Chem 1B Objective 14:
Apply oxidation-reduction reaction principles to electrolytic cells.

Key Ideas: An electrolytic cell converts electrical energy to chemical energy.

An electrolytic involves a non-spontaneous chemical reaction ($\Delta G > 0$).

Electrical energy is supplied to make the NON-spontaneous reaction occur.

In an electrolytic cell, a power supply, e.g., battery, supplies electrons to the cathode where reduction occurs. At the anode, oxidation occurs.

# Metals Tend to Lose Electrons
# Different Metals Have a Different Ability (see Activity Series) to Lose Electrons

1. Connect one metal to another metal with a wire. What happens?

2. A piece of Cu metal is placed into $Zn^{2+}$ (aq). What happens? Why?

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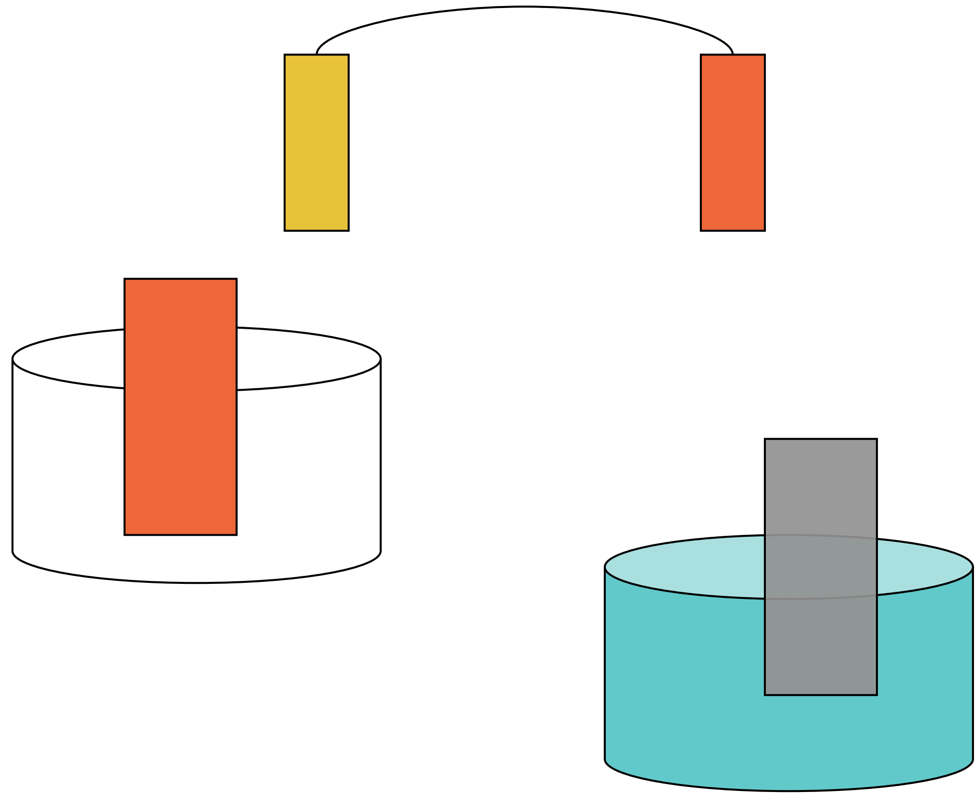

Which reaction is not spontaneous?
How can you make this reaction occur?

# Metals Tend to Lose Electrons
## Different Metals Have a Different Ability (see Activity Series) to Lose Electrons

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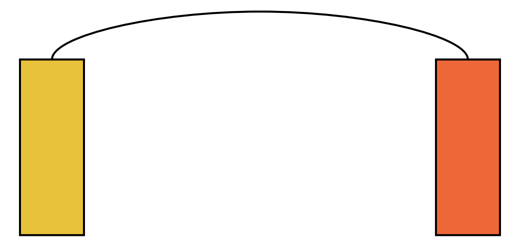

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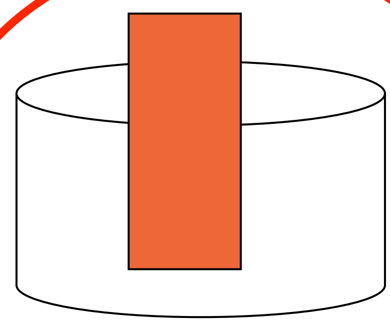

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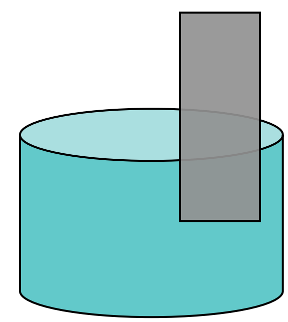


Which reaction is NOT spontaneous? Cu is <u>less</u> active than Zn.
How can you make this reaction occur? Use electricity.

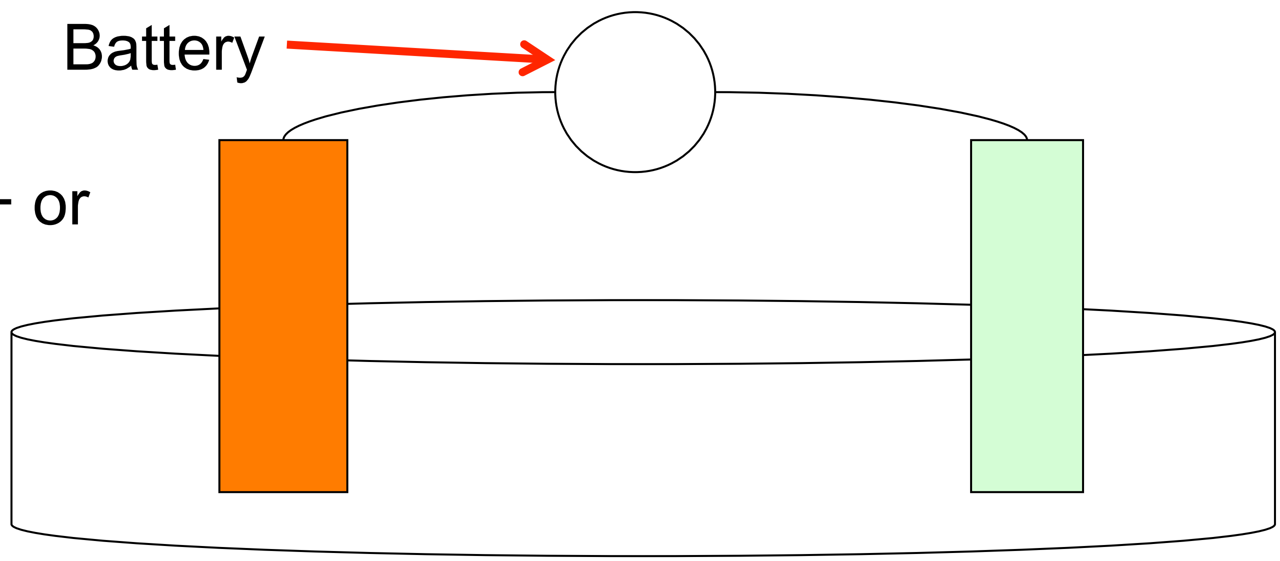
**Objective**: Make an electrolytic cell

***Electrolytic Cell uses Electricity to make Chemical Energy***

No salt bridge needed in electrolytic cell

Use an electrolytic cell to plate Zn metal onto Cu.
Draw a cell diagram.
What should you use for electrodes?
What is the minimum voltage required to plate Zn onto Cu?
Would you add anything to the water? Give reasons.

Which terminal (+ or -) goes where?



**Objective**: Make an electrolytic cell

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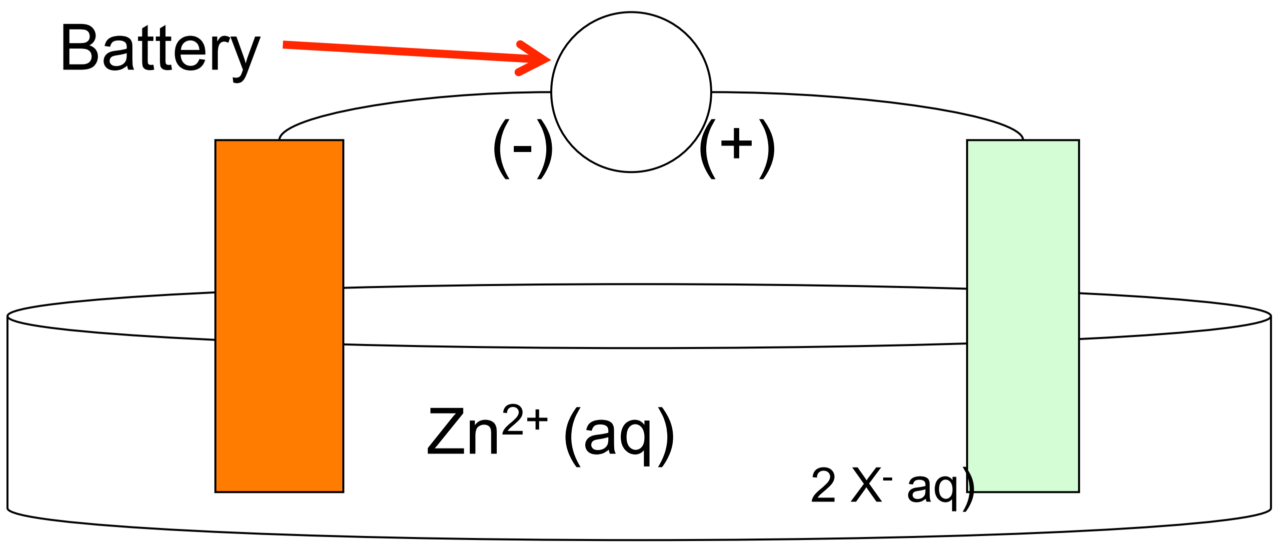
Use an electrolytic cell to plate Zn metal onto Cu.

$Zn^{2+}$ (aq) + 2 $e^-$ ---> Zn (s)
on Cu electrode
Reduce (cathode)

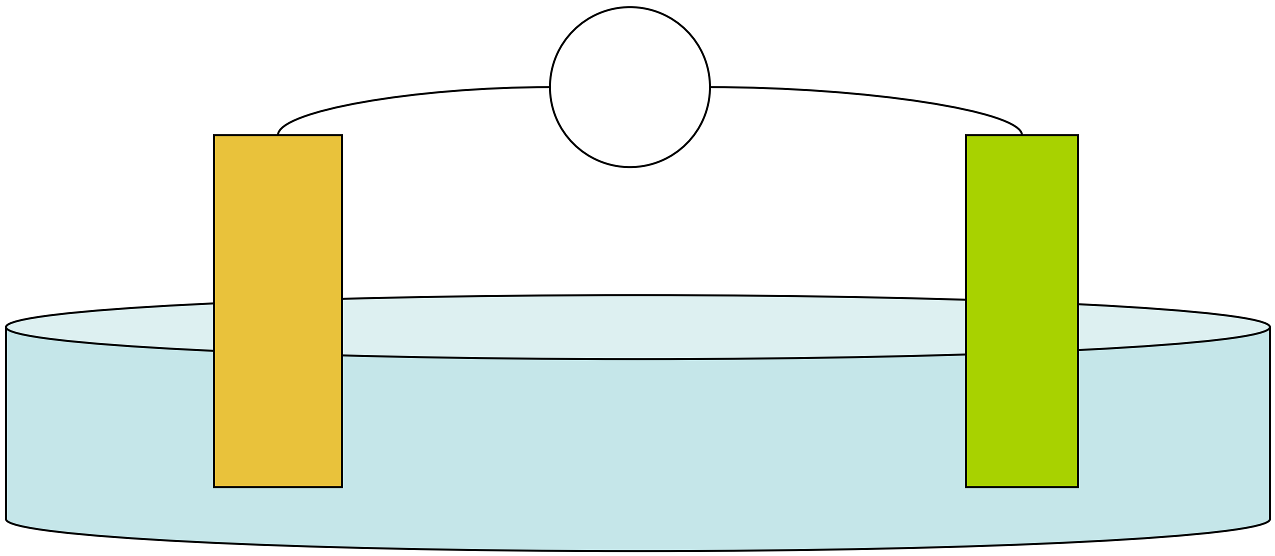
Zn (s) ---> $Zn^{2+}$ (aq) + 2 $e^-$
on Zn electrode
Oxidize (anode)




Overall Reaction:

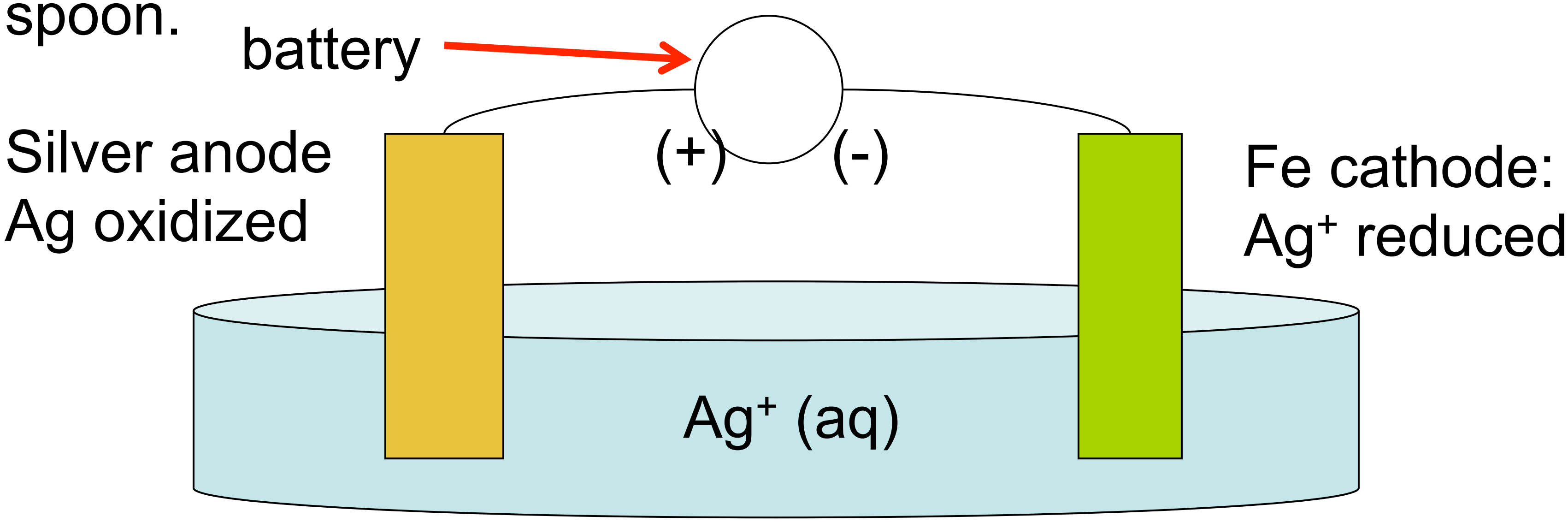
E = ___ V

***Electroplating***: Use an electrolytic cell to silver plate a iron spoon.
Which electrode is the spoon?
What would you use as the electrolyte?
What is the minimum voltage required to plate Ag?



100 mA of current is passed through the cell for 30 min.
Calculate the mass of Ag that is plated onto the spoon.
*Formulas to use*: $I = Q/t$ and $Q = n F$

***Electroplating***: Use an electrolytic cell to silver plate a iron spoon.




100 mA of current is passed through the cell for 30 min. Calculate the mass of Ag that is plated onto the spoon.

Current tells you how much charge (electrons) pass through the cell in a certain time: $I = Q/t$

or $Q = It = (0.1\ A)(30\ min)(60\ sec/min) = 180\ C$

From Charge (Q), calculate the moles of electrons, n

$Q = n F$ or $n = Q/F = 180\ C/96{,}500\ C/mole = 0.0019$ moles electrons

$Ag^+ + 1\ e^- \rightarrow Ag\ (s)$ so 0.0019 moles electrons = 0.0019 moles Ag

0.0019 moles Ag = 0.2 g Ag

**Objective**: Make an electrolytic cell

***Electrolytic Cell uses Electricity to make Chemical Energy***

No salt bridge needed in electrolytic cell

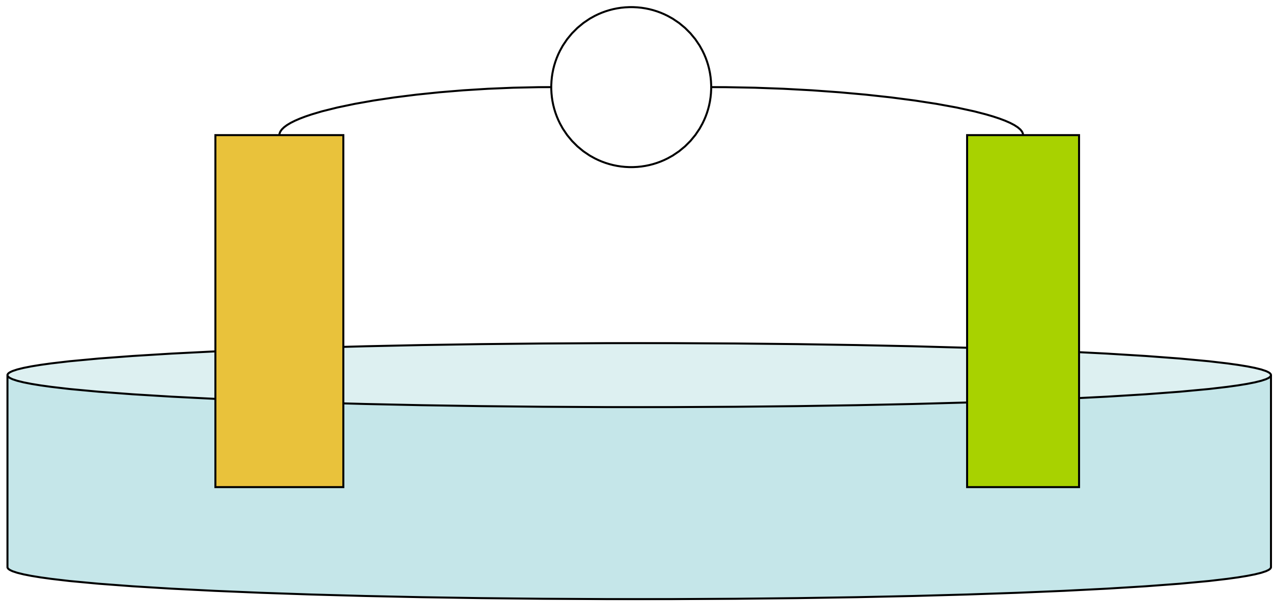
Use an electrolytic cell to Split Water.

Draw a cell to split water.

At which electrode is $H_2$ produced?

What is the minimum voltage required to split water?

Would you add anything to the water? Give reasons.



How Much Energy in Volts are Needed to Split Water?

Acid conditions:

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

$2\ H^+\ (aq) + 2\ e^- \text{--->} H_2\ (g)$ $E^o = 0\ V$

$2\ H_2O \text{--->} 2\ H_2\ (g) + O_2\ (g)$ $E^o = -1.23\ V$

Basic conditions:

$O_2\ (g) + 2\ H_2O + 4\ e^- \text{--->} 4\ OH^-\ (aq)$ $E^o = 0.40\ V$

$2\ H_2O + 2\ e^- \text{--->} H_2\ (g) + 2\ OH^-\ (aq)$ $E^o = -0.83\ V$

$2\ H_2O \text{--->} 2\ H_2\ (g) + O_2\ (g)$ $E^o = -1.23\ V$

# To Split Water:

## *Is -1.23 V a lot of energy?*

$E = QV = (1.6\times10^{-19}\ C/e^-)(2\ e^-)(1.23\ V)(6.02\times10^{23}/mole)$
$= 237\ kJ$

$\Delta G = -\ n\ F\ E = -(2)(96{,}500\ C/mole)(-1.23\ V) = 237.4\ kJ$

Red light (650 nm): $E = hc/\lambda = 184\ kJ$

Blue light (450 nm): $E = hc/\lambda = 266\ kJ$

# <u>To Split Water:</u>

## *Is -1.23 V a lot of energy?*

**1.23 V = 237 kJ**

<u>Electricity</u>: 1 kW hr = $3.6 \times 10^6$ J = 0.034 therm
Cost: PG&E rate = \$0.1323/kW hr

To split one mole (18 g) of $H_2O$ requires 237 kJ of energy:
(\$0.1323/kW hr)(1 kW hr/$3.6 \times 10^6$ J )(237,000 J) = \$0.0087

To split one liter (1000 g) of $H_2O$ requires 13,200 kJ of energy:
(\$0.0087/mole)(1 mole/18 g)(1000 g) = \$0.48

# To Split Water:
## *Is -1.23 V a lot of energy?*
**1.23 V = 237 kJ**

To split one liter (1000 g) of $H_2O$ requires 13,200 kJ of energy:
(\$0.0087/mole)(1 mole/18 g)(1000 g) = \$0.48

It costs \$0.48 to split 1000 g of $H_2O$ to make 111 g of $H_2$.

Combustion:

$$2\ H_2\ (g) + O_2\ (g) \text{ ---> } 2\ H_2O\ (l) \qquad \Delta H = -142.6\ kJ/g$$

111 g of $H_2$ produces 15,800 kJ

NET: 15,800 J – 13,200 J = 2,600 kJ

Currently, on a global scale, **energy usage is on the order of 13 terawatts** (13 trillion W or 13 trillion joules per second), of which roughly **85% is generated by burning fossil fuels**. (CEN, 8/27/07, p. 16)

"***MORE ENERGY—in the form of sunlight—strikes Earth in one hour than all of the energy consumed by humans in an entire year.***" -- Nathan Lewis, Cal Tech Chemistry Professor

Sun showers Earth with an energy flow of some 120,000 TW.

We need to Figure out a way to ***inexpensively*** ***convert sunlight to electricity***.

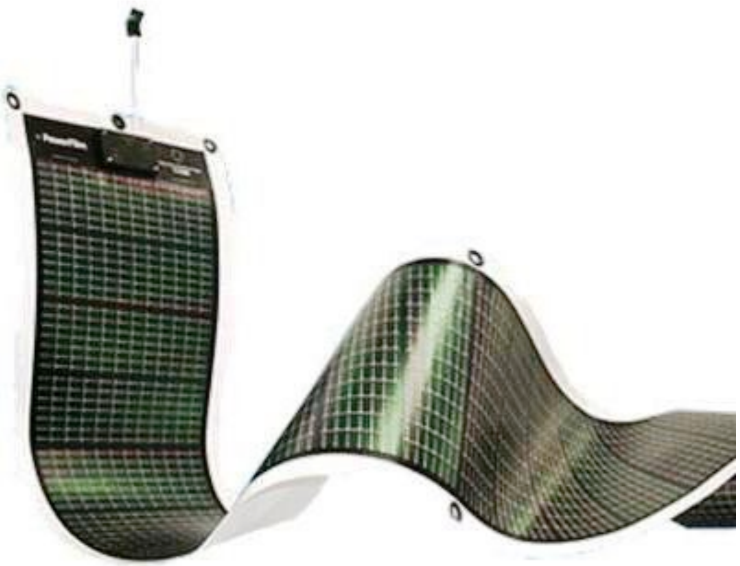
# Solar Energy ≈ 0.125% of U.S. electricity (2008)

CEN, 10/20/08, p. 40

920 MW on Electric Grid = 500 MW photovoltaics + 420 MW concentrating solar power

2260 MW captured solar from solar calculators, road signs, pools,

Polysilicon solar cells
14% efficiency
http://www.topsky-tech.com/poly-silicon-solar-cell-tianwei-supplier.html



Thin Films
8% efficiency
http://www.circuitstoday.com/thin-film-solar-cell

# Solar Cells made of Semiconductors

## Most solar cells use Silicon (Si)

Abundant – from $SiO_2$ (sand)
Good match between solar radiation and Si energy bands
But … fab requires high T and high purity

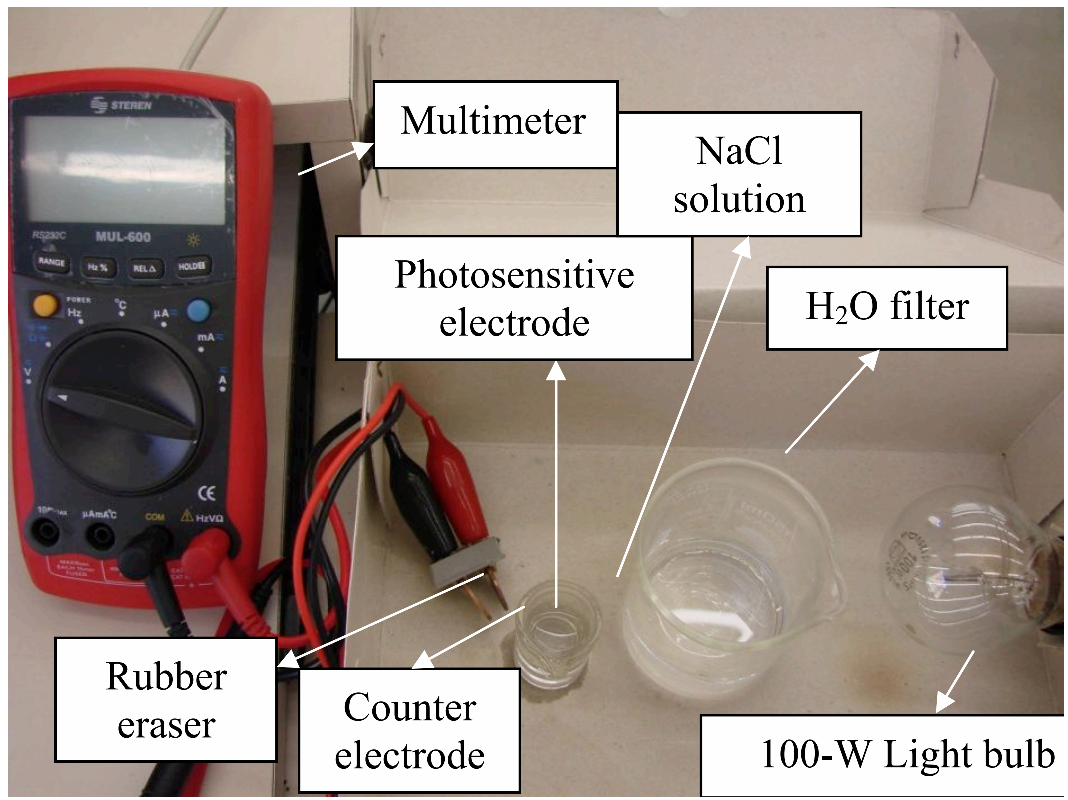
## Lab 8. Make a solar photovoltaic cell using a penny

Cu → $Cu_2O$
$Cu_2O$ = semiconductor
Band gap = 2.0 eV

1 eV = $1.6\times10^{-19}$ J = 60.2 kJ/mole
$E = h\nu = hc/\lambda$

2.0 eV, $\lambda$ = 620 nm (red)
3.2 eV = 390nm (UV) for $TiO_2$

J. Chem. Educ. 2011, 88, 1287



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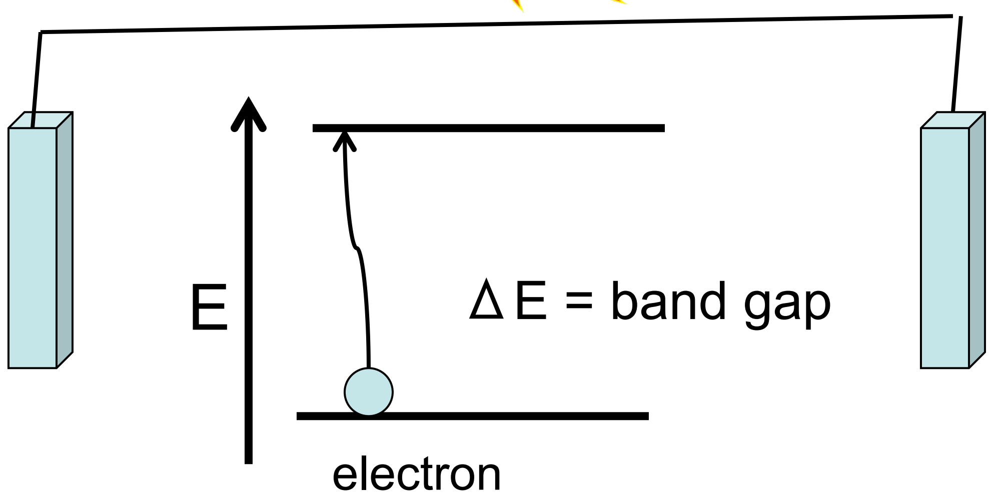
Cu → $Cu_2O$ (semiconductor with Band gap = 2.0 eV, $\lambda$ = 620 nm (red))

http://www.webweaver.nu/clipart/sun.shtml



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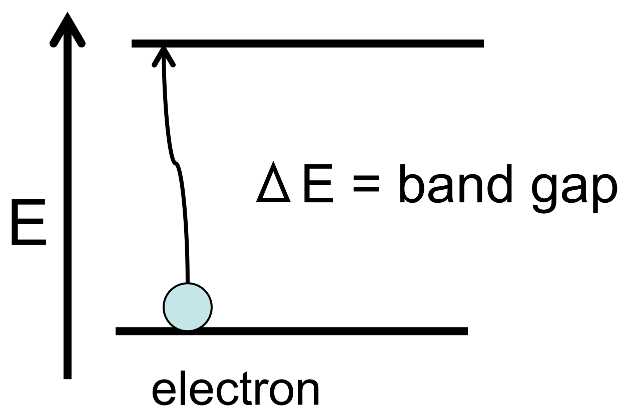


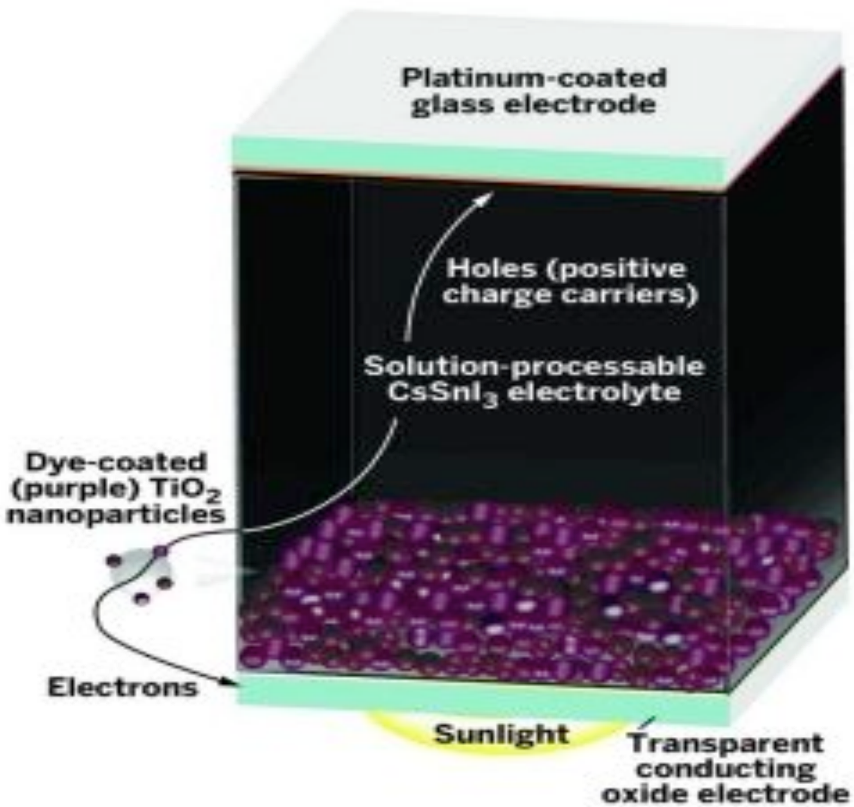

| Substance | Band Gap, eV | Energy, J ($x10^{-19}$) | Wave-length, nm |
|---|---|---|---|
| Si | 1.1 | 1.8 | 1100 |
| $Cu_2O$ | 2.0 | 3.2 | 620 |
| $TiO_2$ | 3.2 | 5.1 | 390 |

http://cen.acs.org/articles/90/i23/Shade-Hot.html

Dye-Sensitized Solar Cells (DSSC) generate electricity from light by mimicking photosynthesis. Efficiency = 26%.

Use ambient indoor light. Use to replace disposable batteries?

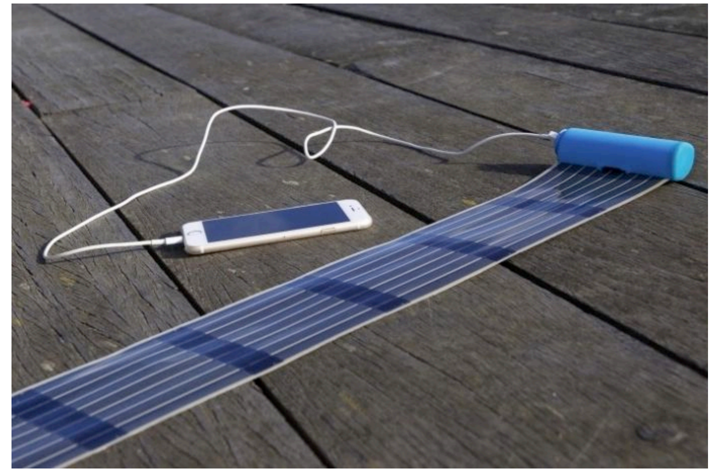
DSSC consists of a film of inexpensive porous $TiO_2$ nanoparticles coated with a sunlight-absorbing dye, often a ruthenium compound, in contact with a liquid electrolyte solution.




http://cen.acs.org/articles/90/i24/Solid-Solar-Cell-Solution.html (CEN, 6/11/12)

Solid Solar-Cell Solution

New solid electrolyte bypasses corrosion and durability problems of traditional dye-sensitized solar cells



Other Types of Solar Cells:
(http://cen.acs.org/articles/94/i18/future-low-cost-solar-cells.html )

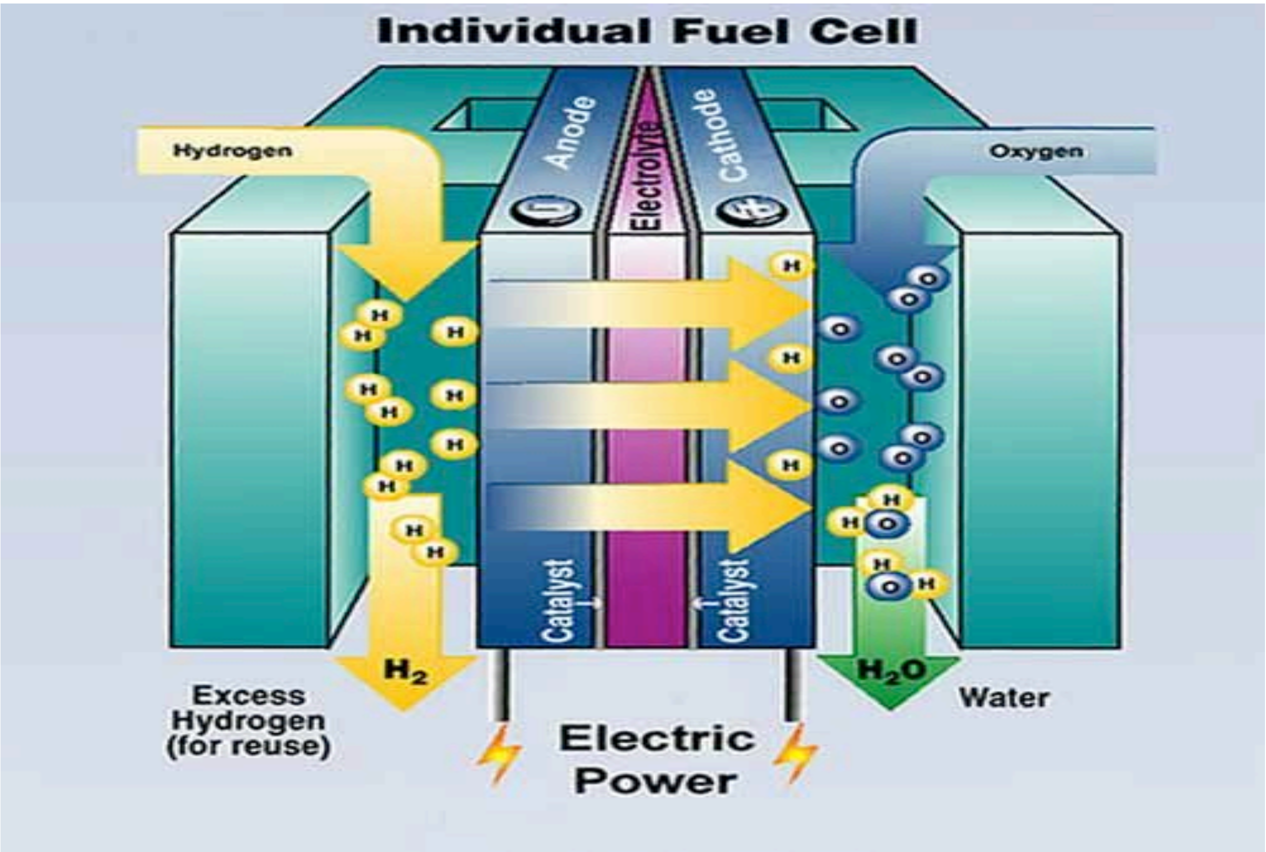
| | |
|---|---|
| Silicon (multicrystalline) | 21% efficiency |
| Silicon (single crystal) | 25% efficiency |
| Gallium-Arsenide | 46% efficiency |
| Organic Photovoltaics | 11.5% efficiency |
| Perovskite Solar Cells | 22.1% efficiency |
| Quantum Dot Photovoltaics | 11.3% efficiency |

## *Fuel Cells Produce Electricity*

http://science.howstuffworks.com/fuel-cell.htm

Hydrogen is thought to be the fuel of the 21st century. It will be used in a fuel cell rather than combusted in a car engine.

a. How does a fuel cell work?




http://www.greenjobs.com/pg/resources/IndustryBackground/IndustryBackground.aspx?id=100000007

Animation: http://www.plugpower.com/Solutions/Technology/OverviewDemo.aspx

## *Honda FCX and MB F-Cell uses $H_2$ Fuel Cells*

$2\ H^+ + 2\ e^- \rightarrow H_2\ (g)$ $\quad E_{red} = 0\ V$

$O_2\ (g) + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$ $\quad E_{red} = +1.23\ V$

$2\ H_2O + 2\ e^- \rightarrow H_2\ (g) + 2\ OH^-$ $\quad E_{red} = -0.83\ V$

$O_2\ (g) + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$ $\quad E_{red} = +0.40\ V$

What reaction occurs at the anode?
What reaction occurs at the cathode?
What is the function of a proton exchange membrane (PEM) in a fuel cell?
How much voltage is produced by a hydrogen fuel cell?

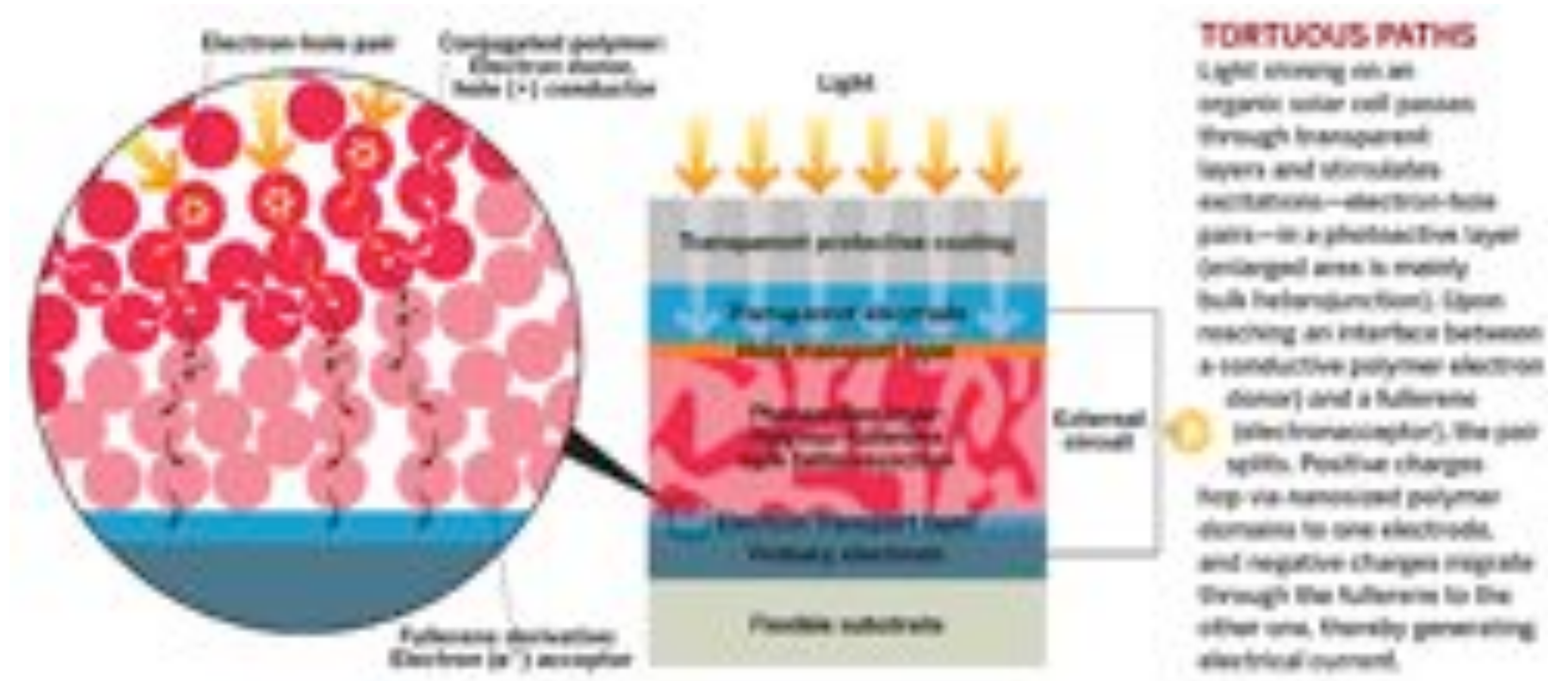
What is the source of hydrogen for a hydrogen fuel cell?
http://auto.howstuffworks.com/fuel-efficiency/fuel-economy/hydrogen-economy4.htm
http://cen.acs.org/articles/89/i45/Still-Chasing-Hydrogen-Economy.html

Why is hydrogen used in a fuel cell to produce electricity rather than in a heat engine?

CEN, 8/10/09, p. 10
$H_2O$ -- sun --> $H_2$ quantum efficiency = 60%
New catalyst = CdS doped with PdS and Pt increases quantum efficiency to 93%. Compare to photosynthesis = 95%

CEN, 5/3/10, p. 11 Splitting water with Goretex coated with PEDOT - PEG catalyst

CEN, 8/23/10, p. 12 Organic PV cell efficiency = 5%
Inorganic semiconductor PV = 10-15%

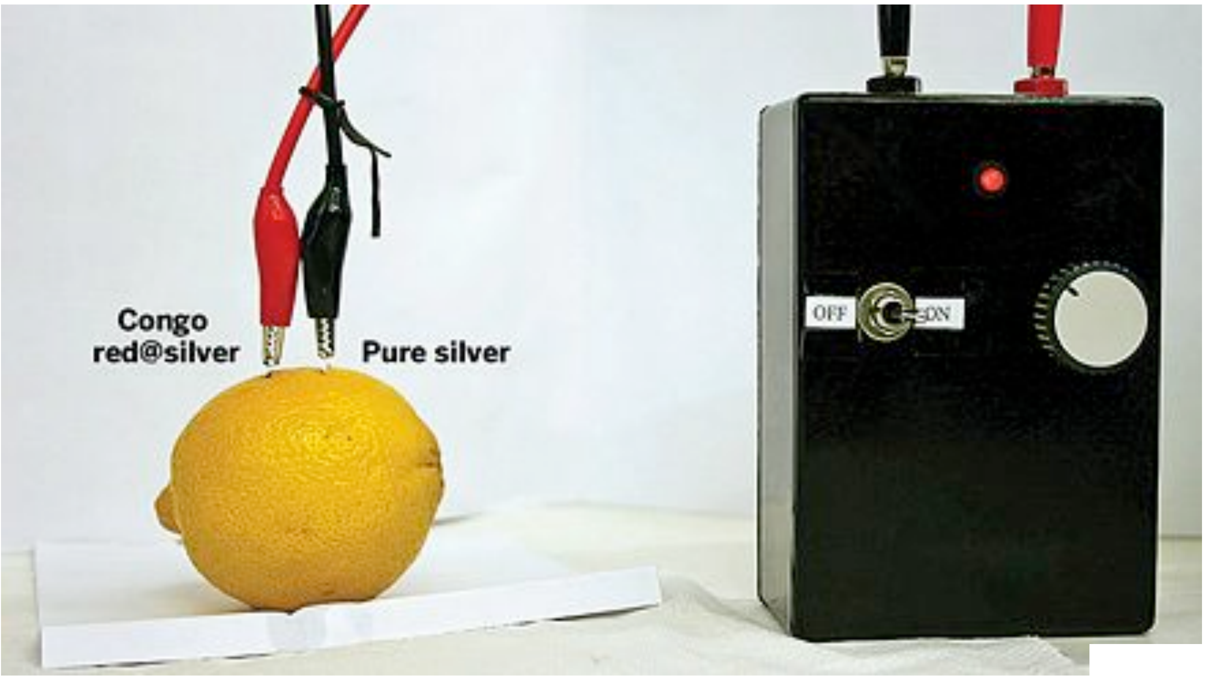


# Efficiency of energy devices

| Energy Source | Efficiency, % |
|---|---|
| $H_2$ → electrical energy | 80 |
| Motor/inverter (EE → ME) | 80 |
| Total: $H_2$ → mechanical energy | 64 |
| Gas engine | 20 |
| Battery powered electric car (90% for battery, 80% for inverter) | 72 |
| Whole cycle: electric car | 72 |
| Charging car | 90 |
| Power plant using combustion | 40 |
| Total | 26 |

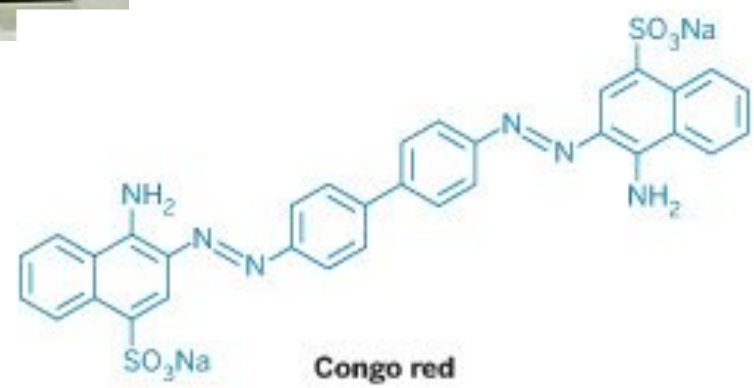
https://pubs.acs.org/cen/news/89/i29/8929notw8.html

7/13/11, CEN, Electrochemical cell based on same-metal electrodes is a first




2 Ag electrodes:
One electrode is pure Ag;
the other electrode doped with Congo red dye.

the potential difference originates from the different **rates** of reactions taking place at the electrodes, rather than by different types of reactions




Congo red

## *Biosensors* uses Electrochemistry


MEDIC chip (top) would be connected to patient's bloodstream to continuously measure a target drug. Inside the device (illustrated at bottom), binding of target (green sphere) to aptamer (gray) causes shape change that boosts electron-transfer rate (curvy arrows) from an electrochemical reporter (blue) to gold electrode (rectangular base), generating detection signal.

http://cen.acs.org/articles/91/i49/NonStop-Biosensor.html

http://www.photographyblogger.net/22-remarkable-pictures-of-rust/

Cost of Corrosion in US in 2002 = $276 billion (3% of GDP)
http://www.nace.org/Publications/Cost-of-Corrosion-Study/

Estimated to be over $1 trillion in US in 2012
http://www.g2mtlabs.com/2011/06/nace-cost-of-corrosion-study-update/

Annual worldwide cost = $2.2 trillion (3% of world GDP)
http://www.corrosion.org/

Name 3 ways to prevent corrosion
http://www.corrosion-doctors.org/index.htm
Corrosion protection, Chang, #19.56, p. 697

CEN, 4/23/12, p. 26. Navy to construct first Titanium hull
Ti is lighter, stronger, and more corrosion resistant than steel but 9 x as expensive and diffcult to weld w/o weakening the Ti.

# Saving Shipwrecks

Electrochemical and spectroscopic methods help conserve historic metal artifacts (CEN, 1/8/07, p. 45)

The electrochemistry of oxygen—in the form of oxidation of metals—is a main cause of damage to shipwrecks. The standard way to treat marine artifacts is to soak them or to perform electrolytic reduction on them in high-pH solutions.

Three main objectives in using electrochemical methods for marine artifact conservation:

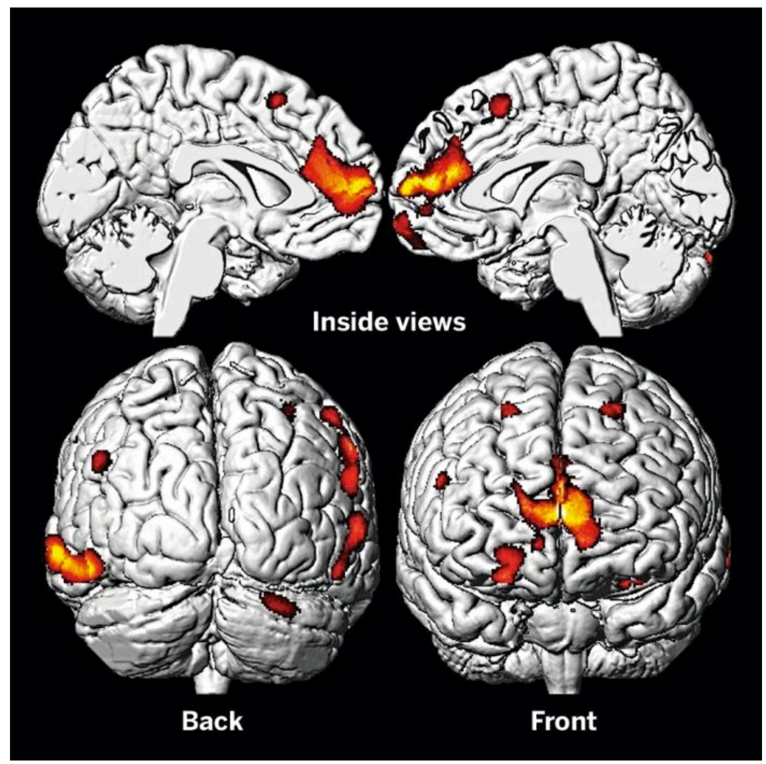
1. convert corrosion products back to a metallic state.
2. remove chlorides, especially from objects containing copper or iron. Chlorides from seawater make metals more prone to attack by dissolved oxygen through formation of complexes and changes in reaction mechanisms.
3. mechanical cleaning.

Mardikian attaches an anode to the interior of the Hunley submarine.

http://cen.acs.org/articles/94/i7/Lead-Ended-Flints-Tap-Water.html

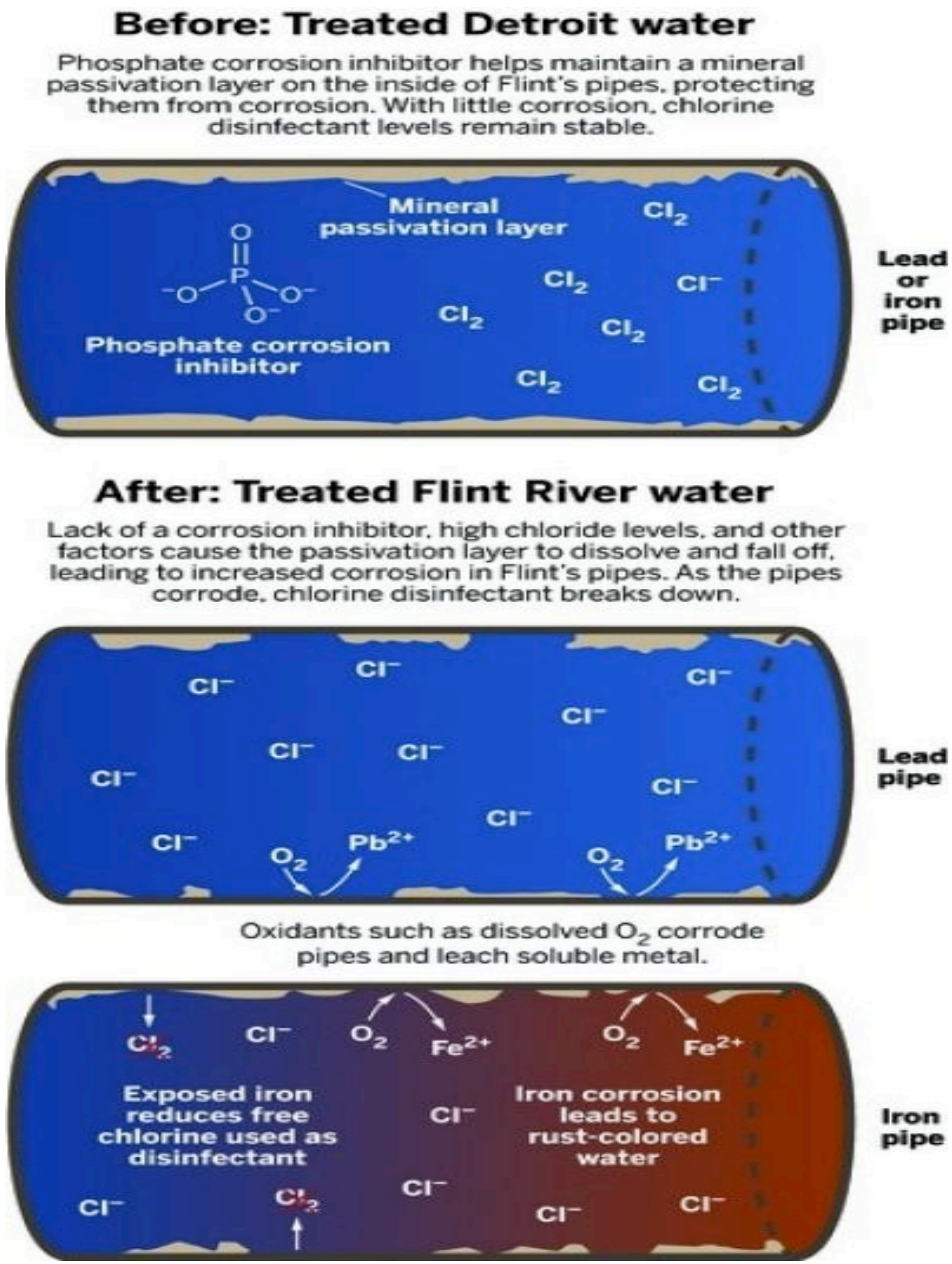
# Lead (Pb) in Tap Water in Flint, MI: How did it get there?

EPA Std = 15 ppb Pb
Flint water = 13,200 ppb




Problem with Lead – cognitive and behavioral issues in children http://cen.acs.org/articles/94/i7/Lead-Ended-Flints-Tap-Water.html

# Lead (Pb) in Tap Water in Flint, MI: How did it get there?



1. a. Fill in the blanks:

| | Voltaic Cell | Electrolytic Cell |
|---|---|---|
| Energy supplied or produced? | | |
| $\Delta G > 0$, $< 0$, or $=0$? | | |
| $\varepsilon_{cell} > 0$, $< 0$, or $=0$? | | |
| Anode separate from cathode? (Yes or No?) | | |

2. The 1.5 V battery that runs your portable radio is dead.
You have Ag, Cu, and Zn and the corresponding metal ion solutions.
Which **two** metals and metal ion solutions would you use to make a 1.5 V battery?
Draw a diagram of your battery. Label the anode and cathode.
Write the half reaction that occurs at each electrode. Calculate the voltage produced by this battery.