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:

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

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 96 500 coulombs per gram equivalent. This is sometimes written as 96 500 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°_{red} (V)
Li^{+}, Li	$Li^{+} + e^{-} \rightarrow Li$	−3.024
K^{+}, K	$K^{+} + e^{-} \rightarrow K$	−2.924
Ca^{2+}, Ca	$Ca^{2+} + 2\,e^{-} \rightarrow Ca$	−2.87
Na^{+}, Na	$Na^{+}e^{-} \rightarrow Na$	−2,714
Mg^{2+}, Mg	$Mg^{2+} + 2\,e^{-} \rightarrow Mg$	−2.34
Ti^{2+}, Ti	$Ti^{2+} + 2\,e^{-} \rightarrow Ti$	−1.75
Al^{3+}, Al	$Al^{3+} + 3\,e^{-} \rightarrow Al$	−1.67
Mn^{2+}, Mn	$Mn^{2+} + 2\,e^{-} \rightarrow Mn$	−1.05
Zn^{2+}, Zn	$Zn^{2+} + 2\,e^{-} \rightarrow Zn$	−0.761
Cr^{3+}, Cr	$Cr^{3+} + 3e^{-} \rightarrow Cr$	−0.71
Fe^{2+}, Fe	$Fe^{2+} + 2\,e^{-} \rightarrow Fe$	−0.441
Co^{2+}, Co	$Co^{2+} + 2\,e^{-} \rightarrow Co$	−0.277
Ni^{2+}, Ni	$Ni^{2+} + 2\,e^{-} \rightarrow Ni$	−0.250
Sn^{2+}, Sn	$Sn^{2+} + 2\,e^{-} \rightarrow Sn$	−0.140
Pb^{2+}, Pb	$Pb^{2+} + 2\,e^{-} \rightarrow Pb$	−0.126
Fe^{3+}, Fe	$Fe^{3+} + 3e^{-} \rightarrow Fe$	−0.036
H^{+}, H_2	$2\,H^{+} + 2\,e^{-} \rightarrow H_2$	−0,000
Saturated calomel	$Hg_2Cl_2 + 2\,e^{-} \rightarrow 2\,Hg + 2\,Cl^{-}$ (Sat. KCl)	0.244
Cu^{2+},Cu	$Cu^{2+} + 2\,e^{-} \rightarrow Cu$	0.344
Cu^{+},Cu	$Cu^{+} + e^{-} \rightarrow Cu$	0.522
Hg_2^{2+}, Hg	$Hg_2^{2+} + 2\,e^{-} \rightarrow 2\,Hg$	0.798
Ag^{+}, Hg	$Ag^{2+} + 2\,e^{-} \rightarrow 2\,Hg$	0.799
Pd^{+}, Pd	$Pd^{+} + 2\,e^{-} \rightarrow Pd$	0.83
Hg^{+}, Hg	$Hg^{+} + e^{-} \rightarrow Hg$	0.854
Pt^{2+}, Pt	$Pt^{2+} + 2\,e^{-} \rightarrow Pt$	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

Element	Symbol	Atomic Number	Molar mass/ (g mol^{-1})
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 $Fe \rightarrow Fe^{+2} + 2e$

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

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

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

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 x 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:

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

where

ρ = density (g/cm^3)

i = current density (A/cm^2)

M = atomic weight (g • 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

= 0.00327 in mm/y

For instant, the above relationship can be used to establish the equivalent of corrosion current of 1 μA/cm^2 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 = 96 500 coulombs/mole.

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

$$\frac{65.38 \times 4.2 \times 10^{-6}}{2 \times 96500} = 1.42 \times 10^{-9}\,\frac{g}{cm^2 s}$$

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 μA/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 μA/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)