CHE 1031: General Chemistry I

5. Electrochemistry

5.1: Galvanic cells (aka voltaic cells)

5.2: Standard reduction potentials

5.3: Batteries & fuel cells

5.4: Corrosion

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5. Electrochemistry

5.1: Galvanic (aka voltaic) cells

- Use cell notation to describe galvanic cells
- Describe the basic components of galvanic cells

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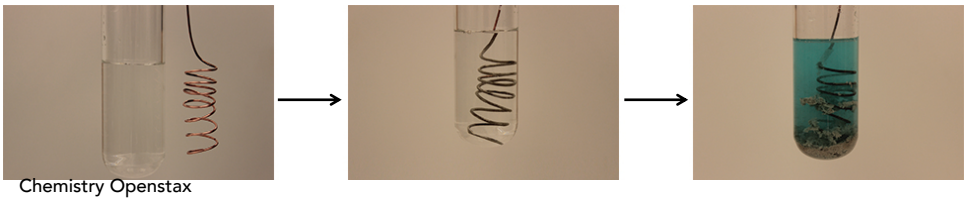
What are galvanic cells?

Galvanic cells (aka voltaic cells) *are electrochemical cells in which* <u>*spontaneous*</u> *redox reactions produce a flow of electrons, ie electricity.*

Example:

A piece of copper wire is placed in a solution of silver (I) nitrate. Immediately, silver metal begins to plate onto the copper metal (reduction), and the copper metal becomes copper ions (oxidation).

$$\left.\begin{array}{l} Cu \rightarrow Cu^{+2} + 2e- \\ 2\,(Ag^{+1} + e- \rightarrow Ag) \end{array}\right] \longrightarrow Cu + 2Ag^{+1} + \cancel{2e-} \rightarrow Cu^{+2} + 2Ag + \cancel{2e-}$$



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Spontaneous? Check the activity series

How does it work?

An elemental metal is **spontaneously** oxidized by ions of any metal <u>below</u> it on the activity series.

Think back to lab:

- Mg <u>is oxidized</u> by H^{+1} ions.
- Cu is <u>not oxidized</u> by H^{+1} ions.

TABLE 4.3 A Partial Activity Series of the Elements

	Oxidation Reaction	
Strongly reducing	$Li \rightarrow Li^+ + e^-$	most easily oxidized
	$K \rightarrow K^+ + e^-$	These elements react rapidly with aqueous H^+ ions (acid) or with liquid H_2O to release H_2 gas.
	$Ba \rightarrow Ba^{2+} + 2e^-$	
	$Ca \rightarrow Ca^{2+} + 2e^-$	
	$Na \rightarrow Na^+ + e^-$	
	$Mg \rightarrow Mg^{2+} + 2e^-$	These elements react with aqueous H^+ ions or with steam to release H_2 gas.
	$Al \rightarrow Al^{3+} + 3e^-$	
	$Mn \rightarrow Mn^{2+} + 2e^-$	
	$Zn \rightarrow Zn^{2+} + 2e^-$	
	$Cr \rightarrow Cr^{3+} + 3e^-$	
	$Fe \rightarrow Fe^{2+} + 2e^-$	
	$Co \rightarrow Co^{2+} + 2e^-$	These elements react with aqueous H^+ ions to release H_2 gas.
	$Ni \rightarrow Ni^{2+} + 2e^-$	
	$Sn \rightarrow Sn^{2+} + 2e^-$	
	$H_2 \rightarrow 2H^+ + 2e^-$	
	$Cu \rightarrow Cu^{2+} + 2e^-$	'precious metals'
	$Ag \rightarrow Ag^+ + e^-$	These elements do not react with aqueous H^+ ions to release H_2.
	$Hg \rightarrow Hg^{2+} + 2e^-$	
	$Pt \rightarrow Pt^{2+} + 2e^-$	
Weakly reducing	$Au \rightarrow Au^{3+} + 3e^-$	least easily oxidized

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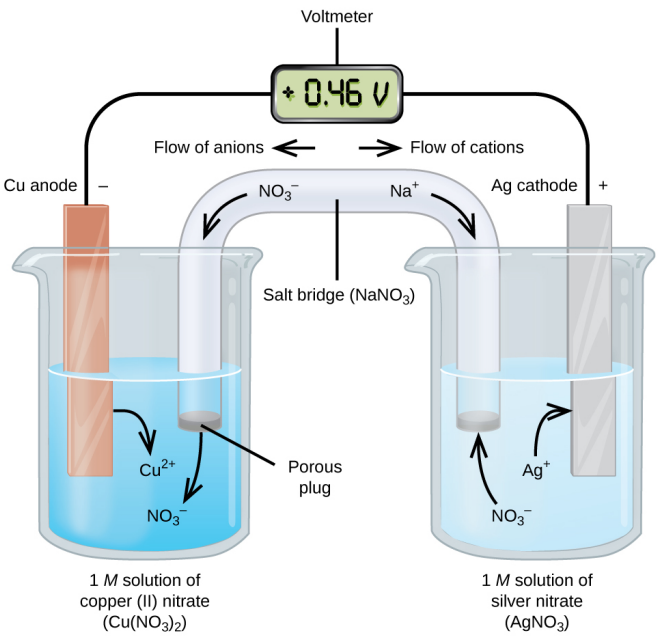
Galvanic cell diagram

Here the redox reaction has been physically separated into two **half-cells,** each corresponding to one **half-reaction.**

The flow of electrons from the anode to the cathode produces **electric current.**



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Galvanic cell diagram

Anode: electrode where oxidation occurs

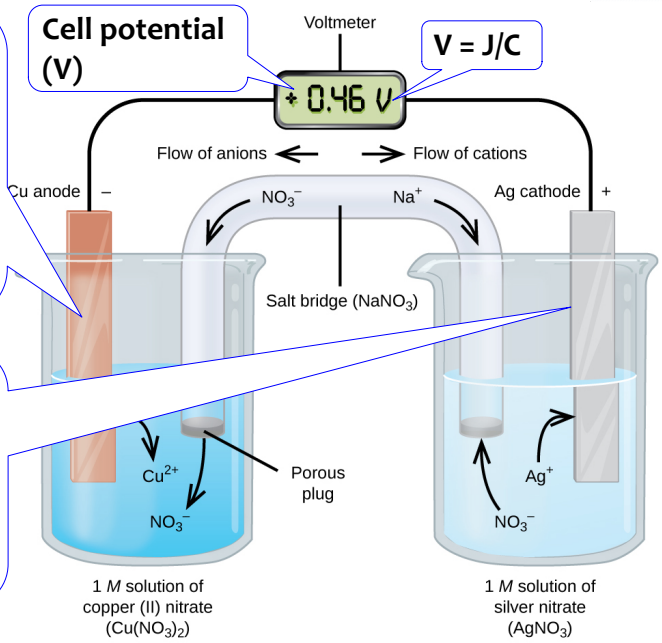
- Electrons flow **<u>from</u>** the anode.
- **<u>A</u> <u>n</u>**egative electr**<u>ode</u>**

Cell potential (V)

V = J/C

Cathode: electrode where reduction occurs

- Electrons flow **<u>to</u>** the cathode
- ca**<u>t</u>**hode



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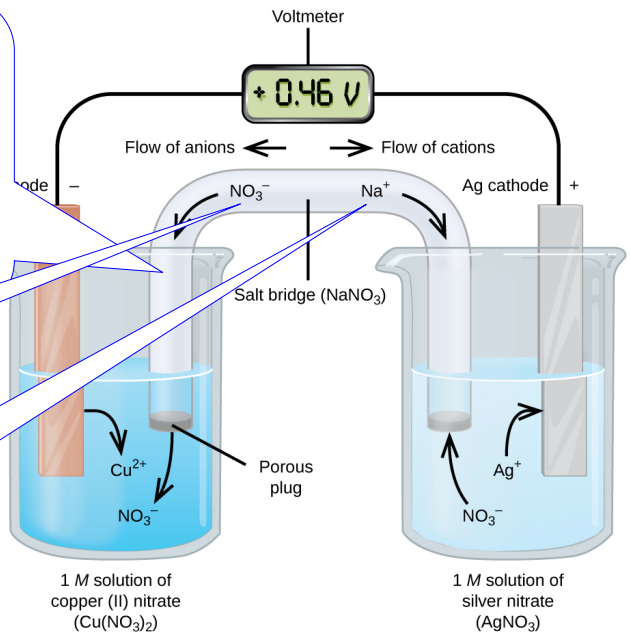
Galvanic cell diagram

Salt bridge: tube that only ions can flow through
- Equalizes the charge of the half cells; maintains redox

Anions flow to the anode (opposing e- flow)

Cations flow to the cathode



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Galvanic cell recap

To summarize what's going on in a galvanic cell:

- Electrons flow from the anode to the cathode.
- The flow of electrons is harvested as electricity.
- The anode slowly degrades as its metal atoms ionize.
- The cathode grows as ions are deposited on it as atoms.
- The salt bridge allows cations to flow to the cathode. This keeps the cathode from becoming so negative that electrons won't flow to it.
- The salt bridge allows anions to flow to the anode. This keeps the anode from becoming too positive as it loses electrons.
- Without the salt bridge the flow of electrons would stop!

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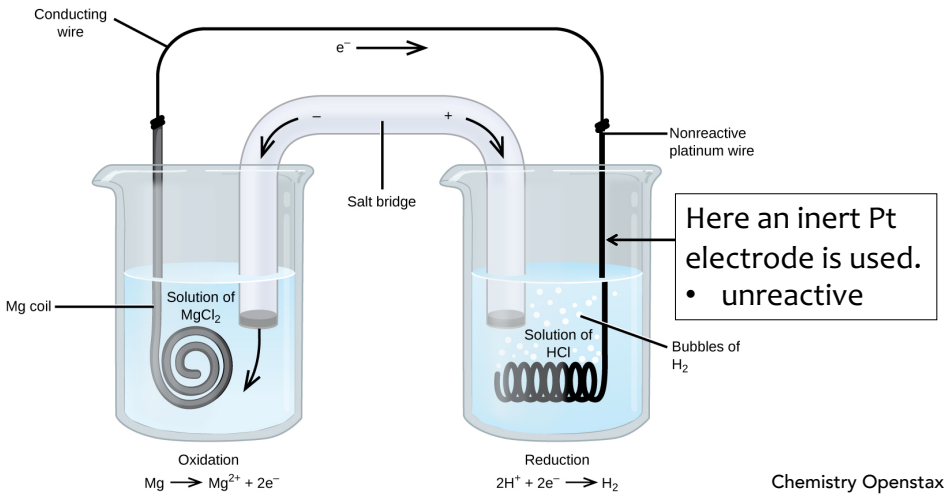
Inert electrodes

When redox reactions involve metals that are poor conductors, an **inert electrode,** *made of a conductive metal that does not participate in the redox reaction*, is used.



Here an inert Pt electrode is used.
- unreactive

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Galvanic cell shorthand

We can use this shorthand to describe a galvanic cell:

$$Cu(s) \mid Cu^{+2}\ (1\ M) \mid\mid Ag^{+1}\ (1\ M) \mid Ag(s)$$

A galvanic cell can be made with this reaction: 1

$$2Cr(s) + 3Cu^{+2}(aq) \rightarrow 2Cr^{+3}(aq) + 3Cu(s)$$

(a) Write oxidation & reduction half-equations.
(b) Label them as oxidation or reduction.
(c) Diagram the half-cells using galvanic cell shorthand.

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Example

A galvanic cells is created using a magnesium anode immersed in a solution of acid. Hydrogen gas is produced and an inert platinum cathode is used. 3

(a) Write oxidation & reduction half-equations.

(b) Label them as oxidation and reduction. Diagram the half-cells using galvanic cell shorthand.

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Example

Consider a galvanic cells using this reaction: 3

$5Fe^{+2}(aq) + MnO4^{-1}(aq) + 8H^{+1}(aq) \rightarrow 5Fe^{+3}(aq) + Mn^{+2}(aq) + 4H2O(l)$

(a) Write oxidation & reduction half-equations.

(b) Label them as oxidation and reduction.

(c) Identify the cathode and the anode.

(d) Diagram the half-cells using galvanic cell shorthand.

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Can you?

(1) Define the term 'galvanic cell' (aka voltaic cell)?

(2) Create a diagram of a galvanic cell?

(3) Locate and identify the functions of: anode; cathode; salt bridge; half-cells.

(4) Explain what an inert electrode is and when it is used?

(6) Represent a galvanic cell using symbols for phase separation and the salt bridge?

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5. Electrochemistry

5.2: Standard reduction potentials

- Use standard reduction potentials to determine the better oxidizing or reducing agent from among choices.

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Using standard reduction potentials

When standard reduction potentials of both half-reactions are known, the cell potential of a galvanic cell can be calculated rather than experimentally determined.

A <u>positive cell potential</u> indicates that a galvanic cell reacts **spontaneously** and will **produce an electric current**.

Calculate the cell potential of this galvanic cell: 4

$$Cu(s) \mid Cu{+}2(1\ M) \parallel Ag^{+1}(1\ M) \mid Ag(s)$$

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Standard reduction potentials

$F_2 + 2e^- \rightarrow 2F^-$ least easily oxidized	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$ most easily oxidized	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

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Try this

A galvanic cell is made with Au^{+3}/Au and Ni^{+2}/Ni half-cells.
(a) Identify the oxidizing & reducing agents. 5
(b) Calculate the cell potential.

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One more

A galvanic cell is made with Mg electrode in a 1 M solution of $Mg(NO_3)_2$ and a Ag electrode and a 1 M $Ag(NO_3)$ solution. 6
(a) Identify the oxidizing & reducing agents.
(b) Calculate the cell potential.

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Can you?

(1) Find both the appropriate SRP for both anode and cathode using a table of SRP values?

(2) Calculate cell potential given a galvanic cell diagram?

(3) Determine if a redox reaction is spontaneous?

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5. Electrochemistry

5.3: Batteries & fuel cells

- Classify batteries as primary or secondary
- List some characteristics & limitations of batteries
- Provide a general description of a fuel cell

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What's a battery?

Battery: *an electrochemical cell (or series of cells) that produces electrical current*

- Galvanic cells suited to practical application

Primary battery: *single use (not rechargeable)*

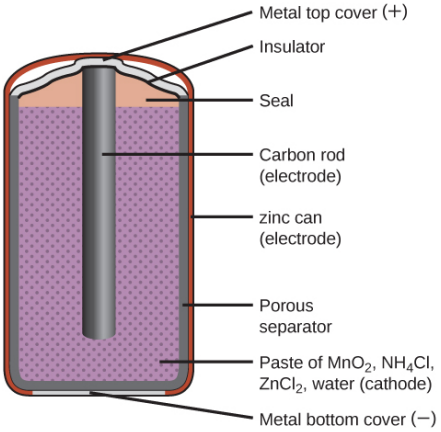
- **Dry cell:** *solid reactants*

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

$2MnO_4^{-1} + 2(NH_4)(Cl) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3 + H_2O + 2Cl^{-1}$

Ecell = +1.5 V

- V same for all sizes (AAA-D), but the larger sizes last longer



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Alkaline batteries

A primary battery developed in the 1950s as improvements of dry cell batteries

- 3-5X more energy
- Alkaline material poses a chemical hazard if they leak

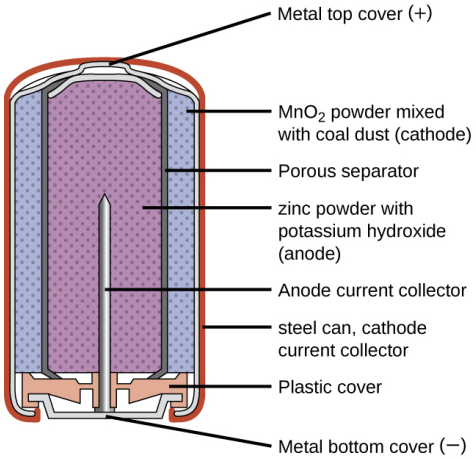
$Zn(s) + 2(OH)^{-1} \rightarrow ZnO + H_2O + 2e^-$

$E° = -1.28$ V

$2MnO_4^{-1} + H_2O + 2e^- \rightarrow Mn_2O_3(s) + 2(OH)^{-1}$

$E° = +0.15$ V

E°cell = + 1.43 V



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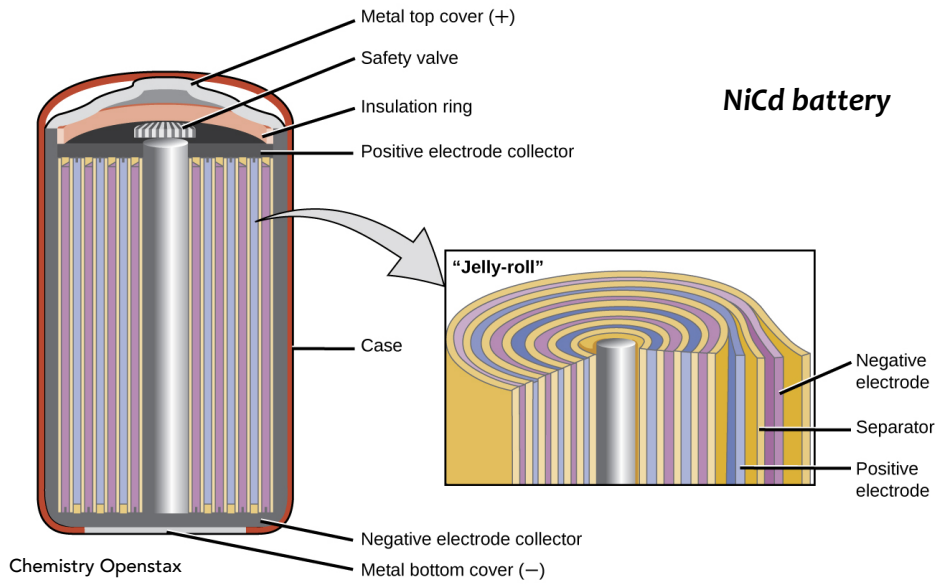
Secondary batteries

Secondary batteries: *are rechargeable*



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Common secondary batteries

The **NiCd battery (nickel – cadmium)** can be charged about 1000 times and provides 1.2 – 1.25 V.

- Cd makes these batteries quite toxic.

$$Cd(s) + 2(OH)^{-1} \rightarrow Cd(OH)2(s) + 2e-$$
$$\underline{NiO2(s) + 2H2O + 2e- \rightarrow Ni(OH)2(s) + 2(OH)^{-1}}$$
$$Cd(s) + NiO2(s) + 2H2O \rightarrow Cd(OH)2(s) + Ni(OH)2(s)$$

The **lithium ion battery** is now ubiquitous. They provide 3.7 V, hold charge well and are lightweight.

$$LiCoO2(s) \rightleftharpoons Li1\text{-}xCoO2 + xLi^{+1} + xe-$$
$$\underline{xLi^{+1} + xe- + xC6 \rightleftharpoons x\ LiC6}$$
$$LiCoO2 + xC6 \rightleftharpoons Li1\text{-}xCoO2 + xLiC6$$

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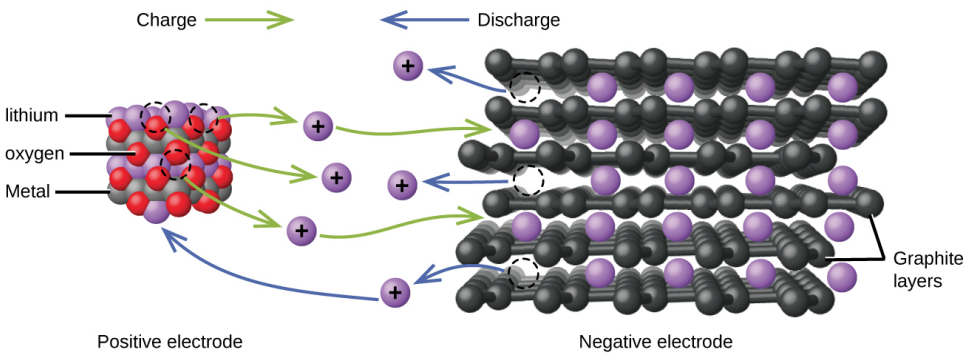
Li ion batteries

The C6 in lithium ion batteries is graphite: thin and very lightweight layers of carbon.



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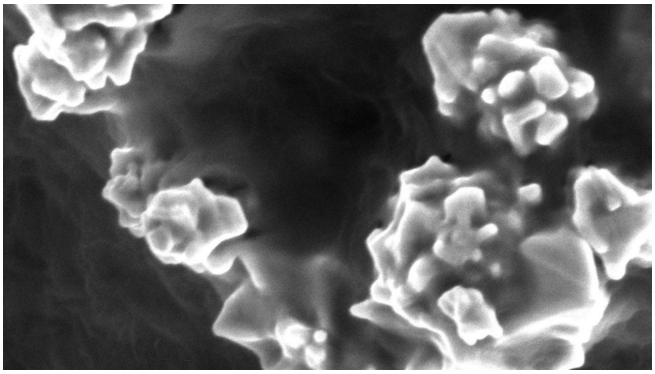
Safer Li ion batteries

Li ion batteries make our addiction to electronics possible, but they sometimes **catch on fire**.

Researchers at Stanford University have developed a thin film of plastic studded with nickel micro-particles to solve this problem.

At normal temps the Ni conducts electricity.

When the battery begins to overheat, plastic film expands & separates Ni, stopping flow of e-.



http://www.sciencemag.org/news/2016/01/cheap-plastic-film-prevents-batteries-catching-fire

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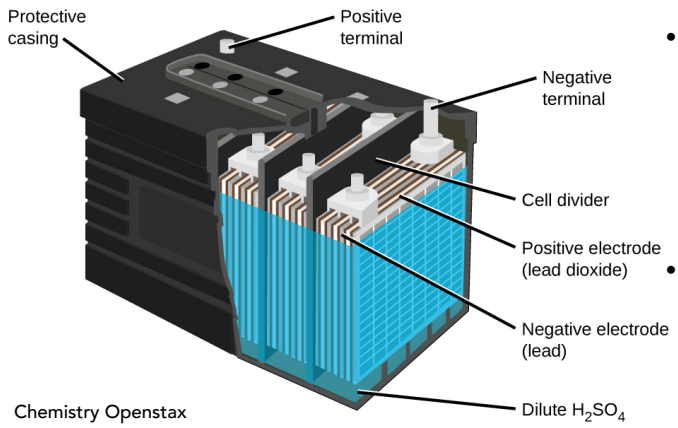
Lead-acid batteries

The **lead-acid batteries** used in cars are an old secondary battery.

$Pb(s) + HSO4^{-1} \rightarrow Pb(SO4) + H^{+1} + 2e-$

$PbO2(s) + HSO4^{-1} + 3H^{+1} + 2e- \rightarrow Pb(SO4) + 2H2O$

$Pb(s) + PbO2(s) + 2H2(SO4) \rightarrow 2Pb(SO4) + 2H2O$



- Each cell produces 2 V, so 6 cells in serial create a 12 V battery.
- Environmental hazard because of both the lead & the acid.

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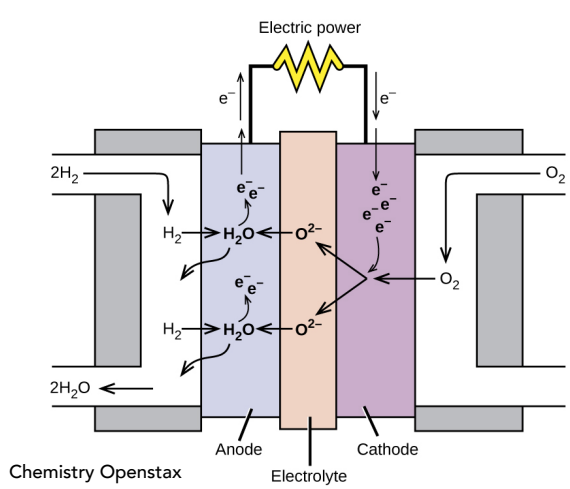
Fuel cells

Fuel cell: *a device that converts chemical energy into electrical energy without combustion*

- Open systems with continuous fuel input & power output
- Redox reactions



Efficiency 40 – 60%, greater than 25-35% for internal combustion.

In this hydrogen fuel cell the only by-product is **water**.

$2H2 + 2O^{-2} \rightarrow 2H2O + 4e-$

$O2 + 4e- \rightarrow 2O^{-2}$

$2H2 + O2 \rightarrow 2H2O$

$E°cell = 0.9\ V$

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Can you?

(1) Define the term battery?

(2) Differentiate between primary and secondary batteries?

(3) Describe what factors govern battery voltage and longevity?

(4) Explain how battery cells can be linked in serial to increase power output?

(5) Explain how a plastic-nickel film can be used to improve the safety of lithium ion batteries?

(6) Explain the differences between batteries and fuel cells and the advantages of fuel cells?

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5. Electrochemistry

5.4: Corrosion

- Define corrosion
- List some methods to slow or prevent corrosion

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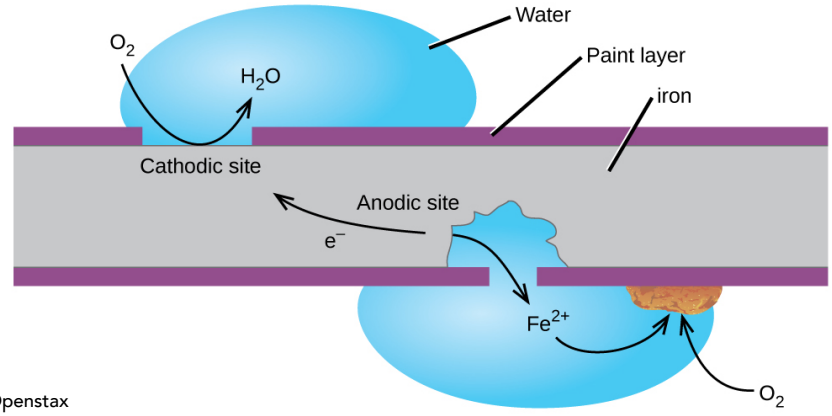
Corrosion

Corrosion: *the undesirable degradation of metals due to spontaneous electrochemical (redox) reactions*

- Aka rust, tarnish, verdigris
- In the US, corrosion causes <u>half a trillion dollars</u> of damage annually.



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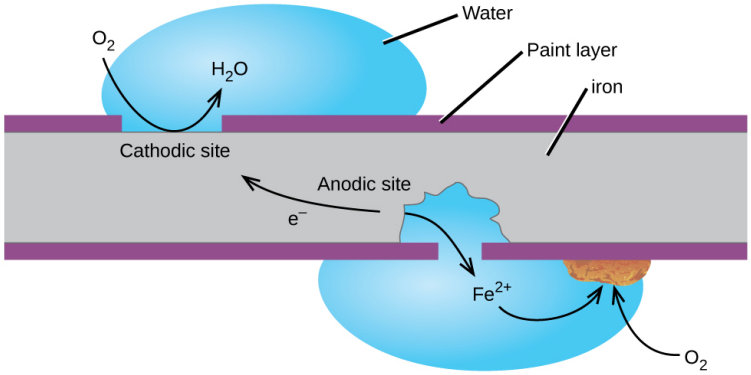
Rust

Iron **rusts** where it is exposed to oxygen gas and water.

$Fe(s) \rightarrow Fe^{+2} + 2e^-$	$E° = -0.44$ V
$O_2 + 4H^{+1} + 4e^- \rightarrow 2H_2O$	$E° = +1.23$ V
$2Fe(s) + O_2 + 4H^{+1} \rightarrow 2Fe^{+2} + 2H_2O$	$E° = +1.67$ ← spontaneous

$4Fe^{+2} + O_2 + (4 + 2x)\,H_2O \rightarrow$ **$2Fe_2O_3\text{-}xH_2O$** $+ 8H^{+1}$

Rust forms when iron ions continue to react with O_2 & H_2O.



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Preventing corrosion?

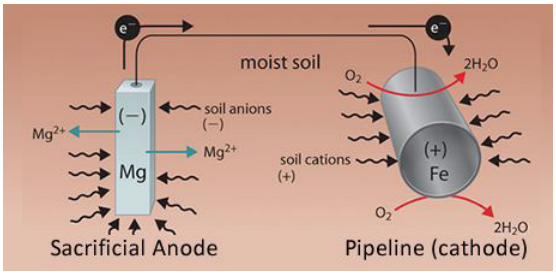
Corrosion can be prevented by preventing access of air and water to metals. **Paint** works but must be kept intact.

Alloys can prevent corrosion from within. The chromium added to stainless steel collects near the surface, reacts with air to form an **oxide** that seals and protects the body of the metal.

Galvanization (Zn-plating) coats valuable metals with a more easily oxidized metal (lower reduction potential).

- The Zn (**sacrificial anode)** is oxidized & protects coated metal.
- Galvanization is also called **cathodic protection**.

- **Wired sacrificial anodes**
- **Trickle charging**



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Can you?

(1) Define the term corrosion?

(2) Use SRP to determine whether a redox reaction could produce corrosion?

(3) Draw a diagram to show where corrosion occurs relative to the anode and cathode of a redox reaction?

(4) List three methods for preventing corrosion?

(5) Explain the concept of self-limiting corrosion?

(6) Explain how sacrificial anodes can provide cathodic protection?

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5. Electrochemistry: terms to know

active electrode
alkaline battery
anode
battery
cathode
cathodic protecdtion
cell notation
cell potential
corrosion
dry cell
electrical potential
fuel cell
galvanic cell
galvanized iron
inert electrode
lead acid battery
lithium ion battery
nickel-cadmium battery
oxidation half-reaction
primary battery
reduction half-reaction
sacrificial anode
secondary battery
standard cell potential (E°cell)
standard reduction potential (E°)
voltaic cell

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