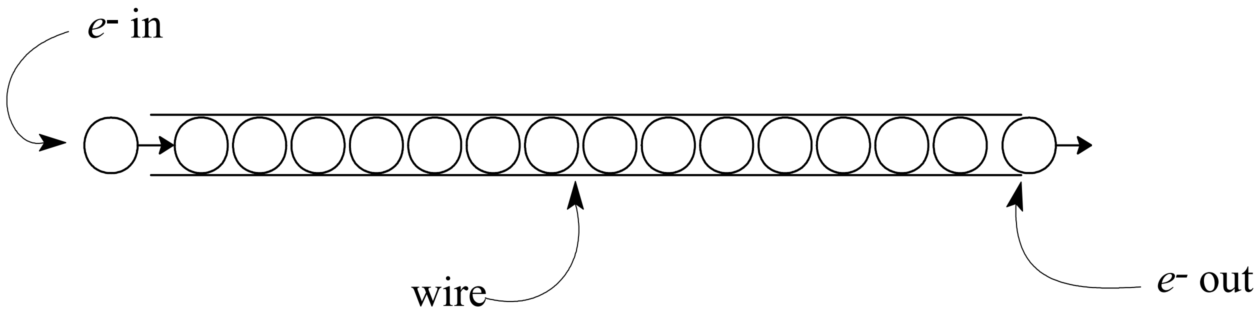
Electrical Conduction



☞ ***Electrical conduction*** is the flow of electric charge produced by the movement of electrons in a conductor.

☞ The rate of electron flow (called the ***current***, *I*, in amperes) is the amount of charge (in coulombs, C) carried per unit time:

$$I = Q/t$$

$$Q = It$$

$$1 \text{ C} = 1 \text{ amp}\cdot\text{s} = 6.24 \times 10^{18} \text{ unit charges}$$

$$\text{Faraday } (\mathscr{F}) = 96,489 \pm 2 \text{ C} \approx 9.65 \times 10^{4} \text{ A}\cdot\text{s}$$
$$= \text{charge of one mole electrons}$$

Electrolytic Conduction

☞ ***Electrolytic conduction*** is the passage of electrical current through an electrolyte (molten salt or electrolyte solution).

- Charge is carried by the movement of ions.

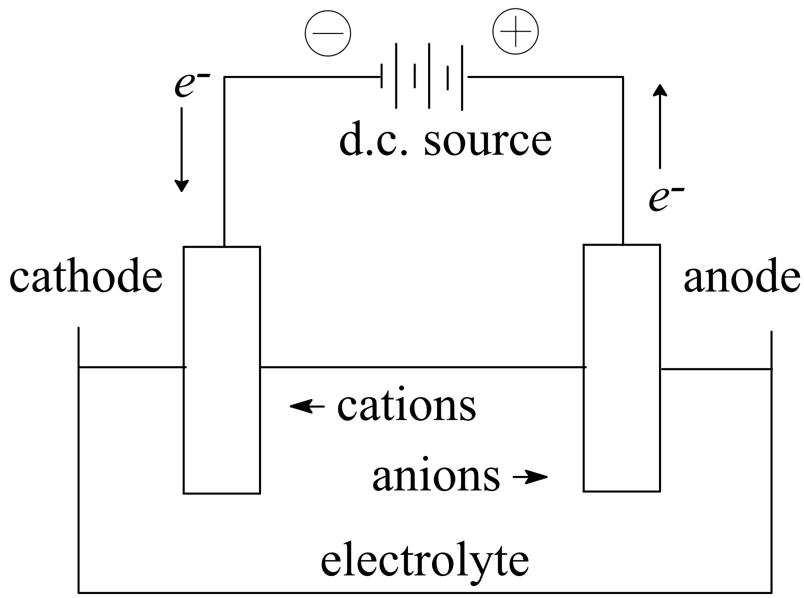
- Electrolytic conduction results in *non-spontaneous* chemical change, called ***electrolysis***.

✓ No ions can move freely in solid ionic salts, so there can be no electrolytic conduction.

⇨ Ionic *solids* are non-conductors.

☞ Electrolysis reactions are most often *non-spontaneous* redox reactions, forced to occur by the imposed electrical potential.

Electrolysis Cell



- Battery or other direct current (d.c.) source forces passage of electrical current through electrolyte.

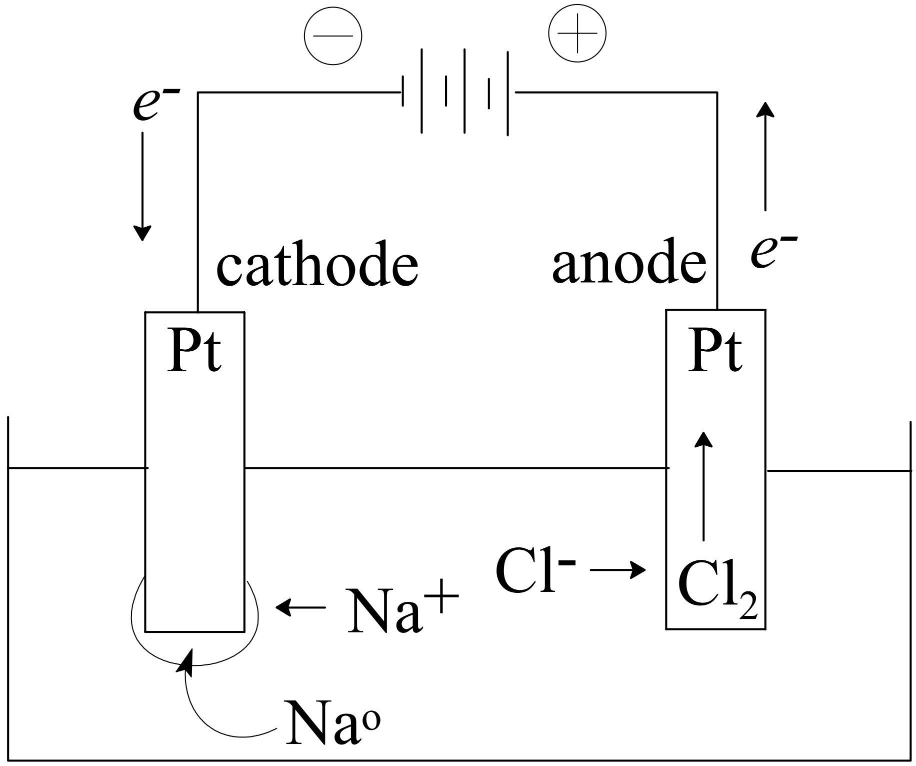
- Cathode is electron source for species that are reduced in the electrolysis reaction.

- Anode is electron sink for species that will be oxidized in the electrolysis reaction.

- Cathode is negative (⊖); anode is positive (⊕).

- In the external circuit, electrons flow from the anode, through the d.c. current source, to the cathode.

Electrolysis of Molten NaCl(*l*)
With Inert Pt Electrodes



Electrolysis in Aqueous Solution

- ☞ In an aqueous solution of an electrolyte, there may be several possible oxidations and several possible reductions.

  - ☞ ***Among possible oxidations and reductions, the overall redox reaction requiring the least applied voltage will occur.***

Electrolysis of NaCl(*aq*) Solution With Inert Pt Electrodes

Possible Reductions at the Cathode:

$Na^+(aq) + e^- \rightarrow Na(s)$ $\qquad E^o = -2.71$ V

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

☞ Reduction of $H_2O(l)$ requires overcoming much less potential, so formation of $H_2(g)$ and $OH^-(aq)$ occurs.

Possible Oxidations at the Anode:

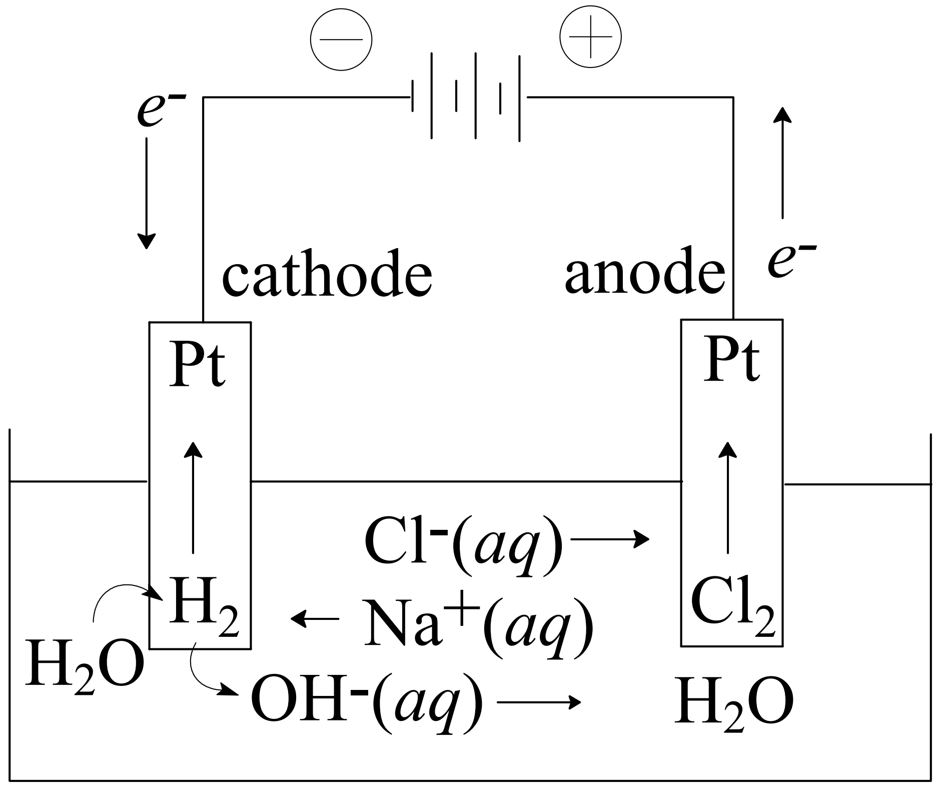
$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $\qquad -E^o = -1.36$ V

$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $\qquad -E^o = -1.23$ V

☞ Applied voltage requirements are similar, but formation of $O_2(g)$ at Pt has a high overvoltage, so $Cl_2(g)$ forms at high concentrations of $Cl^-(aq)$.

✔ Overvoltage is extra voltage that must be supplied to overcome a kinetic inhibition to forming a certain species at a particular kind of electrode.

Electrolysis of NaCl(*aq*) Solution With Inert Pt Electrodes



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

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \qquad -E^o = -1.36\ V$$

$$2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + 2OH^-(aq) + Cl_2(g)$$

$$E^o_{cell} = -2.19\ V$$

Electrolysis of $CuSO_4$(*aq*) Solution With Inert Pt Electrodes

Possible Reductions at the Cathode:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^o = -0.83$ V

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^o = +0.34$ V

☞ $Cu^{2+}(aq)$ is reduced to $Cu(s)$.

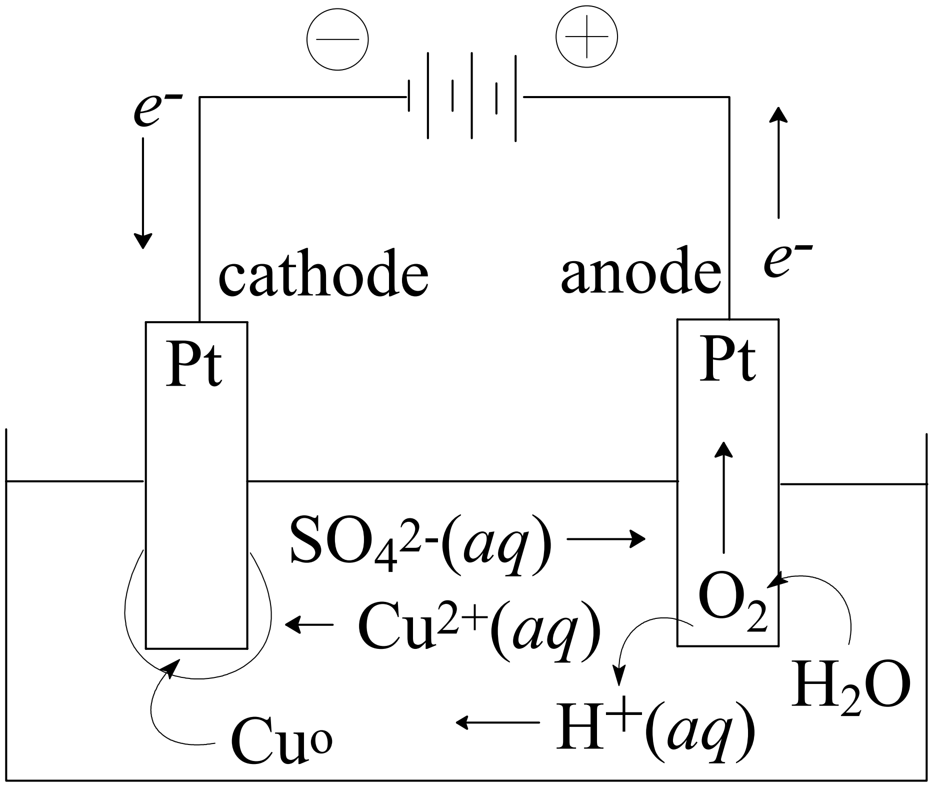
Possible Oxidations at the Anode:

$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^-$ $-E^o = -2.01$ V

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

☞ $H_2O(l)$ is oxidized to $O_2(g)$ and $H^+(aq)$, despite the overvoltage.

Electrolysis of $CuSO_4(aq)$ Solution With Inert Pt Electrodes



$$2\{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)\} \qquad E^o = +0.34\text{ V}$$

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

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

$$E^o_{cell} = -0.89\text{ V}$$

Electrolysis of $CuSO_4(aq)$ Solution With Active Cu Electrodes

Possible Reductions at the Cathode:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^o = -0.83$ V

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^o = +0.34$ V

☞ $Cu^{2+}(aq)$ is reduced to $Cu(s)$.

Possible Oxidations at the Anode:

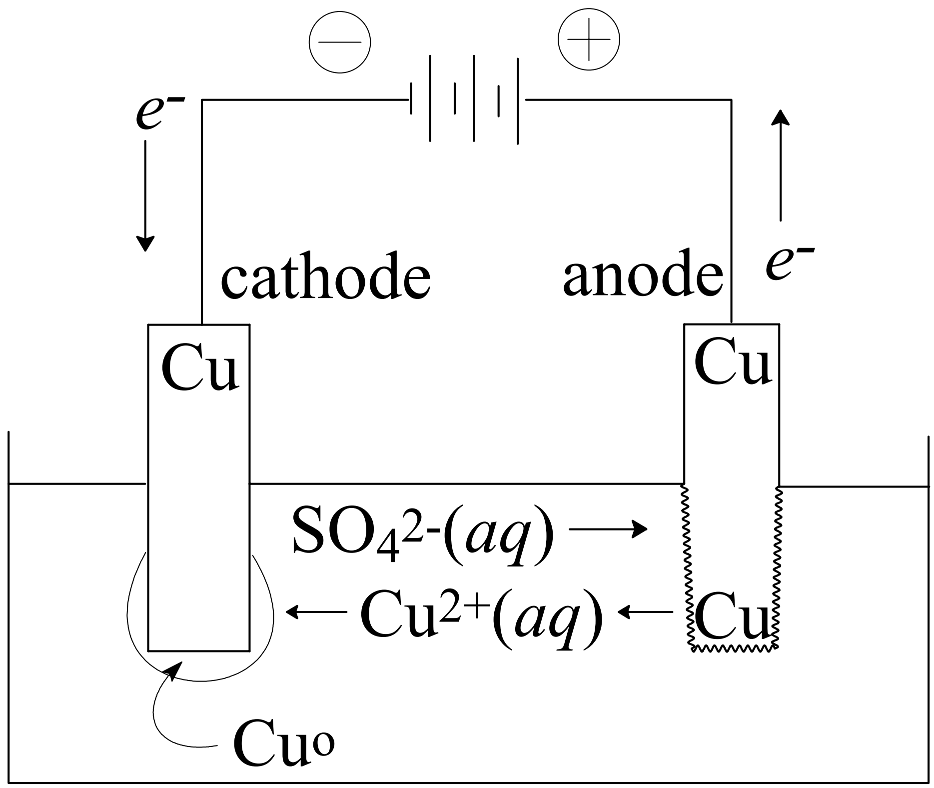
$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^-$ $-E^o = -2.01$ V

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

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $-E^o = -0.34$ V

☞ Now $Cu(s)$ oxidation is the favored process at the anode, so $Cu(s)$ is oxidized to $Cu^{2+}(aq)$.

Electrolysis of $CuSO_4$(*aq*) Solution With Active Cu Electrodes



$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)\ [\text{cathode}] \qquad E^o = +0.34\ V$$

$$Cu(s)\ [\text{anode}] \rightarrow Cu^{2+}(aq) + 2e^- \qquad -E^o = -0.34\ V$$

$$Cu^{2+}(aq) + Cu(s)\ [\text{anode}] \rightarrow Cu(s)\ [\text{cathode}] + Cu^{2+}(aq)$$

$$E^o_{cell} = 0.00\ V$$

Faraday's Law

☞ The amount of substance produced or consumed at an electrode is proportional to the number of electrons transferred from the anode to the cathode.

$$Q = It$$

Faraday ($\mathscr{F}$) = 96, 489 ± 2 C ≈ 9.65 x 10^4 A·s
= charge of one mole electrons

☞ The *equivalent weight* of a substance is that amount produced or consumed at an electrode when the charge equivalent to one mole of electrons (1 $\mathscr{F}$) is passed.