Electrochemistry

Basic terms

electric current
to flow
circuit
cell
electrode
salt bridge
solute
anion
cation

molten state
potential
electromotive force
fuel cell

Electrochemistry and Redox

Oxidation-reduction: “Redox”

Electrochemistry:

study of the interchange between chemical change and electrical work

Electrochemical cells:

systems utilizing a redox reaction to produce or use electrical energy

Redox

Oxidation is loss of e^-

O.N. increases (more positive)

Reduction is gain of e^-

O.N. decreases (more negative)

Oxidation involves loss OIL
Reduction involves gain RIG

Redox Terminology

PROCESS	$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$
OXIDATION • One reactant loses electrons • Reducing agent is oxidized • Oxidation number increases	Zinc **loses** electrons. Zinc is the reducing agent and becomes **oxidized**. The oxidation number of Zn **increases** from 0 to +2.
REDUCTION • Other reactant gains electrons • Oxidizing agent is reduced • Oxidation number decreases	Hydrogen ion **gains** electrons. Hydrogen ion is the oxidizing agent and becomes **reduced**. The oxidation number of H^+ **decreases** from +1 to 0.

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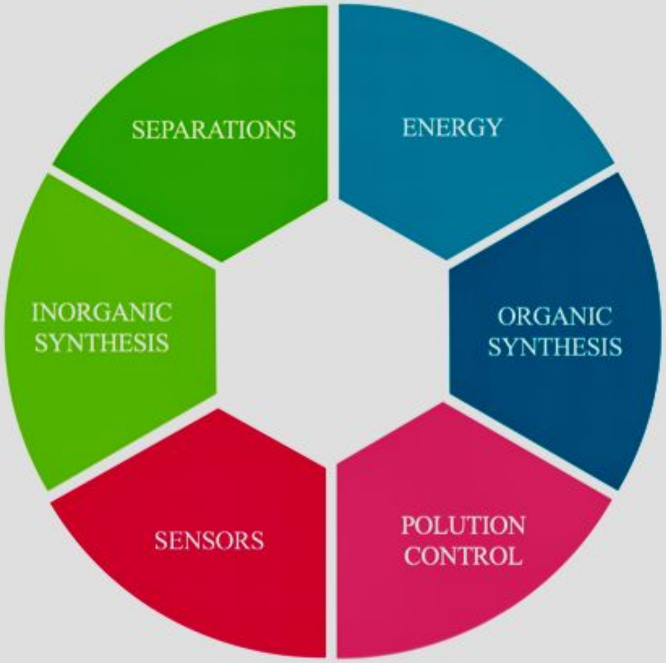
Applications of Electrochemistry



SEPARATIONS

Salt Splitting
Electrodialysis

INORGANIC SYNTHESIS

Chlor-alkali manufacture
Aluminum Refining
Water Electrolysis
Halogens, peracids, peroxide, ferrate
Metals extraction and refining: Al, Na, Mg, Li,

SENSORS

ENERGY

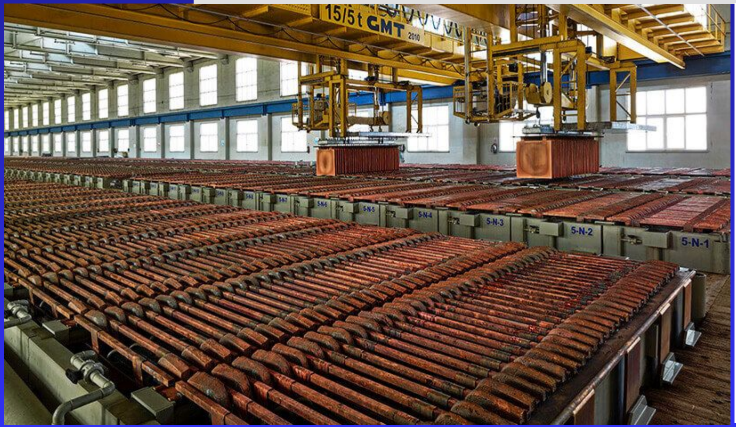
Redox Flow Cells
Fuel Cells
Batteries

ORGANIC SYNTHESIS

Halogenation, Dehalogenation
Methoxylation, Acetoxylation
Hydrogenation
Carboxylation and Decarboxylation
Coupling Reactions
Nitro Reduction

POLUTION CONTROL

Metal Recovery
Recycle of chemicals
Scrubbing of Industrial Gases



Types of cells

- **Voltaic (galvanic) cells:**

a spontaneous reaction generates electrical energy

Chemistry→Electricity

- **Electrolytic cells:**

absorb free energy from an electrical source to drive a nonspontaneous reaction

Electricity→Chemistry

Common Components

- Electrodes:

  conduct electricity between cell and surroundings

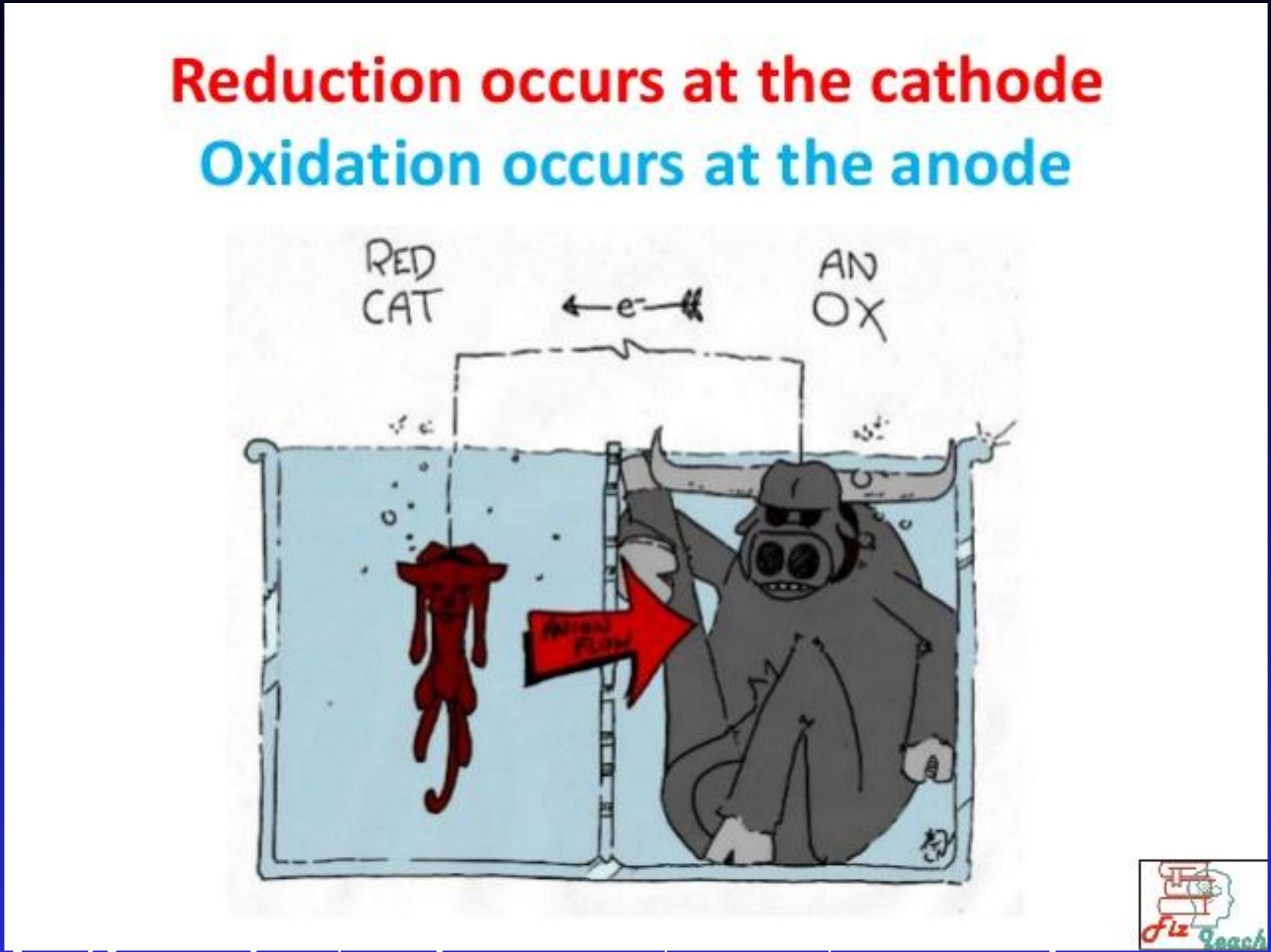
- Electrolyte:

  mixture of ions involved in reaction or carrying charge

- Salt bridge:

  completes circuit (provides charge balance)

Electrodes



Reduction occurs at the cathode

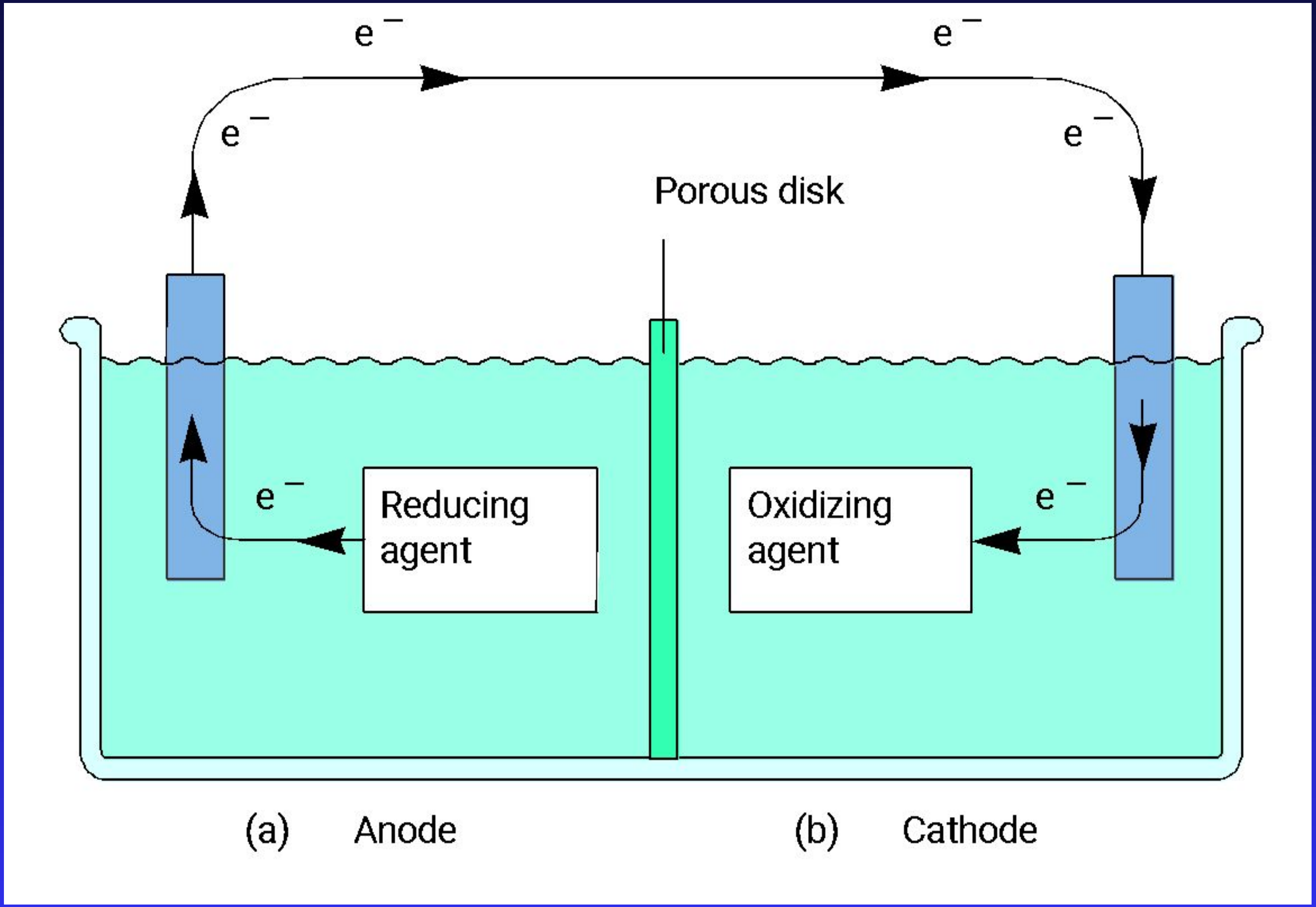
Oxidation occurs at the anode

Active electrodes: participate in redox

Inactive: sites of ox. and red.

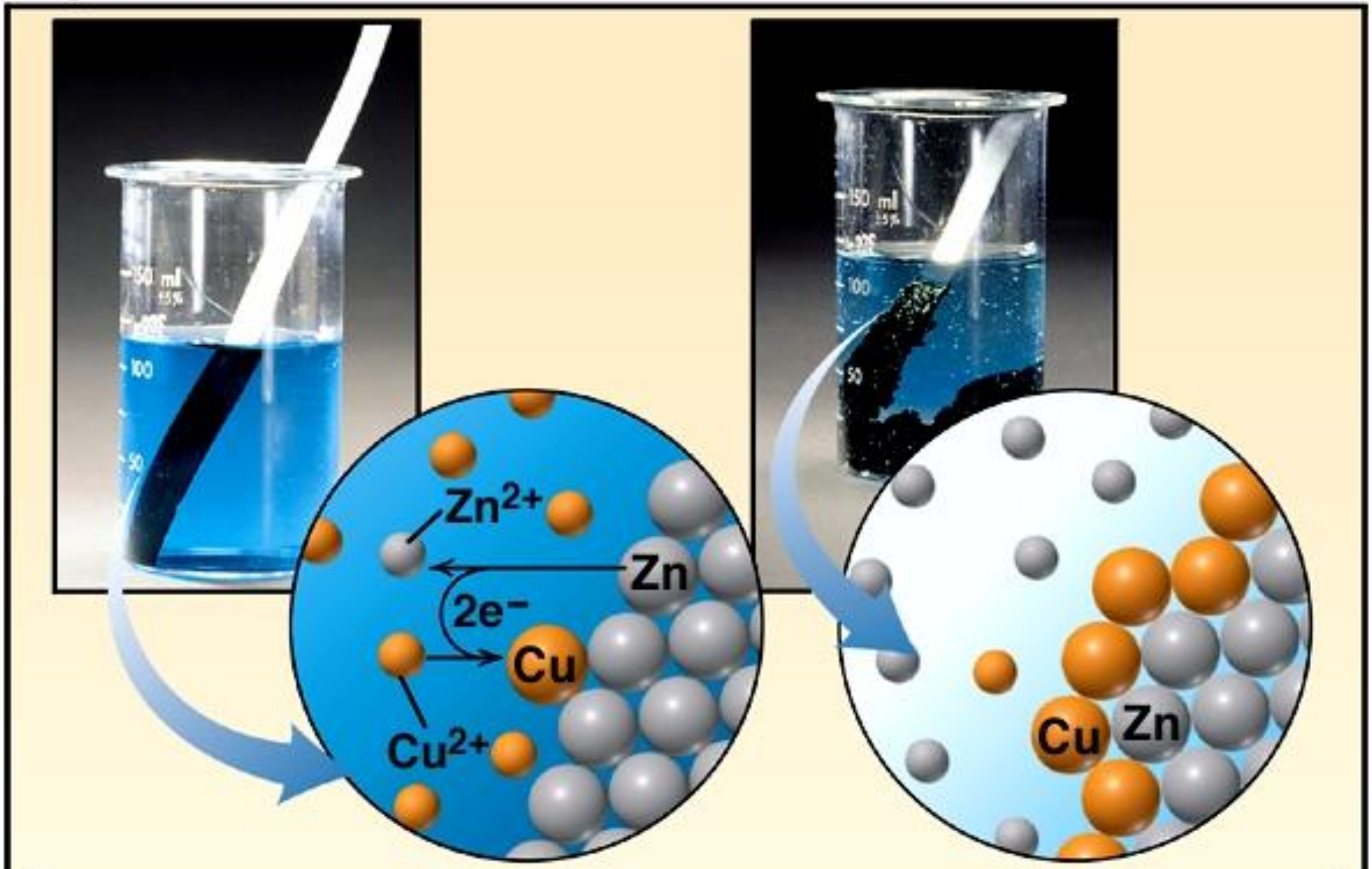
Voltaic (Galvanic) Cells

A device in which chemical energy is changed to electrical energy. Uses a spontaneous reaction.



Alessandro Volta (1745–1827)
Luigi Galvani (1737-1798)

Spontaneous Reaction between Zn and Cu^{2+}



$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

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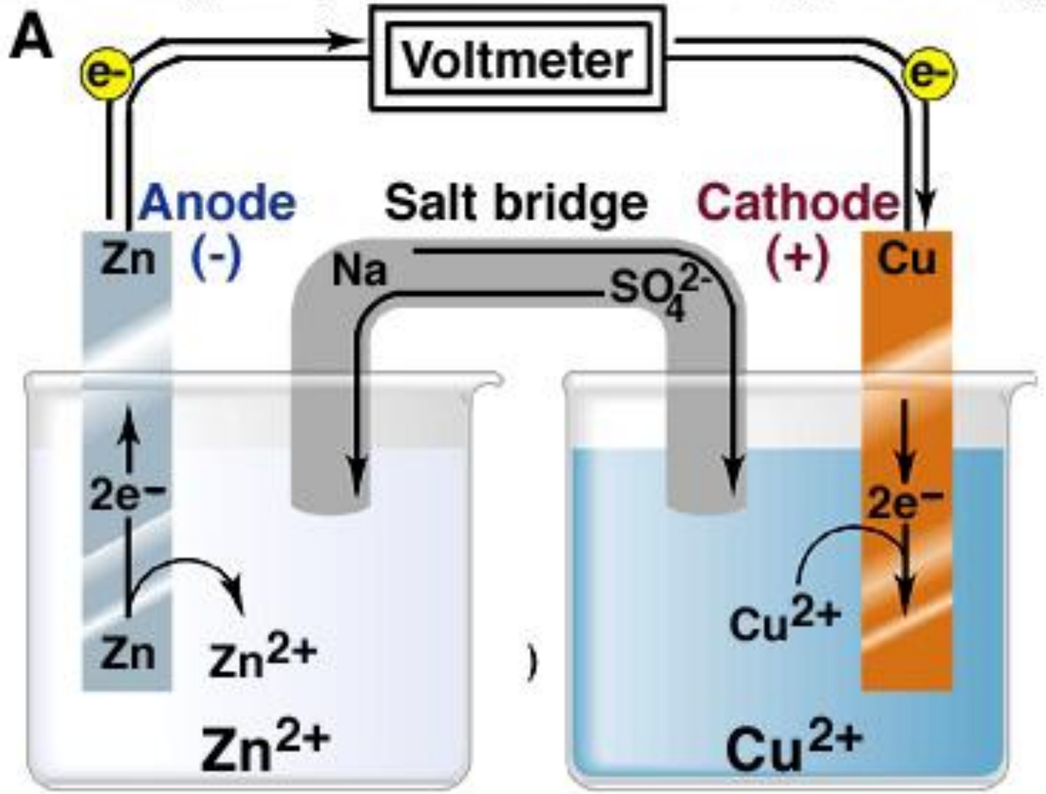
Zinc-Copper Reaction Voltaic Cell



Oxidation half-reaction

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

Reduction half-reaction

$$2e^- + Cu^{2+}(aq) \longrightarrow Cu(s)$$

Overall (cell) reaction

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

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$$Zn^{2+}_{(aq)} + Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + Zn_{(s)}$$

Zn gives up electrons to Cu

- "pushes harder" on e^-
- greater potential energy
- greater "electrical potential"

Spontaneous reaction due to

- relative difference in metals' abilities to give e^-
- ability of e^- to flow

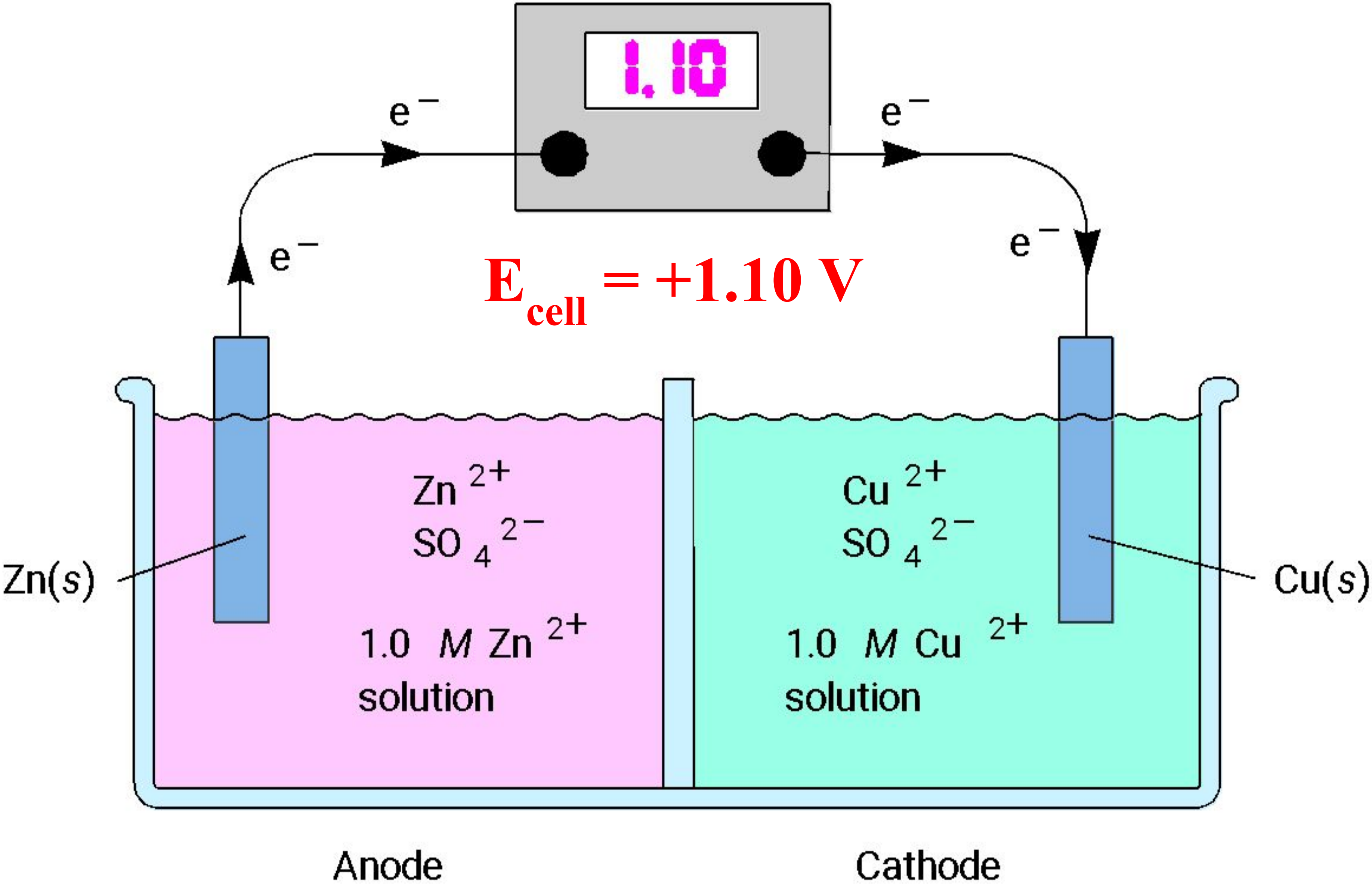
Designing a cell

- half-equations representing reactions in each half-cell
- overall ionic equation
- polarity of electrodes and their nature (anode and cathode)
- oxidizing agent and reducing agent
- direction of flow of electrons through the conducting wires and of ions

through the salt bridge

- physical changes occurring at the electrodes or in their vicinity (metal

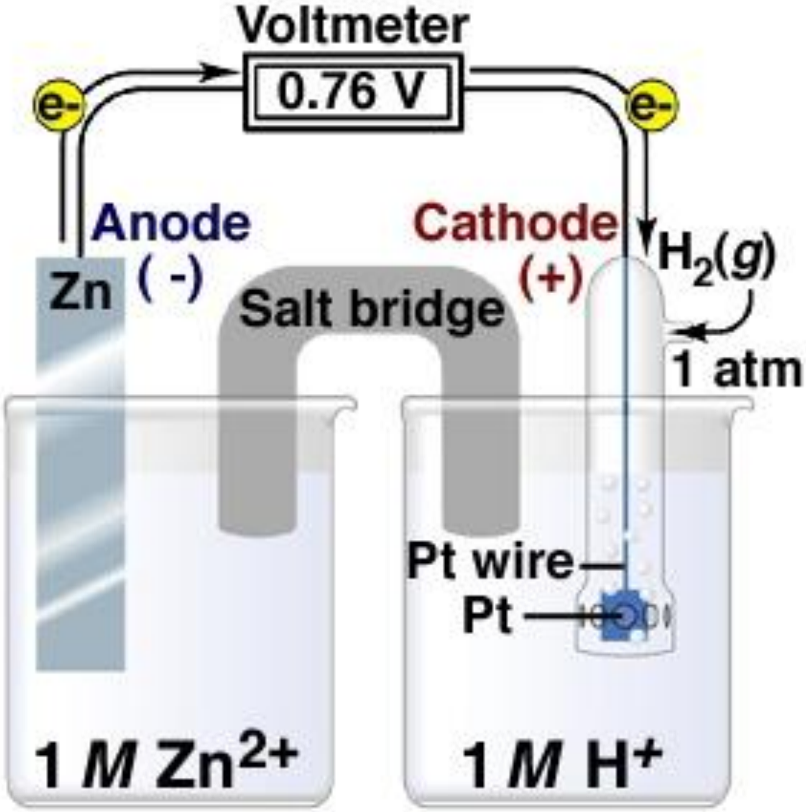
deposition, electrode dissolution, changes in pH and so on).



$E_{cell} = +1.10\ V$

1.10
e^-
e^-
e^-
e^-
$Zn(s)$
Zn^{2+}
SO_4^{2-}
1.0 M Zn^{2+} solution
Cu^{2+}
SO_4^{2-}
1.0 M Cu^{2+} solution
$Cu(s)$
Anode
Cathode

The Standard Hydrogen Electrode



Oxidation half-reaction

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Reduction half-reaction

$2H^+(aq) + 2e^- \rightarrow H_2(g)$

Overall (cell) reaction

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

Cell Potential

A galvanic cell consists of an oxidizing agent (in cathode half-cell) and a reducing agent (in anode half-cell).

Electrons flows through a wire from the anode half-cell to the cathode half-cell.

The driving force that allows electrons to flow is called the electromotive force (emf) or the cell potential (E_{cell}).

- The unit of electrical potential is *volt* (V).

  1 V = 1 J/C of charge transferred.

Standard Reduction Potentials

E^0 values for reduction half-reactions with solutes at 1M and gases at 1 atm

$$Cu^{2+} + 2e^- \rightarrow Cu$$

$$E^0 = 0.34 \text{ V vs. SHE}$$

$$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$$

$$E^0 = 0.20 \text{ V vs. SHE}$$

Standard Electrode Potentials - Part 1

Table 21.2 Standard Electrode (Half-Cell) Potentials (298 K)*

Half-Reaction	E^0 (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$	+2.07
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.70
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	+0.22

*Written as reductions; E^0 value refers to all components in their standard states: 1 *M* for dissolved species; 1 atm pressure for gases; the pure substance for solids and liquids.

Standard Electrode Potentials - Part 2

Table 21.2 Standard Electrode (Half-Cell) Potentials (298 K)*

Half-Reaction	E^0 (V)
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons SO_2(g) + 2H_2O(l)$	+0.20
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	−0.23
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	−0.28
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	−2.90
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.93
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05

*Written as reductions; E^0 value refers to all components in their standard states: 1 *M* for dissolved species; 1 atm pressure for gases; the pure substance for solids and liquids.

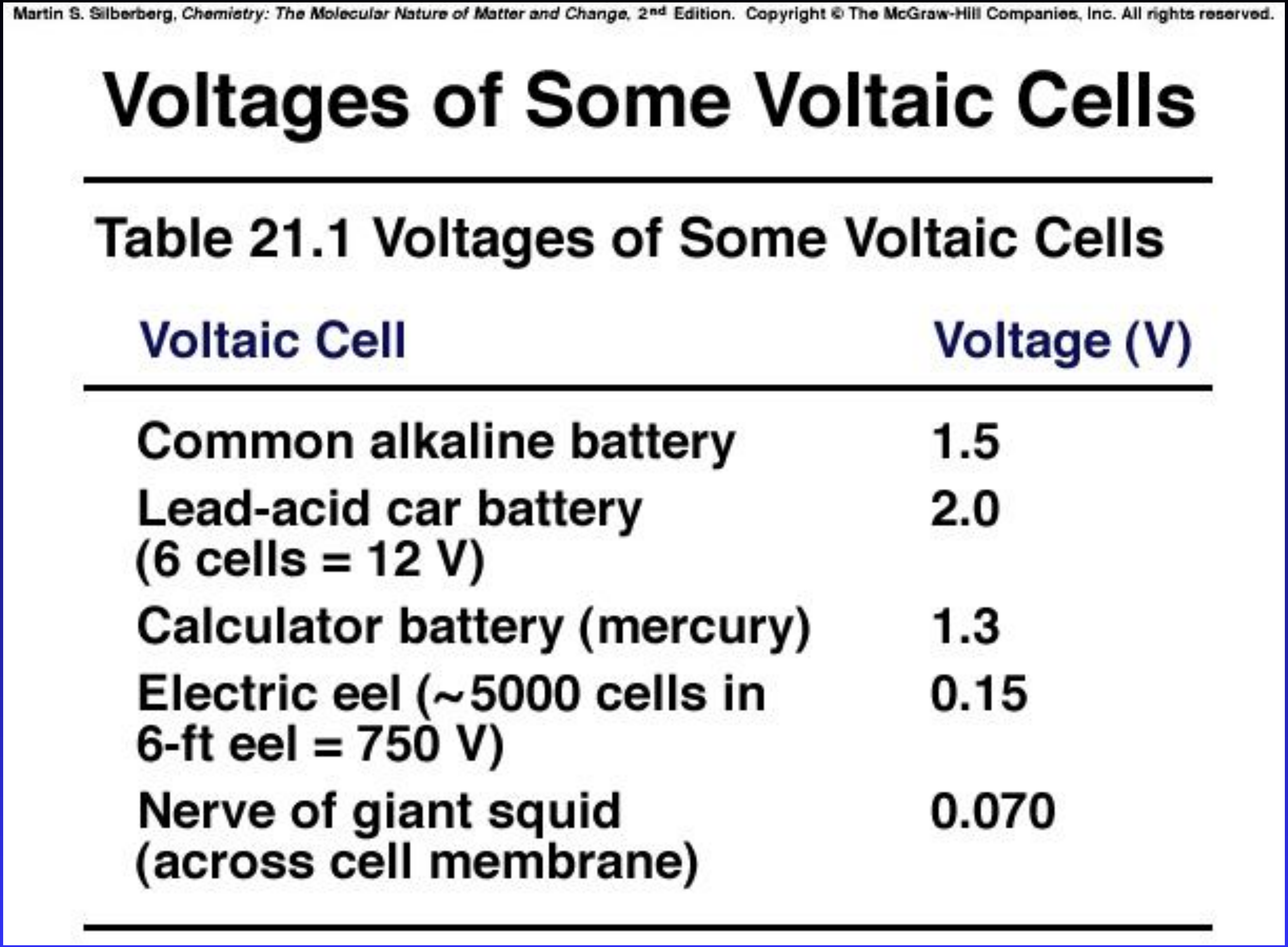
Calculating E^0_{cell}

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$E^0_{cell} > 0$ Spontaneous

$E^0_{cell} < 0$ Not

$E^0_{cell} = 0$ Equilibrium



Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 2nd Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

Voltages of Some Voltaic Cells

Table 21.1 Voltages of Some Voltaic Cells

Voltaic Cell	Voltage (V)
Common alkaline battery	1.5
Lead-acid car battery (6 cells = 12 V)	2.0
Calculator battery (mercury)	1.3
Electric eel (~5000 cells in 6-ft eel = 750 V)	0.15
Nerve of giant squid (across cell membrane)	0.070

The **Nernst equation** is an equation that relates the reduction potential of an electrochemical reaction (half-cell or full cell reaction) to the standard electrode potential, temperature, and activities (often approximated by concentrations) of the chemical species undergoing reduction and oxidation.

Walther Nernst
(1864-1941)

Nernst Equation

Under nonstandard conditions

$$\Delta G = \Delta G^0 + RT\ln Q$$

$$-nFE = -nFE^0 + RT\ln Q$$

$$\boxed{E_{cell} = E^0 - \frac{RT}{nF}\ln Q}$$

$$\boxed{E_{cell}^{298K} = E^0 - \frac{0.0592}{n}\ln Q}$$

E_{cell} is the cell potential (electromotive force) at the temperature of interest,

$E^{\ominus}_{\text{cell}}$ is the standard cell potential,

R is the universal gas constant: $R = 8.314472(15)\ \text{J K}^{-1}\ \text{mol}^{-1}$,

T is the temperature in kelvins

$F = 9.64853399(24)\times10^{4}\ \text{C mol}^{-1}$,

Q_{r} is the reaction quotient of the cell reaction.

Batteries

A **battery** is a galvanic cell or, more commonly, a **group** of galvanic cells connected in series.

Leclanché Acidic Dry Cell

Electrolyte in paste form

- $ZnCl_2 + NH_4Cl$

  Or $MgBr_2$

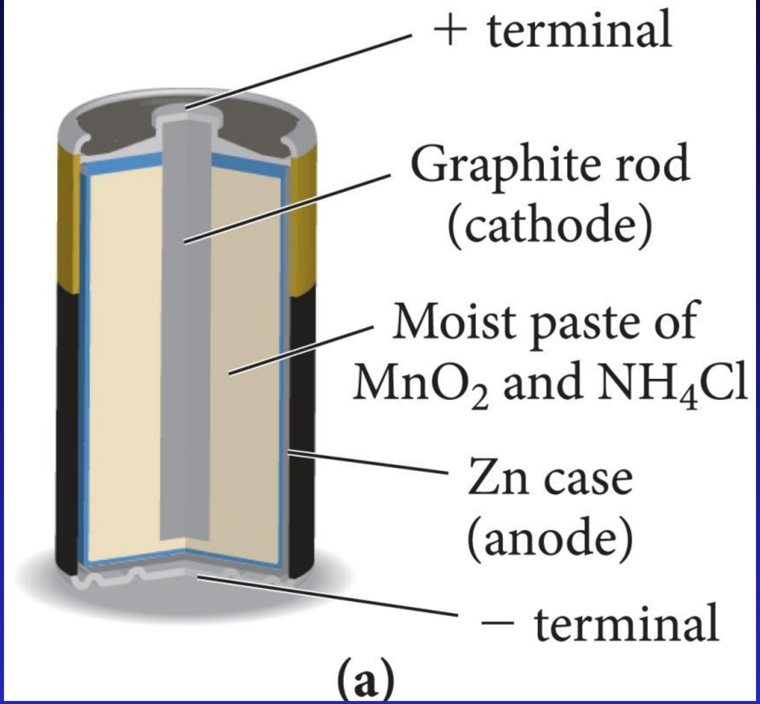
Anode = Zn (or Mg)

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$$

Cathode = graphite rod

MnO_2 is reduced.

$$2\ MnO_2(s) + 2\ NH_4^+(aq) + 2\ H_2O(l) + 2\ e^- \rightarrow 2\ NH_4OH(aq) + 2\ Mn(O)OH(s)$$



Cell voltage = 1.5 V

Expensive, nonrechargeable, heavy, easily corroded

Alkaline Dry Cell

Same basic cell as acidic dry cell, except electrolyte is alkaline KOH paste

Anode = Zn (or Mg)

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^{-}$$

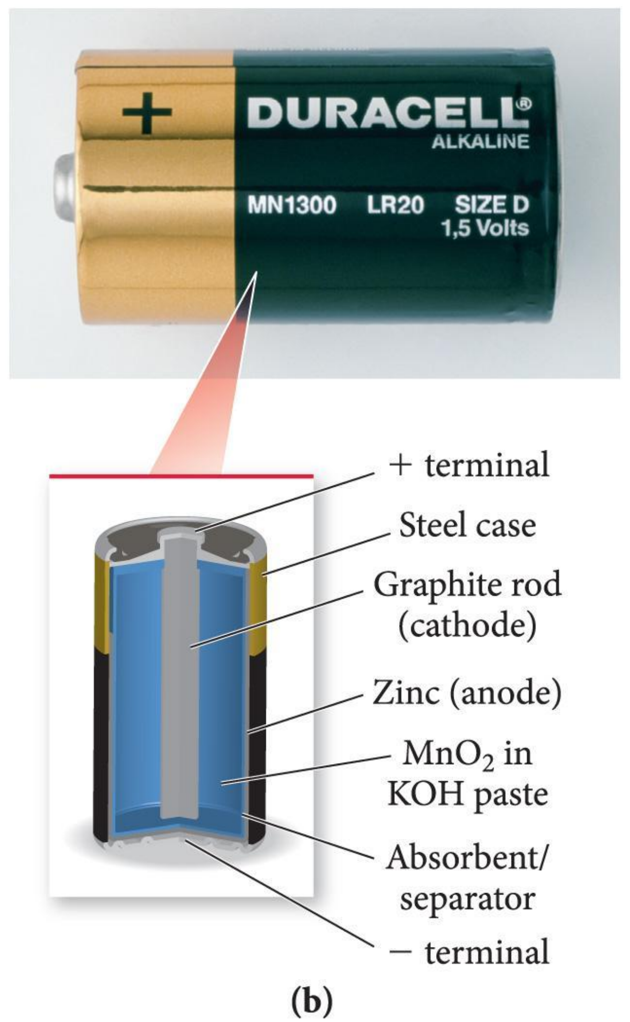
Cathode = graphite or brass rod

MnO_2 is reduced.

$$2\,MnO_2(s) + 2\,NH_4^{+}(aq) + 2\,H_2O(l) + 2\,e^{-} \rightarrow 2\,NH_4OH(aq) + 2\,Mn(O)OH(s)$$

Cell voltage = 1.54 V

Longer shelf life than acidic dry cells and rechargeable, with little corrosion of zinc.



Lead Storage Battery

Six cells in series

Electrolyte = 30% H_2SO_4

Anode = Pb

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2\ e^-$$

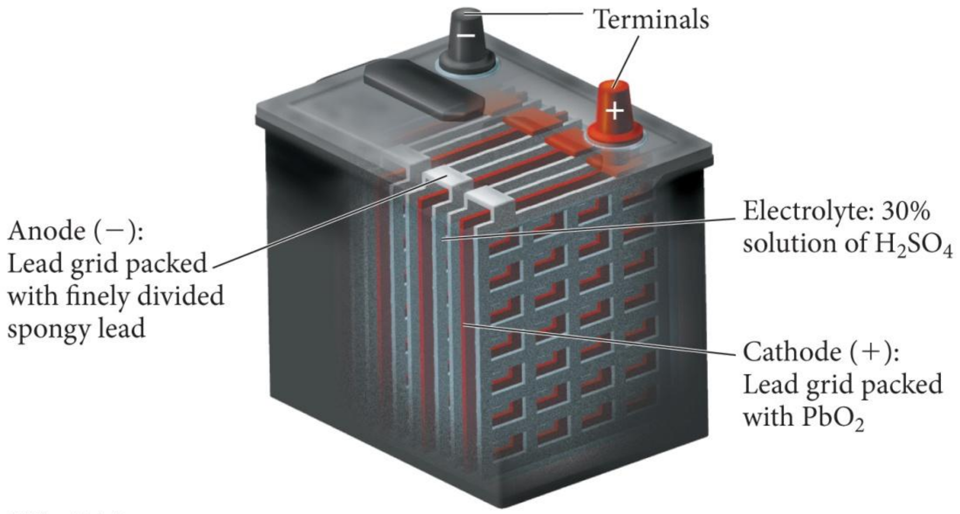
Cathode = Pb coated with PbO_2

PbO_2 is reduced.

$$PbO_2(s) + 4\ H^+(aq) + SO_4^{2-}(aq) +$$
$$\rightarrow PbSO_4(s) + 2\ H_2O(l)$$

Cell voltage = 2.09 V

Rechargeable, heavy



NiCad Battery

Electrolyte is concentrated KOH solution

Anode = Cd

$$Cd(s) + 2\ OH^-(aq) \rightarrow Cd(OH)_2(s) + 2\ e^-$$

$$E^0 = 0.81\ V$$

Cathode = Ni coated with NiO_2

NiO_2 is reduced.

$$NiO_2(s) + 2\ H_2O(l) + 2\ e^- \rightarrow Ni(OH)_2(s) + 2OH^-$$

Cell voltage = 1.30 V

Rechargeable,

long life, light;

however, recharging incorrectly

can lead to battery breakdown

Ni-MH Battery

Electrolyte is concentrated KOH solution

Anode = metal alloy with dissolved hydrogen

- Oxidation of H from H^0 to H^+

$$M \cdot H(s) + OH^-(aq) \rightarrow M(s) + H_2O(l) + e^-$$

$$E° = 0.89\ V$$

Cathode = Ni coated with NiO_2

NiO_2 is reduced.

$$NiO_2(s) + 2\ H_2O(l) + 2\ e^- \rightarrow Ni(OH)_2(s) + 2OH^-$$

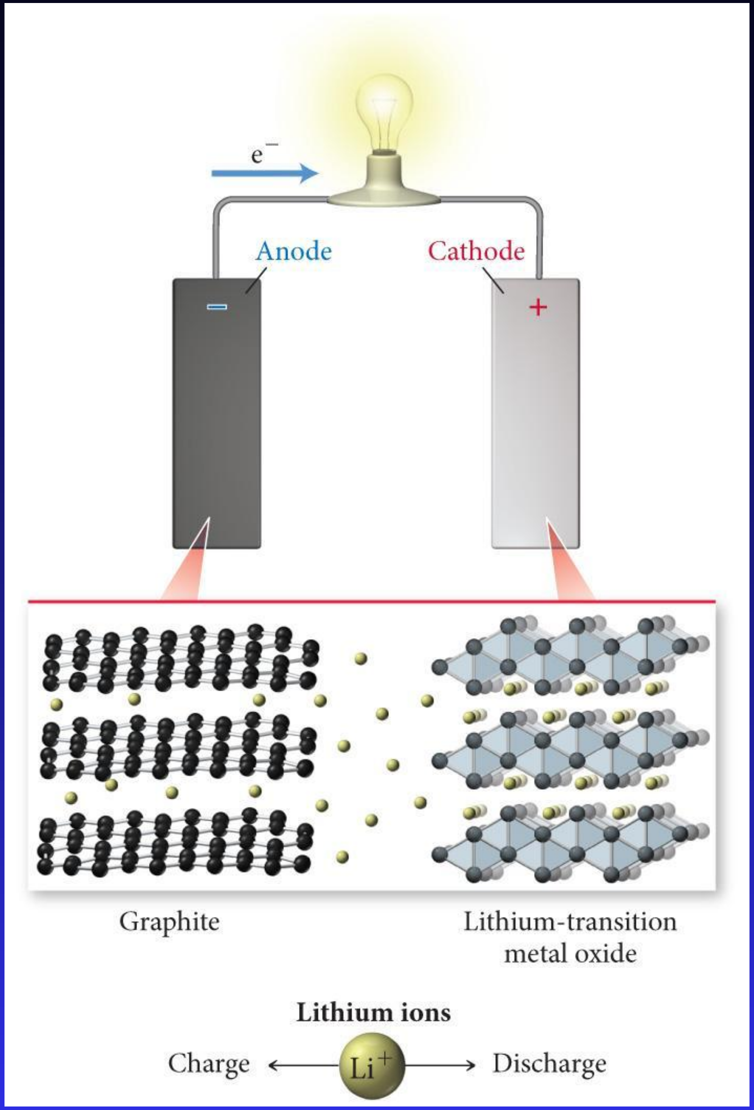
$$E^0 = 0.49\ V$$

Cell voltage = 1.30 V

Rechargeable, long life, light, more environmentally friendly than NiCad, greater energy density than NiCad

Lithium Ion Battery

- Electrolyte is concentrated KOH solution
- Anode = graphite impregnated with Li ions
- Cathode = Li - transition metal oxide
  - Reduction of transition metal
- Work on Li ion migration from anode to cathode causing a corresponding migration of electrons from anode to cathode
- Rechargeable, long life, very light, more environmentally friendly, greater energy density



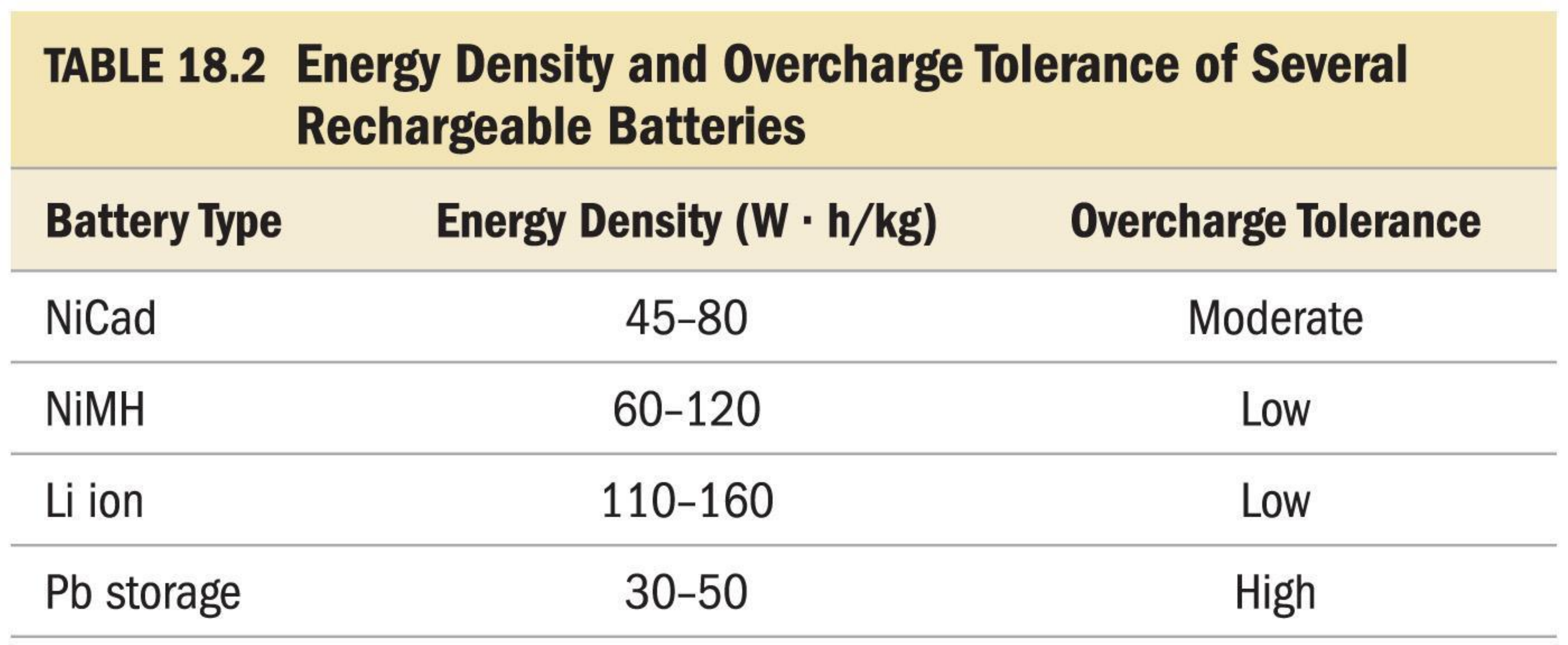
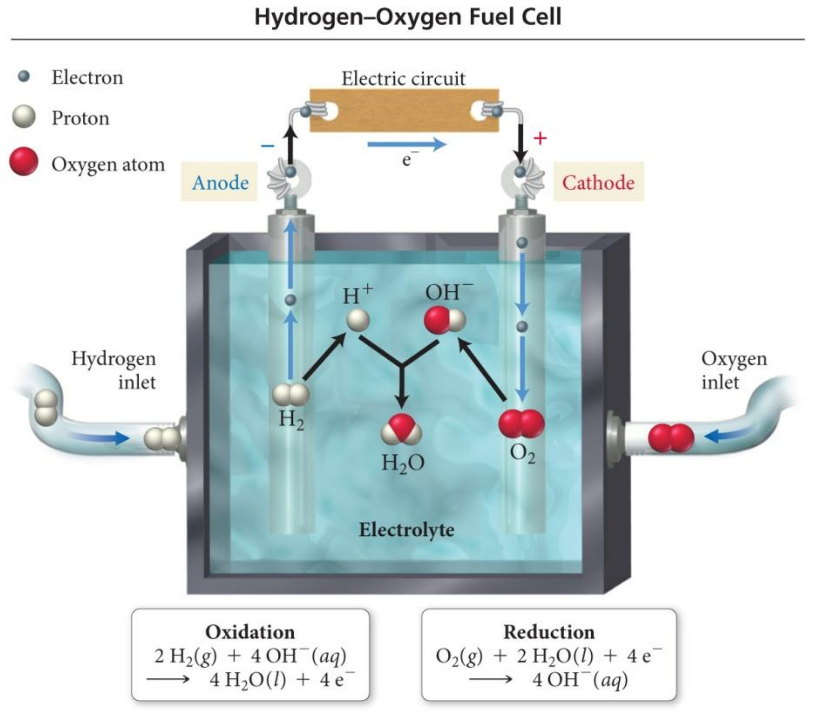


TABLE 18.2 Energy Density and Overcharge Tolerance of Several Rechargeable Batteries

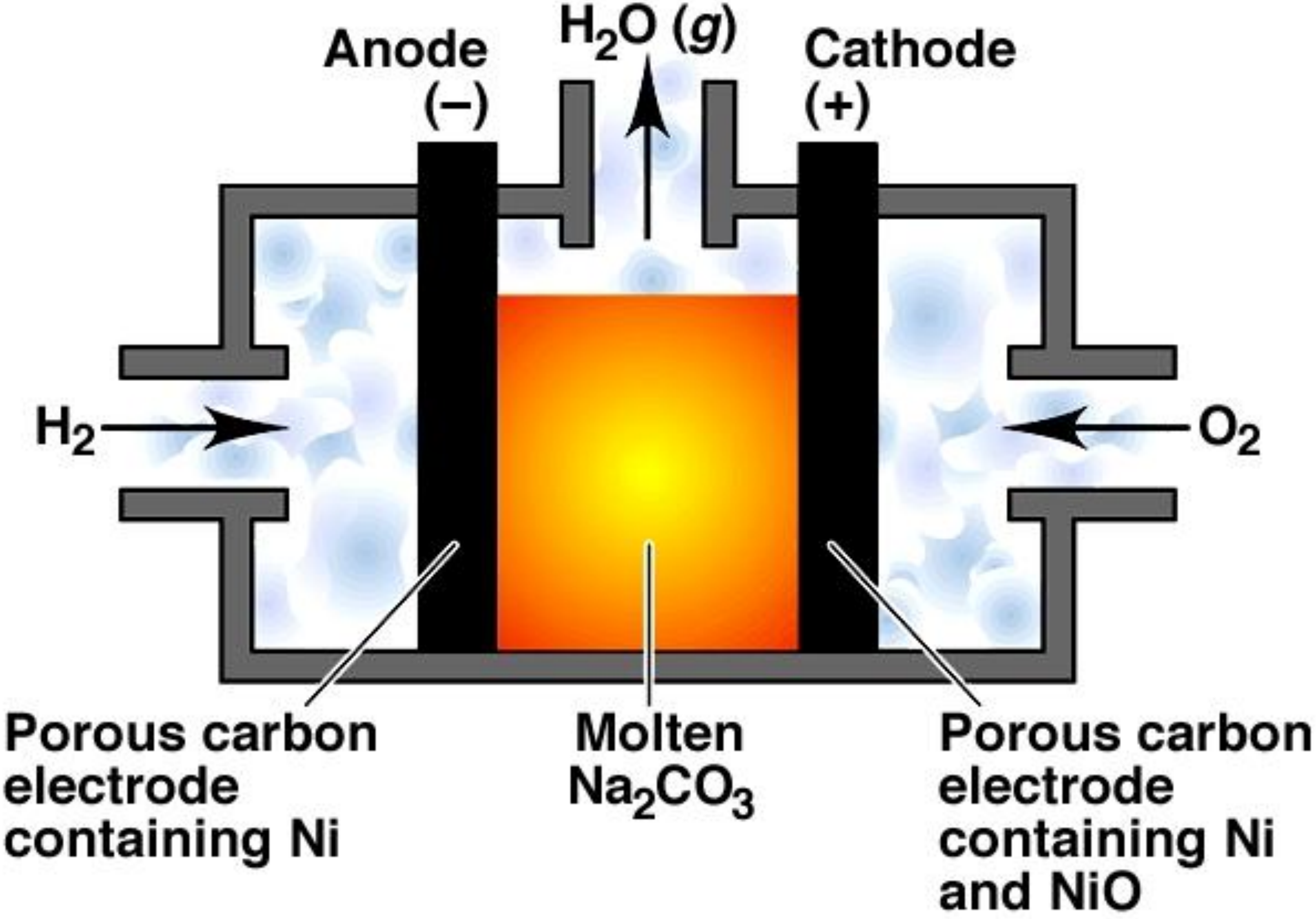
Battery Type	Energy Density ($W \cdot h/kg$)	Overcharge Tolerance
NiCad	45–80	Moderate
NiMH	60–120	Low
Li ion	110–160	Low
Pb storage	30–50	High

Fuel Cells

- Like batteries in which reactants are constantly being added
  - So it never runs down!
- Anode and cathode both Pt coated metal
- Electrolyte is OH^- solution.
- Anode reaction
- $2\ H_2 + 4\ OH^- \rightarrow 4\ H_2O(l) + 4\ e^-$
- Cathode reaction
- $O_2 + 4\ H_2O + 4\ e^- \rightarrow 4\ OH^-$



Flow Batteries (Fuel Cells)

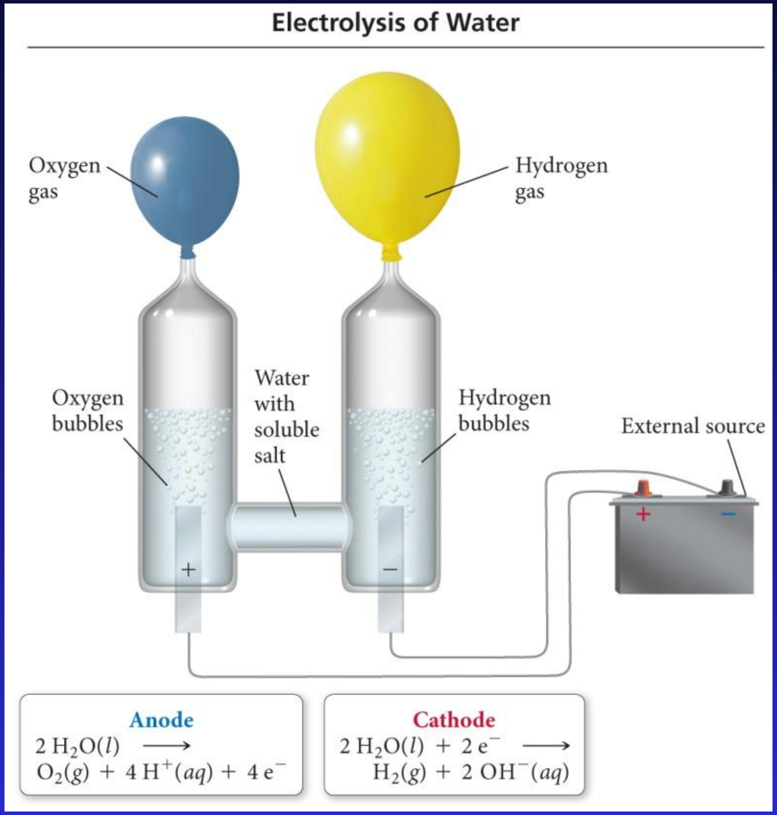


Electrolysis

- the process of using electrical energy to break a compound apart.

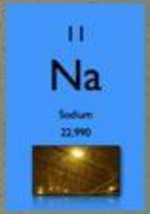
Electrolysis is done in an electrolytic cell.

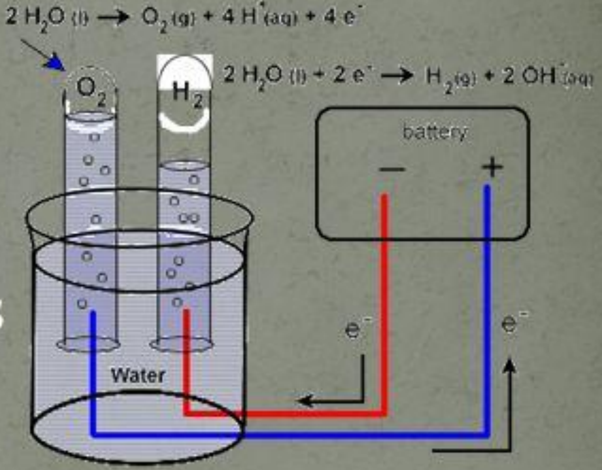
Electrolytic cells can be used to separate elements from their compounds.



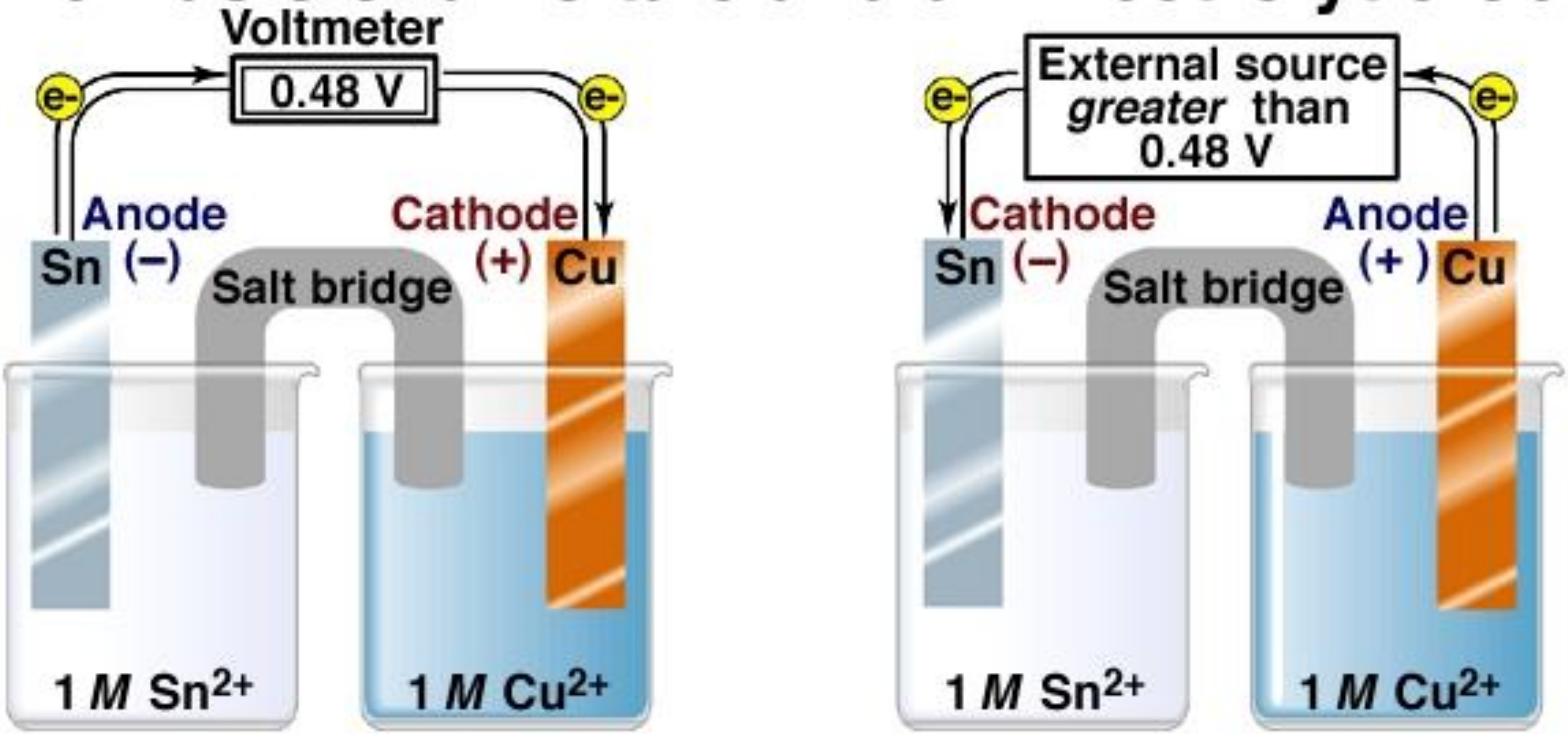
Davy(1778-1825)

- Sir Humphry Davy used electricity as a source of energy for some of his investigations involving chemicals.
- He decomposed water by electrolysis and was responsible for isolating many metals in a pure form, including the reactive metals sodium and potassium.





The Basis of a Voltaic and an Electrolytic Cell



Oxidation half-reaction

$\mathrm{Sn}(s) \longrightarrow \mathrm{Sn}^{2+}(aq) + 2e^-$

Reduction half-reaction

$\mathrm{Cu}^{2+}(aq) + 2e^- \longrightarrow \mathrm{Cu}(s)$

Overall (cell) reaction

$\mathrm{Sn}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Sn}^{2+}(aq) + \mathrm{Cu}(s)$

A Voltaic cell

Oxidation half-reaction

$\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2e^-$

Reduction half-reaction

$\mathrm{Sn}^{2+}(aq) + 2e^- \longrightarrow \mathrm{Sn}(s)$

Overall (cell) reaction

$\mathrm{Cu}(s) + \mathrm{Sn}^{2+}(aq) \longrightarrow \mathrm{Cu}^{2+}(aq) + \mathrm{Sn}(s)$

B Electrolytic cell

Electrolytic Cells

The source of energy: a battery or DC power supply.

The positive terminal of the source is attached to the anode.

The negative terminal of the source is attached to the cathode.

Electrolyte can be either an aqueous salt solution or a molten ionic salt.

Cations in the electrolyte are attracted to the cathode and anions are attracted to the anode.

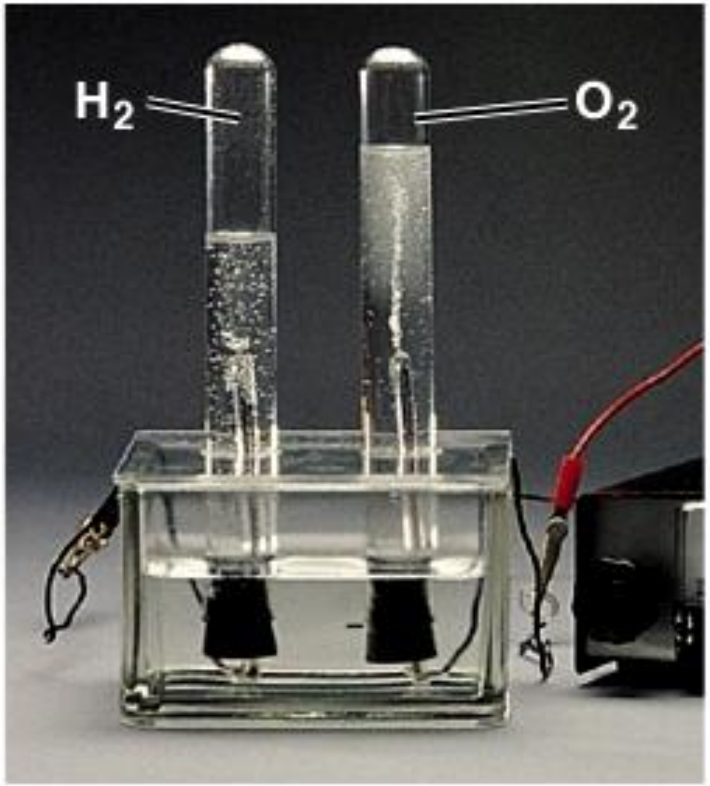
Cations pick up electrons from the cathode and are reduced; anions release electrons to the anode and are oxidized.

Voltaic vs. Electrolytic Cells

Table 21.4 Comparison of Voltaic and Electrolytic Cells

			Electrode		
Cell Type	**ΔG**	**E_{cell}**	**Name**	**Process**	**Sign**
Voltaic	<0	>0	Anode	Oxidation	–
Voltaic	<0	>0	Cathode	Reduction	+
Electrolytic	>0	<0	Anode	Oxidation	+
Electrolytic	>0	<0	Cathode	Reduction	–

The Electrolysis of Water



Oxidation half-reaction
$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Reduction half-reaction
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

Overall (cell) reaction
$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$

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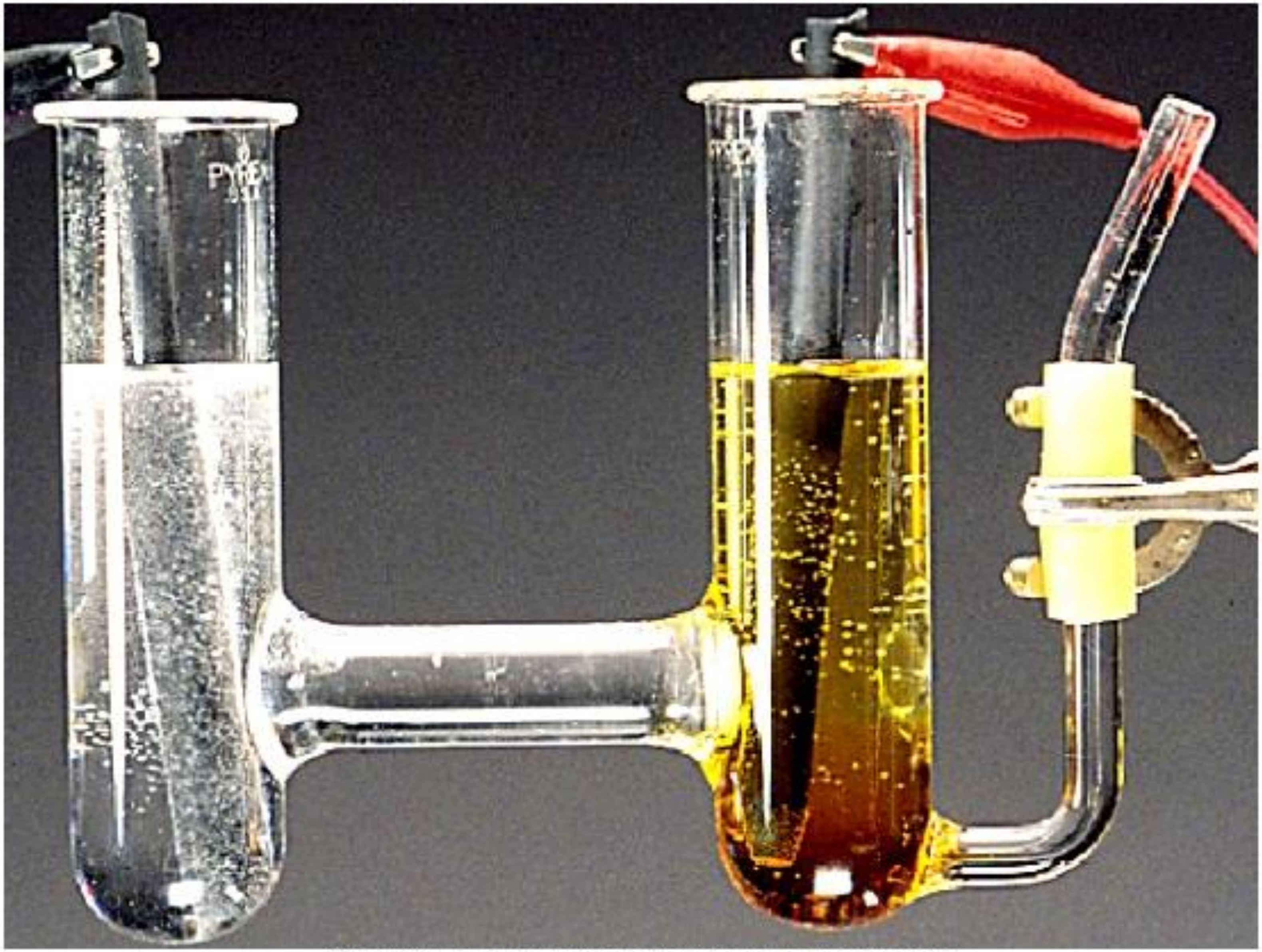
Electrolysis of Aqueous KBr.



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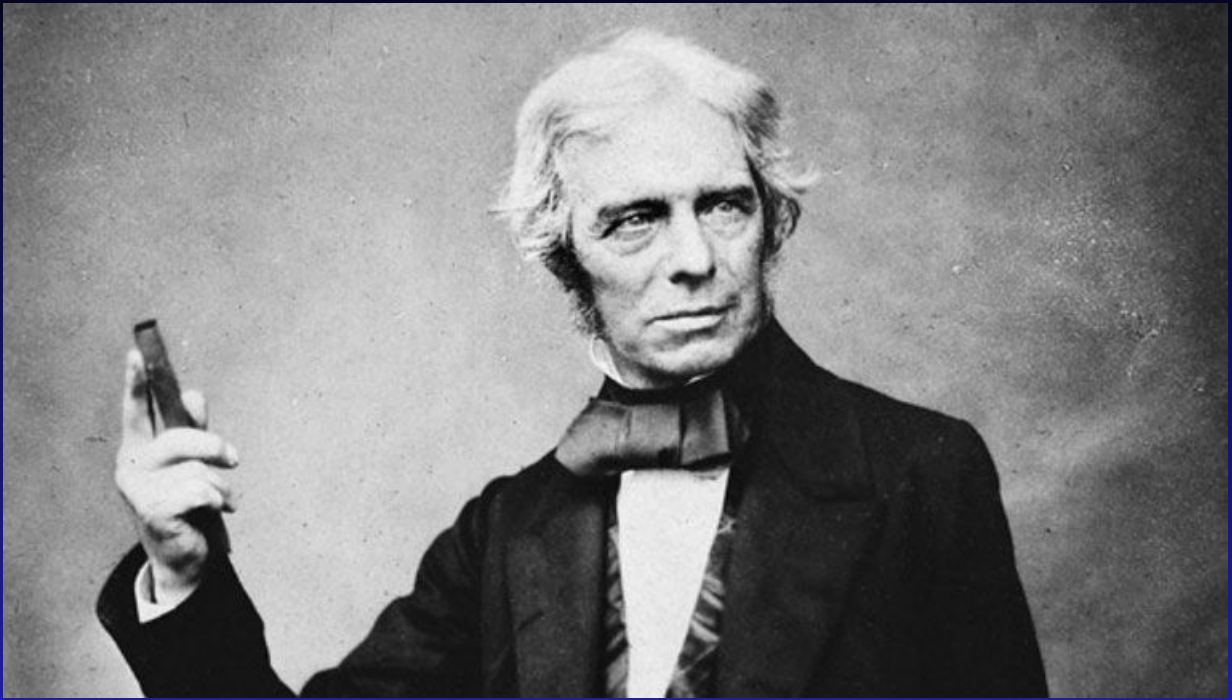
Michael Faraday (1791- 1867)



1821 - discovered electromagnetic rotation.

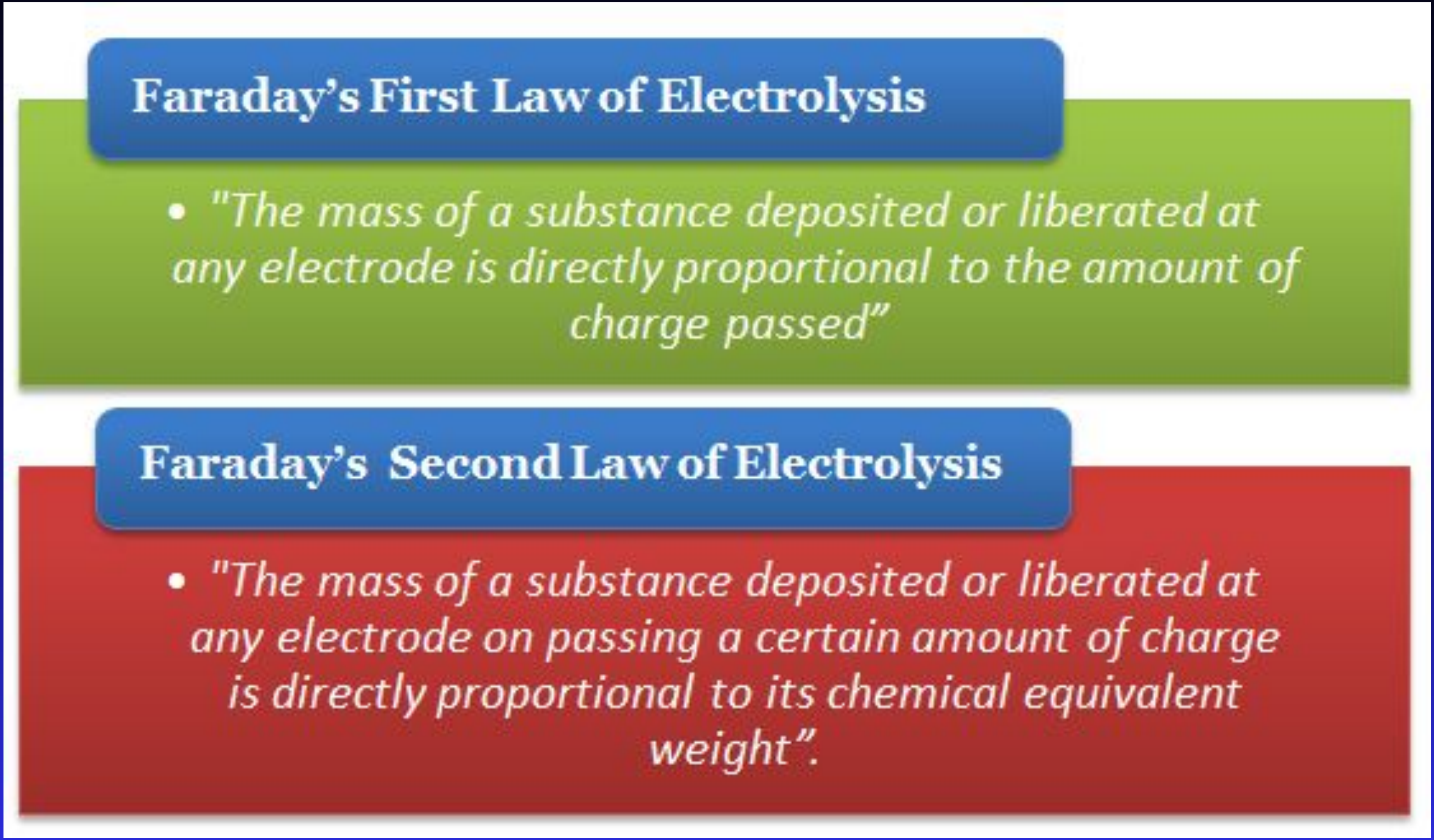
1831 - discovered electromagnetic induction, the principle behind the electricity generator.

1825 - isolated benzene.

1830 - became professor of chemistry at the Royal Military Academy in Woolwich

1834 - laws of electrolysis

Quantitative electrolysis and Faraday's laws



Faraday's First Law of Electrolysis

- *"The mass of a substance deposited or liberated at any electrode is directly proportional to the amount of charge passed"*

Faraday's Second Law of Electrolysis

- *"The mass of a substance deposited or liberated at any electrode on passing a certain amount of charge is directly proportional to its chemical equivalent weight".*

Faraday's Laws of Electrolysis: Expanded Relationship

$$\boxed{n = \frac{q}{zF}}$$

$$\boxed{\frac{w}{M} = \frac{It}{zF}}$$

n = amount of material, mol

w = mass of material, g

M = molar mass of material, g mol^{-1}

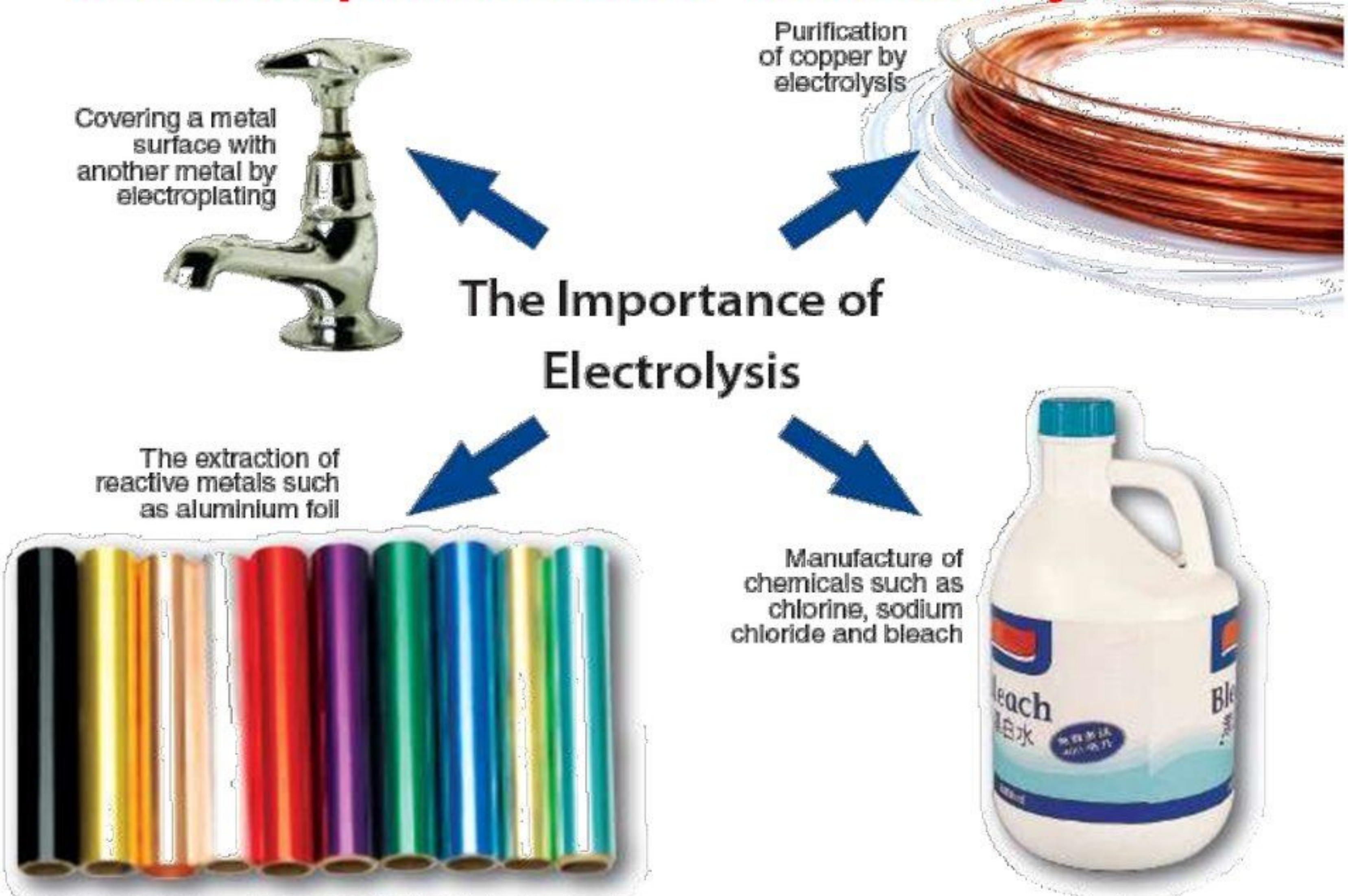
I = current, A

t = time, s

z = number of electrons

F = Faraday constant, 96 485 C mol^{-1}

Some important uses of electrolysis:



The Importance of Electrolysis

Covering a metal surface with another metal by electroplating

Purification of copper by electrolysis

The extraction of reactive metals such as aluminium foil

Manufacture of chemicals such as chlorine, sodium chloride and bleach

Figure 20.1 Some applications of electrolysis in daily life

Home task

Read and memorize pp.333-335. (pp.302-339)

Questions 1-11 p.336

24, 25 p.338

(in writing)

Electrochemistry: Crash Course Chemistry #36

"I'm on the verge of a major breakthrough, but I'm also at that point where chemistry leaves off and physics begins, so I'll have to drop the whole thing."