CHEM 103: Chemistry in Context

Unit 4

Solution Chemistry

Reading: Chapter 8 (parts)

Unit 4.3

Oxidation and Reduction

Colorado State University

Electronegativity and Oxidation

Chapter 5 **Electron pairs not equally shared**

Electronegativity tells us who "wins" in a shared pair

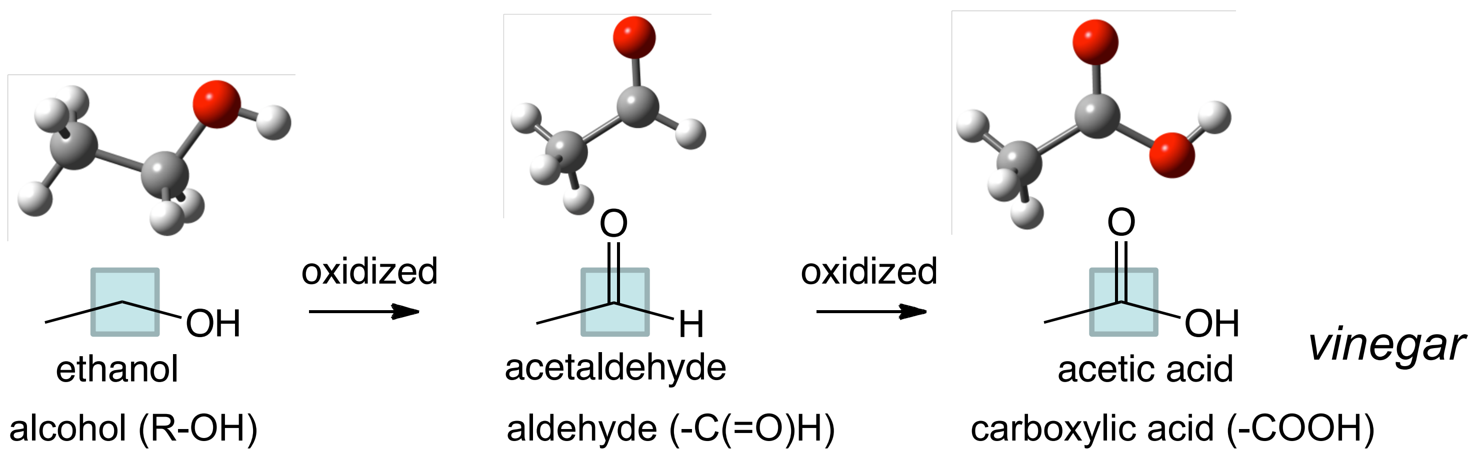
Table 5.3 Electronegativity Values, Arranged by Group Number

1A	2A	3A	4A	5A	6A	7A	8A
H							He
2.1							—
Li	Be	B	C	N	O	F	Ne
1.0	1.5	2.0	2.5	3.0	3.5	4.0	—
Na	Mg	Al	Si	P	S	Cl	Ar
0.9	1.2	1.5	1.8	2.1	2.5	3.0	—

Oxygen more electronegative than all elements except F; we say oxygen takes electrons from almost all other elements

Moving Protons vs Electrons

- Acid-Base chemistry: movement of protons (in the form of hydronium)
- Redox chemistry: transfer of electrons between compounds
  - Electron transfer reactions: think “OIL RIG”
    - Oxidation Is Loss (of electrons)
    - Reduction Is Gain (of electrons)
- Oxidation state—another formalism in chemistry
  - neutral atom: oxidation state = 0
  - ionic compound: oxidation state often the same as the charge of the species
  - atoms in molecules: the charge on the atom assumes that the most electronegative atoms get all the electrons in a bond; organic example from earlier in the semester (C 2.5, H 2.1):



ox. state of C: -1 +1 +3

Rust via Acid Rain: Redox Also Involved

$$4Fe(s) + 2O_2(g) + 8H_3O^+(aq) \rightarrow 4Fe^{2+}(aq) + 12H_2O(l)$$
$$4Fe^{2+}(aq) + O_2(g) + 12H_2O(l) \rightarrow 2Fe_2O_3(s) + 8H_3O^+(aq)$$

acid is catalytic

Net: $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ **rust**

Redox in Energy-Related Materials: Electrons, Cells and Batteries

A galvanic cell is a device that converts the energy released in a spontaneous chemical reaction into electrical energy

A battery is a device consisting of one or more galvanic cells that produces a direct current by converting chemical energy into electrical energy

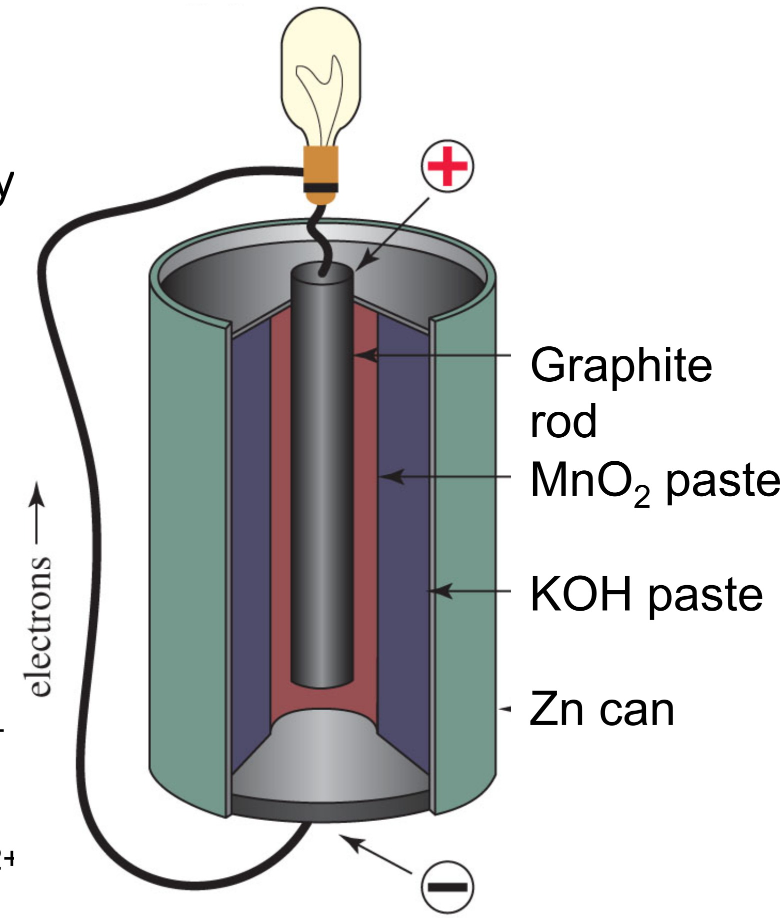
A electrolytic cell is a device that converts electrical energy into chemical energy (a battery running backwards)

Simplified alkaline battery

Oxidation half-reaction: $Zn \rightarrow Zn^{2+} + 2e^-$

Reduction half-reaction: $2e^- + 2Mn^{4+} \rightarrow 2Mn^{3+}$

Overall reaction: $Zn + 2Mn^{4+} \rightarrow 2Mn^{3+} + Zn^{2+}$



Electrons shuttled through an external circuit: Electricity is the flow of electrons from one region to another, driven by a difference in potential energy

Anodes and Cathodes

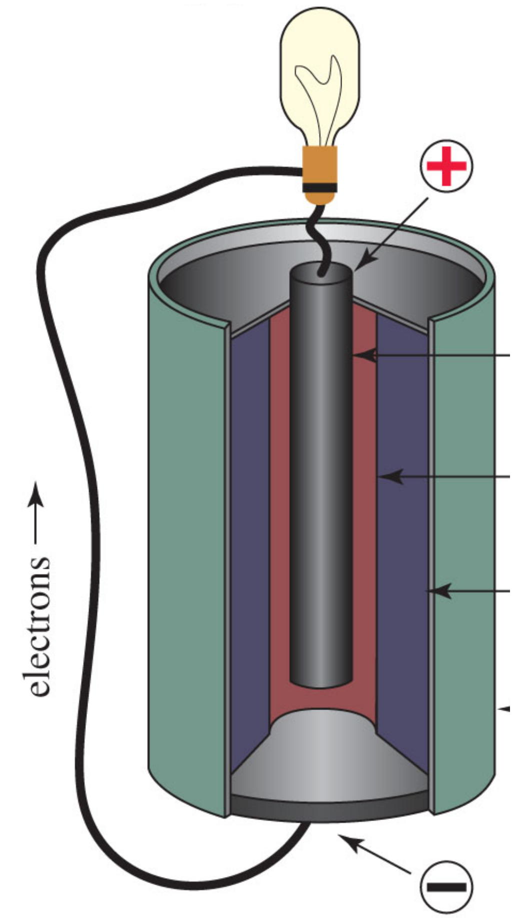
The flow of electrons from one region to another is facilitated by electrodes, which serve as sites for the chemical reactions:

The anode (– on a battery) is electrode where the oxidation takes place, it is the source of electrons for the external circuit

The cathode (+ on a battery) is electrode where the reduction takes place, it receives the electrons from the external circuit

$$Zn + 2Mn^{4+} \rightarrow 2Mn^{3+} + Zn^{2+}$$

For our *simplified* alkaline battery, Zn is losing electrons so it's the anode; meanwhile Mn^{4+} is gaining electrons so it's the cathode



The voltage is the difference in electrochemical potential between the two electrodes (how far downhill the reaction is). Cells are connected in series to increase the potential difference & voltage

$$1\ eV = 96.5\ kJ/mol$$

Lead storage battery

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2\,H_2O(l)$

Highly reversible (many recharges), but heavy

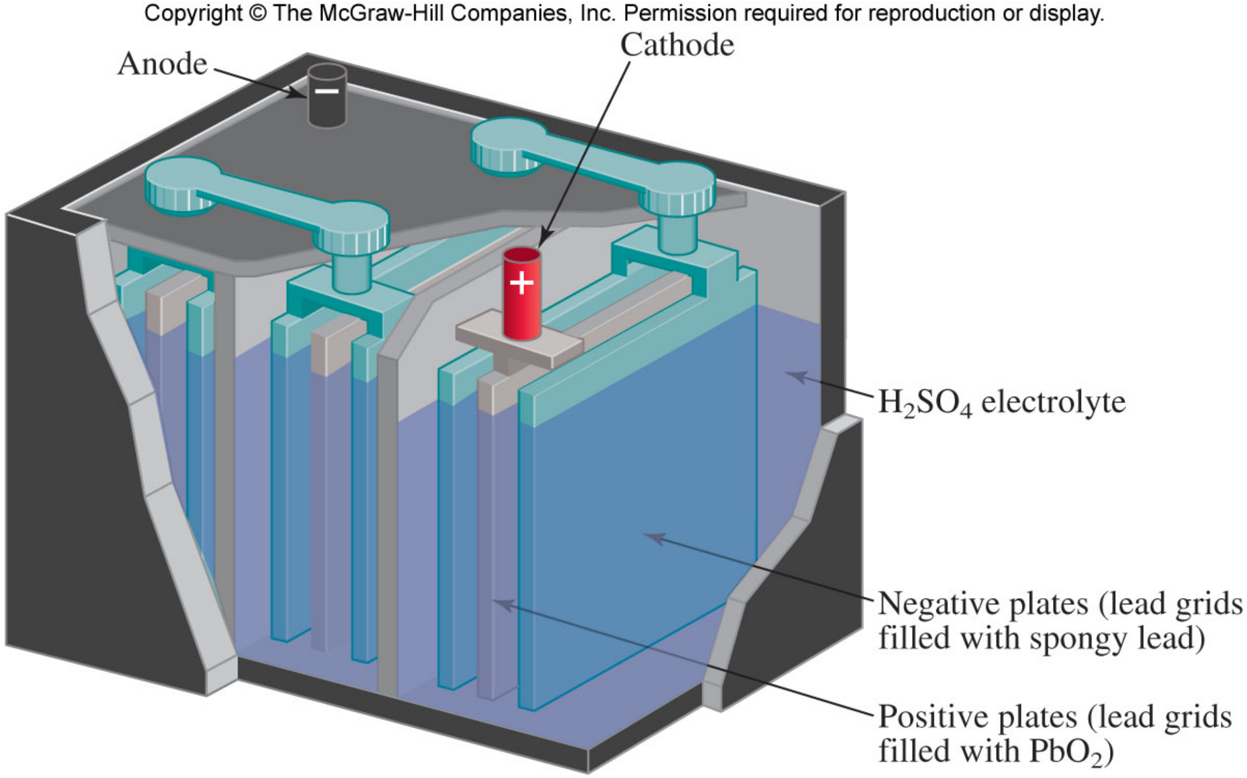
What's being oxidized?
What's being reduced?

Ionic compounds, so charge tells the story

$O=O^{2-}$
$OH=OH^{-}$
$SO_4=SO_4^{2-}$

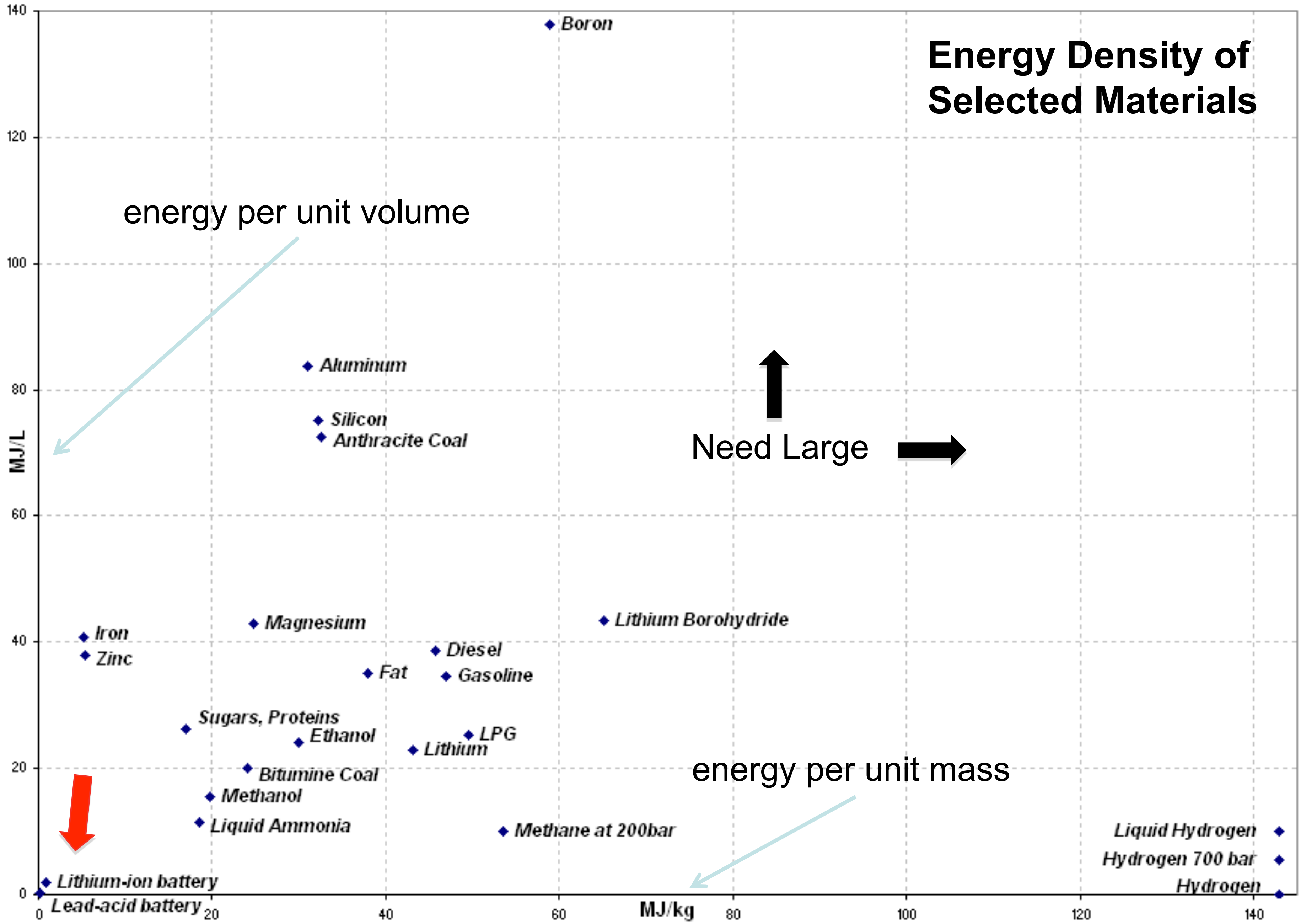
$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2\,H_2O(l)$

Pb^0 Pb^{4+} Pb^{2+}



~2 volts/cell x 6 cells=12 volts

$Pb^0 \rightarrow Pb^{2+} + 2e^-$ oxidation
$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$ reduction



Energy Density of
Selected Materials
energy per unit volume
energy per unit mass
Need Large
MJ/L
MJ/kg
140
120
100
80
60
40
20
0
0
20
40
60
80
100
120
140
Boron
Aluminum
Silicon
Anthracite Coal
Iron
Zinc
Magnesium
Lithium Borohydride
Diesel
Fat
Gasoline
Sugars, Proteins
Ethanol
LPG
Lithium
Bitumine Coal
Methanol
Liquid Ammonia
Methane at 200bar
Liquid Hydrogen
Hydrogen 700 bar
Hydrogen
Lithium-ion battery
Lead-acid battery

Redox

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$

$Zn + 2Mn^{4+} \rightarrow 2Mn^{3+} + Zn^{2+}$

$Zn(s) + 2\ MnO_2(s) + H_2O(l) \rightarrow Mn_2O_3(s) + Zn(OH)_2(s)$

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$

$$2H_3O^{+} + 2e^{-} \rightarrow 2H_2O + H_2$$

Alkaline Cells: Actual Chemistry is a Little More Complex

Anode (oxidation half-reaction): Zn^{2+}

Zn^0 $\quad Zn(s) + 2\,OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$

Cathode (reduction half-reaction):

$2\,MnO_2(s) + H_2O(l)\ 2e^- \rightarrow Mn_2O_3(s) + 2\,OH^-(aq)$

Mn^{4+} $\quad Mn^{3+}$

Overall:

$Zn(s) + 2\,MnO_2(s) + H_2O(l) \rightarrow Mn_2O_3(s) + Zn(OH)_2(s)$

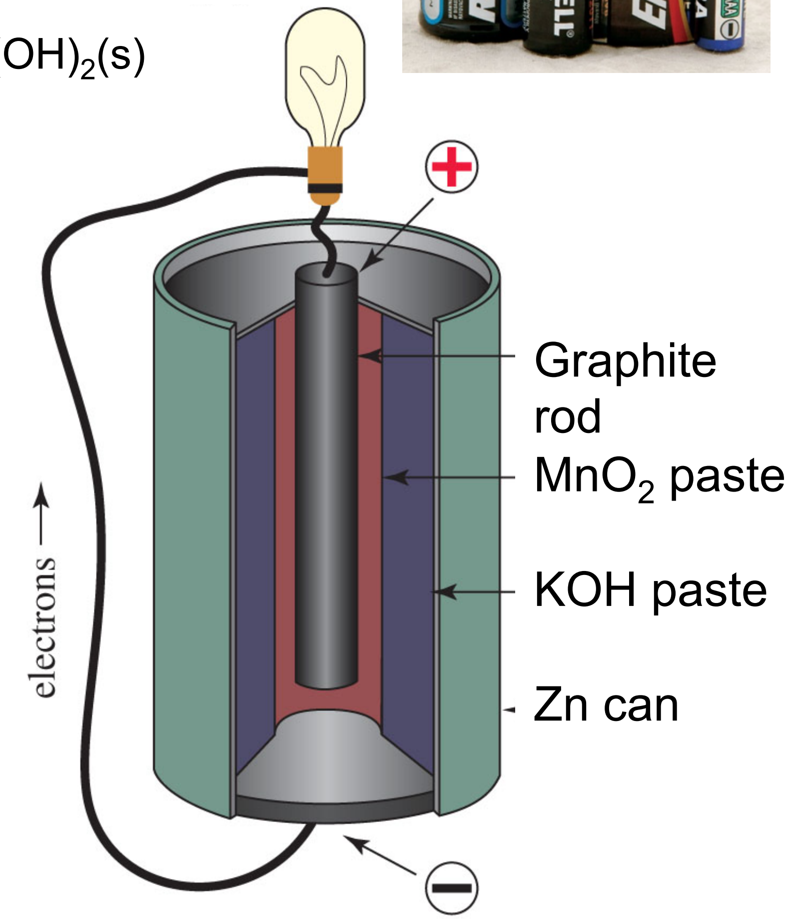
Voltage depends upon the redox chemistry

For alkaline cells, voltage = 1.54 V

1 eV = 96.5 kJ/mol

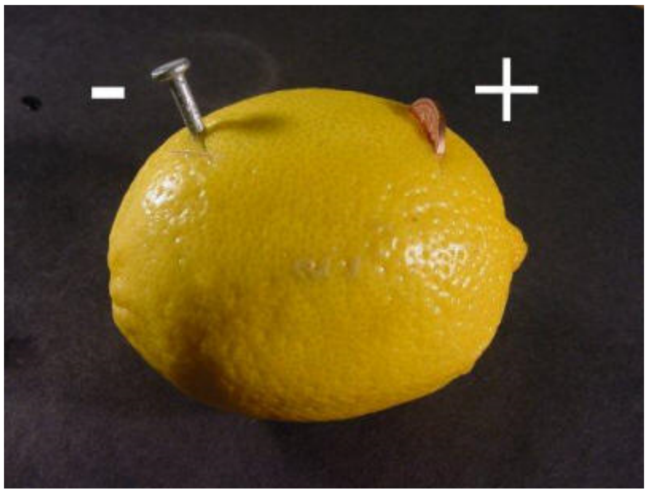
Current, measured in amps (A) or milliamps (mA) is a measure of how fast the electrons flow through the external circuit

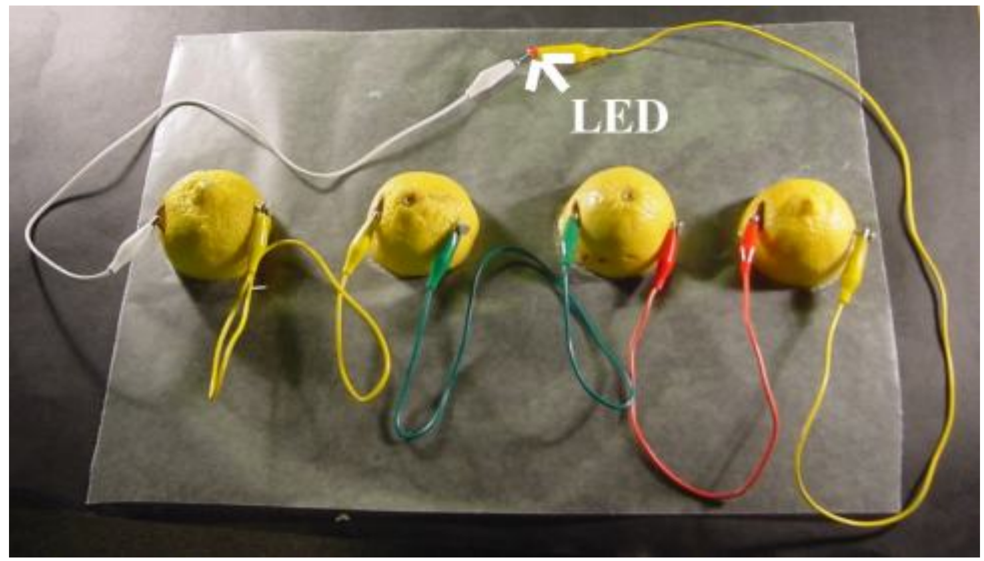
Battery **size** determines how long the charge can be maintained, not the voltage



Citrus Battery

images: http://www.quantumbalancing.com/news/lemon_battery.htm





- Electrodes
  - penny (copper)
  - galanized nail (zinc)
  - what are the ½ reactions for each electrode?
  - which is the cathode? anode?
- Role of lemon
  - electrolyte
  - reduction side of the redox system

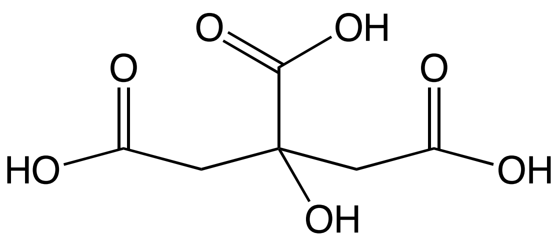
http://franklin.chem.colostate.edu/chem103/movies/Lemon-Battery-large-new.mp4

Lemon Battery

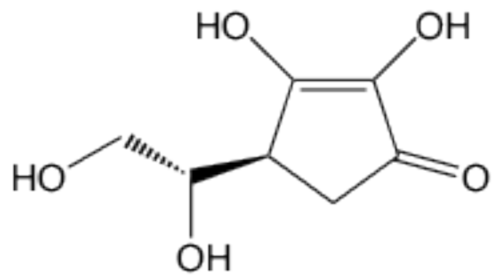
$$Zn \rightarrow Zn^{2+} + 2e^{-}$$

$$2H_3O^{+} + 2e^{-} \rightarrow 2H_2O + H_2$$

Lemon battery:



Citric acid: (prevents scurvy)



Ascorbic acid (vitamin C): antioxidant

Potato battery:

H_3PO_4