POLARIZATION AND CORROSION RATES

POLARIZATION

When there is no net current from an electrode. Then this electrode is at equilibrium state and its potential is the equilibrium potential (E^0) . When net current flows to or from is surface , the potential change from E^0 to $E_{i,}$ the electrode is then said to be polarized and the process is termed as polarization , the polarization is measured in volts as follows :-

$$\eta = E - E_o$$

Polarization divided into three main types :-

1- Activation Polarization ( )

Activation polarization is caused by a slow electrode reaction or another way the electrical reaction for which an activation energy in the form of potential is required for the reation to proceed.

. For example, consider the reduction of hydrogen ions:-

$$2H^+ + 2e^- \rightarrow H_2$$

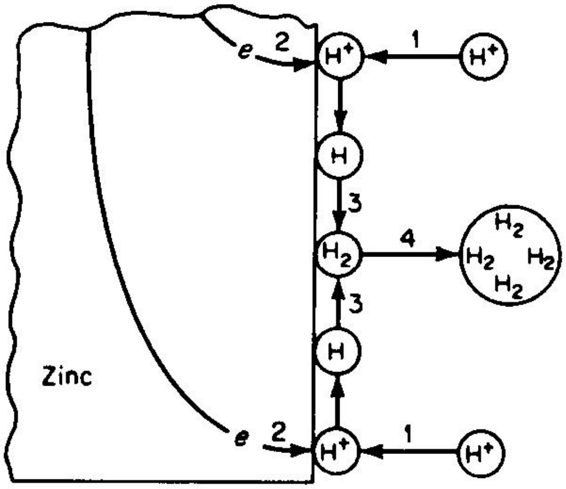
Hydrogen evolution occurs in four major steps:

1- Adsorption of hydrogen ion from solution to metal electrode

2- Electron transfer from zinc to form hydrogen atom

3- Combining of two hydrogen atoms to form a molecule of hydrogen

4- The coalescence of many hydrogen molecules to form a bubble



Factors Affecting Activation Polarization :-

1- **Current Density:** Activation polarization increases with current density

2- **Materials:** Activation polarization varies with one metal to another

3- **Surface Roughness**: Activation polarization is high on a smooth surface compared to a shiny surface

4- **Temperature:** Increased temperatures decrease polarization

5- **Pressure:** Hydrogen over-voltage increases rapidly with decreasing pressure.

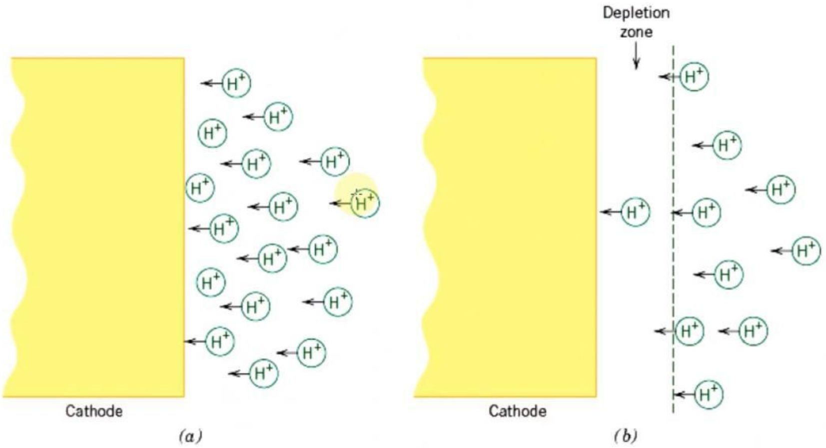
6- **pH:** Over-voltage increase initially and decreases with increased pH value.

7- **Agitation:** It has no effect on activation polarization

2- Concentration Polarization ( )

Concentration Polarization is obtained When the rate of electrode reaction is dependent on mass transfer

Consider the hydrogen reaction at low reduction rate the distribution of hydrogen ions to electrode is uniform , while at high reduction rate will be depleted hydrogen .



Effect of Various Factors on Concentration Polarization:

1- **Agitation:** By agitation, the thickness of the diffusion layer is decreased,

2- **Temperature:-** As the temperature rises, the thick nests of diffusion layer is decreased and the corrosion current is increased.

3- **Velocity:-** The higher the velocity, the less is con concentration polarization. At a sufficiently high velocity, concentration polarization becomes zero

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4- Combined polarization

Is the total polarization of electrode is the sum of activation and concentration

Corrosion Rates Measurements From polarization

There are two technique used in corrosion rate measurements :-

1- Linear Polarization technique :-

The Linear Polarization technique in principle is a convenient and rapid way for determining corrosion rate . The Wanger and Traud represented by :-

$$i = i_{Corr.}\left[\exp\left(\frac{\eta}{b_a}\right) - \exp\left(-\frac{\eta}{b_c}\right)\right] \qquad (1)$$

Equation (1) is derived and simplified by stern and geary and become :-

$$\frac{\Delta E}{\Delta i_{app.}} = \frac{b_a\, b_c}{2.303\, I_{corr.}\,(b_a + b_c)} \qquad (2)$$

b_a & b_c is anode and cathode Tafel slopes

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The stern and geary need anode and cathode Tafel slopes for accurate measurment then assume the values of Tafel slopes in range of 120 mv then the equation reduced to :-

$$\frac{\Delta E}{\Delta i_{app.}} = \frac{0.026}{I_{corr.}} \Rightarrow I_{corr.} = \frac{0.026}{R_p} \qquad (3)$$

The polarization resistance (RP) can determine by :-

$$R_p = d\eta / d_i$$

$$\left[\frac{di}{d\eta}\right] = -i^{o}\,\frac{\alpha nF}{RT}$$

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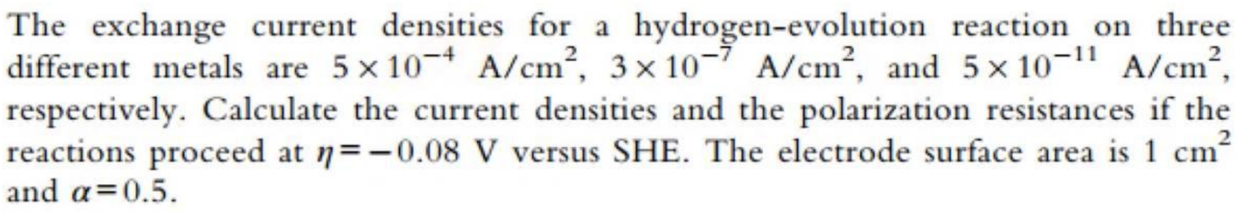
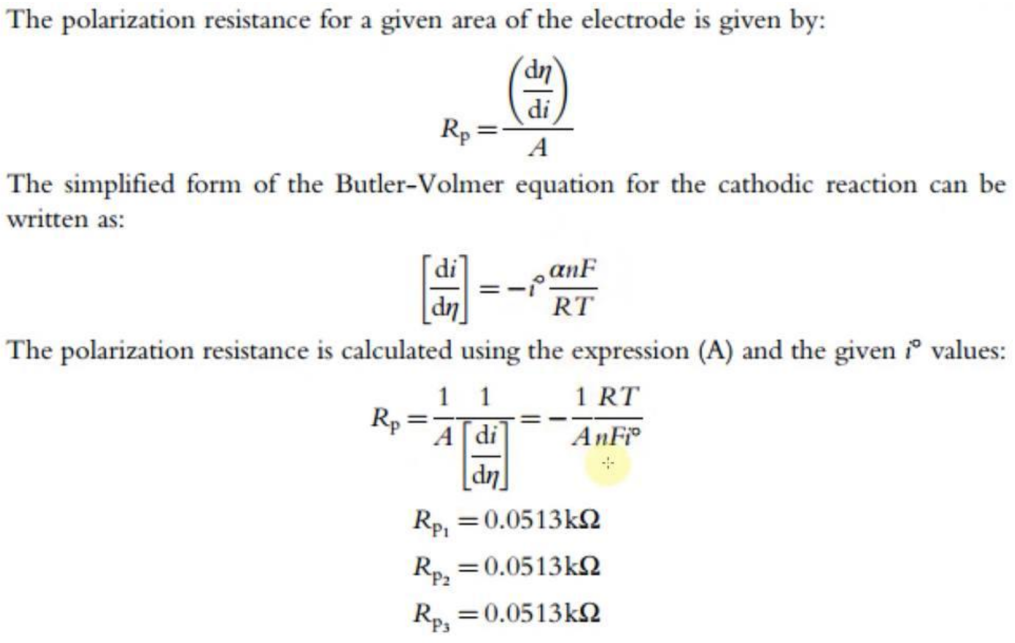
Example 1



The exchange current densities for a hydrogen-evolution reaction on three different metals are 5×10^{-4} A/cm^2, 3×10^{-7} A/cm^2, and 5×10^{-11} A/cm^2, respectively. Calculate the current densities and the polarization resistances if the reactions proceed at $\eta = -0.08$ V versus SHE. The electrode surface area is 1 cm^2 and $\alpha = 0.5$.

SOLUTION



The polarization resistance for a given area of the electrode is given by:

$$R_p = \frac{\left(\frac{d\eta}{di}\right)}{A}$$

The simplified form of the Butler-Volmer equation for the cathodic reaction can be written as:

$$\left[\frac{di}{d\eta}\right] = -i^\circ \frac{\alpha nF}{RT}$$

The polarization resistance is calculated using the expression (A) and the given i° values:

$$R_p = \frac{1}{A}\frac{1}{\left[\frac{di}{d\eta}\right]} = -\frac{1}{A}\frac{RT}{nFi^\circ}$$

$$R_{p_1} = 0.0513\text{k}\Omega$$

$$R_{p_2} = 0.0513\text{k}\Omega$$

$$R_{p_3} = 0.0513\text{k}\Omega$$

Example 2

Calculate the corrosion currents for the metals in **above** Example using the Stearn-Geary equation for cathodic and anodic Tafel slopes of $b_c = -0.1$ V and $b_a = 0.1$ V. Estimate the corrosion rates in mpy.

SOLUTION

Corrosion currents:

$$I_{\mathrm{corr}} = \frac{b_a \times b_c}{2.3(b_a + b_c)} \times \frac{1}{R_p}$$

$$I_{\mathrm{corr}_1} = \frac{0.1\,\mathrm{V} \times 0.1\,\mathrm{V}}{2.3 \times (0.1\,\mathrm{V} + 0.1\,\mathrm{V})} \times \frac{1}{51.3\Omega} = 4.24 \times 10^2\,\mu\mathrm{A/cm^2}$$

$$I_{\mathrm{corr}_2} = \frac{0.1\,\mathrm{V} \times 0.1\,\mathrm{V}}{2.3 \times (0.1\,\mathrm{V} + 0.1\,\mathrm{V})} \times \frac{1}{8.56 \times 10^4\Omega} = 2.54 \times 10^{-1}\,\mu\mathrm{A/cm^2}$$

$$I_{\mathrm{corr}_3} = \frac{0.1\,\mathrm{V} \times 0.1\,\mathrm{V}}{2.3 \times (0.1\,\mathrm{V} + 0.1\,\mathrm{V})} \times \frac{1}{5.13 \times 10^8\Omega} = 4.20 \times 10^{-5}\,\mu\mathrm{A/cm^2}$$

Corrosion rates:

$$\mathrm{C.R}_1 = \frac{0.131 \times (4.24 \times 10^2) \times (\mathrm{E.W}_1)}{d_1}$$

$$\mathrm{C.R}_2 = \frac{0.131 \times (2.54 \times 10^{-1}) \times (\mathrm{E.W}_2)}{d_2}$$

$$\mathrm{C.R}_3 = \frac{0.131 \times (4.20 \times 10^{-5}) \times (\mathrm{E.W}_3)}{d_3}$$

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Example 3

The linear polarization slope for a tin electrode measured in tomato juice is 5 mV/(μA/cm^2). Calculate the corrosion rate in (g/m^2 day). Assume $b_a = b_c = \pm 0.1$ V.

SOLUTION

$$R_p = \frac{\Delta E}{\Delta i} = 5\frac{\text{mV}}{\mu\text{A/cm}^2} \qquad I_{\text{corr}} = \frac{b_a \times b_c}{2.3(b_a + b_c)} \times \frac{\Delta i}{\Delta E} \qquad I_{\text{corr}} = \frac{0.01\,\text{V}^2}{0.46\,\text{V}} \times \frac{\mu\text{A/cm}^2}{5\,\text{mV}} \times \frac{1000\,\text{mV}}{1\,\text{V}}$$

$$I_{\text{corr}} = 4.348\,\mu\text{A/cm}^2$$

$$\text{CR} = \left[4.348\,\mu\text{A/cm}^2\right]\left[\frac{118.710(\text{g/mol})}{2(\text{eq/mol})}\right] \times \frac{1\,\text{cm}^2}{1 \times 10^{-4}\,\text{m}^2} = 2.581 \times 10^6\,\frac{\mu\text{Ag}}{\text{eq}\,\text{m}^2}$$

$$\text{CR} = 2.581 \times 10^6\left(\frac{\mu\text{Ag}}{\text{eq}\,\text{m}^2}\right) \times \left(\frac{1\,\text{eq}}{96{,}487\,\text{C}}\right) \times \left(\frac{1\,\text{C}}{1 \times 10^6\,\mu\text{A}\,\text{s}}\right) \times \left(\frac{3600\,\text{s}}{1\,\text{h}}\right) \times \left(\frac{24\,\text{h}}{1\,\text{day}}\right) = 2.31\,\text{g/m}^2\text{day}$$

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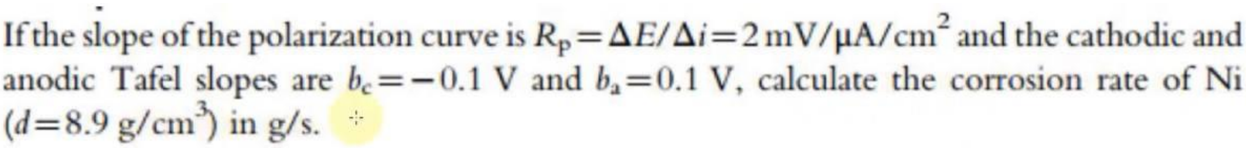
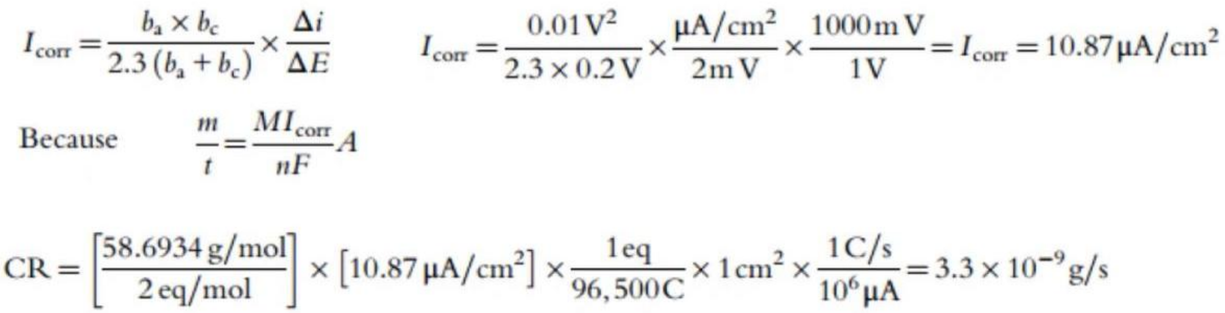
Example4



If the slope of the polarization curve is $R_p = \Delta E/\Delta i = 2\,\text{mV}/\mu\text{A/cm}^2$ and the cathodic and anodic Tafel slopes are $b_c = -0.1$ V and $b_a = 0.1$ V, calculate the corrosion rate of Ni ($d = 8.9\,\text{g/cm}^3$) in g/s.

SOLUTION



$$I_{\text{corr}} = \frac{b_a \times b_c}{2.3\,(b_a + b_c)} \times \frac{\Delta i}{\Delta E} \qquad I_{\text{corr}} = \frac{0.01\,\text{V}^2}{2.3 \times 0.2\,\text{V}} \times \frac{\mu\text{A/cm}^2}{2\text{m V}} \times \frac{1000\text{m V}}{1\text{V}} = I_{\text{corr}} = 10.87\,\mu\text{A/cm}^2$$

$$\text{Because} \qquad \frac{m}{t} = \frac{MI_{\text{corr}}}{nF}A$$

$$\text{CR} = \left[\frac{58.6934\,\text{g/mol}}{2\,\text{eq/mol}}\right] \times \left[10.87\,\mu\text{A/cm}^2\right] \times \frac{1\,\text{eq}}{96{,}500\,\text{C}} \times 1\,\text{cm}^2 \times \frac{1\,\text{C/s}}{10^6\,\mu\text{A}} = 3.3 \times 10^{-9}\,\text{g/s}$$

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