# CORROSION KINETICS

## FARADAY'S LAWS OF ELECTROLYSIS AND ITS APPLICATION IN DETERMINING THE CORROSION RATE

The classical electrochemical work conducted by Michael Faraday in the nineteenth century produced two laws published in 1833 and 1834 named after him. The two laws can be summarized below.

**The First Law**:

The mass of primary products formed at an electrode by electrolysis is directly proportional to the quantity of electricity passed. Thus:

$$m \propto It \text{ or } m = ZIt \quad (1)$$

where

I= current in amperes

t = time in seconds

m = mass of the primary product in grams

Z = constant of proportionality (electrochemical equivalent). It is the mass of a substance liberated by 1 ampere-second of a current (1 coulomb).

**The Second Law:**

The masses of different primary products formed by equal amounts of electricity are proportional to the ratio of molar mass to the number of electrons involved with a particular reaction:

$$m_1 \propto \frac{M_1}{n_1} \propto Z_1 \qquad \text{.....2}$$

$$m_2 \propto \frac{M_2}{n_2} \propto Z_2 \qquad \text{.....3}$$

**where**

m1,m2 = masses of primary product in grams

M1, M2 = molar masses ($g.mol^{-1}$)

n1, n2= number of electrons

Z1, Z2 = electrochemical equivalent.

Combining the first law and the second law, as in equation:

***m = Zit***

Substituting for Z, from equation 2 in 1

$$m = k\frac{M}{n}It \qquad \text{.......4}$$

or

$$m = \frac{1}{F} \cdot \frac{M}{n}It \qquad \text{........5}$$

where F = Faraday's constant. It is the quantity of electricity required to deposit the ratio of mass to the valency of any substance and expressed in coulombs per mole (C (g equiv.)-1). It has a value of 96 485 coulombs per gram equivalent. This is sometimes written as 96 485 coulombs per mole of electrons.

**Applications of Faraday's Laws in Determination of Corrosion Rates of Metals & Alloys**

Corrosion rate has dimensions of mass x reciprocal of time:

$$(g \cdot y^{-1} \text{ or } kg \cdot s^{-1})$$

In terms of loss of weight of a metal with time, from equation (5), we get:

$$\frac{dw}{dt} = \frac{MI}{nF} \quad (I = \text{current}) \qquad \text{........6}$$

The rate of corrosion is proportional to the current passed and to the molar mass. Dividing equation (5) by the exposed area of the metal in the alloy, we get

$$\frac{w}{At} = \frac{MI}{nFA} \qquad \text{........7}$$

But, $\frac{I}{A}$ = current density ($i$). Then:

$$\frac{w}{At} = \frac{Mi}{nF} \quad (i = \text{current density}) \qquad \text{........ 8}$$

The above equation has been successfully used to determine the rates of corrosion. A very useful practical unit for representing the corrosion rate is milligrams per decimeter square per day ($mg.dm^{-2}.day^{-1}$) or mdd. Other practical units are millimeter per year ($mm\ y^{-1}$)

Below are some examples showing how Faraday's laws are used to determine the corrosion rate. ) and mils per year (mpy).

**Table 1.5** *Standard potential series*

| Electrode | Reaction | $E^{\circ}_{red}$ (V) |
|---|---|---|
| $Li^+$, Li | $Li^+ + e^- \rightarrow Li$ | −3.024 |
| $K^+$, K | $K^+ + e^- \rightarrow K$ | −2.924 |
| $Ca^{2+}$, Ca | $Ca^{2+} + 2e^- \rightarrow Ca$ | −2.87 |
| $Na^+$, Na | $Na^+ e^- \rightarrow Na$ | −2,714 |
| $Mg^{2+}$, Mg | $Mg^{2+} + 2e^- \rightarrow Mg$ | −2.34 |
| $Ti^{2+}$, Ti | $Ti^{2+} + 2e^- \rightarrow Ti$ | −1.75 |
| $Al^{3+}$, Al | $Al^{3+} + 3e^- \rightarrow Al$ | −1.67 |
| $Mn^{2+}$, Mn | $Mn^{2+} + 2e^- \rightarrow Mn$ | −1.05 |
| $Zn^{2+}$, Zn | $Zn^{2+} + 2e^- \rightarrow Zn$ | −0.761 |
| $Cr^{3+}$, Cr | $Cr^{3+} + 3e^- \rightarrow Cr$ | −0.71 |
| $Fe^{2+}$, Fe | $Fe^{2+} + 2e^- \rightarrow Fe$ | −0.441 |
| $Co^{2+}$, Co | $Co^{2+} + 2e^- \rightarrow Co$ | −0.277 |
| $Ni^{2+}$, Ni | $Ni^{2+} + 2e^- \rightarrow Ni$ | −0.250 |
| $Sn^{2+}$, Sn | $Sn^{2+} + 2e^- \rightarrow Sn$ | −0.140 |
| $Pb^{2+}$, Pb | $Pb^{2+} + 2e^- \rightarrow Pb$ | −0.126 |
| $Fe^{3+}$, Fe | $Fe^{3+} + 3e^- \rightarrow Fe$ | −0.036 |
| $H^+$, $H_2$ | $2H^+ + 2e^- \rightarrow H_2$ | −0,000 |
| Saturated calomel | $Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$ (Sat. KCl) | 0.244 |
| $Cu^{2+}$,Cu | $Cu^{2+} + 2e^- \rightarrow Cu$ | 0.344 |
| $Cu^+$,Cu | $Cu^+ + e^- \rightarrow Cu$ | 0.522 |
| $Hg_2^{2+}$, Hg | $Hg_2^{2+} + 2e^- \rightarrow 2Hg$ | 0.798 |
| $Ag^+$, Hg | $Ag^{2+} + 2e^- \rightarrow 2Hg$ | 0.799 |
| $Pd^+$, Pd | $Pd^+ + 2e^- \rightarrow Pd$ | 0.83 |
| $Hg^+$, Hg | $Hg^+ + e^- \rightarrow Hg$ | 0.854 |
| $Pt^{2+}$, Pt | $Pt^{2+} + 2e^- \rightarrow Pt$ | 1.2 (ca) |
| $Au^{3+}$, Au | $Au^{3+} + 3e^- \rightarrow Au$ | 1.42 |
| $Au^+$, Au | $Au^+ + e^- \rightarrow Au$ | 1.68 |

| Element | Symbol | Atomic Number | Molar mass/ (g mol$^{-1}$) |
|---|---|---|---|
| Actinium | Ac | 89 | 227.03 |
| Aluminium | Al | 13 | 26.98 |
| Americium | Am | 95 | (243) |
| Antimony | Sb | 51 | 121.75 |
| Argon | Ar | 18 | 39.95 |
| Arsenic | As | 33 | 74.92 |
| Astatine | At | 85 | 210 |
| Barium | Ba | 56 | 137.34 |
| Berkelium | Bk | 97 | (247) |
| Beryllium | Be | 4 | 9.01 |
| Bismuth | Bi | 83 | 208.98 |
| Bohrium | Bh | 107 | (264) |
| Boron | B | 5 | 10.81 |
| Bromine | Br | 35 | 79.91 |
| Cadmium | Cd | 48 | 112.40 |
| Caesium | Cs | 55 | 132.91 |
| Calcium | Ca | 20 | 40.08 |
| Californium | Cf | 98 | 251.08 |
| Carbon | C | 6 | 12.01 |
| Cerium | Ce | 58 | 140.12 |
| Chlorine | Cl | 17 | 35.45 |
| Chromium | Cr | 24 | 52.00 |
| Cobalt | Co | 27 | 58.93 |
| Copper | Cu | 29 | 63.54 |
| Curium | Cm | 96 | 247.07 |
| Dubnium | Db | 105 | (263) |
| Dysprosium | Dy | 66 | 162.50 |
| Einsteinium | Es | 99 | (252) |
| Erbium | Er | 68 | 167.26 |
| Europium | Eu | 63 | 151.96 |
| Fermium | Fm | 100 | (257.10) |
| Fluorine | F | 9 | 19.00 |
| Francium | Fr | 87 | (223) |
| Gadolinium | Gd | 64 | 157.25 |
| Gallium | Ga | 31 | 69.72 |
| Germanium | Ge | 32 | 72.61 |
| Gold | Au | 79 | 196.97 |
| Hafnium | Hf | 72 | 178.49 |
| Hassium | Hs | 108 | (269) |
| Helium | He | 2 | 4.00 |
| Holmium | Ho | 67 | 164.93 |
| Hydrogen | H | 1 | 1.0079 |
| Indium | In | 49 | 114.82 |
| Iodine | I | 53 | 126.90 |
| Iridium | Ir | 77 | 192.2 |
| Iron | Fe | 26 | 55.85 |
| Krypton | Kr | 36 | 83.80 |
| Lanthanum | La | 57 | 138.91 |
| Lawrencium | Lr | 103 | (262.1) |
| Lead | Pb | 82 | 207.19 |
| Lithium | Li | 3 | 6.94 |
| Lutetium | Lu | 71 | 174.96 |
| Magnesium | Mg | 12 | 24.31 |
| Manganese | Mn | 25 | 54.94 |
| Meitnerium | Mt | 109 | (268) |
| Mendelevium | Md | 101 | 258.10 |
| Mercury | Hg | 80 | 200.59 |
| Molybdenum | Mo | 42 | 95.94 |
| Neodymium | Nd | 60 | 144.24 |
| Neon | Ne | 10 | 20.18 |
| Neptunium | Np | 93 | (237.05) |
| Nickel | Ni | 28 | 58.71 |
| Niobium | Nb | 41 | 92.91 |
| Nitrogen | N | 7 | 14.0067 |
| Nobelium | No | 102 | (259) |
| Osmium | Os | 76 | 190.2 |
| Oxygen | O | 8 | 16.00 |
| Palladium | Pd | 46 | 106.4 |
| Phosphorus | P | 15 | 30.97 |
| Platinum | Pt | 78 | 195.09 |
| Plutonium | Pu | 94 | (244) |
| Polonium | Po | 84 | 210 |
| Potassium | K | 19 | 39.10 |
| Praseodymium | Pr | 59 | 140.91 |
| Promethium | Pm | 61 | (145) |
| Protactinium | Pa | 91 | 231.04 |
| Radium | Ra | 88 | (226) |
| Radon | Rn | 86 | (222) |
| Rhenium | Re | 75 | 186.2 |
| Rhodium | Rh | 45 | 102.91 |
| Rubidium | Rb | 37 | 85.47 |
| Ruthenium | Ru | 44 | 101.07 |
| Rutherfordium | Rf | 104 | (261) |
| Samarium | Sm | 62 | 150.35 |
| Scandium | Sc | 21 | 44.96 |
| Seaborgium | Sg | 106 | (266) |
| Selenium | Se | 34 | 78.96 |
| Silicon | Si | 14 | 28.08 |
| Silver | Ag | 47 | 107.87 |
| Sodium | Na | 11 | 22.99 |
| Strontium | Sr | 38 | 87.62 |
| Sulphur | S | 16 | 32.06 |
| Tantalum | Ta | 73 | 180.95 |
| Technetium | Tc | 43 | (98.91) |
| Tellurium | Te | 52 | 127.60 |
| Terbium | Tb | 65 | 158.92 |
| Thallium | Tl | 81 | 204.37 |
| Thorium | Th | 90 | 232.04 |
| Thulium | Tm | 69 | 168.93 |
| Tin | Sn | 50 | 118.69 |
| Titanium | Ti | 22 | 47.88 |
| Tungsten | W | 74 | 183.85 |
| Ununbium | Uub | 112 | (277) |
| Ununnilium | Uun | 110 | (269) |
| Unununium | Uuu | 111 | (272) |
| Uranium | U | 92 | 238.03 |
| Vanadium | V | 23 | 50.94 |
| Xenon | Xe | 54 | 131.30 |
| Ytterbium | Yb | 70 | 173.04 |
| Yttrium | Y | 39 | 88.91 |
| Zinc | Zn | 30 | 65.37 |
| Zirconium | Zr | 40 | 91.22 |

The value given in parenthesis is the molar mass of the isotope of largest known half-life.

**Example 1**

Steel corrodes in an aqueous solution, the corrosion current is measured as 0.1 mA • $cm^{-2}$ . Calculate the rate of weight loss per unit area in units of mdd.

**Solution**

For Fe —> $Fe^{+2}$ + *2e*

$$\frac{w}{At} = \frac{Mi}{nF}$$

**Where:**
M= 55.9 $g.mol^{-1}$
i = 0.1 $mA.cm^{-2}$ =0.0001 $A.cm^{-2}$
n = 2

$$\frac{w}{At} = 2.897 \times 10^{-8}\ \mathrm{g\,cm^{-2}s^{-1}}$$

Now converting g to mg (x $10^3$), we get $\frac{w}{At}$ = 2.897 x $10^{-5}$ mg $cm^{-2}$ $s^{-1}$

$$2.897 \times 10^{-5} \frac{mg}{cm^2 s} * \frac{100cm^2}{dm^2} * \frac{24h}{day} * \frac{3600\ s}{h} = 250.3\ mdd$$

**Example 2**
Iron is corroding in seawater at a current density of 1.69 x $10^{-4}$ $A/cm^2$. Determine the corrosion rate in
(a) mdd (milligrams per $decimeter^2$ day)
(b) ipy (inches per year) (density for Iron = 7.86)

**Solution**

**(a)** Apply Faraday's law $\frac{w}{At} = \frac{Mi}{nF}$

= 422.8 mg $dm^{-2}$ $day^{-1}$

**(b)** ipy = mdd * 0.00144/ρ, ρ = density

$$= 422.8 \times \frac{0.00144}{7.86} = 0.077\ \text{ipy}$$

**Example 3**

A sample of zinc anode corrodes uniformly with a current density of $4.27 \times 10^{-7}$ $A/cm^2$ in an aqueous solution. What is the corrosion rate of zinc in mdd?

**Penetration** unit time can be obtained by dividing equation (8) by density of the alloy. The following equation can be used conveniently:

$$\text{Corrosion rate, } r = C \cdot \frac{Mi}{n\rho} \qquad \ldots\ldots 9$$

**where**

$\rho$ = density ($g/cm^3$)

i = current density ($A/cm^2$)

M = atomic weight ($g \cdot mol^{-1}$)

n = number of electrons involved

C = constant which includes F and any other conversion factor for units (depending on units)

**= 0.129 in mpy**

**= 3.27 in mm/y**

For instant, the above relationship can be used to establish the equivalent of corrosion current of 1 μA/cm² with the rate of corrosion for iron in mpy as shown below

$$1\ \mu A/cm^2 = 0.129\left[\frac{(55.8)(1)}{(2)(7.86)}\right] = 0.46\ \text{mpy}$$

**Example 4**

A sample of zinc corrodes uniformly with a current density of 4.2 x $10^{-6}$ A/$cm^2$ in an aqueous solution.

**(a)** What is the corrosion rate of zinc in mg/$dm^2$

**(b)** What is the corrosion rate of zinc in mm/year?

**Solution**

**(a)** Given current density, i = 4.2 x $10^{-6}$ A/$cm^2$ , zinc atomic weight, M = 65.38 g/mol, density, ρ = 7.1 g/$cm^3$, n = 2, F = 96 485 coulombs/mole.

$$\frac{w}{At} = \frac{Mi}{nF}$$

$$\frac{65.38 \times 4.2 \times 10^{-6}}{2 \times 96485} = 1.42 \times 10^{-9}\frac{g}{cm^2 s}$$

Now converting g to mg (x $10^3$), we get $= 1.42 \times 10^{-6}\frac{mg}{cm^2 s}$

$$1.42 \times 10^{-6}\frac{mg}{cm^2 s} * \frac{100cm^2}{dm^2} * \frac{24h}{day} * \frac{3600\ s}{h} = 12.27\ mdd$$

**(b)** We can also use the relationship given below to determine the rate of corrosion in mm/year or other units by changing the constants. The constant for mm/year is 0.00327.

$$\text{Corrosion rate, } r = C \cdot \frac{Mi}{n\rho}$$

Where ρ is the density in $g/cm^3$, *i* is the current density in $\mu A/cm^2$, and C is the constant = 0.00327 for mm/year.

$$\text{Corrosion rate} = \frac{0.00327 \times 65.38\,\text{g/mol} \times 4.2}{2 \times 7.13}$$

Corrosion rate = 0.0629 mm/year

**Example 5**
AISI 316 steel has the following nominal composition:

| | | | |
|---|---|---|---|
| Cr = 18% | n = 1 | ρ = 7.1 $g/cm^2$ | At. wt. = 52.01 g/mol |
| Ni = 8% | n = 2 | ρ = 8.9 $g/cm^2$ | At. wt. = 58.68 g/mol |
| Mo = 3% | n = 1 | ρ = 10.2 $g/cm^2$ | At. wt. = 95.95 g/mol |
| Fe = 70% | n = 2 | ρ = 7.86 $g/cm^2$ | At. wt. = 55.85 g/mol |

Find the equivalence between the current density of 1 $\mu A/cm^2$ and the corrosion rate (mpy).

**Solution:**

$$\text{Corrosion rate} = C \cdot \frac{Mi}{n\rho}$$

Where C is the constant for conversion depending on unit.

$$\text{C.R} = 0.129\left\{\left(\frac{52.01}{1 \times 7.1}\right)0.18 + \left(\frac{58.68}{2 \times 8.9}\right)0.08 + \left(\frac{95.95}{1 \times 10.2}\right)0.03 + \left(\frac{55.85}{2 \times 7.86}\right)0.70\right\}$$

= 0.129 [1.318 + 0.263 + 0.282 + 2.48]
= 0.55 mpy (mils/year)