11_Electrochemistry

Jocelyn S. Sonquit-Sorrilla

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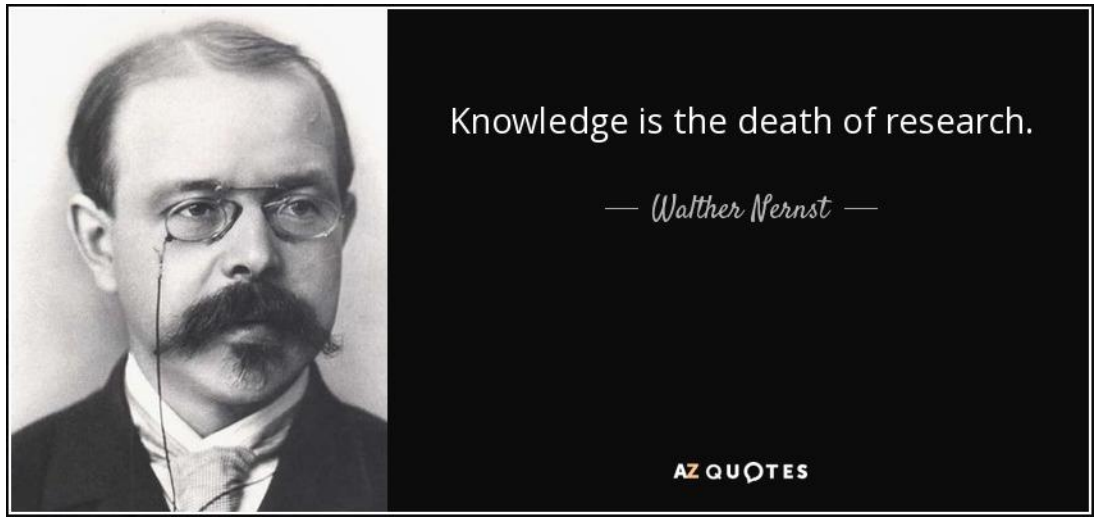
Cell emf Under Non-Standard Condition

- Calculated by using an equation first derived by **Walther Nernst** (**1864-1941**), a **German chemist** who established many of the theoretical foundations of electricity



The Nernst Equation

Deriving the Nernst Equation

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$
$$-nF E_{\text{cell}} = -nF E^\circ_{\text{cell}} + RT \ln Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\,\text{V}}{n} \log Q$$

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- E cell – cell emf under non-standard condition
- E^o cell- cell emf at standard condition
- n – no. of electrons involved
- Q – reaction quotient

Q, Reaction Quotient

$$wW + xX \longrightarrow yY + zZ$$

$$Q = \frac{[a_Y]^y [a_Z]^z}{[a_W]^w [a_X]^x}$$

- Q - product of the activity terms for the substances on the right of the chemical equation.
- The denominator of Q is the product of the activity terms for the substances on the left of a chemical equation.
- The activity of a pure solid is assumed to be unity at all times, the activity for a solid is always equal to 1.
- The activity of a substance in a solution is given by the molar concentrations of the substance.
- The activity of a gas is equal to the partial pressures of the gas in atmospheres.

Example

- $Zn(s) + Cu^{+2}(aq, 1M) \longrightarrow Zn^{+2}(aq, 1M) + Cu(s)$ $\quad E^0 cell = 1.10V$
- Given: T – 298K
  [Cu+2] = 5.00M
  [Zn+2] = 0.050M
- Find: E cell
- Equation: $E = E^o cell – (0.0592V/n) \log Q$
- $E = 1.10V – (0.0592/2) \log [Zn+2]/[Cu+2]$
- $E = 1.10V – (0.0592/2) \log (0.050M/5.00M)$
- $E = 1.10V – (0.0296) (-2)$
- $E = 1.16V$

The Nernst Equation

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592\,\text{V}}{n} \log Q$$

$$Q = \frac{[a_Y]^y [a_Z]^z}{[a_W]^w [a_X]^x}$$

- As reactants are converted to products, the value of Q increases, so the value of E decreases, eventually reaching E=0.
- Ehen E = 0, the cell reaction has reached equilibrium, and no net reaction is occurring.
- In general, increasing the concentration of reactants or decreasing the concentration of the products increases the driving force for the reaction, resulting in a higher emf.
- Conversely, decreasing the concentration of the reactants or increasing the concentration of the products decreases the emf.

Problems

Sample Problem 7.11. Calculate the emf at 298K generated by the cell:

$$Cr_2O_7^{+2}{}_{(aq)} + 14H^+{}_{(aq)} + 16I^-{}_{(aq)} \longrightarrow 2Cr_2^{+3}{}_{(aq)} + 3I_{2(s)} + 7H_2O_{(l)}$$

When, $[Cr_2O_7^{-2}] = 2.0$ M; $[H^+] = 1.0$ M; $[I^-] = 1.0$ M; and $[Cr^{+3}] = 1.0 \times 10^{-5}$ M:

$$Cr_2O_7^{+2}{}_{(aq)} + 14H^+{}_{(aq)} + 16I^-{}_{(aq)} \longrightarrow 2Cr_2^{+3}{}_{(aq)} + 3I_{2(s)} + 7H_2O_{(l)}$$

Solution:

This problem has been solved in the previous example.

Cathode: $Cr_2O_7^{-2}{}_{(aq)} + 14H^+{}_{(aq)} + \cancel{6e^-} \longrightarrow 2Cr^{+3}{}_{(aq)} + 7H_2O_{(l)}$ $\quad E^0{}_{red} = 1.33V$

Anode: $6I^-{}_{(aq)} \longrightarrow 3I_{2(s)} + \cancel{6e^-}$ $\quad E^0{}_{red} = 0.54V$

$$Cr_2O_7^{-2}{}_{(aq)} + 14H^+{}_{(aq)} + 6I^-{}_{(aq)} \longrightarrow 3I_{2(s)} + 2Cr^{+3}{}_{(aq)} + 7H_2O_{(l)}$$

n = 6.0 (6electrons involved)

$E^0{}_{cell} = E^0{}_{red}$(cathode) - $E^0{}_{red}$ (anode) = 1.33 V – 0.54 V = 0.79 V

Solving for Q:

$$Q = \frac{[Cr^{+3}]^2}{[Cr_2O_7^{-2}][H^+]^{14}[I^-]^6} = \frac{[1.0x10^{-5}]^2}{[2.0][1.0]^{14}[1.0]^6} = \frac{1.0x10^{-10}}{2.0} = 5.0x10^{-11}$$

Solving for E:

$$E = 0.79\ V - \frac{0.0592V}{6.0}\log 5.0x10^{-11}$$

$$E = 0.79\ V - \frac{0.0592V}{6.0}(-10.3) \qquad = 0.79V + 0.10V = 0.89V$$

The result is qualitatively what we expect. Because the concentration of $Cr_2O_7^{-2}$ (a reactant) is above 1 M and the concentration of Cr^{+3} (a product) is below 1M, the emf is greater than E^0.

Sample Problem 7.12. If the voltage of Zn-H^+ cell is 0.45 V at 25^{0}C when $[Zn^{+2}] = 1.0$ M and $P_{H2(g)} = 1.0$ atm, what is the concentration of H^+?

Solution:

The cell reaction is:

$$Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + H_{2(g)}$$

Solution:

Identifying the cathode and anode half-cell reactions:

Analyzing the reaction: Zn from 0 to +2 losing 2e$^-$ (oxidation – anode), thus H^+ to H_2 gaining 2e- (reduction – cathode).

Cathode: $2H^+_{(aq,\ 1M)} + 2e^- \longrightarrow H_{2(g,\ 1\ atm)}$ - involving gases (reduction) $E^0_{Red} = 0.000V$

Anode: $Zn_{(s)} \longrightarrow Zn^{+2}_{(aq,\ 1M)} + 2e^-$ -aqueous solution $(oxidation)$ $E^0_{Red} = -0.760V$

$E^0_{cell} = E^0_{Red(Cathode)} - E^0_{Red(anode)} = 0.000V$ - (-0.763V) = 0.763V

E^0 = +0.760 V

E = 0.450V

n = 2.0

$[Zn^{+2}]$ = 1.0 M; $P_{H_{2(g)}} = 1.0$ atm

Solving for Q:

$$Q = \frac{[Zn^{+2}_{(aq)}][H_{2(aq)}]}{[H^+_{(aq)}]^2} = \frac{[1.0M][1.0\ atm]}{[H^+_{(aq)}]^2}$$

Option 1: Solving the $[H^+_{(aq)}]$ using 1.0 atm pressure

$$0.450V = 0.760\ V - \frac{0.0592V}{2.0} \log \frac{[1.0M][1.0\ atm]}{[H^+_{(aq)}]^2} = 0.763\ V - \frac{0.0592V}{2.0} \log \frac{1.0}{[H^+_{(aq)}]^2}$$

$\log \frac{1.0}{[H]^2}$ = -2 log H, so

$$0.450V = 0.763\ V - \frac{0.0592V}{2.0}(-2 \log H^+)$$

0.450V - 0.763 V = 0.0592V (log H^+)

-0.313V = 0.0592V (log H^+)

$$\log [H^+] = \frac{-0.310}{0.0592} = -5.2$$

$[H^+]$ = - antilog 5.29 = 6.3x10^{-6} M

This example shows how a voltaic cell whose cell reaction involves H^+ that can be used to measure $[H^+]$ or pH. A pH meter is especially designed voltaic cell with a voltmeter calibrated to read pH directly.

Sample Problem 7.13.

In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a Zn/Zn^{+2} half-cell and an H_2/H^+ half-cell under the following conditions:

$[Zn^{+2}] = 0.010$ M $[H^+] = 2.5$ M $P_{H_2} = 0.30$ atm

Calculate E_{cell} at 298.15K.

Solution:

Identifying the half-cell reactions for cathode and anode:

Zn/Zn^{+2} – oxidation (anode)

H_2/H^+ - reduction (cathode)

Half-cell (anode) : $Zn_{(s)} \rightarrow Zn^{+2} + \cancel{2e^-}$ $E^0_{red} = -0.76$V

Half-cell (cathode): $2H^+ + \cancel{2e^-} \rightarrow H_{2(g)}$ $E^0_{red} = 0.00$V

Overall reaction: $2H^+ + Zn_{(s)} \rightarrow Zn^{+2} + H_{2(g)}$

$E^0_{cell} = E^0_{red(cathode)} - E^0_{red(anode)} = 0.00\text{V} - (-0.76\text{V}) = 0.76\text{V}$

n = 2.0 (2e- lost/gained)

$[Zn^{+2}] = 0.010$ M

$[H^+] = 2.5$ M

$P_{H_2} = 0.30$ atm

Solving for Q:

$$Q = \frac{[Zn^{+2}](H_2)}{[H^+_{(aq)}]^2} = \frac{[0.010](0.30)}{[2.5]^2} = 4.8\text{x}10^{-4}$$

Solving for E_{cell} at 298.15K (25°C),

$$E_{cell} = E^0_{cell} - \frac{0.0592V}{(2.0)} \log Q = 0.76\text{V} - \frac{0.0592V}{2.0} \log (4.8\text{x}10^{-4})$$

$$= 0.76\text{V} - \frac{0.0592V}{2.0}(-3.32) = 0.76\text{V} + 0.0983\text{V} = 0.86\text{V}$$

Another Option: For consistency of units, let us convert atm to mol/L (M):

Using the PV = nRT

Rearranging the equation gives:

$$\frac{n}{V} = \frac{P}{RT} = \frac{0.30\ \cancel{atm}}{\left(0.08206\frac{L-\cancel{atm}}{\cancel{K}-mol}\right)(298.15\cancel{K})} = 0.012\ \frac{mol}{L} = 0.012\text{ M}$$

Solving for Q:

$$Q = \frac{[Zn^{+2}](H_2)}{[H^+_{(aq)}]^2} = \frac{[0.010](0.012)}{[2.5]^2} = 1.9\text{x}10^{-5}$$

Solving for E_{cell} at 298.15K:

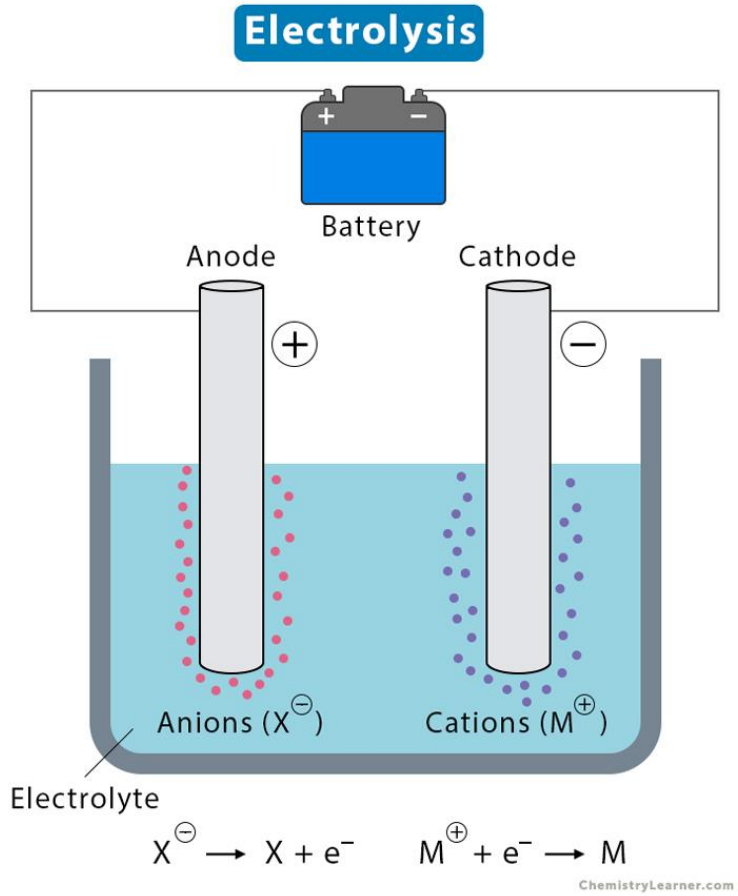
$$E_{cell} = E^0_{cell} - \frac{0.0592V}{(2.0)} \log Q = 0.76\text{V} - \frac{0.0592V}{2.0} \log (1.9\text{x}10^{-5})$$

$$= 0.76\text{V} - \frac{0.0592V}{2.0}(-4.7) = 0.76\text{V} + +0.139\text{V} = 0.90\text{V}$$

This type of problems can be solved using either of the options (using atm as unit for pressures or converting atm to M).

Electrolysis

- Such types of processes driven by an outside source of electrical energy are called **electrolysis** reactions and are taking place in **electrolytic cells.**
- **2NaCl(l) ⟶ 2Na(l) + Cl2(g)**



Electrolytic Cells

- Like in the voltaic cell, the electrode at which reduction occurs – **cathode**, and the electrode at which oxidation occurs – **anode**.
- In the electrolysis of molten NaCl, sodium ions pick up electrons and reduced to Na metal at the cathode.
- As the Na+ ions near the cathode are depleted, additional Na+ ions migrate in.
- Similarly, there is net movement of Cl- ions to the anode, where they are oxidized.
- The electrode reactions for the electrolysis

Cathode: 2Na + (l) + 2e -⟶ 2Na(l)

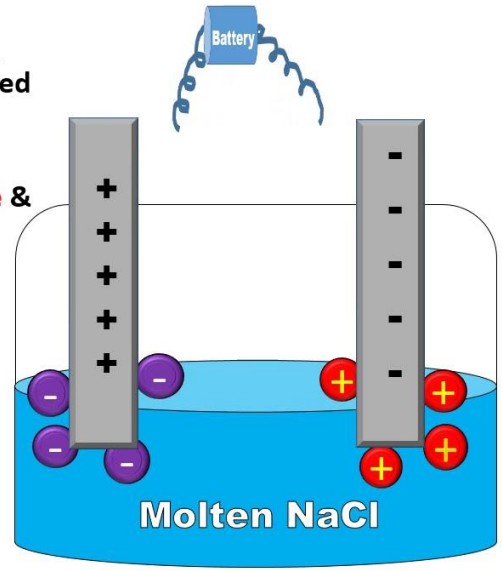
Anode: 2Cl - (l)⟶ Cl2(g) + 2e –

2Na + (l) +2Cl - (l)⟶Cl2(g) + 2Na(l)

Electrolysis of molten NaCl

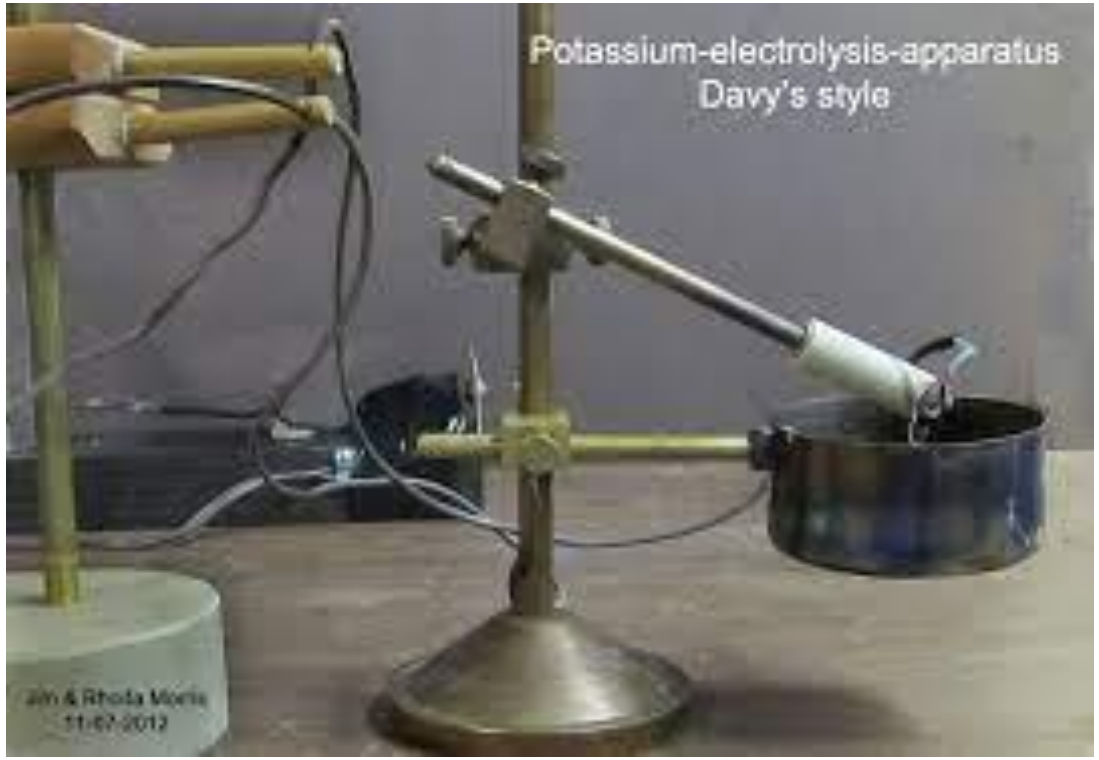
A source of direct current is connected to a pair of inert electrodes inserted In molten sodium chloride.
Na+ ions flows towards the negative & Cl- ions towards the positive electrode.

- **Anode is +ve**
- **Cathode is -ve**
- **Oxidation takes place at Anode**
- **Reduction at Cathode.**

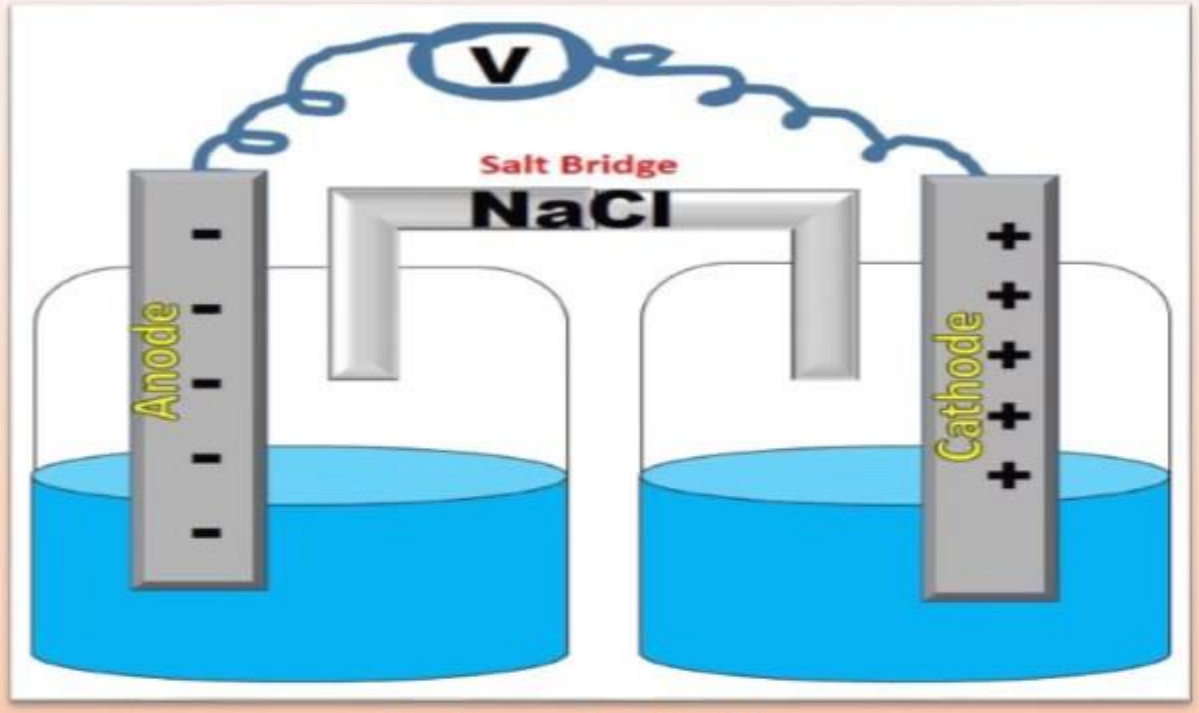


Electrolysis

- **Electrolysis** also refers to the decomposition of a substance by an electric current.
- The electrolysis of sodium and potassium hydroxides, first carried out in 1808 by **Sir Humphrey Davey**, led to the discovery of these two metallic elements and showed that these two hydroxides which had previously been considered un-decomposable and thus elements, were in fact compounds.



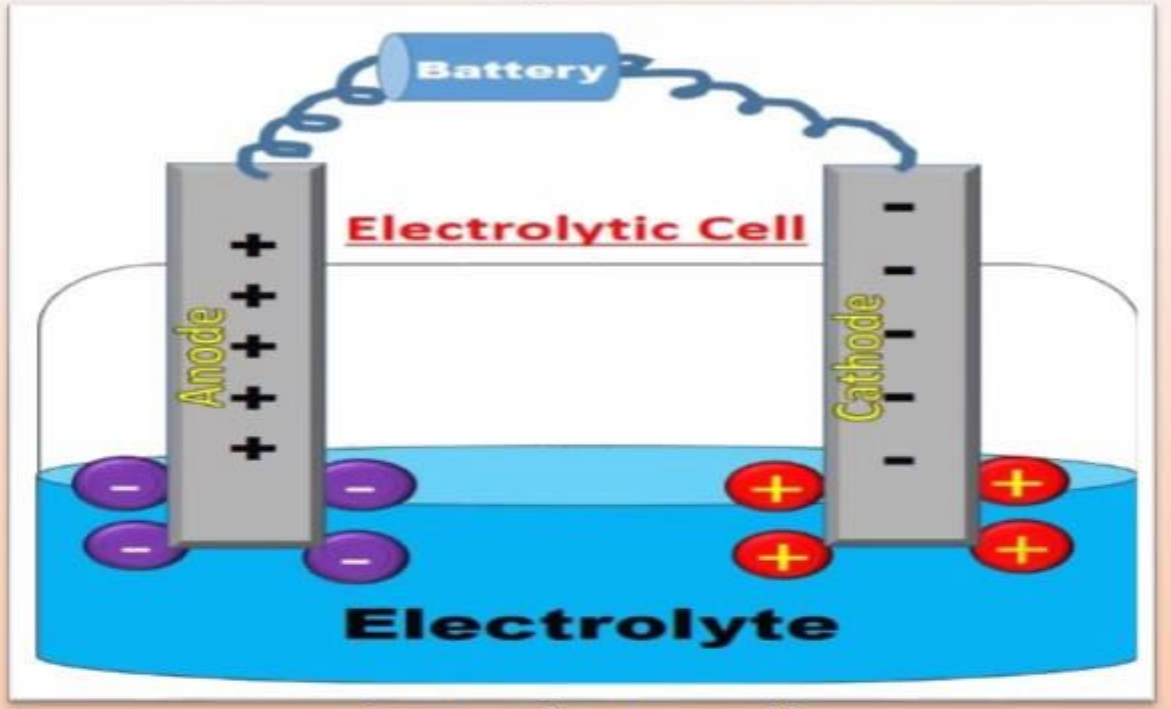
Difference b/w Galvanic Cell & Electrolytic Cell



Galvanic Cell

Changes chemical energy into Electrical energy .

1. Anode is –ve
2. Cathode is +ve
3. Spontaneous reaction occurs.
4. Does not require external voltage source.



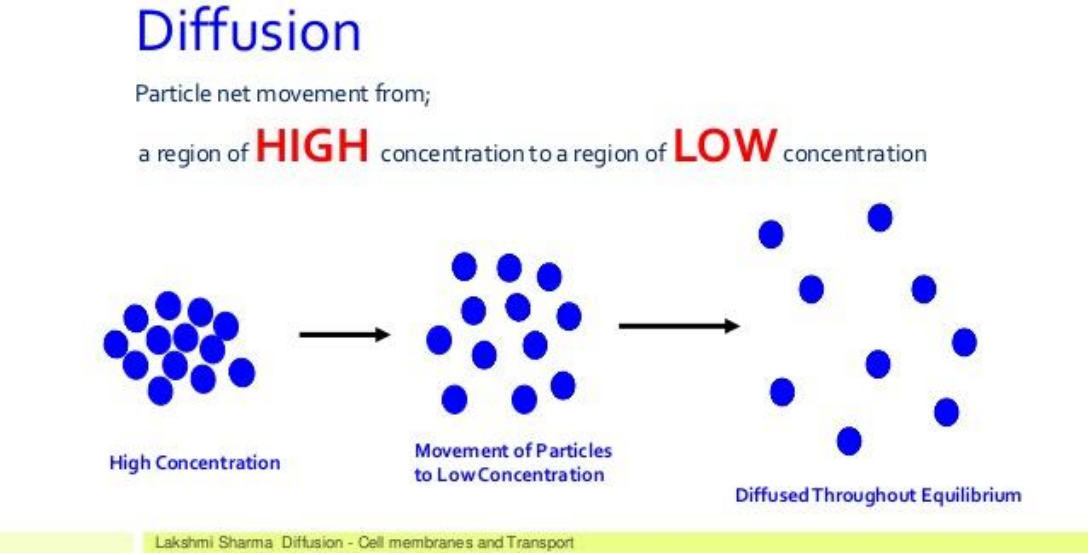
Electrolytic Cell

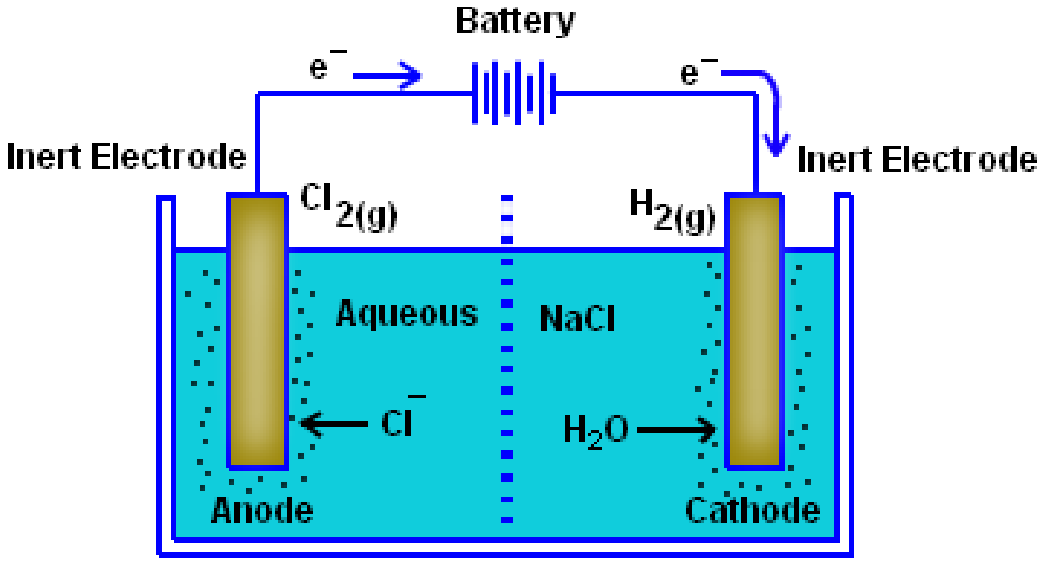
Changes electrical energy into chemical energy.

1. Anode is +ve
2. Cathode is -ve
3. Non-Spontaneous reaction occurs.
4. Require external voltage source.

Electrolysis

- Ionic motion throughout the bulk of the solution occurs mostly by **diffusion**, which is the transport of molecules in response to a concentration gradient.
- **Migration**— the motion of a charged particle due to an applied electric field, is only a minor player, producing only about one non-random jump out of around 100,000 random ones for a 1 volt cm^{-1} electric field.
- Only those ions that are near the interfacial region are likely to undergo migration.





Electrolysis in Aqueous Solution

- Water is capable of undergoing both **oxidation**, releasing oxygen at the anode,

H2O →½O2(g) + 2 H+ + 2 e –

E° = –1.23 v

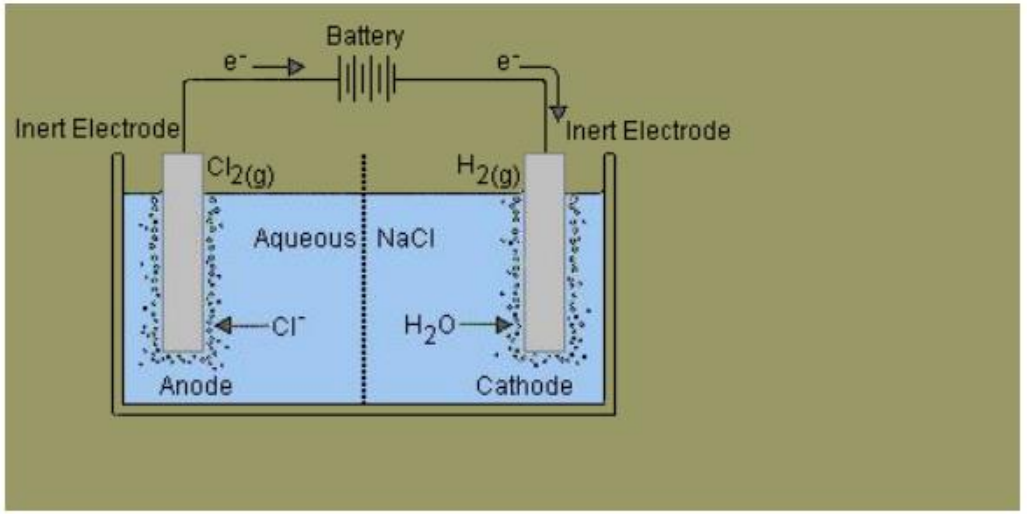
- and **reduction**, producing hydrogen gas at the cathode,

2 H2O + 2 e– →H2(g) + 2 OH–

E° = -0.83 v

- Electrolysis of salt ("brine") is carried out on a huge scale and is the basis of the **chlor-alkali** industry.

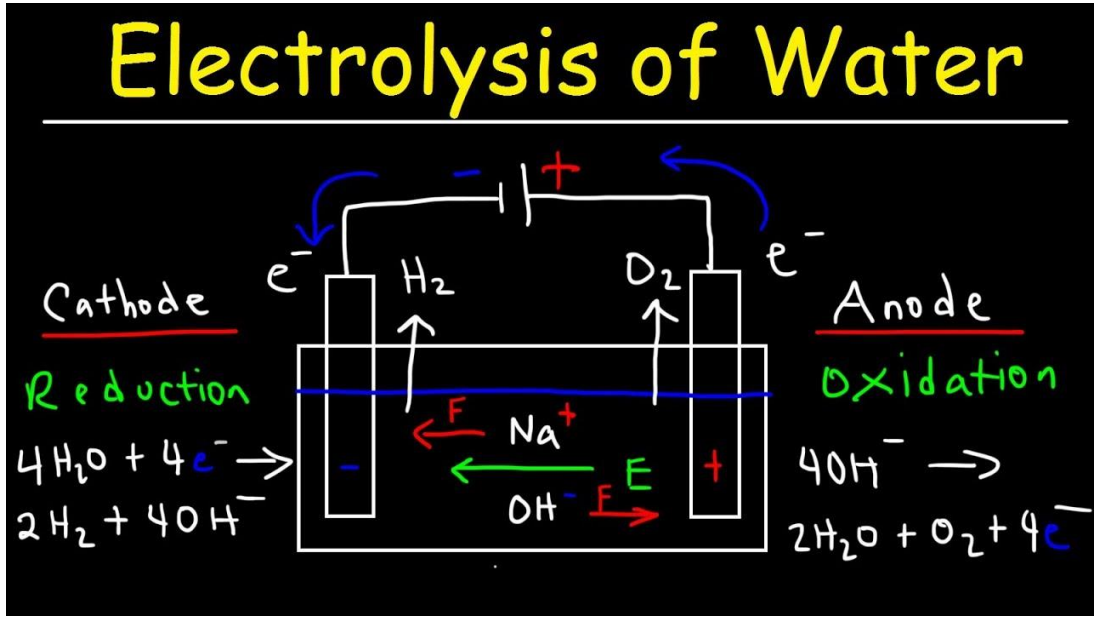
cathode:	$2\ H_2O + 2\ e^- \rightarrow H_2(g) + 2\ OH^-$	E =+0.41 v ([OH⁻] = 10-7 M)
anode:	$Cl^- \rightarrow ½\ Cl_2(g) + e^-$	$E° = –1.36$ v
net:	$Cl^- + H_2O \rightarrow 2\ H_2(g) + ½\ Cl_2(g) + 2\ OH^-$	$E = –0.95$ v



Reduction of Na^+ ($E° = –2.7$ v) is energetically more difficult than the reduction of water (–1.23 v), so in aqueous solution the latter will prevail.

Electrolysis of Water

cathode:	$2\ H_2O + 2\ e^- \rightarrow H_2(g) + 2\ OH^-$	$E° = -0.83$ v
anode:	$H_2O \rightarrow ½\ O_2(g) + 2\ H+ + 2\ e^-$	$E° = -1.23$ v
net:	$3\ H_2O(l) \rightarrow H_2(g) + ½\ O_2(g)$	$E = -2.06$ v

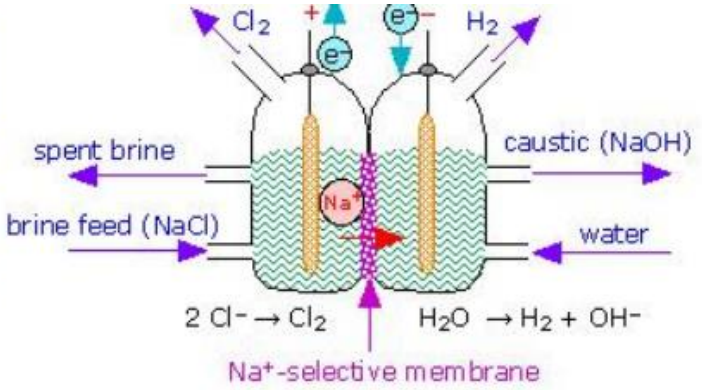


. Industrial Electrolytic Process – The Chloralkali Industry

anode reactions	$2\ Cl^- \rightarrow Cl_{2(g)} + 2\ e^-$	-1.36 v	i
	$4\ OH^- \rightarrow O_{2(g)} + 2\ H_2O + 4\ e^-$	-0.40 v	ii
cathode reactions	$Na+ + e^- \rightarrow Na_{(s)}$	-2.7 v	iii
	$H_2O + 2\ e^- \rightarrow H_{2(g)} + 2\ OH^-$	+.41 v	iv

2 NaCl + 2 H2O → 2 NaOH + Cl2(g) + H2(g)

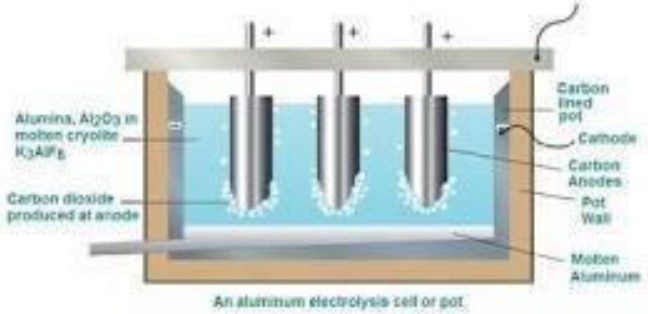
A modern industrial chloralkali plant



Schematic diagram of a cell for the production of chlorine

Electrolytic Refining of Aluminum

Hall-Heroult Process for Aluminum



An aluminum electrolysis cell or pot

Chemical reactions in the processing of aluminium

Alumina reacts with cryolite:

$$Al_2O_3 + 4\,AlF_6^{3-} \rightarrow 3\,Al_2OF_6^{2-} + 6\,F^-$$

Cathode: $AlF_6^{3-} + 3\,e^- \rightarrow Al + 6\,F^-$

Anode: $2\,Al_2OF_6^{2-} + 12\,F^- + C \rightarrow 4\,AlF_6^{3-} + CO_2 + 4\,e^-$

The overall cell reaction:

$$Al_2O_3 + 3\,C \rightarrow 4\,Al + 3\,CO_2$$

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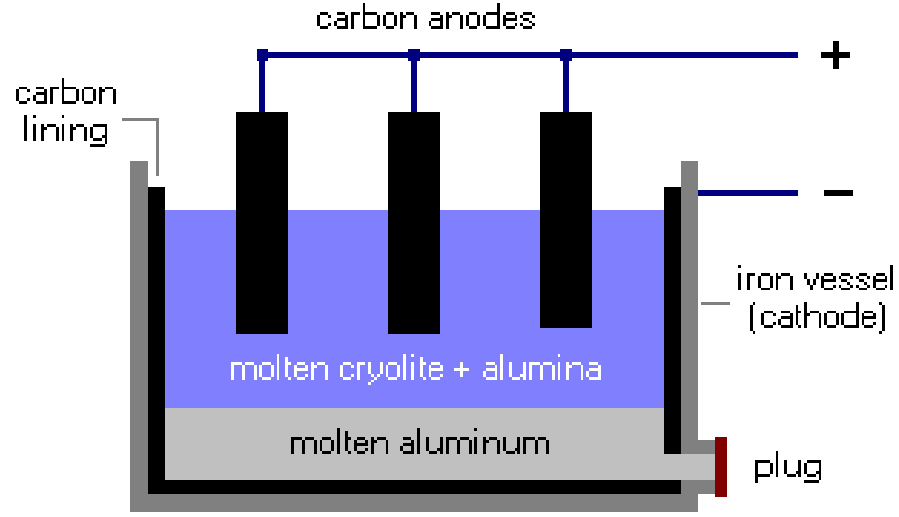
GVG/PD/1.2



HALL-HEROULT PROCESS

Stoichiometry of Electrolysis

- **Faraday's law of electrolysis**: the amount of substance deposited or liberated at any electrode is directly proportional to the amount of charge passed.
    1. The weights of substances formed at an electrode during electrolysis are directly proportional to the quantity of electricity that passes through the electrolyte.
    2. The weights of different substances formed by the passage of the same quantity of electricity are proportional to the equivalent weight of each substance
- The **equivalent weight** of a substance is defined as the molar mass, divided by the number of electrons required to oxidize or reduce each unit of the substance.

- Basic electrical units
- current (amperes) is the rate of charge transport

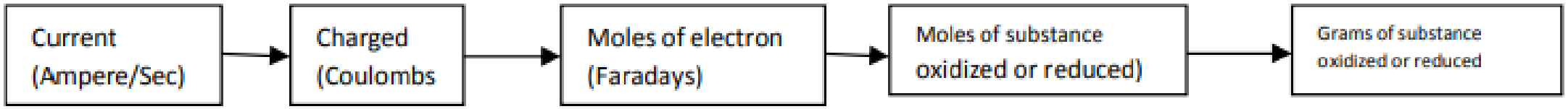
  1 amp = 1 C/sec
- power (watts) is the rate of energy production or consumption

  1 w = 1 J/sec = 1 volt-amp

  1 watt-sec = 1 J

  1 kw-h = 3600 J

Steps relative to the stoichiometric calculations of substances oxidized or reduced



Note: Current is the rate of flow of electricity. An ampere (amp) is the one associated with the flow of 1 C (Coulomb) past a point per second

Sample Problem 7.14. The charge of a single electron is 1.6022×10^{-29} C. Calculate the Avogadro's number from the fact that 1F = 96500 C.

Solution:

1F = 96500 C

Charge for $1e^- = 1.6022 \times 10^{-29}$ C

? number of electrons = 96,500 ~~C~~ x $\left(\frac{1\ e-}{1.6022x10^{-19}\cancel{C}}\right) = 6.023 \times 10^{23}\ e^-$

Recall the Avogadro's number is dependent upon the variables:

- for molecules $= 6.023 \times 10^{23}$ molecules
- for ions $= 6.023 \times 10^{23}$ ions, etc.

Sample Problem 7.15. In the electrolysis of $CuSO_4$, how much copper is plated out on the cathode by a current of 0.750 A in 10.0 min?

Solution:

Atomic mass: Cu = 63.5 S = 32.0 O = 16.0

$A = \frac{1\,C}{s} = 0.750\,\frac{C}{s}$

1 F = 96,500 C

$t = 10.0\ min.\ x\ \frac{60\,s}{min} = 600.\ s$

Using dimensional analysis:

$? \text{ no. of Faradays (F)} = 600.\ s\ (\frac{0.750\,\cancel{C}}{\cancel{s}})(\frac{1F}{96500\cancel{C}}) = 4.66x10^{-3}\ F$

Half-cell reaction for the formation of $Cu_{(s)}$:

$Cu^{+2} + 2e^- \rightarrow Cu_{(s)}$ – for every 1.0 mole of Cu there are $2e^-$ (equivalent to 2.0F) available:

1 mol Cu(s) ≅ 63.5 g ≅ 2*F*

$? \text{ g } Cu_{(s)} = 4.66x10^{-3}\,\cancel{F}(\frac{63.5\,g\,Cu_{(s)}}{2.0\cancel{F}}) = 0.148\ g$

Sample Problem 7.16. The half-reaction for formation of magnesium metal upon electrolytes of molten $MgCl_2$ is $Mg^{+2} + 2e^- \rightarrow Mg_{(s)}$. Calculate the mass of Mg formed upon passage of 60.0 A for a period of 4.00×10^3 s.

Solution:

A = 60.0

t = 4.00×10^3 s

C = A x t = A x s

Atomic mass: Mg = 24.3

$$? \text{ g Mg} = (60.0 \cancel{\text{A}})(4.00 \times 10^3 \cancel{\text{s}})\left(\frac{1.0 \cancel{\text{mol e}^-}}{96500 \cancel{\text{C}}}\right)\left(\frac{1.o \cancel{\text{mol Mg}}}{2.0 \cancel{\text{mol e}^-}}\right)\left(\frac{24.3 \text{ g Mg}}{1.0 \cancel{\text{mol Mg}}}\right) = 30.2 \text{ g Mg}$$

Batteries

- A **battery** is a portable self-contained electrochemical power source that consists of one or more voltaic cells.
- The common **1.5 V batteries** used to power flashlights and many consumer electronic devices are single voltaic cells.
- Greater voltages can be achieved by using multiple voltaic cells in a single battery, as in the case of **12-V automotive batteries**.
- When cells are connected in series (with the cathode of one attached to the anode of another), the battery produces a voltage that is the sum of the emfs of the individual cells.
- The electrodes of batteries are marked following the convention- **the cathode is labeled with a plus sign** and the **anode with a minus sign.**

Primary vs. Secondary Cells

Cells are devices that add electrical potential energy to charges moving through them (they add voltage or emf). They do this using chemical reactions in the cell. There are two types of cells:

Primary Cells

Non-rechargeable. Once the cell gives up all its energy, the chemicals cannot react again.

Examples:

- Zinc-carbon cells
- (anything non-rechargeable)

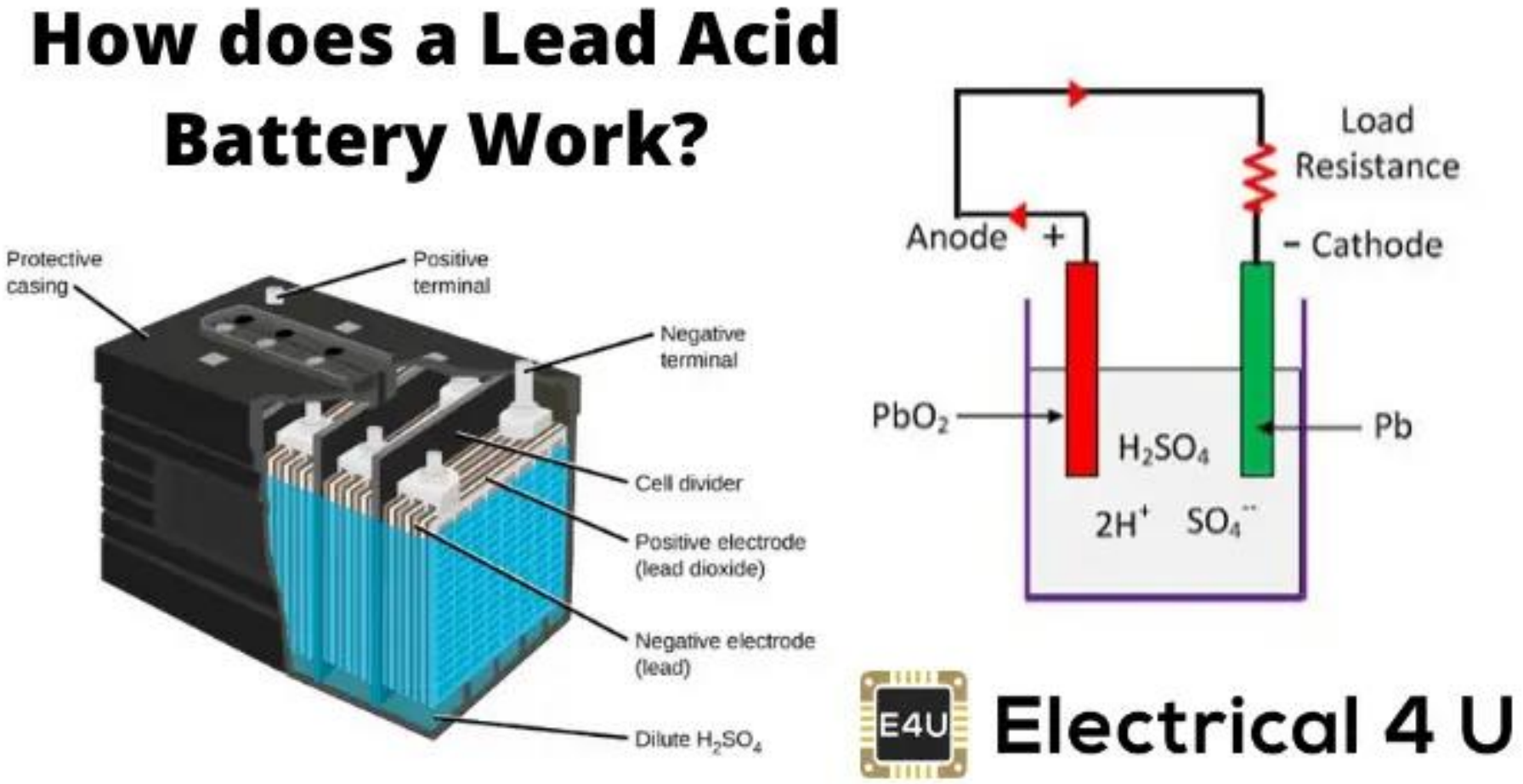
Secondary Cells

Rechargeable. Once the cell gives up all its energy, the chemical reaction that causes it to lose energy can be reversed by a charger, giving it more energy to use in circuits.

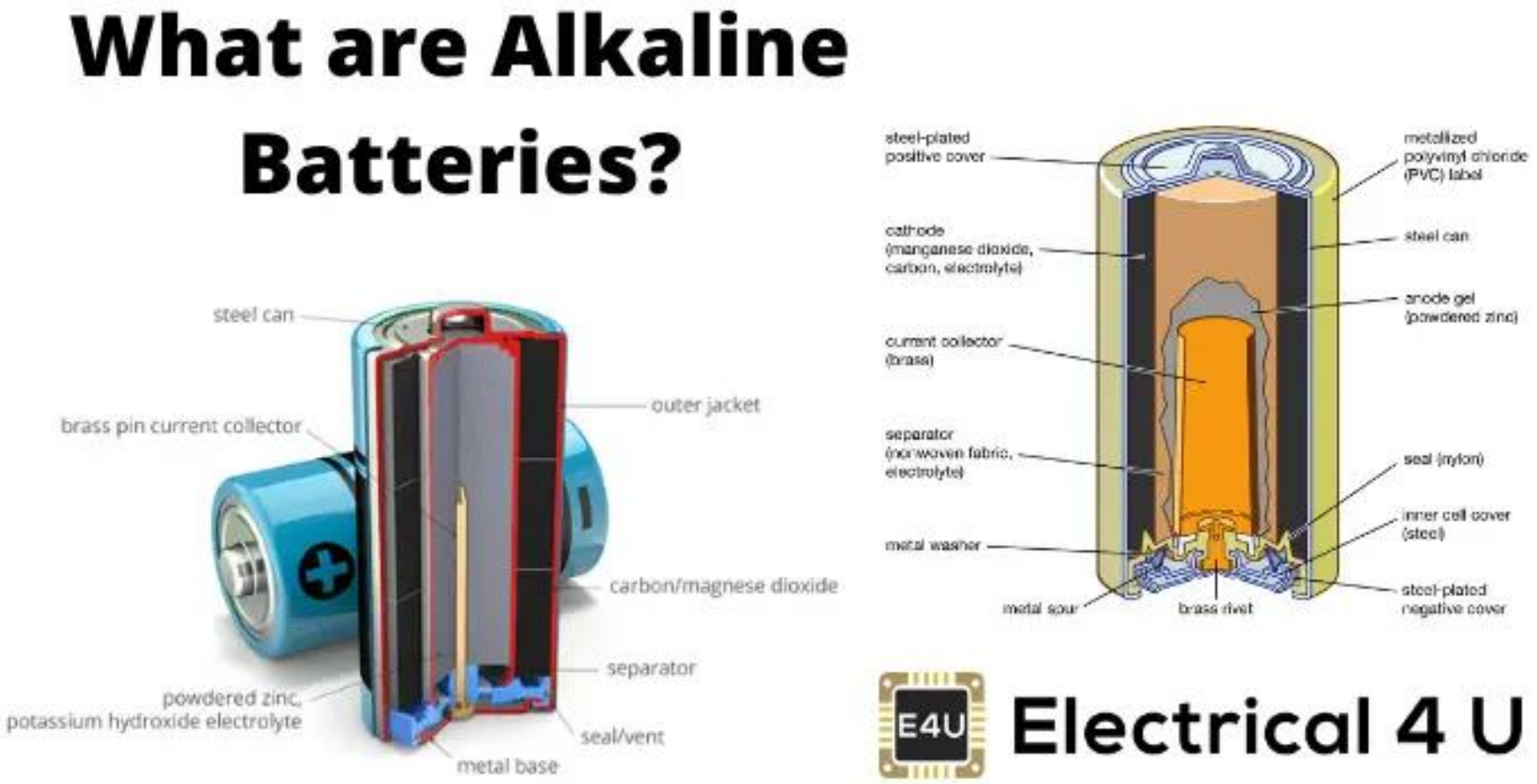
Examples:

- Zinc-carbon cells
- Car batteries

Lead-Acid Storage Battery

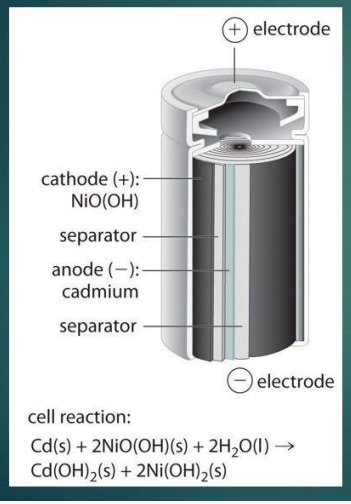


Alkaline Battery



Nickel-Cadmium, Nickel Metal-Hydride, and Lithium-Ion Batteries

1- Ni-Cd (Nickel Cadmium battery)



Battery reactions:

At the negative

$Cd + 2OH \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Cd(OH)_2 + 2e^-$

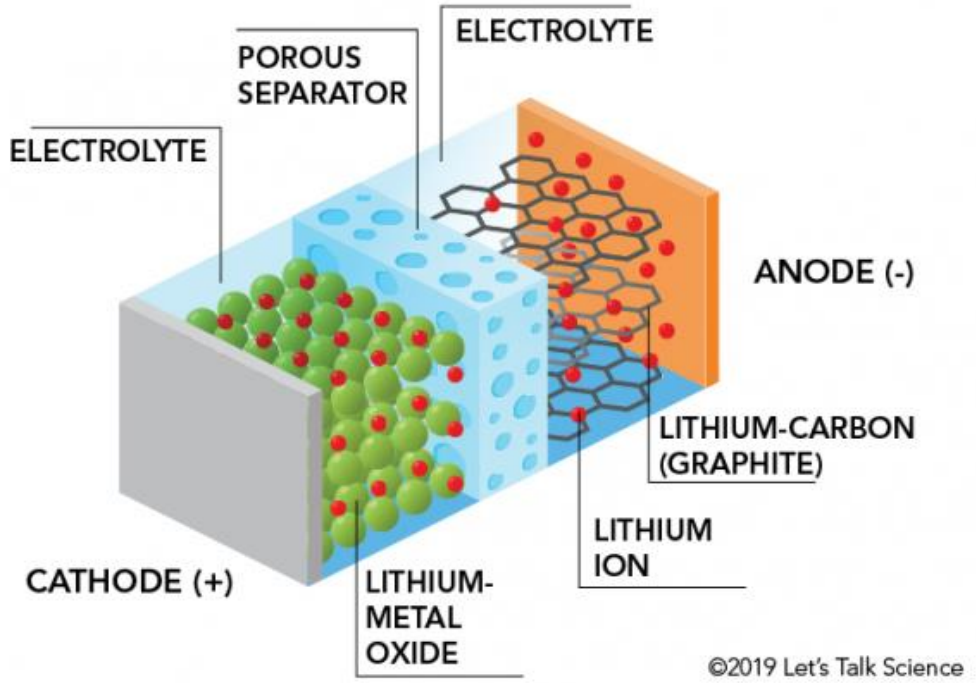
At the positive

$NiOOH + H_2O + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Ni(OH)_2 + OH$

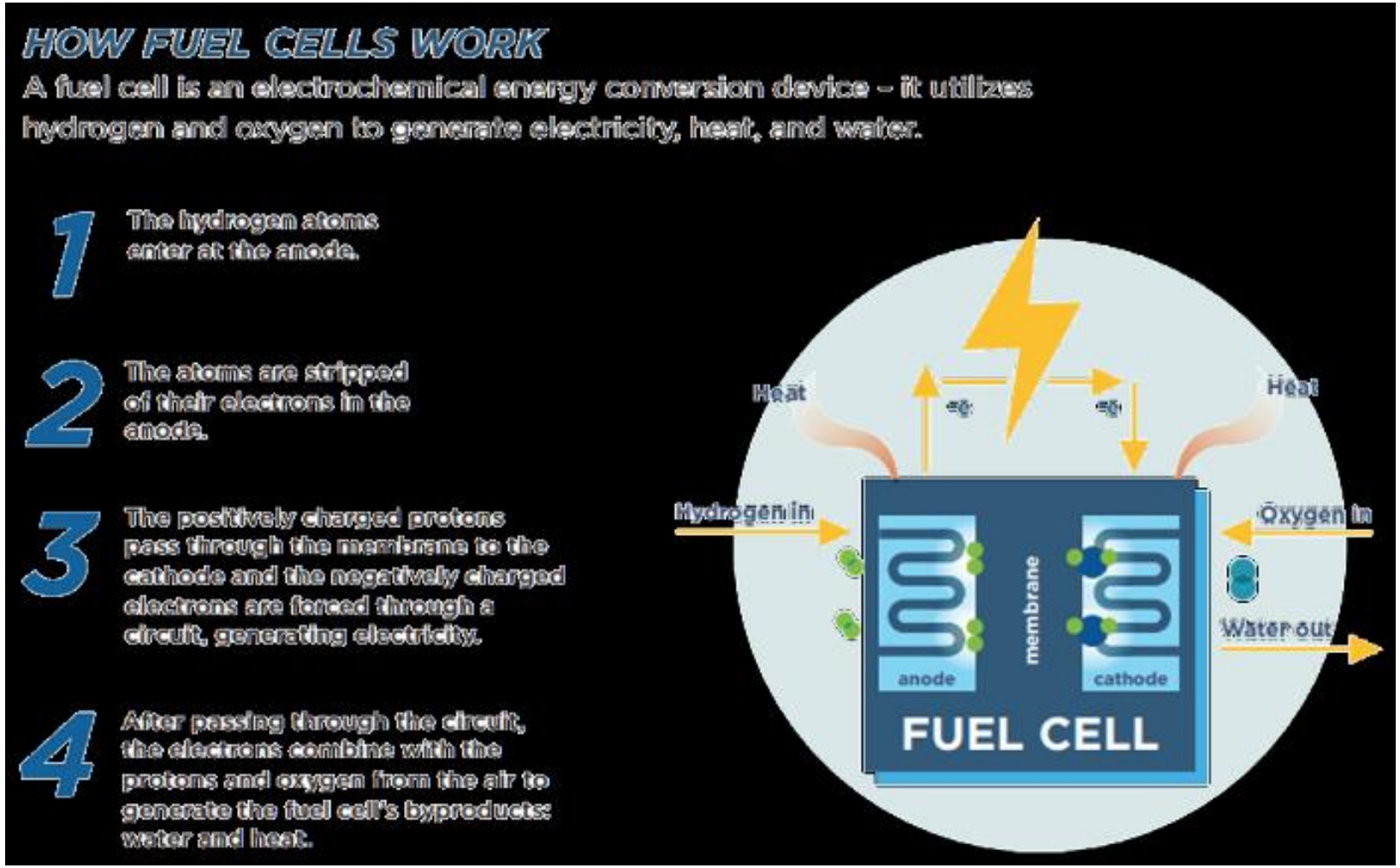
Overall reaction

$2NiOOH + Cd + 2H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} 2Ni(OH)_2 + Cd(OH)_2$

PARTS OF A LITHIUM-ION BATTERY



Fuel Cells

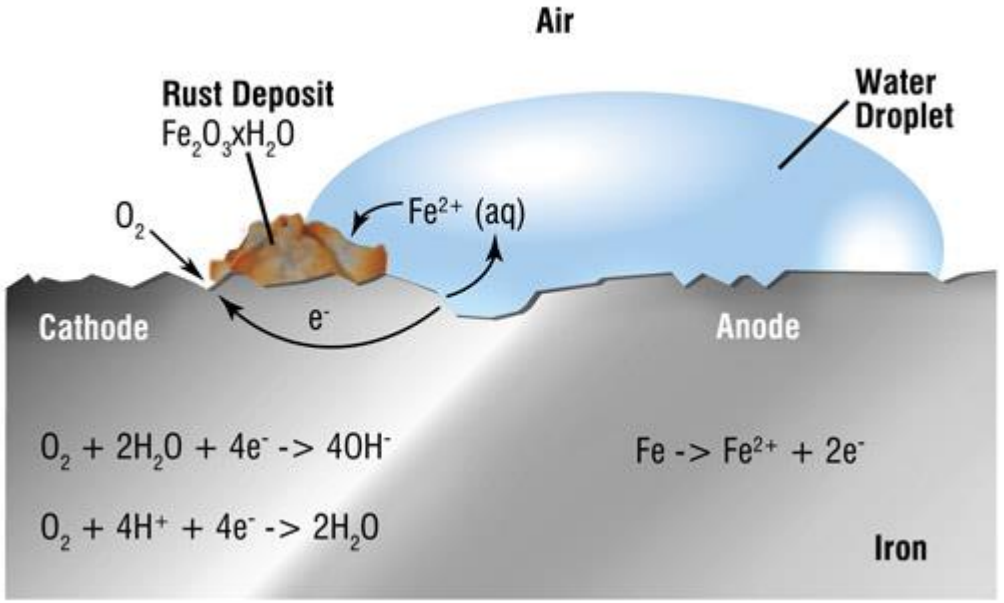

HOW FUEL CELLS WORK
A fuel cell is an electrochemical energy conversion device – it utilizes hydrogen and oxygen to generate electricity, heat, and water.
1
The hydrogen atoms enter at the anode.
2
The atoms are stripped of their electrons in the anode.
3
The positively charged protons pass through the membrane to the cathode and the negatively charged electrons are forced through a circuit, generating electricity.
4
After passing through the circuit, the electrons combine with the protons and oxygen from the air to generate the fuel cell's byproducts: water and heat.
Heat
Heat
Hydrogen in
Oxygen in
Water out
anode
membrane
cathode
FUEL CELL

Corrosion of iron in contact with water

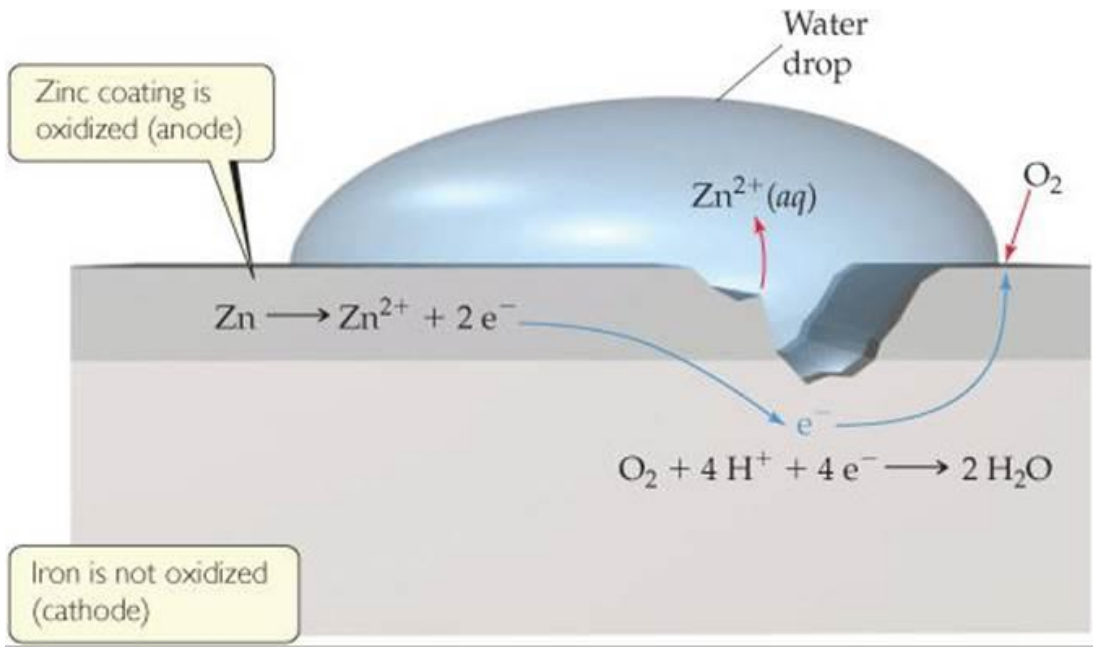
Iron and steel rust when they come into contact with **water and oxygen**.

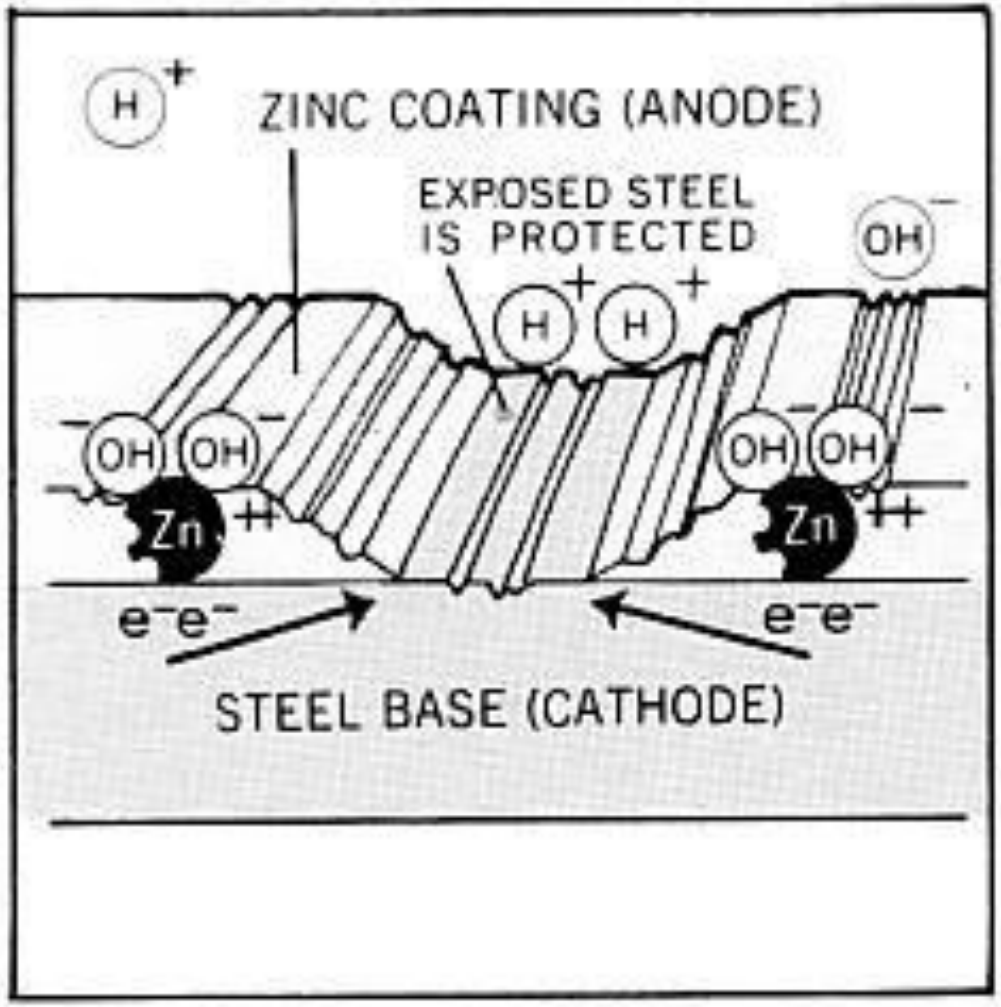
They rust faster in **salty water** or **acid rain**.

Aluminium, on the other hand, does not corrode easily, because its surface is protected by a layer of aluminium oxide.



Cathodic protection of iron in contact with zinc





11_Electrochemistry

Jocelyn S. Sonquit-Sorrilla

Mar.14.2023

end