

ELECTROCHEMISTRY

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For- B.Sc.**

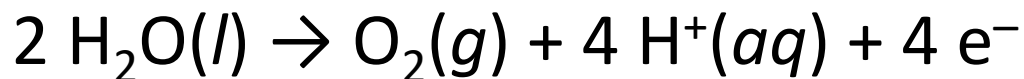
Electrolysis

- **Electrolysis:** is the process in which electrical energy is used to drive a *nonspontaneous* chemical reaction.
- **An electrolytic cell** is an apparatus for carrying out electrolysis.
- Processes in an electrolytic cell are the *reverse* of those in a galvanic cell.

Electrolysis

- **Electrolysis of Water:** Requires an electrolyte species, that is less easily oxidized and reduced than water, to carry the current.

- **Anode:** Water is oxidized to oxygen gas.



- **Cathode:** Water is reduced to hydrogen gas.



Electrolysis

- **Electrolysis of Aqueous Sodium Chloride:** uses different processes to molten sodium chloride.
- Based on cell potentials, water (-0.83 V) would be preferentially reduced over sodium ions (-2.71 V).
- Based on cell potentials, water ($+1.23$ V) should be preferentially oxidized over chloride ions ($+1.36$ V).
- The observed product at the anode is Cl_2 , not O_2 , because of a phenomenon called *overvoltage*.

Electrolysis

- **Overvoltage:** Additional voltage needed to maintain the rate of electron transfer at the electrode –solution interface.
- Overvoltage is required when a half-reaction has a significant activation energy, and so a slow rate.
- Overvoltage for formation of O_2 or H_2 is much greater than for the formation of Cl_2 .

Electrolysis

- **Quantitative Electrolysis:** The amount of substance produced at an electrode by electrolysis depends on the quantity of charge passed through the cell.
- Reduction of 1 mol of sodium ions requires 1 mol of electrons to pass through the system.
- The charge on 1 mol of electrons is 96,500 coulombs.

Electrolysis

- To determine the moles of electrons passed, we measure the current and time that the current flows:

$$\text{Charge (C)} = \text{Current (A)} \times \text{Time (s)}$$

- Because the charge on 1 mol of e^- is 96,500 C, the number of moles of e^- passed through the cell is:

$$\text{Moles of } e^- = \text{Charge (C)} \times \frac{1 \text{ mole } e^-}{96,500\text{C}}$$

Redox Reactions

Redox reactions are those involving the oxidation and reduction of species.

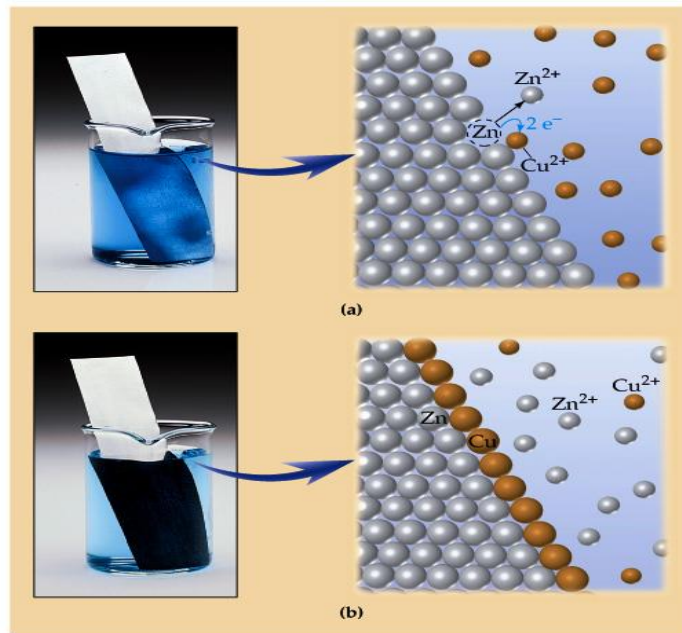
OIL – **O**xidation **I**s **L**oss of electrons.

RIG – **R**eduction **I**s **G**ain of electrons.

Oxidation and reduction *must* occur together.

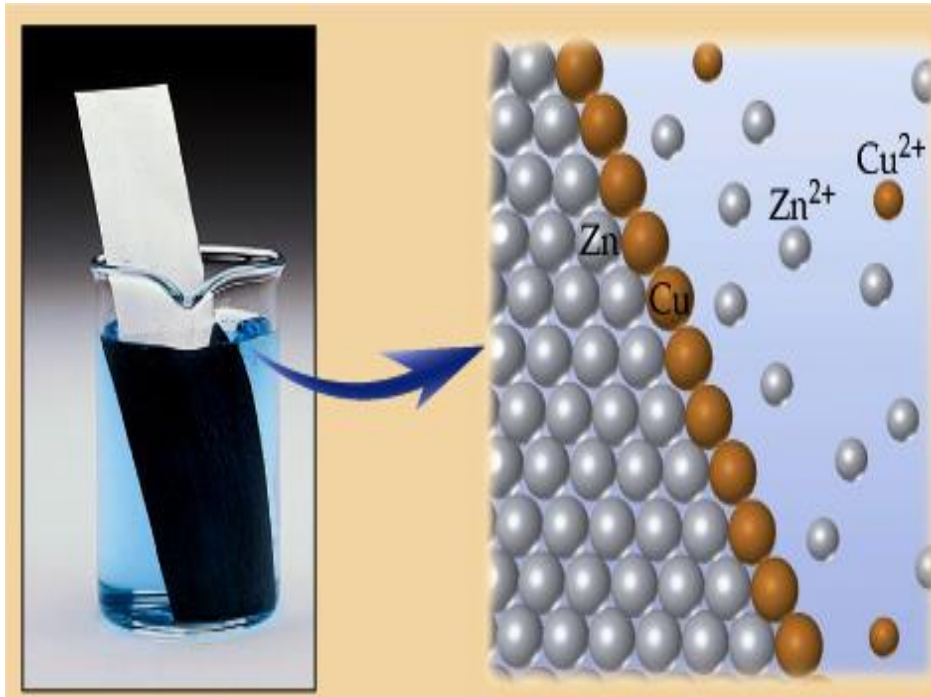
Redox Reactions

- **Oxidation Half-Reaction:** $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2 e^{-}$.
- The Zn loses two electrons to form Zn^{2+} .



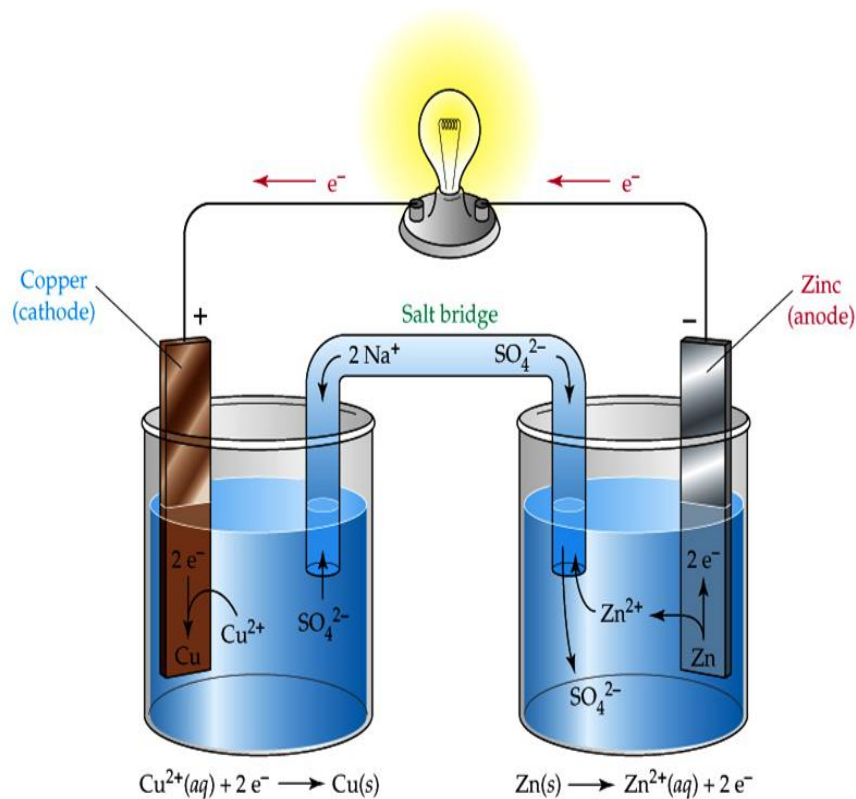
Redox Reactions

- **Reduction Half-Reaction:** $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightarrow \text{Cu}(\text{s})$
- The Cu^{2+} gains two electrons to form copper.



Redox Reactions

- Overall: $\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$



Electrochemical Cells

- **Electrodes:** are usually metal strips/wires connected by an electrically conducting wire.
- **Salt Bridge:** is a U-shaped tube that contains a gel permeated with a solution of an inert electrolyte.
- **Anode:** is the electrode where oxidation takes place.
- **Cathode:** is the electrode where reduction takes place.

Electrochemical Cells

- **Convention for expressing the cell:**

Anode Half-Cell || Cathode Half-Cell

Electrode | Anode Soln. || Cathode Soln. |
Electrode

$\text{Zn}(s) | \text{Zn}^{2+} (1 \text{ M}) || \text{Cu}^{2+} (1 \text{ M}) | \text{Cu}(s)$

$\text{Pt}(s) | \text{H}_2 (1 \text{ atm}) | \text{H}^+ (1 \text{ M}) || \text{Fe}^{3+}(aq),$
 $\text{Fe}^{2+}(aq) | \text{Pt}(s)$

- Electrons flow from anode to cathode.
Anode is placed on left by convention.

Electrochemical Cells

- The standard potential of any galvanic cell is the sum of the standard half-cell potentials for the oxidation and reduction half-cells.

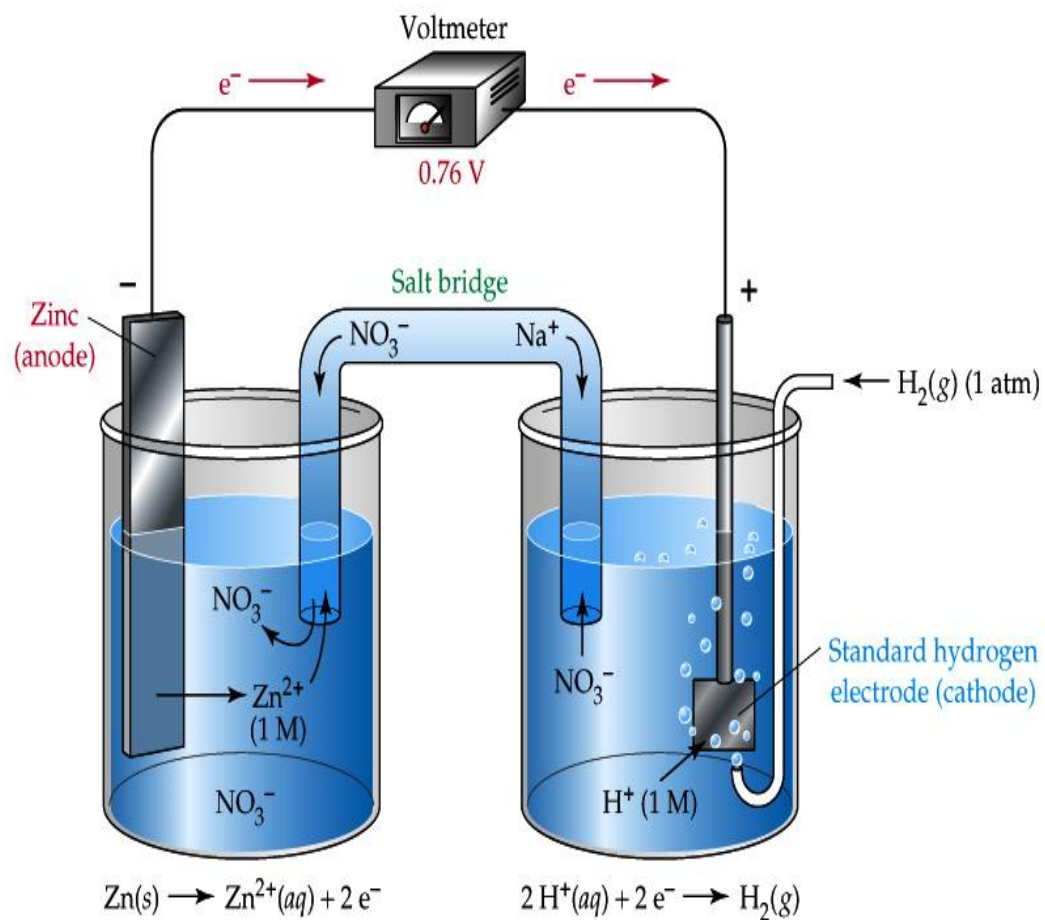
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidation}} + E^{\circ}_{\text{reduction}}$$

- Standard half-cell potentials are always quoted as a reduction process. The sign must be changed for the oxidation process.

Electrochemical Cells



- The *standard half-cell potentials* are determined from the *difference* between the two electrodes.
- The reference point is called the *standard hydrogen electrode (S.H.E.)* and consists of a platinum electrode in contact with H₂ gas (1 atm) and aqueous H⁺ ions (1 M).
- The *standard hydrogen electrode* is assigned an arbitrary value of exactly **0.00 V**.

Electrochemical Cells



Electrochemical Cells

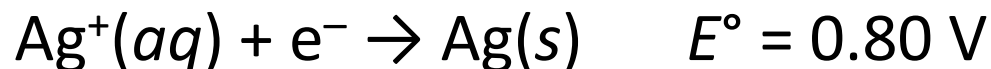
TABLE 18.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction	E° (V)	
<p>Stronger oxidizing agent</p> 	$F_2(g) + 2 e^- \longrightarrow 2 F^-(aq)$	2.87	<p>Weaker reducing agent</p> 
	$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51	
	$Cl_2(g) + 2 e^- \longrightarrow 2 Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33	
	$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$	1.23	
	$Br_2(l) + 2 e^- \longrightarrow 2 Br^-(aq)$	1.09	
	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2 e^- \longrightarrow 2 I^-(aq)$	0.54	
	$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2 e^- \longrightarrow Sn^{2+}(aq)$	0.15	
		$2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$	
<p>Weaker oxidizing agent</p>	$Pb^{2+}(aq) + 2 e^- \longrightarrow Pb(s)$	-0.13	
	$Ni^{2+}(aq) + 2 e^- \longrightarrow Ni(s)$	-0.26	
	$Cd^{2+}(aq) + 2 e^- \longrightarrow Cd(s)$	-0.40	
	$Fe^{2+}(aq) + 2 e^- \longrightarrow Fe(s)$	-0.45	
	$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s)$	-0.76	
	$2 H_2O(l) + 2 e^- \longrightarrow H_2(g) + 2 OH^-(aq)$	-0.83	
	$Al^{3+}(aq) + 3 e^- \longrightarrow Al(s)$	-1.66	
	$Mg^{2+}(aq) + 2 e^- \longrightarrow Mg(s)$	-2.37	
	$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71	
	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.04	

Electrochemical Cells

- When selecting two half-cell reactions the more negative value will form the oxidation half-cell.

- Consider the reaction between zinc and silver:



- Therefore, zinc forms the oxidation half-cell:



Spontaneity of a Reaction

- The value of E°_{cell} is related to the thermodynamic quantities of ΔG° and K .
- The value of E°_{cell} is related to ΔG° by:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

- The value of K is related to ΔG° by:

$$\Delta G^\circ = -RT \ln K$$

Spontaneity of a Reaction

- These are combined:

$$-nFE^{\circ}_{\text{cell}} = -RT \ln K$$

- and rearranged at 25°C to give:

$$E^{\circ}_{\text{cell}} = (0.0257/n) \ln K$$

or
$$E^{\circ}_{\text{cell}} = (0.0592/n) \log K$$

- (Units = volts, n = moles, F = 96,500 coulombs)

The Nernst Equation

- Cell potentials can be modified by temperature and composition changes according to the equation:

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

$$\therefore -nFE = -nFE^\circ + RT \ln K$$

- Giving: $E = E^\circ - (RT/nF) \ln K$

E = Potential of electrode/cell E° = Standard Potential

R = Molar Gas Constant
Kelvin

T = Temperature in

n = No. of electrons involved in rxn.

F = Faradays (96500 C)
Constant

K = Equilibrium

Therefore,

$$E = E^{\circ} - (RT/ nF) \ln K$$

$$E = E^{\circ} - 2.303(RT/ nF) (\log K)$$

$$R = 8.314 \text{ J/K.mol} \quad T = 298 \text{ K}$$

$$F = 96500 \text{ Coulomb}$$

Putting Values

$$E = E^{\circ} - (0.0592/ n) (\log K)$$

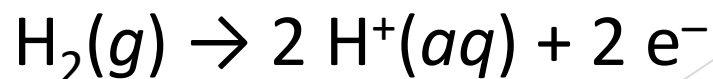
The Nernst Equation

- A particularly important use of the Nernst equation is in the electrochemical determination of pH.

Pt | H₂ (1 atm) | H⁺ (? M) || Reference
Cathode

$$E_{\text{cell}} = E_{\text{H}_2 \rightarrow \text{H}^+} + E_{\text{ref}}$$

- The Nernst equation can be applied to the half-reaction:



The Nernst Equation

- For the half-reaction: $\text{H}_2(g) \rightarrow 2 \text{H}^+(aq) + 2 e^-$

$$E_{\text{H}_2 \rightarrow \text{H}^+} = (E_{\text{H}_2 \rightarrow \text{H}^+}^{\circ}) - \left(\frac{0.0592\text{V}}{n} \right) \left(\log \frac{[\text{H}^+]^2}{P_{\text{H}_2}} \right)$$

- $E^{\circ} = 0 \text{ V}$ for this reaction (standard hydrogen electrode). P_{H_2} is 1 atm.

$$E_{\text{H}_2 \rightarrow \text{H}^+} = 0 \text{ V} - \left(\frac{0.0592\text{V}}{n} \right) (\log [\text{H}^+]^2)$$

The Nernst Equation

- The overall potential is given by:

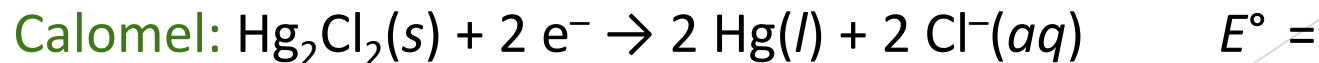
$$E_{\text{cell}} = (0.0592\text{V})(\text{pH}) + E_{\text{ref}}$$

- Which rearranges to give an equation for the determination of pH:

$$\frac{E_{\text{cell}} - E_{\text{ref}}}{0.0592\text{V}} = \text{pH}$$

The Nernst Equation

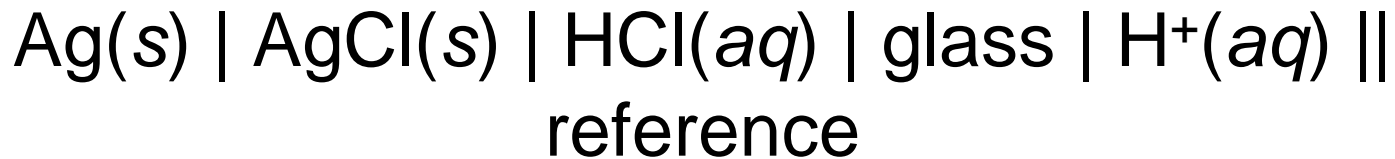
- A higher cell potential indicates a higher pH, therefore we can measure pH by measuring E_{cell} .
- A glass electrode (Ag/AgCl wire in dilute HCl) with a calomel reference is the most common arrangement.



0.28 V

The Nernst Equation

- The glass pH probe is constructed as follows:



- The difference in $[\text{H}^+]$ from one side of the glass membrane to the other causes a potential to develop, which adds to the measured E_{cell} .

$$\frac{E_{\text{cell}} - E_{\text{ref}}}{0.0592\text{V}} = \text{pH}$$

Batteries

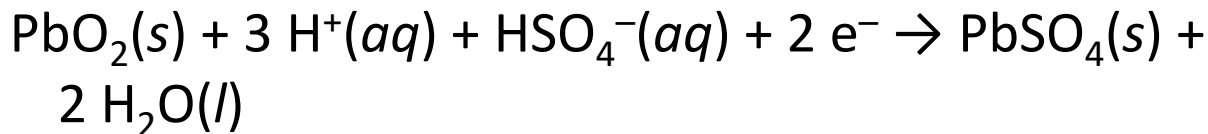
- Batteries are the most important practical application of galvanic cells.
- Single-cell batteries consist of one galvanic cell.
- Multi cell batteries consist of several galvanic cells linked in series to obtain the desired voltage.

Batteries

- **Lead Storage Battery:** A typical 12 volt battery consists of six individual cells connected in series.
 - **Anode:** Lead grid packed with spongy lead.



Cathode: Lead grid packed with lead oxide.



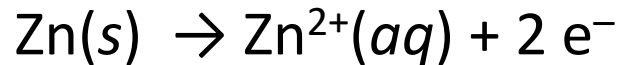
Electrolyte: 38% by mass sulfuric acid.

Cell Potential: 1.924 V

Batteries

- **Zinc Dry-Cell:** Also called a Leclanché cell, uses a viscous paste rather than a liquid solution.

Anode: Zinc metal can on outside of cell.



- **Cathode:** MnO_2 and carbon black paste on graphite.
- $2 \text{MnO}_2(s) + 2 \text{NH}_4^{+}(aq) + 2 e^{-} \rightarrow \text{Mn}_2\text{O}_3(s) + 2 \text{NH}_3(aq) + 2 \text{H}_2\text{O}(l)$
- **Electrolyte:** NH_4Cl and ZnCl_2 paste.
- **Cell Potential:** 1.5 V but deteriorates to 0.8 V with use.

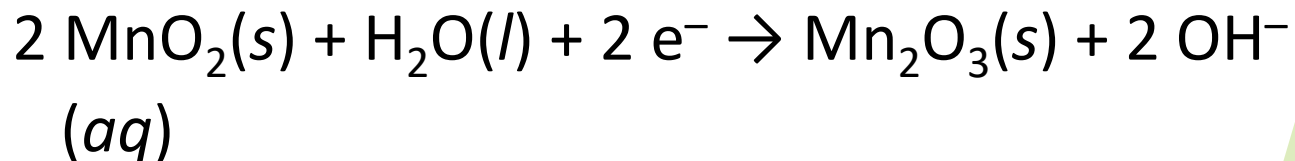
Batteries

- **Alkaline Dry-Cell:** Modified Leclanché cell which replaces NH_4Cl with NaOH or KOH .

Anode: Zinc metal can on outside of cell.



Cathode: MnO_2 and carbon black paste on graphite.



Electrolyte: NaOH or KOH , and $\text{Zn}(\text{OH})_2$ paste.

Cell Potential: 1.5 V but longer lasting, higher power, and more stable current and voltage.

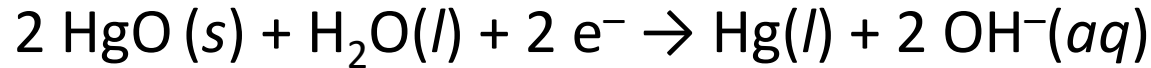
Batteries

- **Mercury Dry-Cell:** Modified Leclanché cell which replaces MnO_2 with HgO and uses a steel cathode.

Anode: Zinc metal can on outside of cell.



Cathode: HgO in contact with steel.



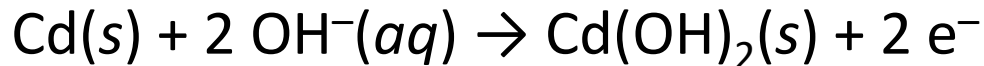
Electrolyte: KOH , and $\text{Zn}(\text{OH})_2$ paste.

Cell Potential: 1.3 V with small size, longer lasting, and stable current and voltage.

Batteries

- **Nickel–Cadmium Battery:** Modified Leclanché cell which is rechargeable.

Anode: Cadmium metal.



Cathode: Nickel(III) compound on nickel metal.

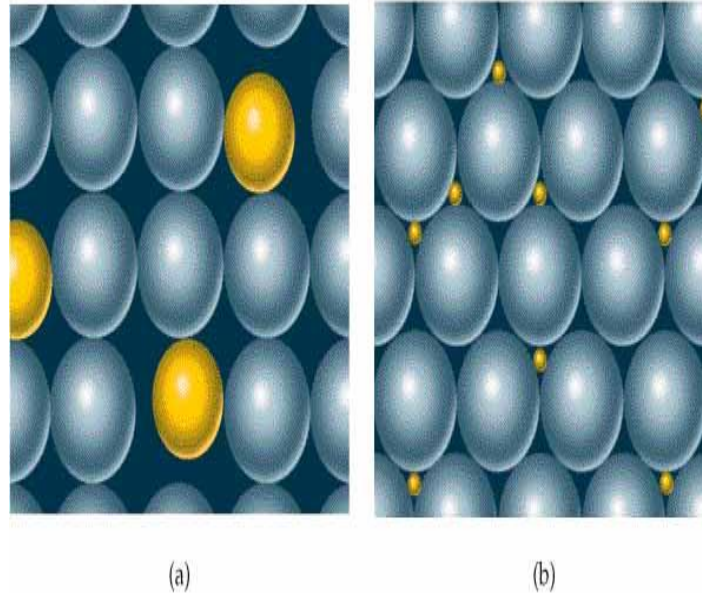


Electrolyte: Nickel oxyhydroxide, NiO(OH).

Cell Potential: 1.30 V

Batteries

- **Nickel–Metal–Hydride (NiMH):**
- Replaces toxic Cd anode with a hydrogen atom impregnated ZrNi_2 metal alloy.
- During oxidation at the anode, hydrogen atoms are released as H_2O .
- Recharging reverses this reaction.

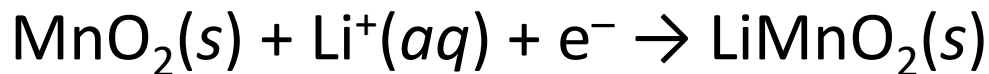


Batteries

- **Lithium Ion (Li-ion):** The newest rechargeable battery is based on the migration of Li^+ ions.
- **Anode:** Li metal, or Li atom impregnated graphite.



Cathode: Metal oxide or sulfide that can accept Li^+ .



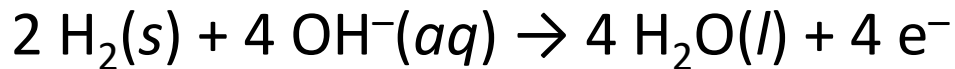
Electrolyte: Lithium-containing salt such as LiClO_4 , in organic solvent. Solid state polymers can also be used.

Cell Potential: 3.0 V

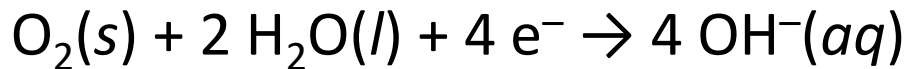
Batteries

- **Fuel Cell:** Uses externally fed CH_4 or H_2 , which react to form water. The most common is H_2 .

- **Anode:** Porous carbon-containing metallic catalysts.



- Cathode:** Porous carbon-containing metallic catalysts.

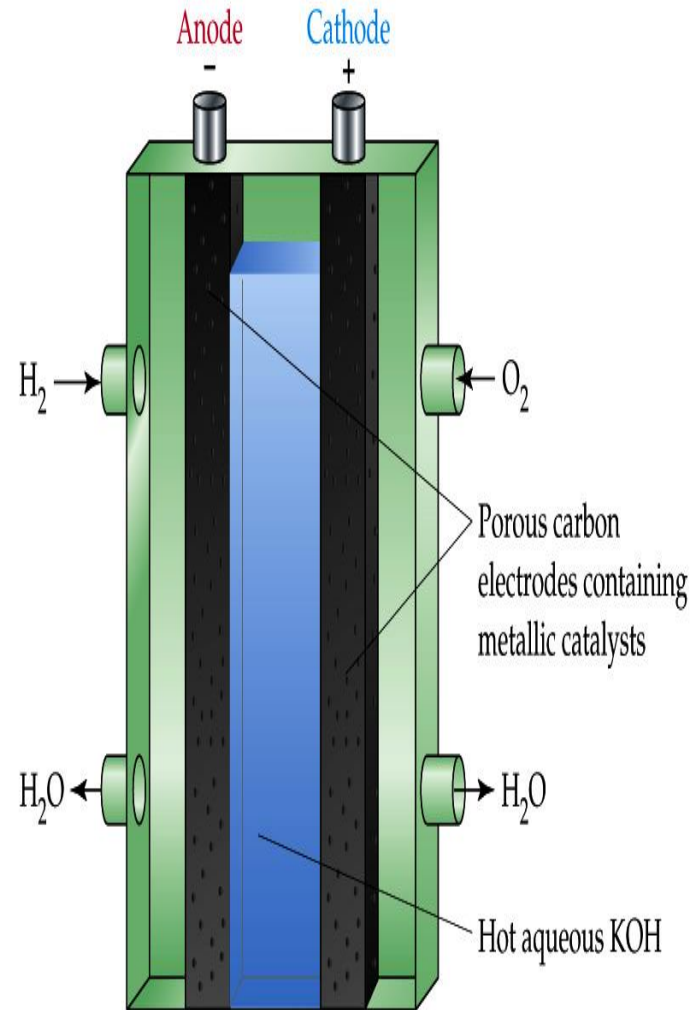


Electrolyte: Hot aqueous KOH solution.

Cell Potential: 1.23 V, but is only 40% of cell capacity.

Batteries

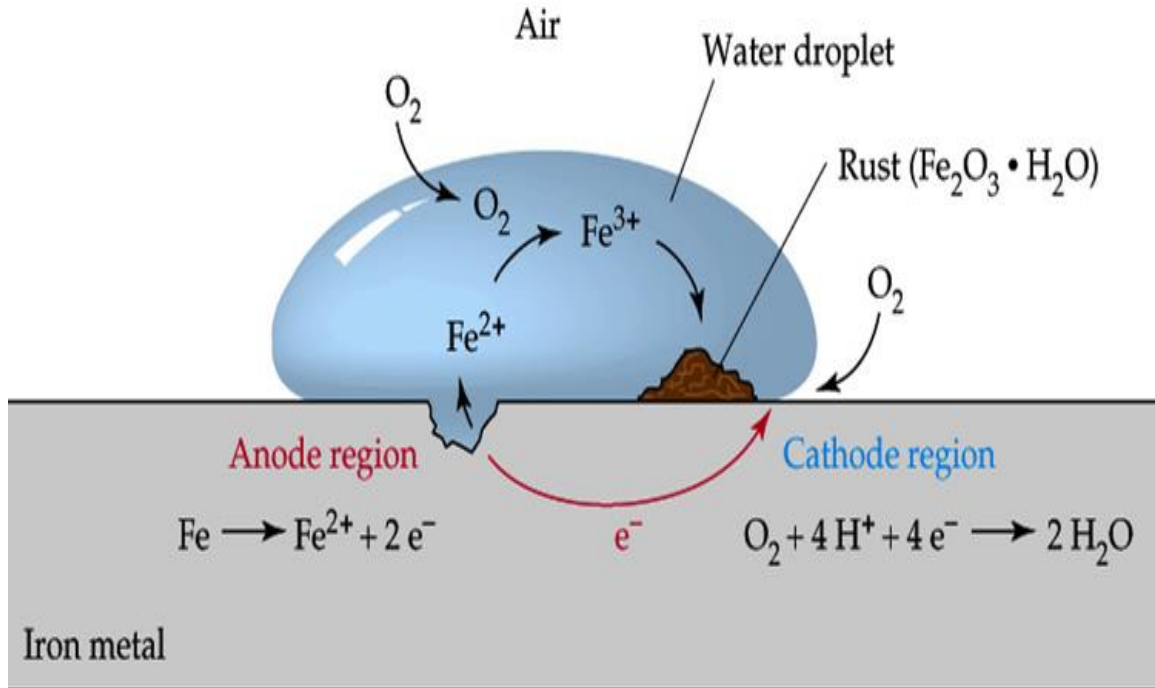
- Fuel cells are not batteries because they are not self-contained.
- Fuel cells typically have about 40% conversion to electricity; the remainder is lost as heat.
- Excess heat can be used to drive turbine generators.



Corrosion

- Corrosion is the oxidative deterioration of metal.
- 25% of steel produced in USA goes to replace steel structures and products destroyed by corrosion.
- Rusting of iron requires the presence of BOTH oxygen and water.
- Rusting results from tiny galvanic cells formed by water droplets.

Corrosion



Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

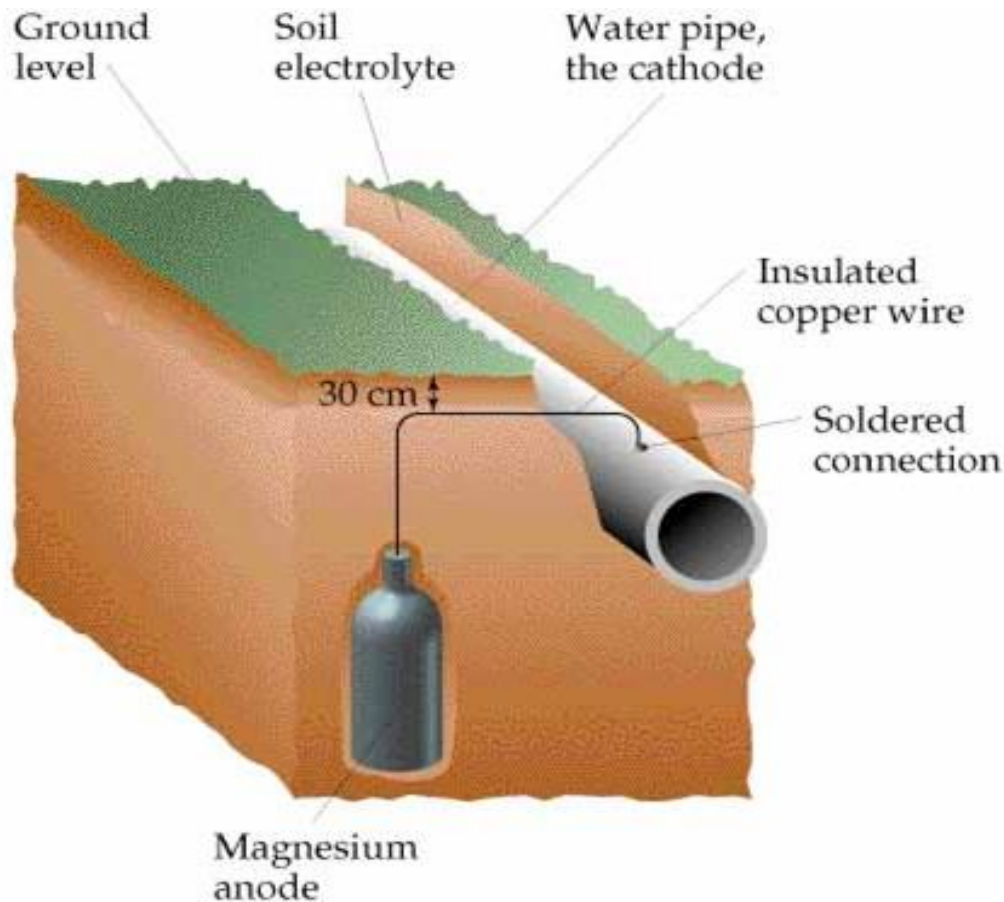
Overall: $2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

Corrosion

- **Galvanizing:** is the coating of iron with zinc. Zinc is more easily oxidized than iron, which protects and reverses oxidation of the iron.
- **Cathodic Protection:** is the protection of a metal from corrosion by connecting it to a metal (*a sacrificial anode*) that is more easily oxidized.
- All that is required is an electrical connection to the *sacrificial anode* (usually magnesium or zinc).

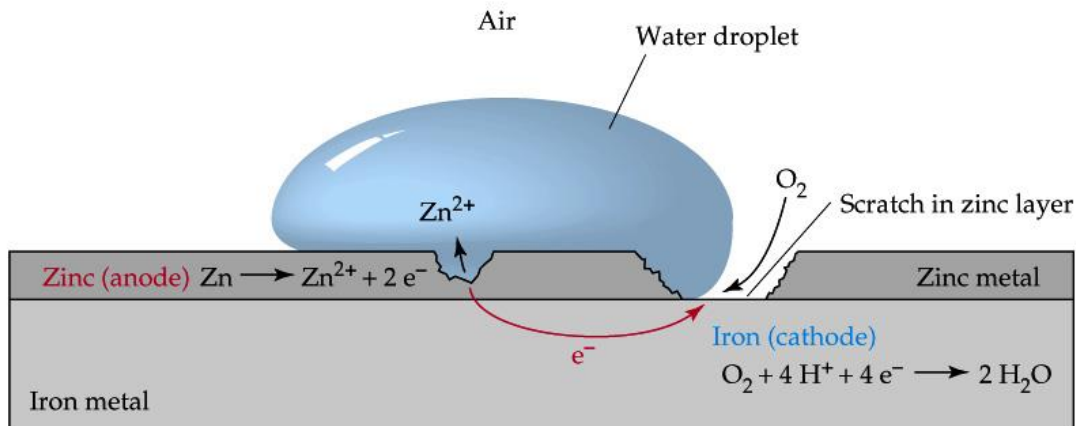
Corrosion

- Cathodic Protection with Magnesium Anode



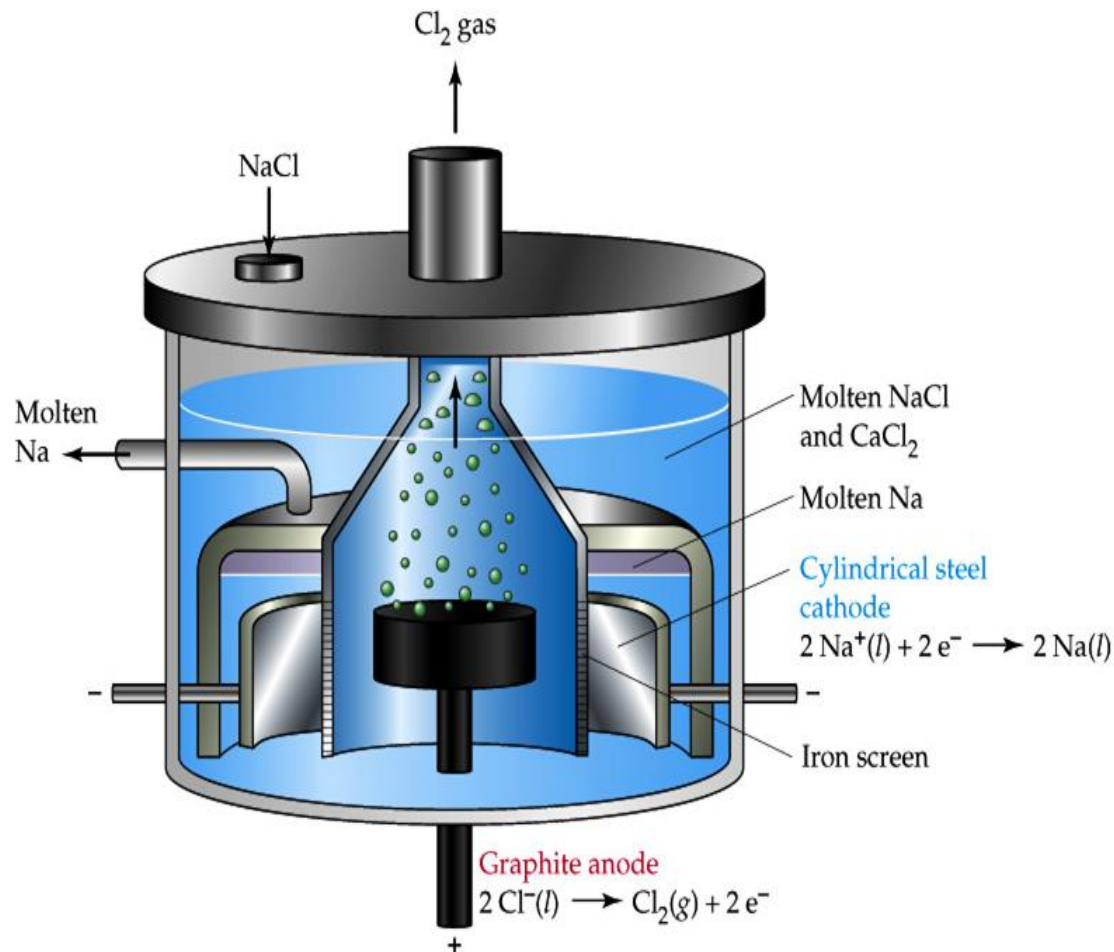
Corrosion

- Cathodic Protection with Zinc Layer



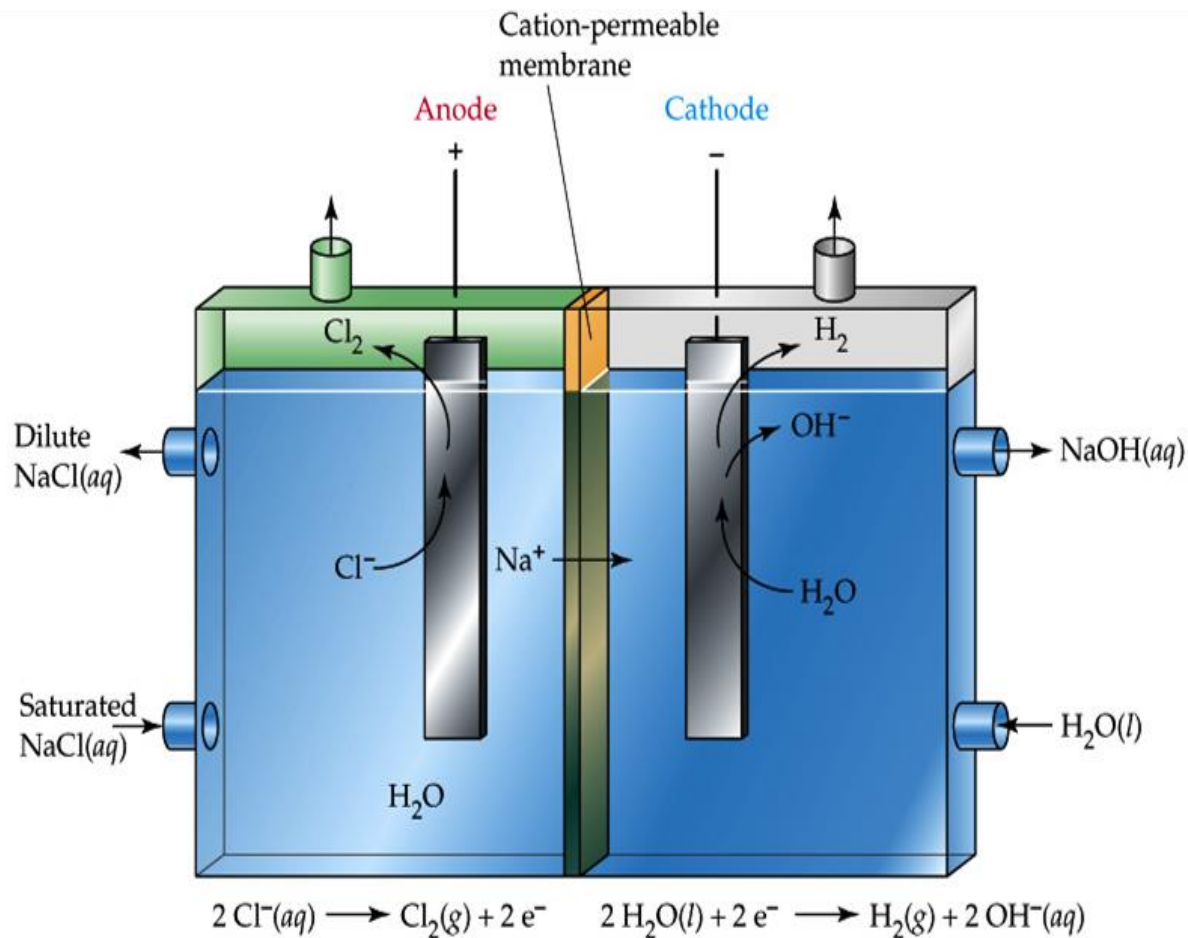
Electrolysis Applications

- **Manufacture of Sodium (Downs Cell):**



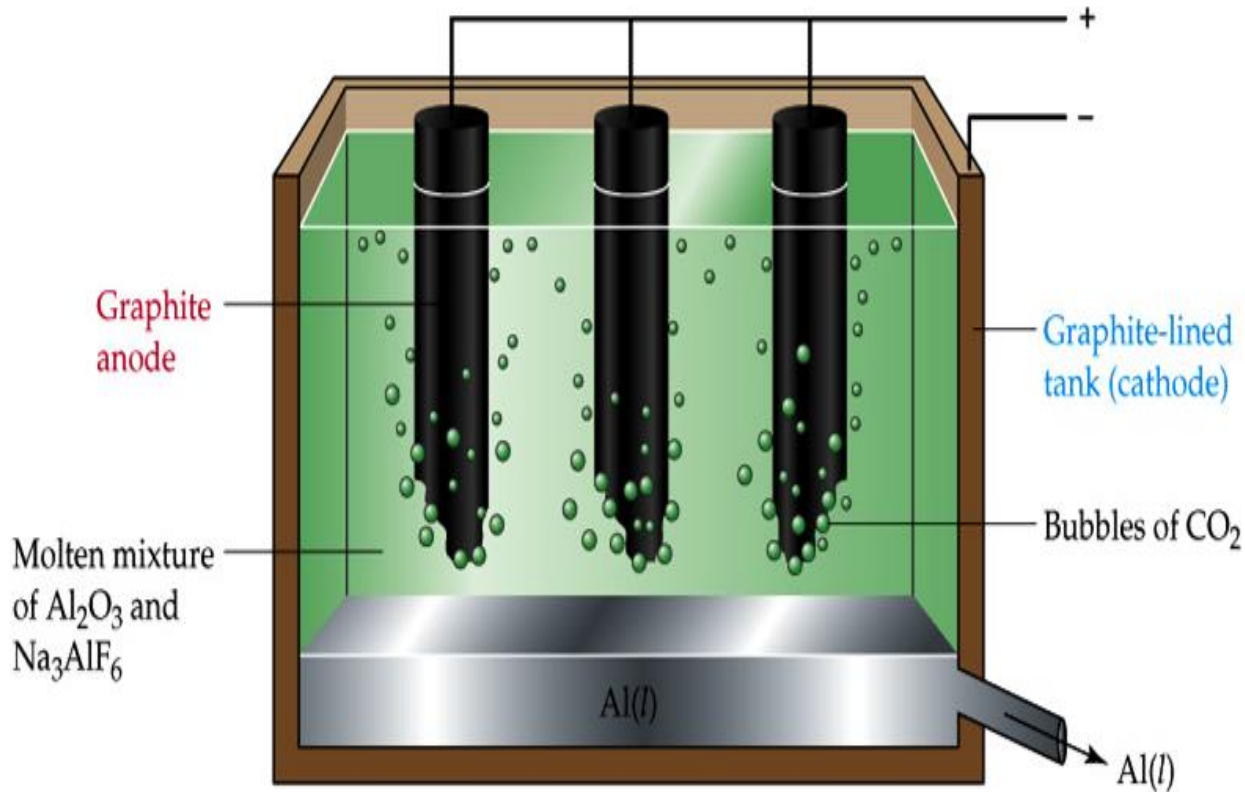
Electrolysis Applications

- **Manufacture of Cl_2 and NaOH (Chlor–Alkali):**



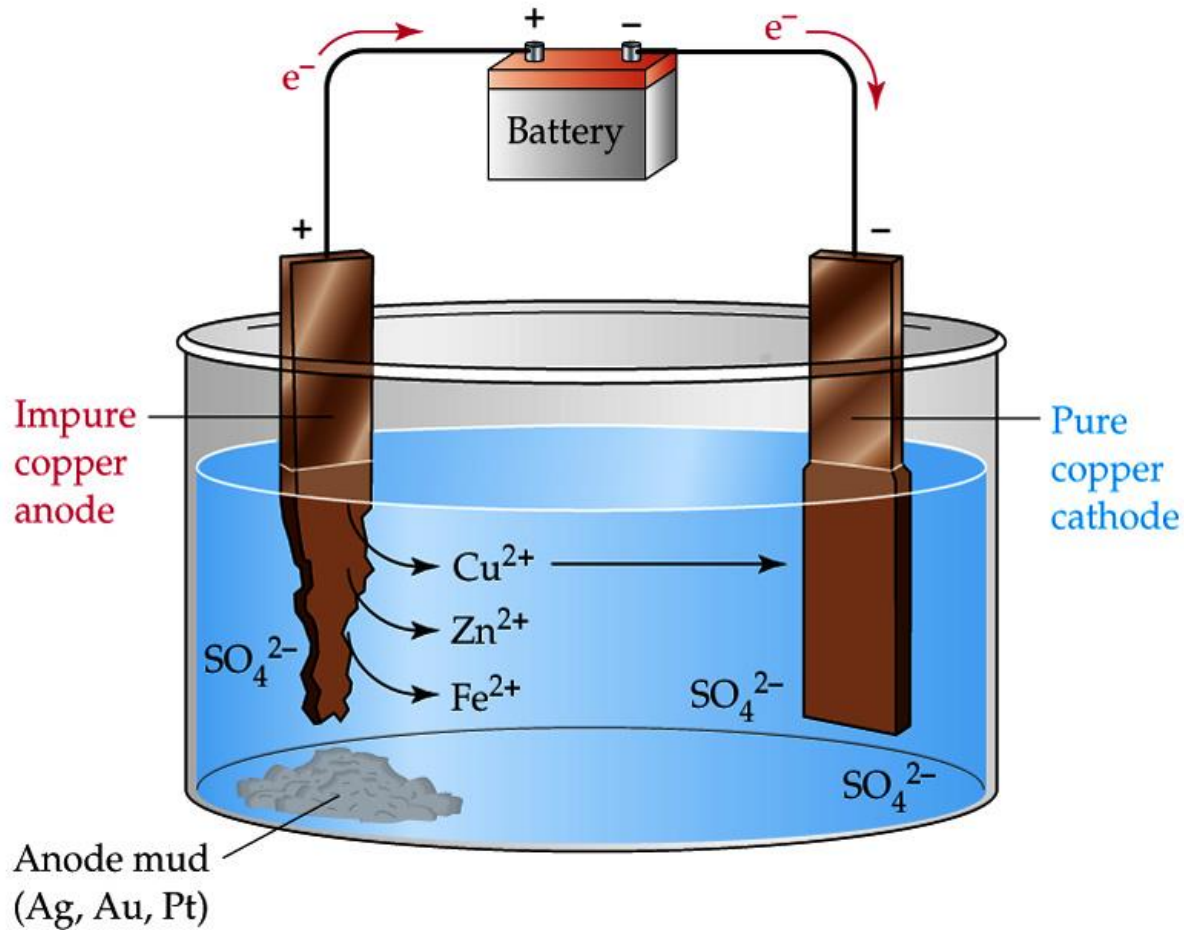
Electrolysis Applications

- **Manufacture of Aluminum (Hall– Heroult):**



Electrolysis Applications

- **Electrorefining and Electroplating:**



THANK

YOU