Adama Science and Technology University

Chapter 4 part IV

Electrochemistry

By

Yilkal Matebie

Introduction

- **Electrochemistry** is the branch of chemistry that deals with the interconversion of **electrical energy** and **chemical energy**.
- **Electrochemical processes are redox (oxidation-reduction) reactions.**
- **Oxidation-Reduction**
  - **Oxidation is the loss of electrons and**
  - **Reduction is the gain of electrons.**

  Both occur *simultaneously*

- **Oxidation results in an *increase* in O.N. X(F, Cl, Br, and I) or decrease H while reduction results in a *decrease* in O.N. and halogen((F, Cl, Br, and I) or increase H**

- **Example reaction of Mg(s) with HCl**

$$\overset{0}{\mathrm{Mg}}(s) + 2\overset{+1}{\mathrm{H}}\mathrm{Cl}(aq) \longrightarrow \overset{+2}{\mathrm{Mg}}\mathrm{Cl}_2(aq) + \overset{0}{\mathrm{H}_2}(g)$$

- **Mg metal is oxidized and H^+ ions are reduced.**

- **An oxidizing agent is the species that does the oxidizing, taking electrons from the substance being oxidized.**
- **A reducing agent is the species that does the reducing, giving electrons to the substance being reduced.**

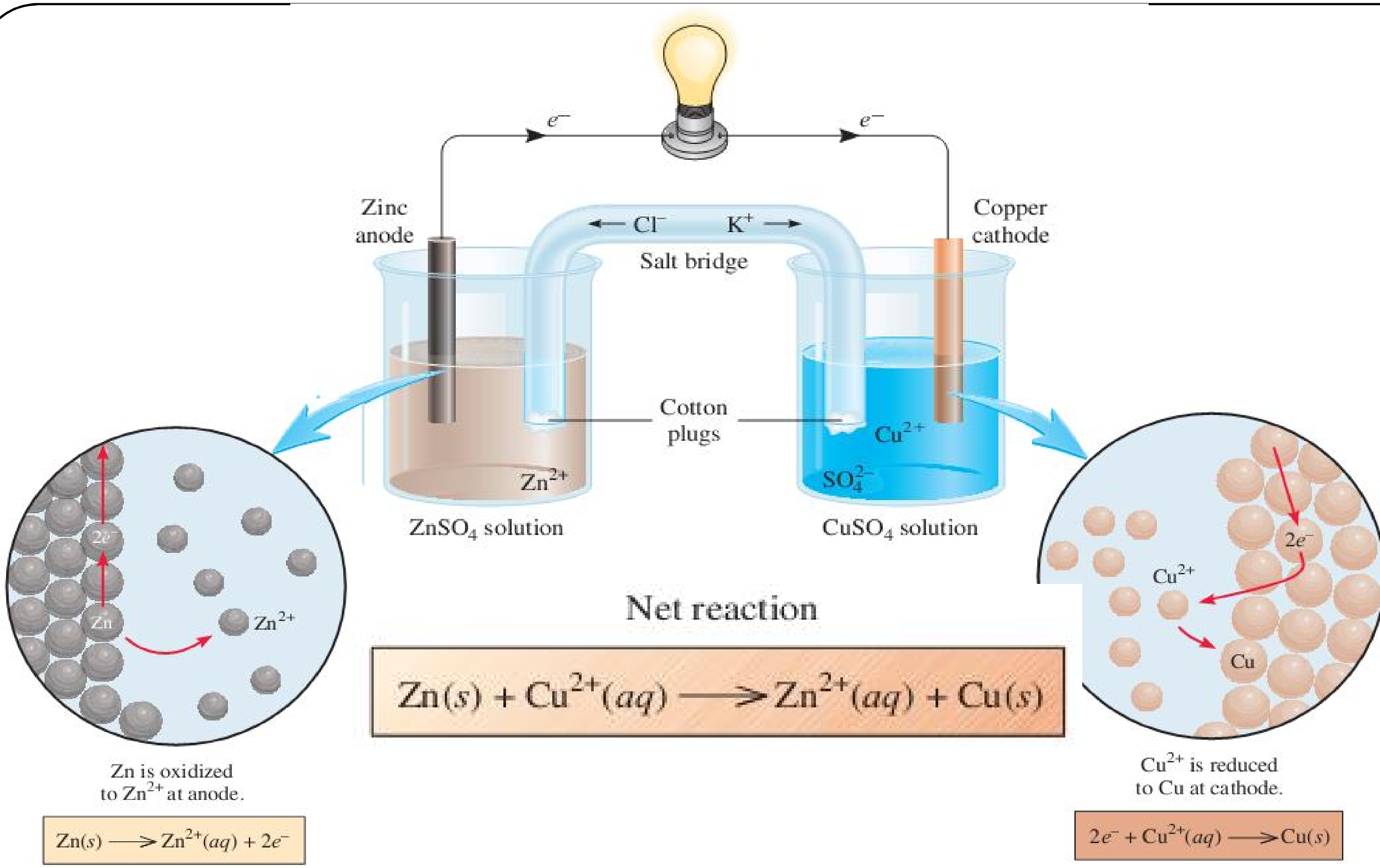
- **The oxidizing agent is reduced, and the reducing agent is oxidized.**
- **The total number of electrons gained by the oxidizing agent always equals the total number lost by the reducing agent.**
- **A summary of redox terminology.**

$$\overset{0}{Zn}(s) + 2\overset{+1}{H}{}^{+}(aq) \rightarrow \overset{+2}{Zn}{}^{2+}(aq) + \overset{0}{H_2}(g)$$

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.

Electrochemical cell

- An electrochemical cell is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current.
- The experimental apparatus for generating electricity through the use of a spontaneous reaction is called a galvanic cell or voltaic cell
- A *voltaic cell* uses a *spontaneous* redox reaction ($\Delta G < 0$) to generate electrical energy.
- A *electrolytic cell* uses electrical energy to drive a *nonspontaneous* reaction ($\Delta G > 0$).
- Both types of cell are constructed using two *electrodes* placed in an *electrolyte* solution
- The *anode* is the electrode at which *oxidation* occurs
- The *cathode* is the electrode at which *reduction* occurs.



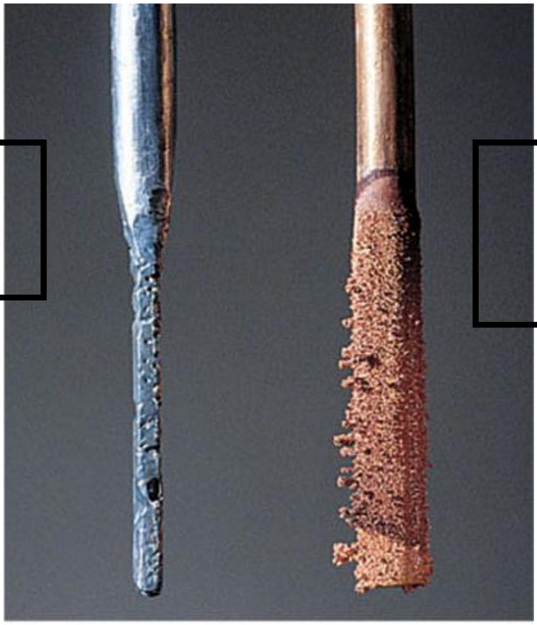
A galvanic cell. The salt bridge (an inverted U tube) containing a KCl solution provides an electrically conducting medium between two solutions. The openings of the U tube are loosely plugged with cotton balls to prevent the KCl solution from flowing into the containers while allowing the anions and cations to move across. The lightbulb is lit as electrons flow externally from the Zn electrode (anode) to the Cu electrode (cathode).

A voltaic cell based on the zinc-copper reaction.

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

Oxidation half-reaction

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



Reduction half-reaction

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

After several hours, the Zn anode weighs less as Zn is oxidized to Zn^{2+}.

The Cu cathode gains mass over time as Cu^{2+} ions are reduced to Cu.

The *anode* produces e^- by the oxidation of Zn(*s*).

Anode is the *negative* electrode in a voltaic cell.

Electrons flow through the external wire *from the anode to the cathode*, where they are used to reduce Cu^{2+} ions.

The cathode is the *positive* electrode in a voltaic cell.

Notation for a Voltaic Cell

The anode components are written on the *left*.

The cathode components are written on the *right*.

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

The single line shows a phase boundary between the components of a half-cell.

The double line shows that the half-cells are physically separated.
denote the salt bridge

Write the cell diagram for the following redox reaction.

$3Fe^{+2}(aq) + 2Al(s) \longrightarrow 3Fe(s) + 2Al^{+3}(aq)$

- **Salt bridge is a tube of an electrolyte in a gel that is connected to the two half-cells of a voltaic cell; the salt bridge allows the flow of ions but prevents the mixing of the different solutions that would allow direct reaction of the cell reactants.**

Example

- **Draw a diagram, show balanced equations, and write the notation for a voltaic cell that consists of one half-cell with a Cr bar in a $Cr(NO_3)_3$ solution, another half-cell with an Ag bar in an $AgNO_3$ solution, and a KNO_3 salt bridge. Measurement indicates that the Cr electrode is negative relative to the Ag electrode.**

SOLUTION:

The half-reactions are:

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ [reduction; cathode

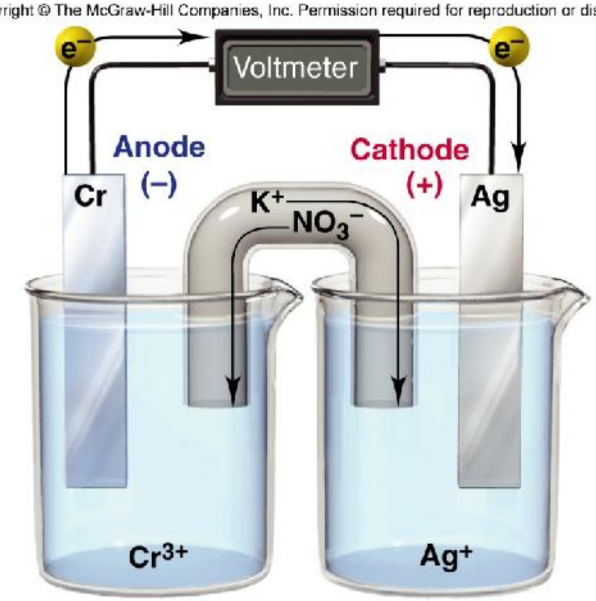
$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^{-}$ [oxidation; a

The balanced overall equation is:

$3Ag^{+} + Cr(s) \rightarrow 3Ag(s) + Cr^{3+}(aq)$

The cell notation is given by:

$r(s) \mid Cr^{3+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$



The cell diagram shows the anode on the left and the cathode on the right.

Standard Reduction Potentials

The *standard cell potential* is designated $E°_{cell}$ and is measured at a specified temperature with no current flowing and *all components in their standard states*

$$E°_{cell} = E°_{cathode\ (reduction)} - E°_{anode\ (oxidation)}$$

A positive E° means the redox reaction will favor the formation of products at equilibrium.

a negative E° means that more reactants than products will be formed at equilibrium.

Selected Standard Electrode Potentials (298 K)

strength of oxidizing agent

Half-Reaction	$E°$(V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$MnO_2(g) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(g) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	−0.23
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05

strength of reducing agent

Example

- A voltaic cell houses the reaction between aqueous bromine and zinc metal:

$$Br_2(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Br^-(aq) \qquad E°_{cell} = 1.83\ V.$$

- Calculate $E°_{bromine}$, given that $E°_{zInc}$ = -0.76 V

SOLUTION:

$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$ [reduction; cathode]

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ [oxidation; anode] $E°_{zinc} = -0.76\ V$

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$1.83 = E°_{bromine} - (-0.76)$$

$$1.83 - 0.76 = E°_{bromine}$$

$$\boxed{E°_{bromine} = 1.07\ V}$$

Exercise: galvanic cell consists of a Mg electrode in a 1.0 M $Mg(NO_3)_2$ solution and a Ag electrode in a 1.0 M $AgNO_3$ solution. Calculate the standard emf of this cell at 25°C

- **Standard electrode potentials refer to the half-reaction as a reduction.**
- ***E*° values therefore reflect the ability of the reactant to act as an *oxidizing agent*.**
- **The *more positive* the *E*° value, the more readily the *reactant* will act as an *oxidizing agent*.**
- **The *more negative* the *E*° value, the more readily the *product* will act as a *reducing agent*.**

Free Energy and Electrical Work

$$\Delta G = -nFE_{cell}$$

n = mol of e^- transferred

F is the Faraday constant

= 9.65×10^4 J/V·mol e^-

- **Both n and F are positive quantities and ΔG is negative for a spontaneous process, so E_{cell} must be positive.**

Under standard conditions, $\Delta G^\circ = -nFE^\circ_{cell}$ and

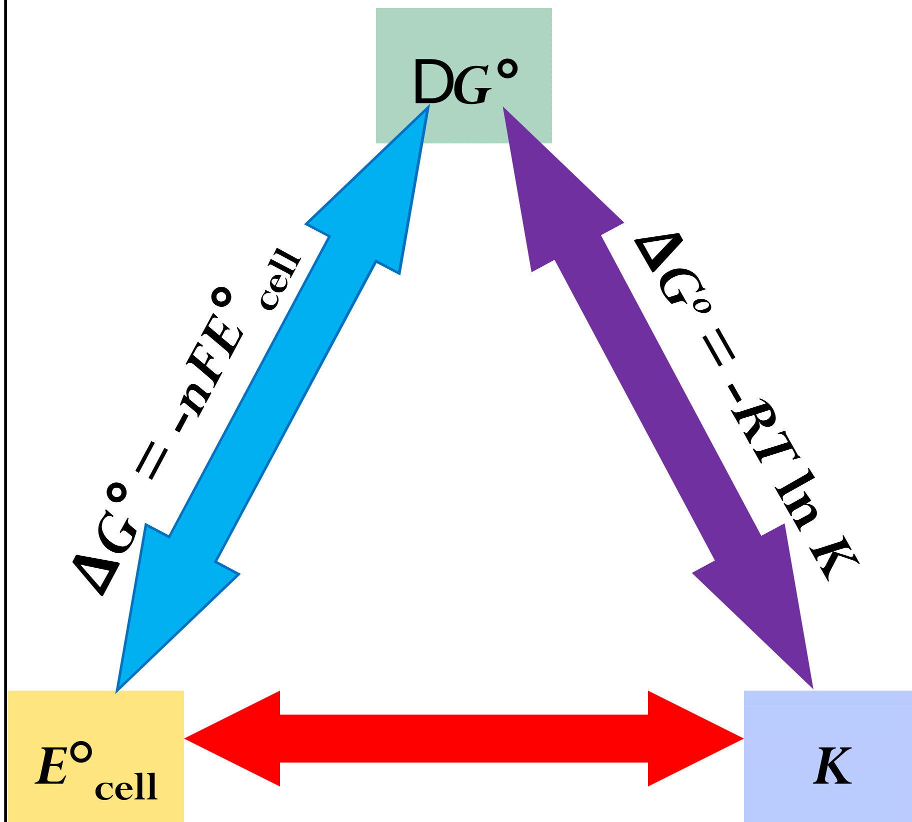
$$E^\circ_{cell} = \frac{RT}{nF} \ln K$$

$$E^\circ_{cell} = \frac{0.0592\,V}{n} \log K$$

for $T = 298.15$ K

$$E^\circ_{cell} = \frac{0.0257}{n} \ln K$$

Relationships among E°_{cell}, K, and ΔG°.



$$E^\circ_{cell} = \frac{RT}{nF} \ln K$$

Reaction Parameters at the Standard State			
DG°	*K*	E°_{cell}	Reaction at standard-state conditions
< 0	> 1	> 0	spontaneous
0	1	0	at equilibrium
> 0	< 1	< 0	Non-spontaneous

Example

- Calculate the equilibrium constant for the following reaction at 25°C:

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

- Solution The half-cell reactions are
- Anode (oxidation): $Sn(s) \longrightarrow Sn_{+2}(aq) + 2e_{-}$
- Cathode (reduction): $2Cu^{+2}(aq) + 2e^{-} \longrightarrow 2Cu^{+}(aq)$
  - $E°_{cell} = E°_{cathode} - E°_{anode}$

$$= E°_{Cu^{+2}/Cu^{+}} - E°_{Sn^{+2}/Sn}$$

$$= 0.15\,V - (-0.14\,V)$$

$$= 0.29\,V$$

$$\ln K = \frac{nE°_{cell}}{0.0257V}$$

$n = 2$

$$\ln K = \frac{2 \times 0.29V}{0.0257V} = 22.6$$

- **Calculate the standard free-energy change for the following reaction at 25°C:**

$$2Au(s) + 3Ca^{2+}(1.0\,M) \longrightarrow 2Au^{3+}(1.0\,M) + 3Ca(s)$$

Solution The half-cell reactions are

$$\text{Anode (oxidation):} \quad 2Au(s) \longrightarrow 2Au^{3+}(1.0\,M) + 6e^-$$
$$\text{Cathode (reduction):} \quad 3Ca^{2+}(1.0\,M) + 6e^- \longrightarrow 3Ca(s)$$

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= E^\circ_{Ca^{2+}/Ca} - E^\circ_{Au^{3+}/Au} \\ &= -2.87\text{ V} - 1.50\text{ V} \\ &= -4.37\text{ V} \end{aligned}$$

$$\Delta G^\circ = -nFE^\circ$$

The overall reaction shows that $n = 6$, so

$$\begin{aligned} \Delta G^\circ &= -(6)(96{,}500\text{ J/V}\cdot\text{mol})(-4.37\text{V}) \\ &= 2.53 \times 10^6\text{ J/mol} \\ &= 2.53 \times 10^3\text{ kJ/mol} \end{aligned}$$

Effect of Concentration on Cell Emf

- Nernst Equation
  - $\Delta G = \Delta G° + RT \ln Q$
  - $\Delta G = -nFE$ and $\Delta G° = -nFE°$, the equation can be expressed as
  - $-nFE = -nFE° + RT \ln Q$, **Dividing the equation through by -nF**

$$E = E° - \frac{RT}{nF} \ln Q$$

$$E = E° - \frac{0.0257\ \text{V}}{n} \ln Q$$

$$E = E° - \frac{0.0592\ \text{V}}{n} \log Q$$

- **Example: Predict whether the following reaction would proceed spontaneously as written at 298 K:**

$$Co(s) + Fe^{+2}(aq) \longrightarrow Co^{+2}(aq) + Fe(s)$$

given that $[Co^{+2}] = 0.25$ M and $[Fe^{+2}] = 0.94$ M.

Solution The half-cell reactions are

Anode (oxidation): $Co(s) \longrightarrow Co^{+2}(aq) + 2e^-$

Cathode (reduction): $Fe^{+2}(aq) + 2e^- \longrightarrow Fe(s)$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= E^\circ_{Fe^{+2}/Fe} - E^\circ_{Co^{+2}/Co}$$

$$= -0.44 - (-0.28\ V)$$

$$= -0.16\ V$$

$$E = E^\circ - \frac{0.0257\ V}{n}\ln Q$$

$$= E^\circ - \frac{0.0257\ V}{n}\ln\frac{[Co^{2+}]}{[Fe^{2+}]}$$

$$= -0.16\ V - \frac{0.0257\ V}{2}\ln\frac{0.25}{0.94}$$

$$= -0.16\ V + 0.017\ V$$

$$= -0.14\ V$$

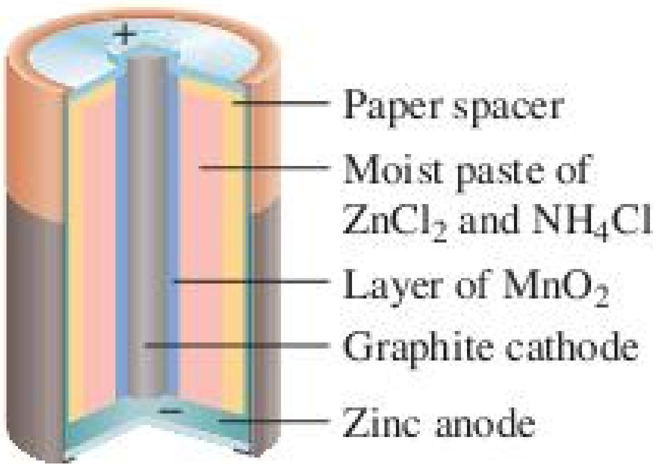
E is negative, the reaction is not spontaneous.

- **Exercise :Will the following reaction occur spontaneously at 25°C, given that $[Fe^{+2}]$ = 0.60 M and $[Cd^{+2}]$ = 0.010 M?**

$$Cd(s) + Fe^{+2}(aq) \qquad Cd^{+2}(aq)\ 1\ Fe(s)$$

Batteries

- **A battery is a galvanic cell, or a series of combined galvanic cells, that can be used as a source of direct electric current at a constant voltage.**
- **Dry Cell Battery**
  - **The most common dry cell, that is, a cell without a fluid component, is the Leclanché cell used in flashlights and transistor radios.**



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

Cathode: $2NH_4^+(aq) + 2MnO_2(s) + 2e \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

erall: $Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) \quad Zn^{+2}(aq) + Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

Alkaline dry cell

- **is similar to the dry cell, but it has potassium hydroxide in place of ammonium chloride.**

© Jill Braaten

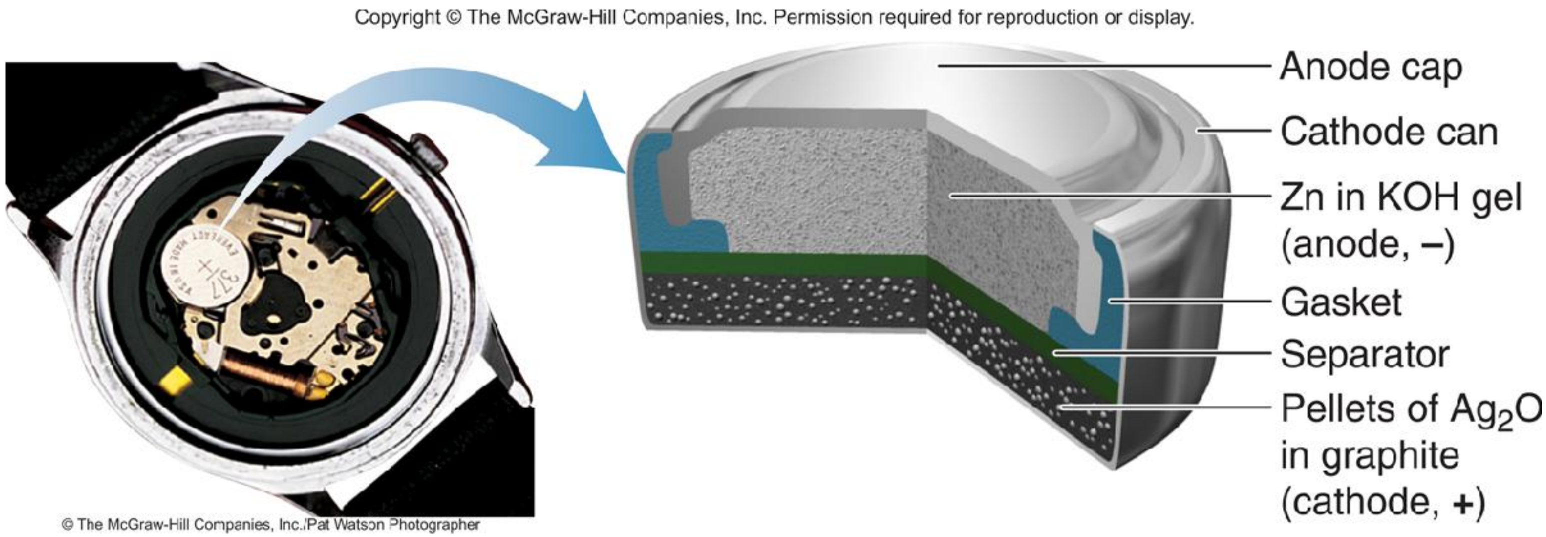
Anode (oxidation): $Zn(s) + 2OH^{-}(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^{-}$

Cathode (reduction): $MnO_2(s) + 2H_2O(l) + 2e^{-} \rightarrow Mn(OH)_2(s) + 2OH(aq)$

Overall (cell) reaction:

$$Zn(s) + MnO_2(s) + H_2O(l) \rightarrow ZnO(s) + Mn(OH)_2(s) \quad E_{cell} = 1.5\ V$$

Silver button



Anode (oxidation): $\mathbf{Zn}(s) + \mathbf{2OH^-}(aq) \rightarrow \mathbf{ZnO}(s) + \mathbf{H_2O}(l) + \mathbf{2e^-}$

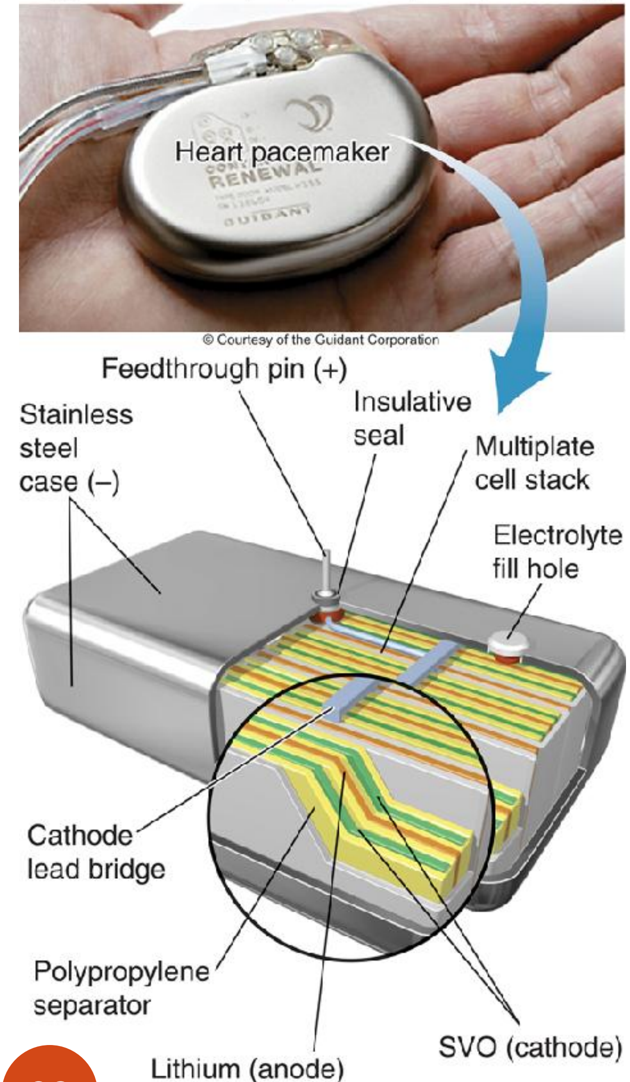
Cathode (reduction): $\mathbf{Ag_2O}(s) + \mathbf{H_2O}(l) + \mathbf{2e^-} \rightarrow \mathbf{2Ag}(s) + \mathbf{2OH^-}(aq)$

Overall (cell) reaction: $\mathbf{Zn}(s) + \mathbf{Ag_2O}(s) \rightarrow \mathbf{ZnO}(s) + \mathbf{2Ag}(s)$

$E_{cell} = 1.6$ V

The mercury battery uses HgO as the oxidizing agent instead of Ag_2O and has cell potential of 1.3 V.

Lithium battery



The primary lithium battery is widely used in watches, implanted medical devices, and remote-control devices.

Anode (oxidation): $Li(s) \rightarrow Li^+ + e^-$

***Cathode (reduction)*:** $CoO_2 + Li^+ + e^- \rightarrow LiCo_2O_2(s)$

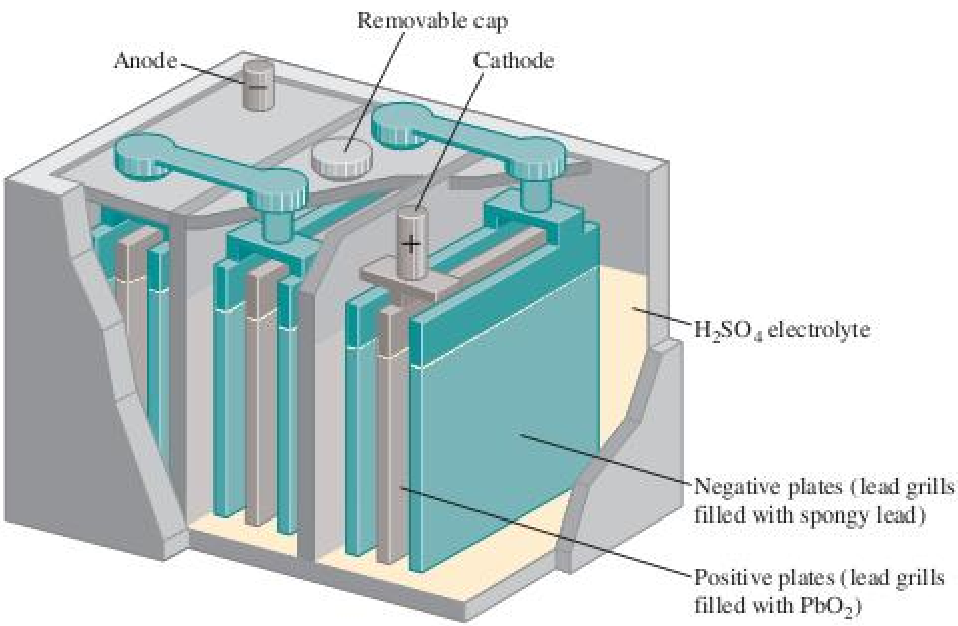
***Overall (cell) reaction*:**

$CoO_2 + Li(s) \rightarrow LiCoO_2(s)$

The advantage of the battery is that lithium has the most negative standard reduction potential and hence the greatest reducing strength

Lead-acid battery.

- **lead storage battery commonly used in automobiles consists of six identical cells joined together in series.**



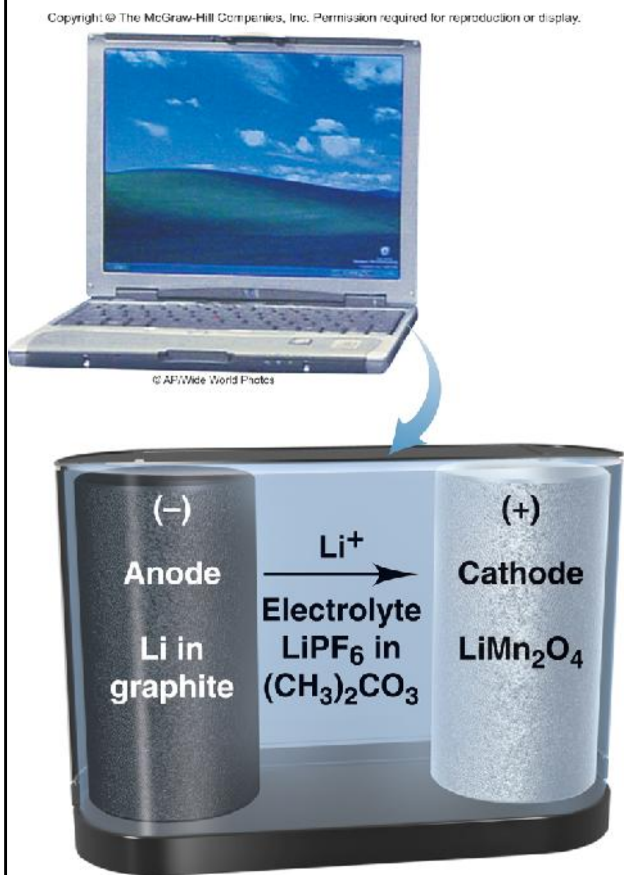
Anode: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

Overall: $Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

e lead-acid car battery is a secondary battery and is rechargeable.

Lithium-ion battery



Anode (oxidation):

$$Li_xC_6(s) \rightarrow xLi^+ + xe^- + C_6(s)$$

Cathode (reduction):

$$Li_{1-x}Mn_2O_4(s) + xLi^+ + xe^- \rightarrow LiMn_2O_4(s)$$

Overall (cell) reaction:

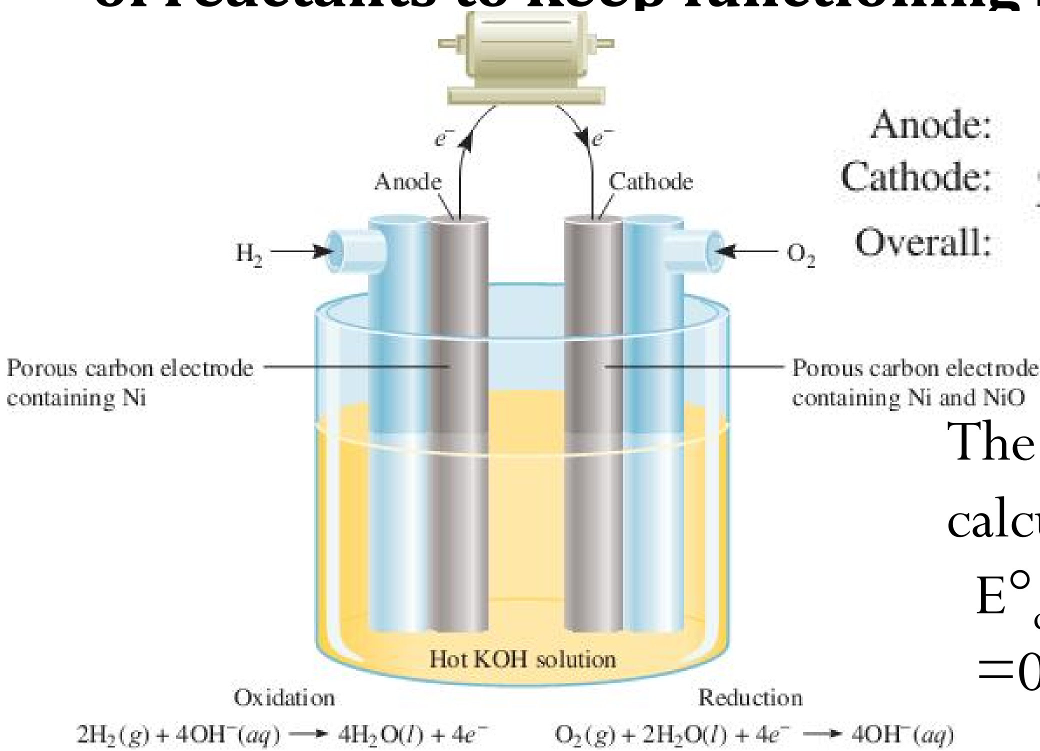
$$Li_xC_6(s) + Li_{1-x}Mn_2O_4(s) \rightarrow LiMn_2O_4(s)$$

$$E_{cell} = 3.7\,V$$

The secondary (rechargeable) lithium-ion battery is used to power laptop computers, cell phones, and camcorders.

Fuel Cells

- **Fossil fuels are a major source of energy, but conversion of fossil fuel into electrical energy is a highly inefficient process.**
- **fuel cell, a galvanic cell that requires a continuous supply of reactants to keep functioning .**



Anode: $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

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

The standard emf of the cell can be calculated as follows, :

$E°_{cell} = E°_{cathode} - E°_{anode}$

$= 0.40\,V - (-0.83\,V)$

$= 1.23\,V$

A hydrogen-oxygen fuel cell.

Electrolysis

- **Galvanic cell is spontaneous redox reactions, which result in the conversion of chemical energy into electrical energy.**
- **Electrolysis is the process in which electrical energy is used to cause a nonspontaneous chemical reaction to occur**

Electrolysis of Molten Sodium Chloride

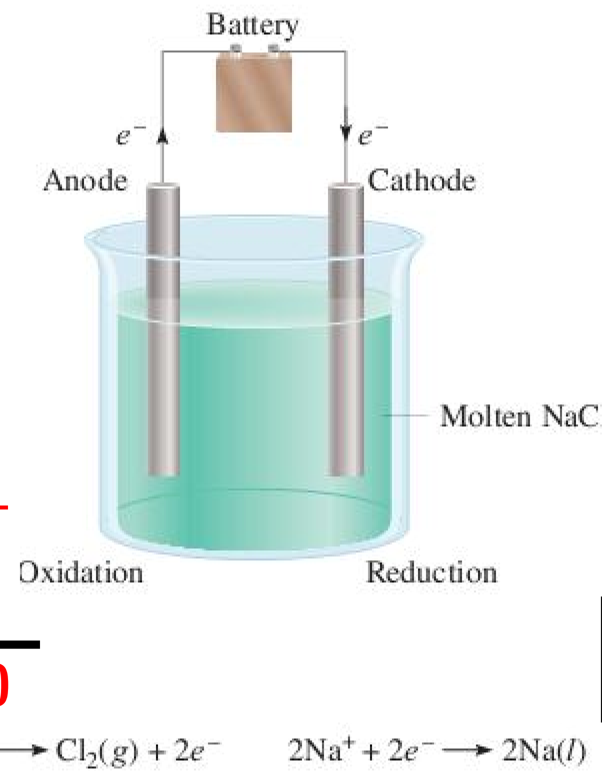
sodium chloride, an ionic compound, can be electrolyzed to form sodium metal and chlorine.

Downs cell, which is used for large-scale electrolysis of NaCl.

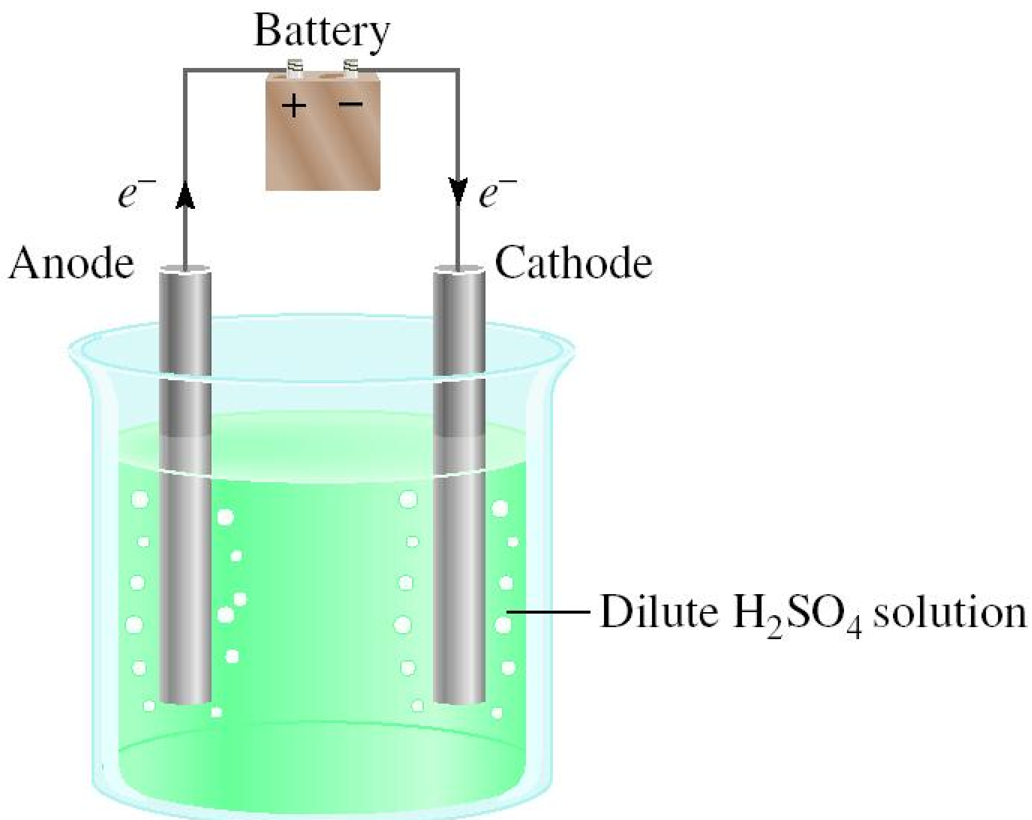
Anode (oxidation): $2Cl^-(l) \longrightarrow 2Cl_2(g) + 2e^-$

Cathode (reduction): $2Na^+(l) + 2e^- \longrightarrow 2Na(s)$

Overall : $2Na^+(l) + 2Cl^-(l) \longrightarrow 2Na(s) + 2Cl_2(g)$



Electrolysis of Water



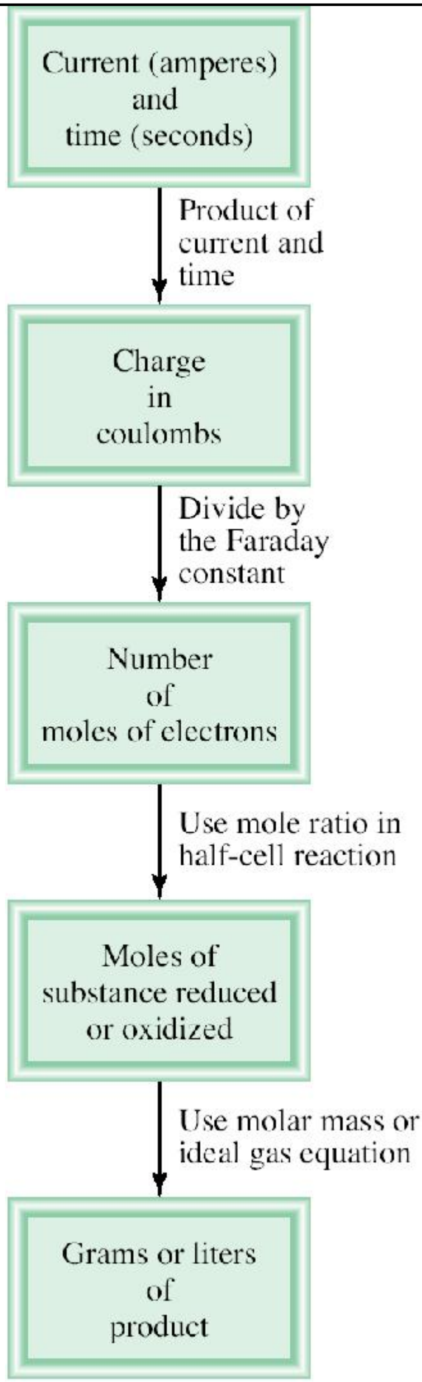
Oxidation

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

Reduction

$$4H^+(aq) + 4e^- \longrightarrow 2H_2(g)$$

$$\begin{array}{rl} \text{Anode (oxidation):} & 2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \\ \text{Cathode (reduction):} & 4[H^+(aq) + e^- \longrightarrow \tfrac{1}{2}H_2(g)] \\ \hline \text{Overall:} & 2H_2O(l) \longrightarrow 2H_2(g) + O_2(g) \end{array}$$



Electrolysis and Mass Changes

charge (C) = current (A) x time (s)

$1 \text{ mol } e^- = 96{,}500 \text{ C}$

How much Ca 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?

Anode: $2Cl^- (l) \longrightarrow Cl_2 (g) + 2e^-$

Cathode: $Ca^{2+} (l) + 2e^- \longrightarrow Ca (s)$

$$Ca^{2+} (l) + 2Cl^- (l) \longrightarrow Ca (s) + Cl_2 (g)$$

2 mole e⁻ = 1 mole Ca

$$\text{mol Ca} = 0.452 \frac{\text{C}}{\text{s}} \times 1.5 \text{ hr} \times 3600 \frac{\text{s}}{\text{hr}} \times \frac{1 \text{ mol e}^-}{96{,}500 \text{ C}} \times \frac{1 \text{ mol Ca}}{2 \text{ mol e}^-}$$

$$= 0.0126 \text{ mol Ca}$$

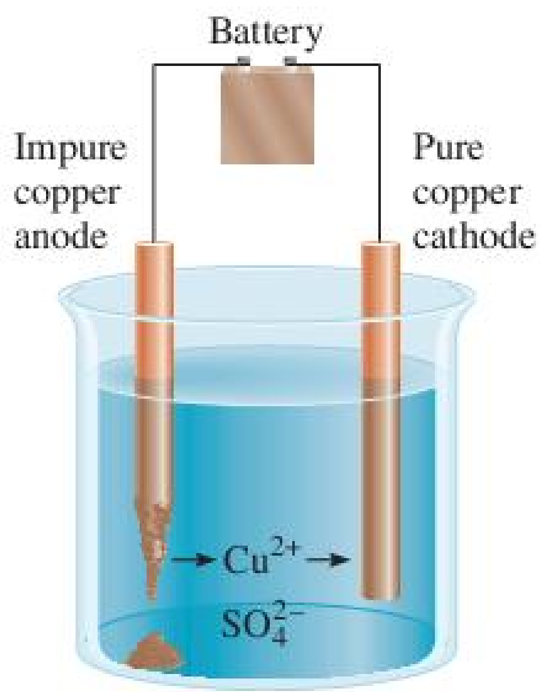
$$= 0.50 \text{ g Ca}$$

Electrometallurgy

- **Electrometallurgy is processes of electrolysis method that are useful to obtain a pure metal from its ores or for refining (purifying) the metal.**
- **Production of Aluminum Metal**
  - **Aluminum is usually prepared from bauxite ore ($Al_2O_3.2H_2O$).**

$$\begin{aligned} &\text{Anode:} && 3[2O^{2-} \longrightarrow O_2(g) + 4e^-] \\ &\text{Cathode:} && 4[Al^{3+} + 3e^- \longrightarrow Al(l)] \\ \hline &\text{Overall:} && 2Al_2O_3 \longrightarrow 4Al(l) + 3O_2(g) \end{aligned}$$

Purification of Copper Metal



$$\text{Anode:} \quad Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$

$$\text{Cathode:} \quad Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$