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:

$$m \propto It \text{ or } m = ZIt$$

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)

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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:

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

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

where

m1,m2 = masses of primary product in grams

M1, M2 = molar masses (g.mol-1)

n 1, n2 = number of electrons

Z1, Z2 = electrochemical equivalent

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

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

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

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

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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:

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

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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) and mils per year (mpy).

Below are some examples showing how Faraday's laws are used to determine the corrosion rate.

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.

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

Now converting g to mg (×103) , cm^{-2} to dm^{-2} , s to d

Sol.:

For Fe $\longrightarrow$ $Fe^{+2} + 2e$

$$\frac{w}{At} = \frac{Mi}{nF}\quad 2.897\text{x }10^{-5}\,\frac{mg}{cm^2 s} * \frac{100\,Cm^2}{dm^2} * \frac{3600\ S}{h} * \frac{24\ h}{day} = 250.3\ \text{mdd}$$

Where:

M= 55.9 $g.mol^{-1}$

i = 0.1 $mA.cm^{-2}$

n = 2

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Example 2

Iron is corroding in seawater at a current density of 1.69 x 10-4 A/cm2 . Determine the corrosion rate in
(a) mdd (milligrams per decimeter2) mdd
(b) ipy (inches per year)

(a) Apply Faraday's law as before

$$\text{mdd} = 1.69 \times 10^{-4}\ \text{A/cm}^2 \times 3600\ \text{s/h} \times 24\ \text{h/day} \times 100\ \text{cm}^2/\text{dm}^2 \times \frac{55.85}{2}\ \text{g/mol} \times 10^3\ \text{mg/g} \times \frac{1}{96\,495}\ \text{A}\cdot\text{s}\cdot\text{mole}$$

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

(b) Converting 422.8 mg dm^{-2} day^{-1} to inches per year (ipy) with the conversion factor [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 x 10^{-7} A/cm2 in an aqueous solution. What is the corrosion rate of zinc in mdd?

Solution:

$$\text{Zn} \rightarrow \text{Zn}^{+2} + 2e$$

$$\text{CR} = \left(4.27 \times 10^{-7}\ \text{A/cm}^2\right)\left(1 \times 10^2\ \text{cm}^2/\text{dm}^2\right)\left(24 \times 3600\,\text{s}\cdot\text{h/h}\cdot\text{day}\right)\left(\frac{65.38}{2}\ \text{g/mol}\right) \times 10^3\text{mg/g}\left(\frac{1}{96\,495}\ \text{A}\cdot\text{s}\cdot\text{mol}\right)$$

$$= 1.25\,\text{mdd}$$

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

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$$Mi$$

where

ρ = density (g/cm^3)
i = current density (A/cm^2)
M = atomic weight ($\text{g}\cdot\text{mol}^{-1}$)
n = number of electrons involved
C = constant which includes F and any other conversion factor for units, for instance, $C = 0.129$ when corrosion rate is in mpy, 3.27 when in mm/year and 0.00327 when units are in mm^3/year.

Example 4

Determine the corrosion rate of AISI 316 steel corresponding to 1 µA/cm2
Ni = 10%
Mo = 3%
Mn = 2%
Fe = balance, 67%
Cr = 18%

Sol.: $$1\ \mu A/cm^2 = 0.128\left[\frac{52.3}{(1)(7.19)}\right]0.18 + 0.128\left[\frac{54.94}{(2)(7.45)}\right]0.02 + 0.128\left[\frac{95.95}{(2)(10.1)}\right]0.03 + 0.128\left[\frac{55.65}{(2)(7.86)}\right]0.07\ \text{mpy} \quad = 0.514587\ \text{mpy}$$

Example 5

A sample of zinc corrodes uniformly with a current density of 4.2 x 10-6 A/cm2 in an aqueous .
(a) What is the corrosion rate of zinc in mg/dm2 /day?
(b) What is the corrosion rate of zinc in mm/year?

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