*Fe*) immersed in an aerated aqueous solution of pH = 9. The dissociation constant for ferrous hydroxide,  $Fe(OH)_2$ , is  $1.64x10^{-14}$ . Given data:

$$\begin{split} i_{o,Fe} &= 10^{-2} \ \mu A/cm^2 & E_{corr} = -0.30 \ V \\ A_{w,Fe} &= 55.85 \ g/mol & \rho_{Fe} = 7.86 \ g/cm^3 \end{split} \qquad \beta_a = 0.10 \ V \\ \text{[Solution: } [Fe^{+2}] &= 1.64x10^{-4} \ mol/l \ \text{and} \ C_R = 232 \ \mu m/y]. \end{split}$$

3.7 Plot the anodic data given below and determine the polarization resistance  $(R_p)$  and the anodic Tafel slope  $(\beta_a)$  for a metal *M*. Use  $\beta_c = 0.07 V$  and  $i_{corr} = 0.019 \ A/cm^2$ .

$M = M^{+2} + 2e^{-1}$	$i~\left(\mu A/cm^2 ight)$	$E(V_{SHE})$
$2H^+ + 2e^- = H_2$	0.08	-0.32
	0.10	-0.30
	0.15	-0.25
	0.18	-0.22
	0.20	-0.20

[Solution:  $R_p = 1 \ ohm \cdot cm^2$  and  $\beta_a = 0.12 \ V$ ].

**3.8** Why does a pearlitic steel corrode rapidly in an acidic solution?

**3.9** Why will the tip and the head of an iron nail behave as anodes relative to the shank? See Figure 1.10a.

**3.10** It is known that the standard electrode potential  $(E^{\circ})$  for pure crystalline zinc is -0.763 V. Will this value change by cold working and impurities? Explain.

**3.11** An electrolyte contains a very low activity  $(8x10^{-9} mol/l)$  of silver cations  $(Ag^+)$  and an unknown concentration of copper cations. If the cell potential difference between the copper anode and the silver cathode is -0.04 V, determine a) which cation will be reduced (electroplated) on the cathode and b) the concentration of  $[Cu^{+2}]$  in g/l at 40°C. Neglect the effects of other ions that might react with silver. [Solution: a) Ag will be reduced and b)  $[Cu^{+2}] = 60.19 g/l]$ .

**3.12** Suppose that a cold worked copper electrode has 8,000 *J/mol* stored energy and it dissolves in an aqueous electrolyte. Calculate the overpotential.

**3.13** What is the significant differences between the overpotential  $(\eta)$  and the Ohmic potential (E)?

**3.14** If a sheet of zinc (Zn) is placed in hydrochloric acid (HCl), Zn goes into solution. Why?

**3.15** Calculate the equilibrium constant at  $25^{\circ}C$  for the electrochemical cell shown in Figure 2.4. [Solution:  $K = 1.64x10^{37}$ ].

3.16 Show that  $\Delta G = zF\beta_a \log(i_a/i_{corr})$  where the local potential *E* can be defined by the Nernst equation.

**3.17** If an electrochemical cell operates at 10 *amps*,  $25^{\circ}C$ , and 101 *kPa* for 30 minutes, calculate a) the number of moles and b) the weight of copper would be produced. [Solution: a) N = 0.093 moles and b) W = 5.93 grams].

**3.18** a) Derive the Arrhenius equation from the general definition of the activation energy of any rate reaction process and determine the Arrhenius constants if  $r_1 = 10^{11} s^{-1}$ ,  $r_2 = 4r_1$ ,  $T_1 = 200^{\circ}K$  and  $T_2 = 400^{\circ}K$ . b) Plot r vs.  $1/T @ 200^{\circ}K \le T \le 400^{\circ}K$ .

**3.19** Plot the given conductivity data vs. the aqueous  $Cu^{+2}SO_4^-$  concentration at 25°C and 1 *atm*. (The data was taken from Ref. [5]). Conduct a nonlinear regression analysis on these data and explain the resultant curve.

C	$K_c$
$(mol/cm^3)$	$(ohm^{-1} \cdot cm^{-1})$
$x10^{-6}$	x10 <sup>-3</sup>
0	0
25.00	3.00
50.00	5.10
75.00	7.40
100.00	8.50
102.50	10.00
105.00	12.00
107.50	14.00
200.00	15.00
202.50	16.00

**3.20** An electrochemical cell operates at a small overpotential and the corroding metal is exposed to a  $H^+$  ion-containing electrolyte. Use the given data

$\eta=0.005~V$	$T = 25^o C$
$i = 3.895  imes 10^{-8} \; A/cm^2$	$ ho=7.14~g/cm^3$
$i_o = 10^{-7} \; A/cm^2$	$D = 10^{-5} \ cm^2/s$
$C_R = 5.8277 x 10^{-4} mm/y$	

in order to determine a) the corroding metal by calculating the atomic weight  $A_w$  and determining its anodic reaction. Assume that there is a linear relationship between the current density and the overpotential. b) The activity of the corroding metal if  $a_{H^+} = 1 \ mol/l$ , c) the free energy change  $\Delta G$ . Will the reaction you have chosen occur?, d) the ionic velocity of the corroding metal. As a crude approximation, neglect the ionic velocity of other ions in solution, e) The ionic mobility  $B_e$  and f) electrolyte conductivity neglecting other ions present in the electrolyte. [Solution: b)  $6.77x10^{-4} \ mol/cm^3$ , d)  $v_i \simeq 2.98x10^{-10} \ cm/s$ ].

**3.21** If an electrochemical copper reduction process is carried out at 5 *amperes.* for 20 minutes, determine a) the electric charge (amount of coulombs of electricity), b) the number of electrons if there are  $1/(1.6022x10^{-19}) = 6.24x10^{18}$  electron/C, c)the number of moles, d) Faraday's weight reduced on a cathode, and the reduction rate (production rate in Chapter 7). Data:  $A_w = 63.55 \ g/mol$  and  $T = 35^{\circ}C$ . [Solutions: a)  $Q = 6,000 \ C$ , b)  $\simeq 4x10^{22}$  electrons, c)  $N = 0.0311 \ moles$ , d)  $W = 1.98 \ g$ , and e)  $P_R = 5.94 \ g/h$ ].

**3.22** Calculate the overpotential that causes hydrogen evolution on a flat platinum (*Pt*) electrode surface immersed in an acid solution, when the applied cathodic and exchange current densities are 6,000  $\mu A/cm^2$  and  $100 \mu A/cm^2$ , respectively. Assume a symmetry factor of 0.50 at room temperature (25°*C*). [Solution:  $\eta_c = -0.21 V$ ].

**3.23** Consider a discharge (chemical desorption) mechanism as the rate determining for  $Ni^{+2} + 2e^{-} = Ni$  at 25°C in a nickel battery. Calculate the cathodic Tafel slope per decade if the symmetry factor is 0.50, the exchange current density is constant, and the cathodic overpotential is  $\eta_c < 0$ . [Solution:  $\beta_c = -0.06 \ V/decade$ ].

**3.24** Plot the normalized current profile as a function of both symmetry factor ( $\alpha$ ) and overpotential; that is,  $i/i_o = f(\alpha, \eta)$  when the oxidation state is defined is z = 2 and  $\alpha = 0.35$ , 0.50 and 0.75 at room temperature (25°C). Explain the polarization behavior very succinctly.

**3.25** Calculate the number of moles and mass of a) the battery zinc (Zn) casing and b) the manganese dioxide  $(MnO_2)$  in the electrolyte if the battery has a stored energy of **36** kJ/V and a power of 3 *Watts*. Calculate c) the time it takes to consume the stored energy if the battery operates at a current of 2 A and d) the potential (voltage). The thickness of the cell casing is x = 1 mm and other dimensions are indicated below. The discharging reaction is



 $MnO_2 + H^+ + e \rightarrow MnOOH$ 

[Solution: a) 40.34 g and 0.62 moles, b) 0.37 moles and 32.17 g, c) 5 h and 1.5 V]

**3.26** A plate of pure nickel (Ni) oxidizes in an electrochemical cell containing an acid solution at 25°C. The total surface area of the nickel plate is 100 cm<sup>2</sup>. If  $2x10^{16}$  electrons per second are relieved on the plate surface, then calculate a) the corrosion rate in mm/y and b) the mass of nickel being lost in a year. [Solution: a)  $C_R = 0.35 mm/y$  and b) m = 31.15 g].

**3.27** Use the data listed in Table 3.3 to perform a least squares analysis and subsequently, determine the polarization proportionality constant  $\beta$ . Let the atomic weight and the density of the steel be  $A_{w,steel} \simeq A_{w,Fe} = 55.85$  g/mol and  $\rho = 7.85$  g/cm<sup>3</sup>, respectively. [Solution:  $\beta = 0.03$  V].

**3.28** Equal amounts of  $CuSO_4$  and  $NiSO_4$  are dissolved with water to make up an electrolyte. Hypothetically, the ion velocities and concentrations are

$$v_{Cu^{+2}} = 0.22 \ cm/s$$
  $C_{Ni^{+2}} = 10^{-5} \ mol/cm^3$   
 $v_{SO_4^{-2}} = 0.1 \ cm/s$   $C_{SO^{-2}} = 10^{-5} \ mol/cm^3$   
 $C_{Cu^{+2}} = 10^{-5} \ mol/cm^3$ 

If the current density is  $1 \ A/cm^2$ , calculate the velocity of the nickel ions  $(Ni^{+2})$ . [Solution: 0.20 cm/s].

**3.29** An electrochemical cell operates at 10 *A*,  $R_x = 0.25$  ohm, and  $\omega = 50$  *Hz*. Determine a) the electrolyte resistance  $(R_s)$ , b) the potential  $E_x$  when the external resistance and the capacitance are  $R_x = 0.25$  ohm and  $C_x = 20$  *A.s/V* at 30°*C* and c) the electrolyte conductivity  $K_c$ . The distance between electrodes is L = 15 cm and the effective electrode surface is A = 8,000 cm<sup>2</sup>. [Solution: a)  $Z(w)_x = 0.25$  ohm, b)  $E_x = 2.5$  V and c)  $K_c = 7.50x10^{-3}$  ohm<sup>-1</sup>.cm<sup>-1</sup>].

**3.30** Determine and analyze the impedance profile by varying the angular frequency for fixed  $R_x = 0.25$  ohm and  $C_x = 20$  A.s/V.

**3.31** Assume that an electrolytic cell is used for recovering nickel from a solution containing  $10^{-4} \ mol/cm^3$  of  $Ni^{+2}$  at 35° C. The nickel ionic mobility and the electric-field strength are  $B = 55x10^{-5} \ cm^2V^{-1}s^{-1}$  and  $F_x = 10 \ V/cm$  [Taken from reference 5], respectively, calculate a) the ionic velocity (v), b) the solution electric conductivity  $(K_c)$  and the electric resistivity  $(\rho_c)$ . [Solution: a)  $v = 0.0055 \ cm/s$ , b)  $K_c = 0.0106 \ ohm^{-1}.cm^{-1}$  and c)  $\rho_c = 94.21 \ ohm.cm$ ].

**3.32** It is known that current flows when there exists a gradient of electric potential  $(d\phi/dx)$  within an electric conductor, such as an electrolyte. Consider a current-carrying homogeneous conductor with constant cross-sectional area  $(A_c)$  so that the electric-field strength  $(E_x)$  is constant at every point in the conductor. Derive an expression for the current as a function of the gradient of electric potential. In this particular problem "x" stands for direction as well as length of the electric conductor. Start with the following current density definition  $i = K_c E_x$ , where  $K_c$  is the electric conductivity  $(ohm^{-1}.cm^{-1})$ .

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