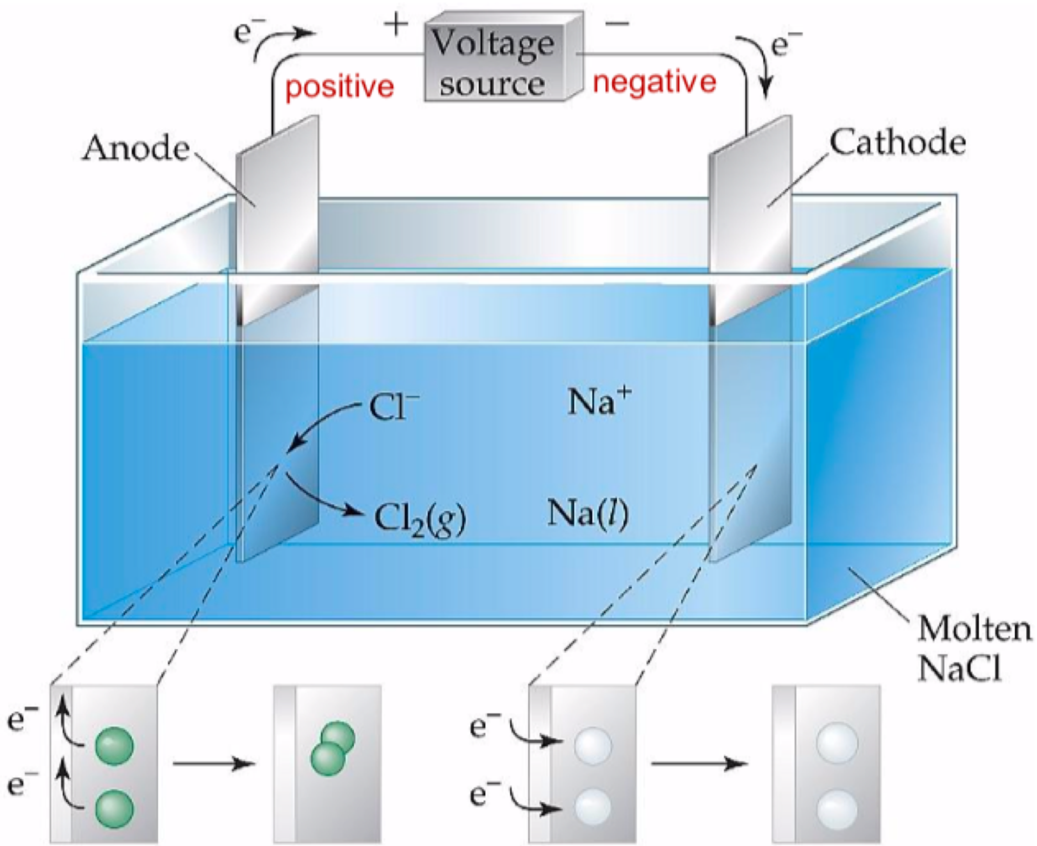
Electrolysis

The process in which electrical energy is used to cause a nonspontaneous chemical reaction to occur

Electrolysis takes place in electrolytic cells

- Electrons are forced to flow from the anode to the cathode



$2\,Cl^- \longrightarrow Cl_2(g) + 2\,e^-$ $\quad 2\,Na^+ + 2\,e^- \longrightarrow 2\,Na(l)$

Electrolysis of Molten Salts

- Cation will be reduced, anion will be oxidized
  - Ex: $FeCl_3$ – Fe(s) formed at cathode, Cl_2(g) at anode
- In mixtures of molten salts, the cation with the highest (most positive) reduction potential will be reduced.

Electrolysis of Aqueous Salts

- Redox reaction of water needs to be taken into account
- At the **cathode**, the reduction of H_2O will compete with reduction of the cation.
- Metal cation will only be reduced if it has a more positive reduction potential than water.
  - Ex: Electrolysis of $CaBr_2$(aq):

  $2\ H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ_{red} = -0.83V$

  $Ca^{2+}(aq) + 2e^- \rightarrow Ca(s) \qquad E^\circ_{red} = -2.87V$

H_2 will be produced, not Ca(s)

Electrolysis of Aqueous Salts con't

- Redox reaction of water also needs to be taken into account at the anode
- At the **anode**, the oxidation of H_2O will compete with oxidation of the anion.
- The anion will only be oxidized if it has a more positive oxidation potential than water.
- Note that oxidation potential of an ion is the reduction potential with the opposite sign (not true for water).
  - Ex: Electrolysis of $CaBr_2(aq)$:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E^\circ_{ox} = -1.23V$

$2Br^-(aq) \rightarrow Br_2(l) + 2e^-$ $E^\circ_{ox} = -1.07V$

Br_2 will be produced instead of O_2

- Under acidic conditions, oxidation of H^+ must also be considered.

Electrolysis

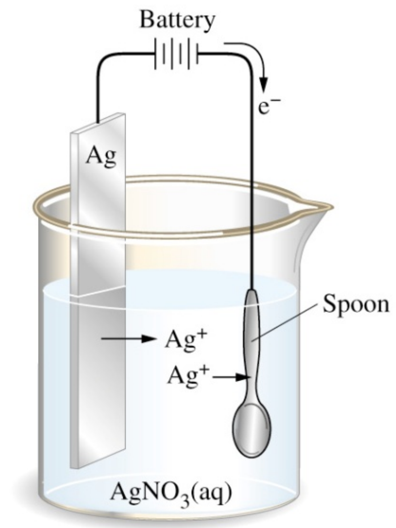
1.) A 1M aqueous solution of iron (III) chloride is electrolyzed. What are the products? $Fe(s)$, $O_2(g)$, $H^+(aq)$

2.) A 1M solution of potassium iodide is electrolyzed under acidic conditions. What are the products? $H_2(g)$, $I_2(s)$

Producing Products by Electrolysis

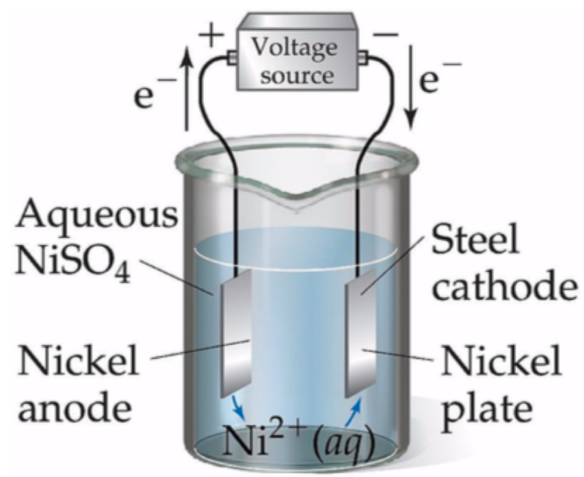
Electroplating:

- Coating one metal onto another
- Often silver or gold over iron or steel
- Cheaper/more durable product
- Method of protecting materials from corrosion
- **Ex: plating nickel**
  - Ni^{2+} preferentially reduced at cathode
  - Ni plates onto the inert electrode



Cathode (steel strip): $Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$ $\quad E^\circ_{red} = -0.28$ V

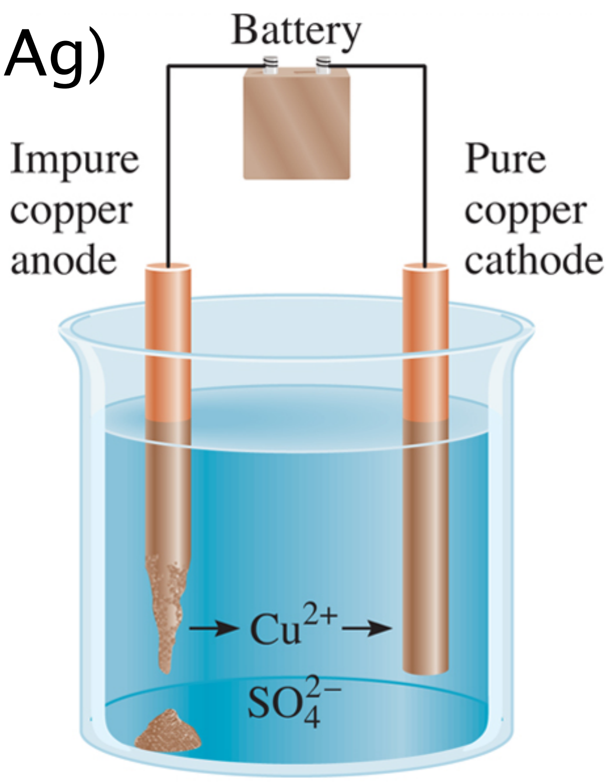
Anode (nickel strip): $Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$ $\quad E^\circ_{red} = -0.28$ V



Producing Products by Electrolysis

Purification:

- Impure metal anode (ex: copper)
- More reactive impurities are oxidized
- Less reactive impurities fall to bottom
  - Isolate unreactive metals (Au, Ag)
- Build up pure metal on cathode
  - Copper up to 99.5% pure



Producing Products by Electrolysis

Amount of material produced through or consumed in electrolysis depends on amount of electrical charge that is used.

Coulomb: Amount of charge passing a point in a circuit in 1 second when the current is 1 ampere (A).

Coulomb = I•t

C = coulomb
I = current in amperes
t = time in seconds

nF = At

n = # moles electrons
F = Faraday's constant
A = current in amperes
t = time in seconds

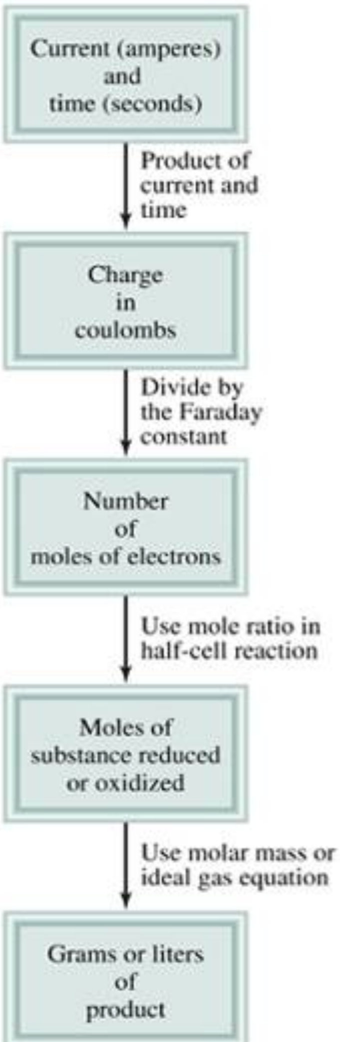
96,485C = charge on one mole of electrons = 1 Faraday

Faraday's constant = 96485 C/mol

Producing Products by Electrolysis

1.) How many grams of Ca(s) will be produced in an electrolytic cell of molten $CaCl_2$ if a current of 0.452 A is passed through the cell for 1.5 hours?

A: 0.51g



Producing Products by Electrolysis

2.) Water is electrolyzed in a cell at 25mA for 15 minutes. How many mL of oxygen gas are produced at 1.0 atm and 25˚C?

A: 1.4mL

Producing Products by Electrolysis

3.) How many minutes are needed to plate out 25.00g Mg from molten $MgCl_2$ using 3.50 A of current?

A: 945 min

Electrical Work

Free Energy (ΔG) is a measure of the maximum amount of work that can be obtained from a system, $\Delta G = w_{max}$. Since $\Delta G = -nFE$,

$$w_{max} = -nFE$$

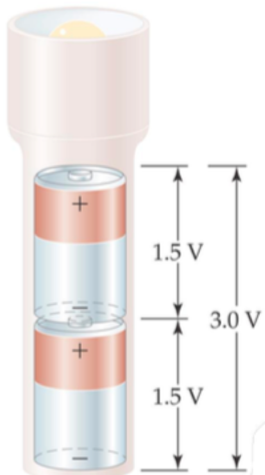
- The cell potential can be thought of as a measure of the driving force for a redox process.
- For a voltaic cell (spontaneous), E_{cell} is positive and w_{max} is negative (work is done by the system on the surroundings).
- For an electrolytic cell (nonspontaneous), the external electromotive force must be greater than E_{cell} to cause the redox reaction to occur.
  - w for an electrolytic cell is positive because work is being done by the surroundings on the system.

Electrical Work

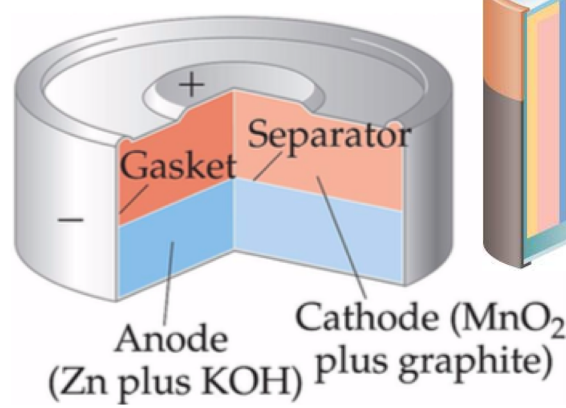
1.) Consider the voltaic cell which is based on the cell reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
Under standard conditions, what is the maximum electrical work, in Joules, that the cell can accomplish if 50.0g of copper is plated out? A: -1.67×10^5 J

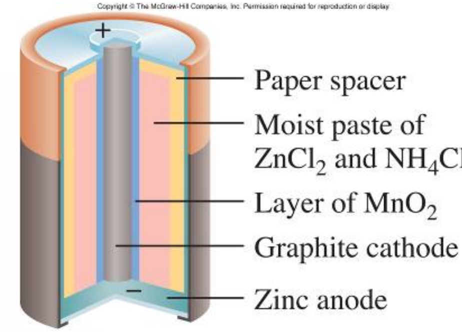
Batteries

A Battery is a self-contained electrochemical power source consisting of one or more voltaic cells.



The cells can be connected in a series to produce a voltage that is the sum of the cell potentials of each individual cell.





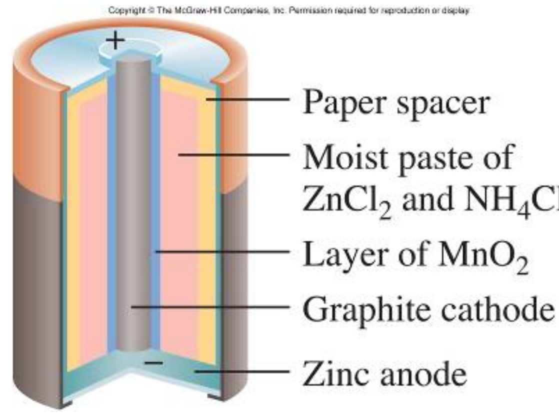
Alkaline Battery:

Most common non-rechargeable battery

- Irreversible reaction
- Reported voltage: +1.5V
- Anode: $Zn(s) + 2\ OH^-(aq) \rightarrow Zn(OH)_2 + 2e^-$
- Cathode: $2MnO_2(s) + 2H_2O(l) + 2e^- \rightarrow MnO(OH)(s) + 2OH^-(aq)$

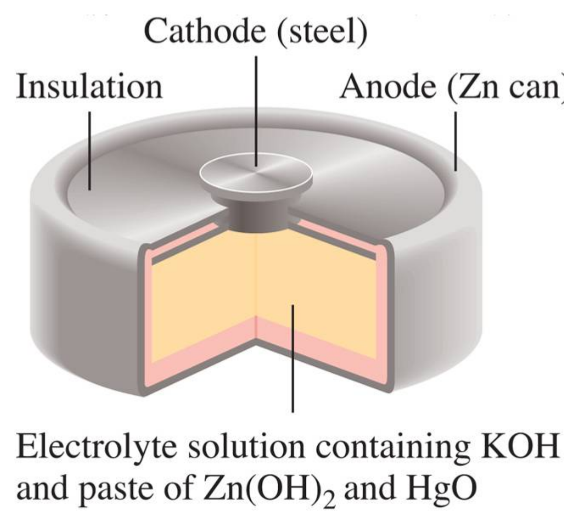
Batteries

Dry Cell Battery:



- Used in portable electronics
- Irreversible reaction
- Reported voltage: +1.5V
- Anode: $Zn \rightarrow Zn^{2+} + 2e^-$
- Cathode: $2MnO_2 + 2NH_4^+ + 2e^- \rightarrow Mn_2O_3 + 2NH_3 + H_2O$

Mercury (Button) Battery:

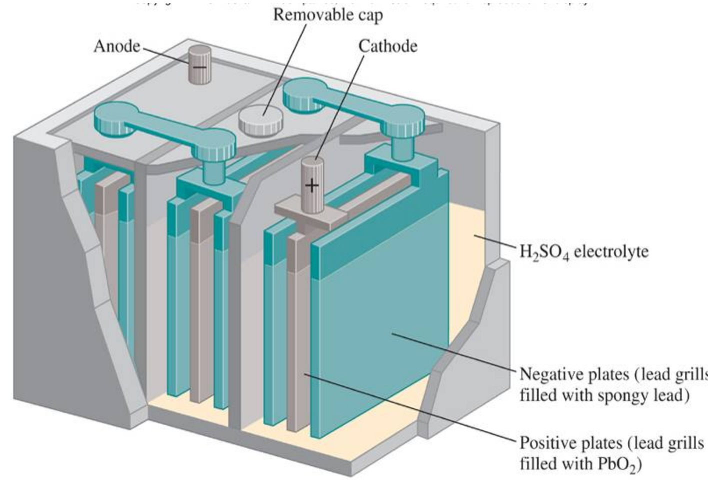


- Pacemakers, hearing aids, watches
- Irreversible reaction
- Constant OH^- composition
- More constant voltage
- Reported voltage: +1.5V
- Anode: $Zn(s) + 2OH^- \rightarrow ZnO + H_2O + 2e^-$
- Cathode: $HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$

Batteries

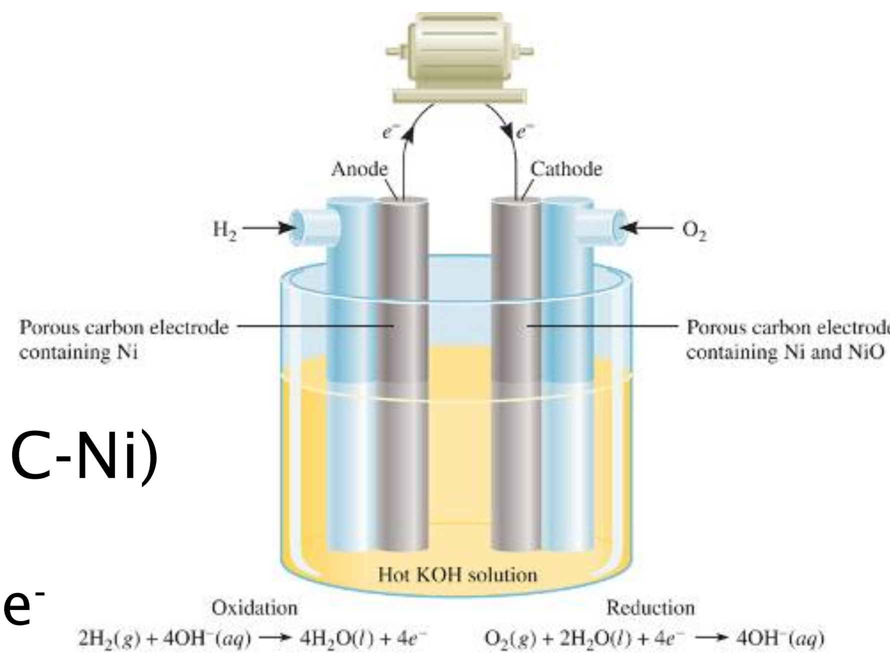
Lead Storage:

- Car & boat batteries
- Reversible reaction - reaction reverses when engine is running
- Reported voltage: +2.0V/cell
  Usually 6 cells = 12V
- Anode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$
- Cathode: $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$



Fuel Cells:

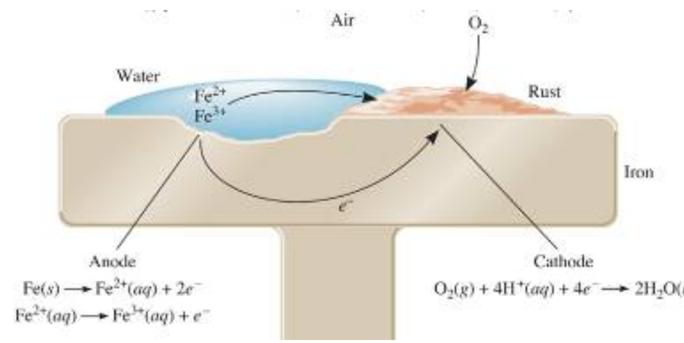
- Galvanic cells
- Irreversible reaction
  - Need to replenish reactants
  - Need to remove products
- Require electrocatalysts (ex: C-Ni)
- Reported voltage: +1.23V
- Anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$
- Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$



Corrosion

A spontaneous redox reaction in which a metal is attacked by some substance in its environment converting it into an unwanted compound.

Deterioration of metal through an electrochemical process.



Products often referred to as rust, tarnish, or patina.

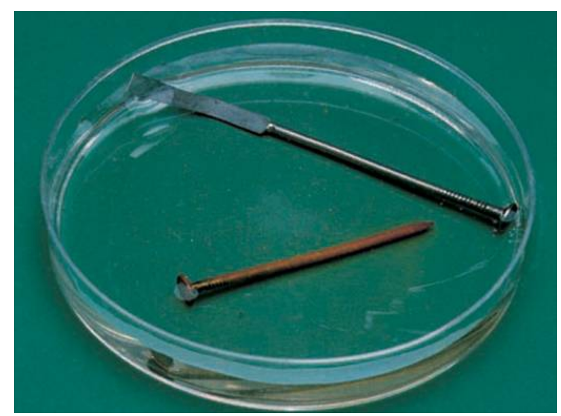
Ex: Rusting of iron

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E^\circ_{red} = 1.23V$

Anode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ $E^\circ_{red} = -0.44V$

$E^\circ_{red}(Fe^{2+}) < E^\circ_{red}(O_2)$

- Iron can be reduced by O_2
- Dissolved O_2 in water usually causes the oxidation of iron
- Fe^{2+} is further oxidized to the Fe^{3+} in rust (Fe_2O_3)



Corrosion Prevention

Cathodic protection – protection of a metal by making it the cathode

- Corrosion of iron can be prevented by coating iron with paint or other metals
  - Galvanized iron – coated with zinc
  - Zinc is easier to oxidize than iron
  - Zn^{2+} $E^{\circ}_{red} = -0.763V$; Fe^{2+} $E^{\circ}_{red} = -0.440V$
  - Zinc becomes the sacrificial anode
- Same reason "zincs" are added to the propeller shafts on boats