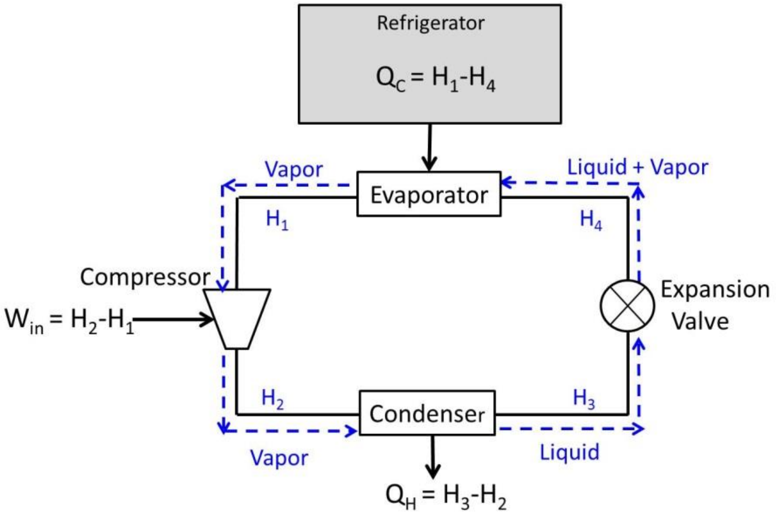
Refrigeration example

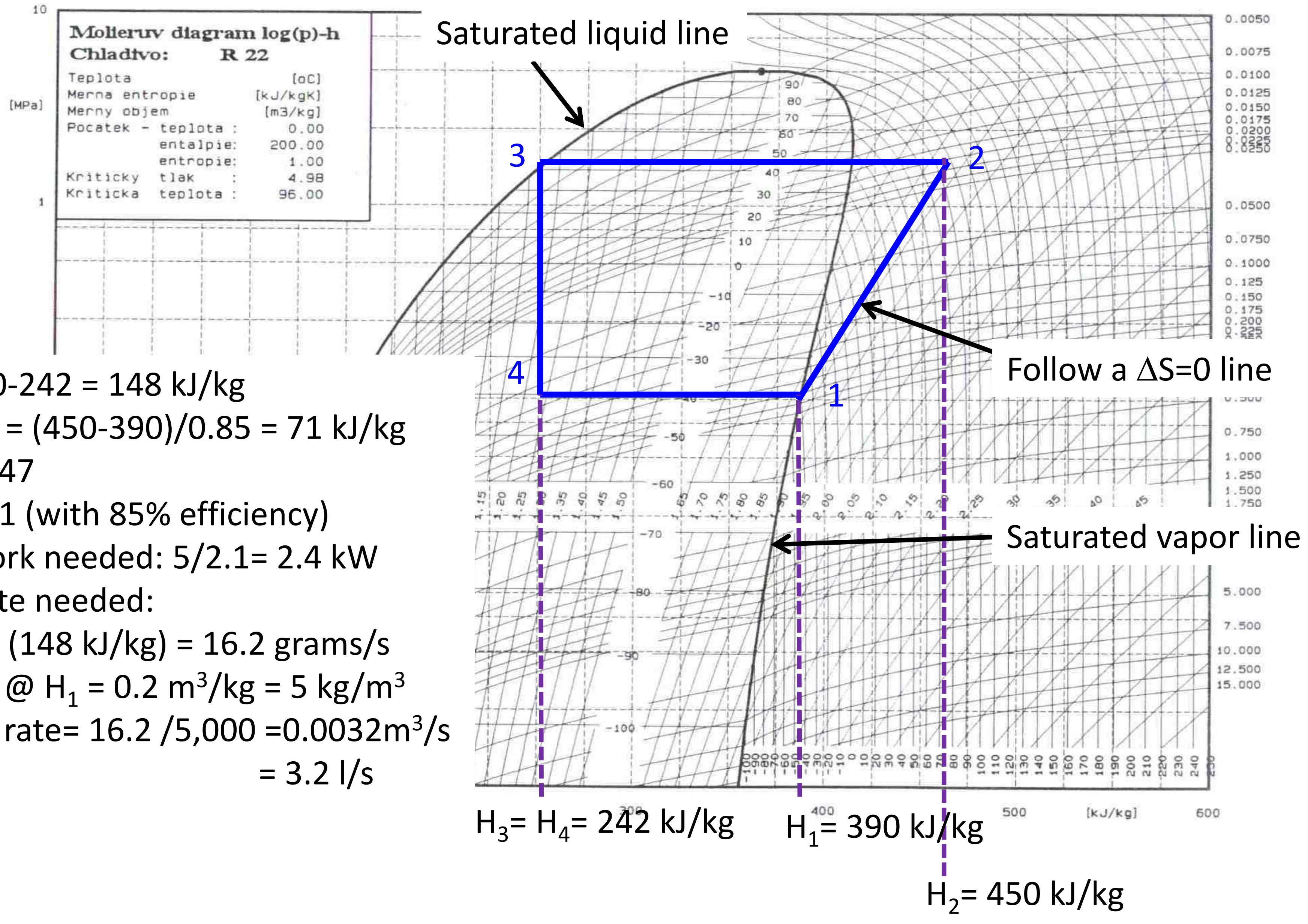
- You are given 2 options for an air conditioner:
  - Group A- You use R-22 as a coolant. You compress your fluid from atmospheric pressure to 20 bar at 100% efficiency (ΔS) = 0. You then let it condense at a constant pressure to saturated liquid. Next you use your expansion valve to take it back to atmospheric pressure. You then let it evaporate until it is a saturated vapor.
  - Group B- You use CO_2 as a coolant. You compress your fluid from 10 bar to 65 bar at 100% efficiency (ΔS) = 0. You then let it condense at a constant pressure to saturated liquid. Next you use your expansion valve to take it 10 bar. You then let it evaporate until it is a saturated vapor.

<u>Questions:</u>

- What is your COP?
- How much work do you need to put in to get 5 kW of cooling with an 85% efficient compressor?
- What is your vapor flow rate at H_1?
- How could you improve efficiency?



Refrigeration example R22 Solution



Q_c = 390-242 = 148 kJ/kg

Work in = (450-390)/0.85 = 71 kJ/kg

COP= 2.47

COP= 2.1 (with 85% efficiency)

Total work needed: 5/2.1= 2.4 kW

Mass rate needed:

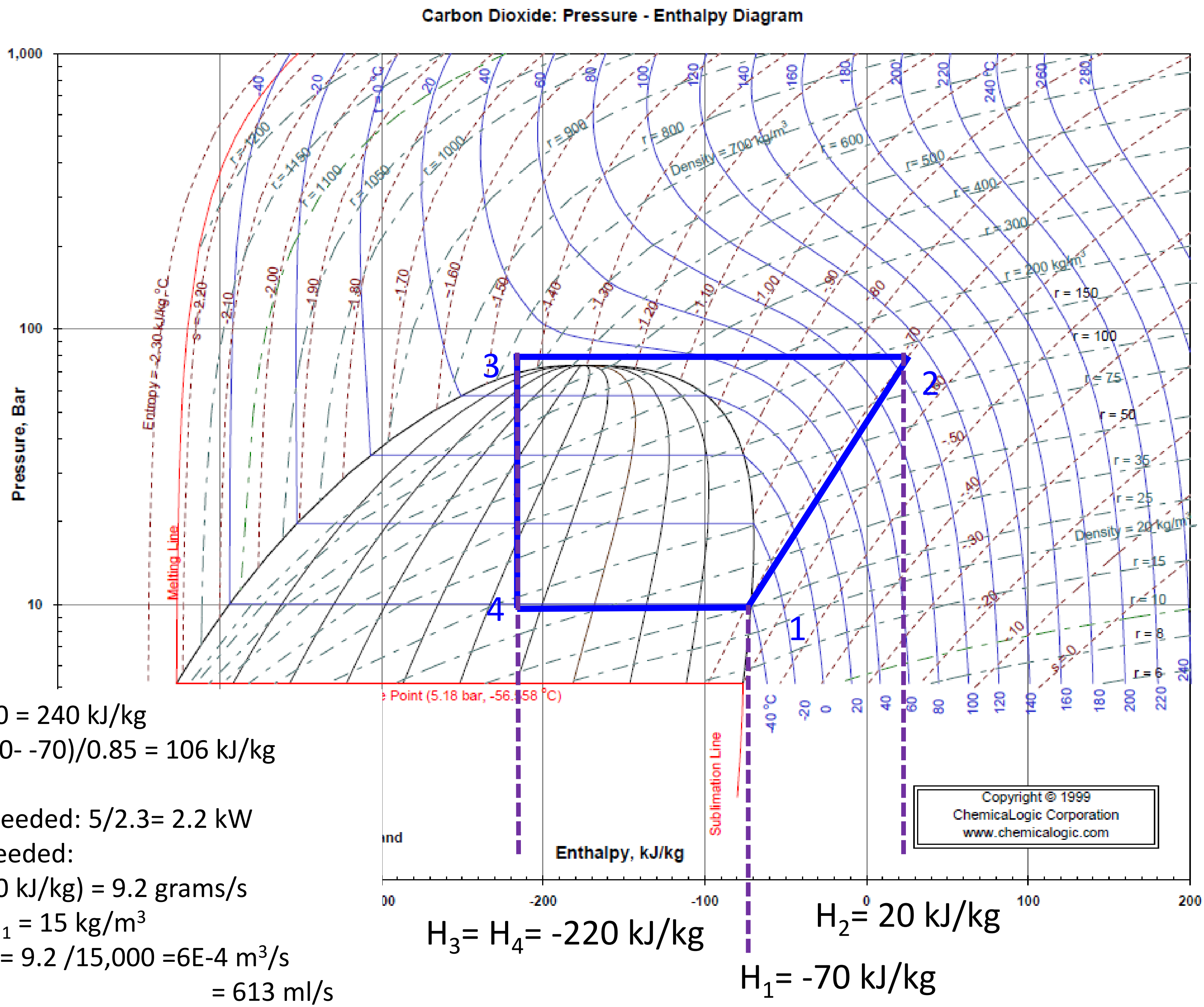
2.4 kW/ (148 kJ/kg) = 16.2 grams/s

Volume @ H_1 = 0.2 m^3/kg = 5 kg/m^3

Volume rate= 16.2 /5,000 =0.0032m^3/s

= 3.2 l/s

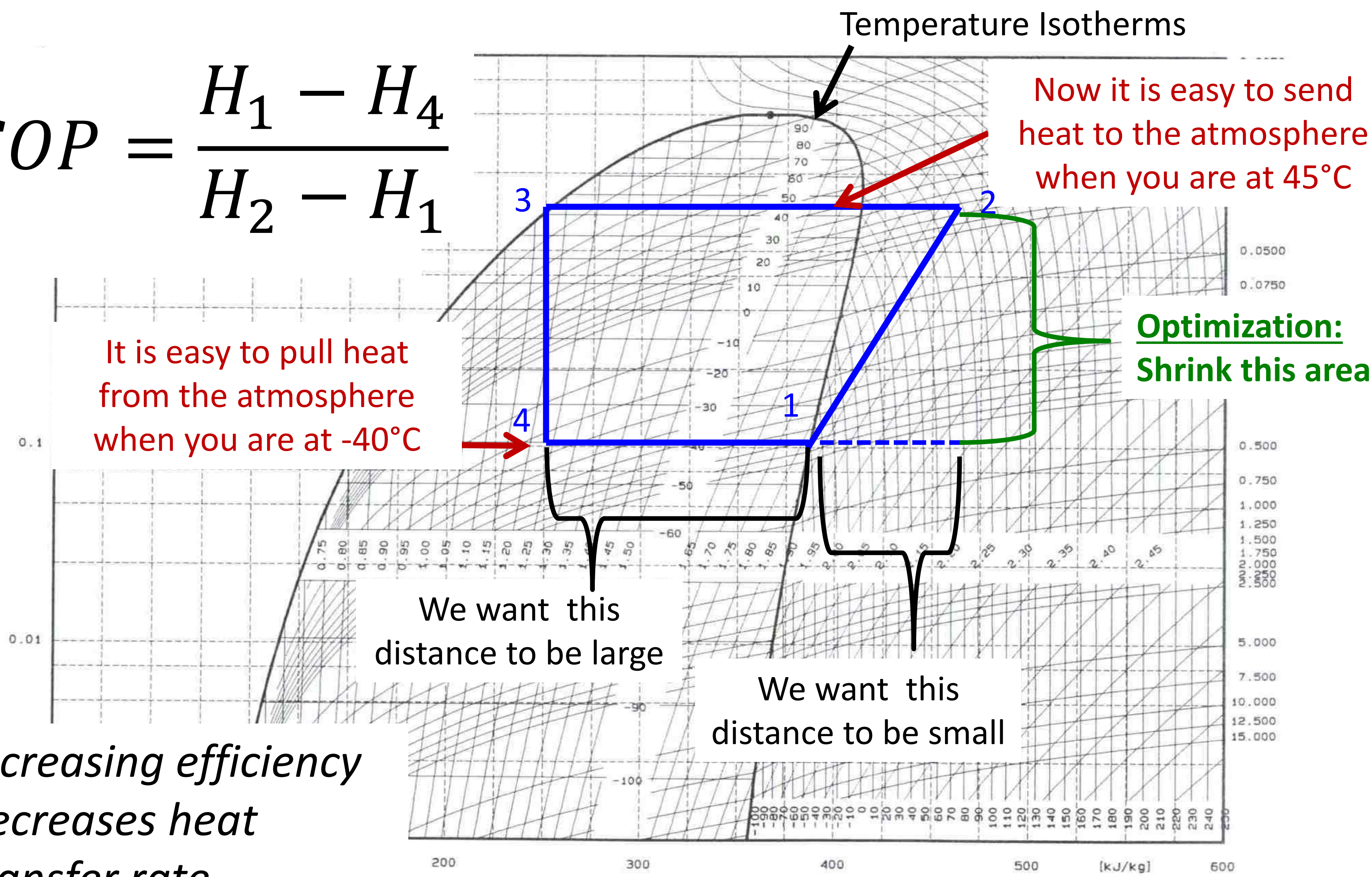
Refrigeration example CO_2 solution



Q_c = 20- -220 = 240 kJ/kg
Work in = (10- -70)/0.85 = 106 kJ/kg
COP= 2.3
Total work needed: 5/2.3= 2.2 kW
Mass rate needed:
2.2 kW/ (240 kJ/kg) = 9.2 grams/s
Density @ H_1 = 15 kg/m^3
Volume rate= 9.2 /15,000 =6E-4 m^3/s
= 613 ml/s

Refrigeration example R22 Solution

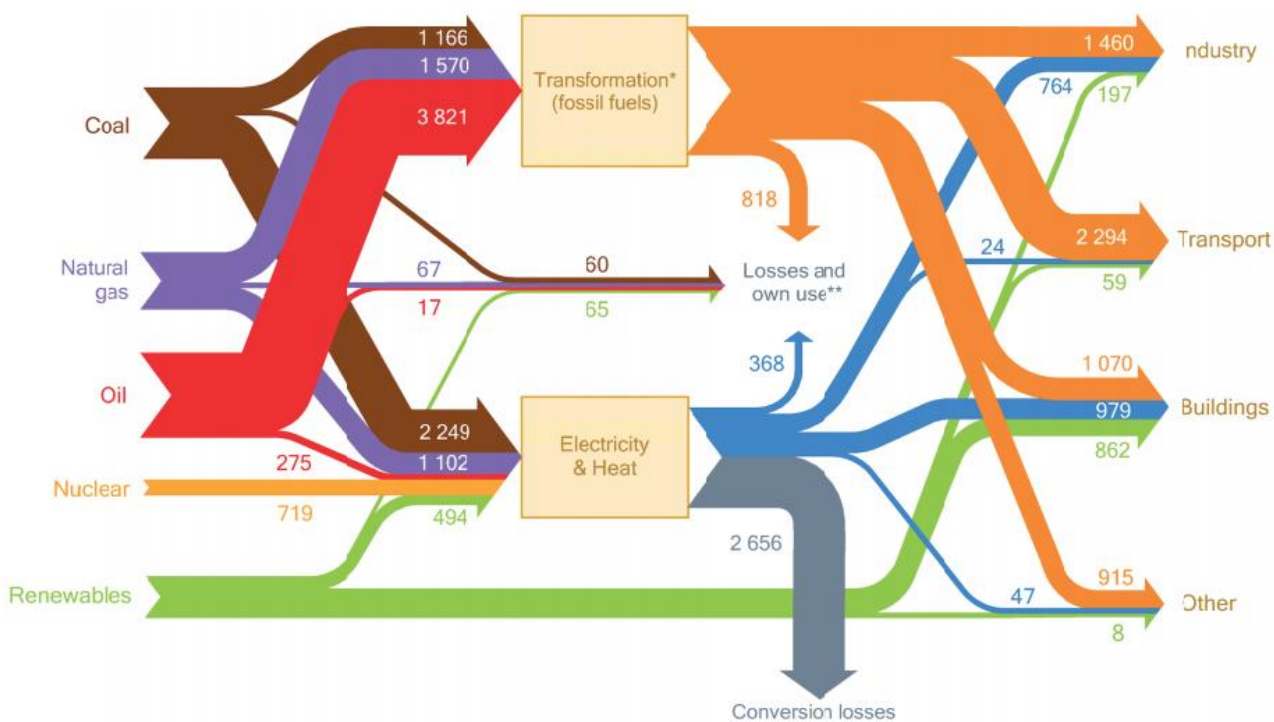
$$COP = \frac{H_1 - H_4}{H_2 - H_1}$$



Increasing efficiency decreases heat transfer rate

Energy Conversion

Energy Produced → Conversion of Energy → Energy Used



Sankey Diagram- numbers correspond to mtoe

Lecture - Learning Objectives

At the end of this lecture you should be able to:

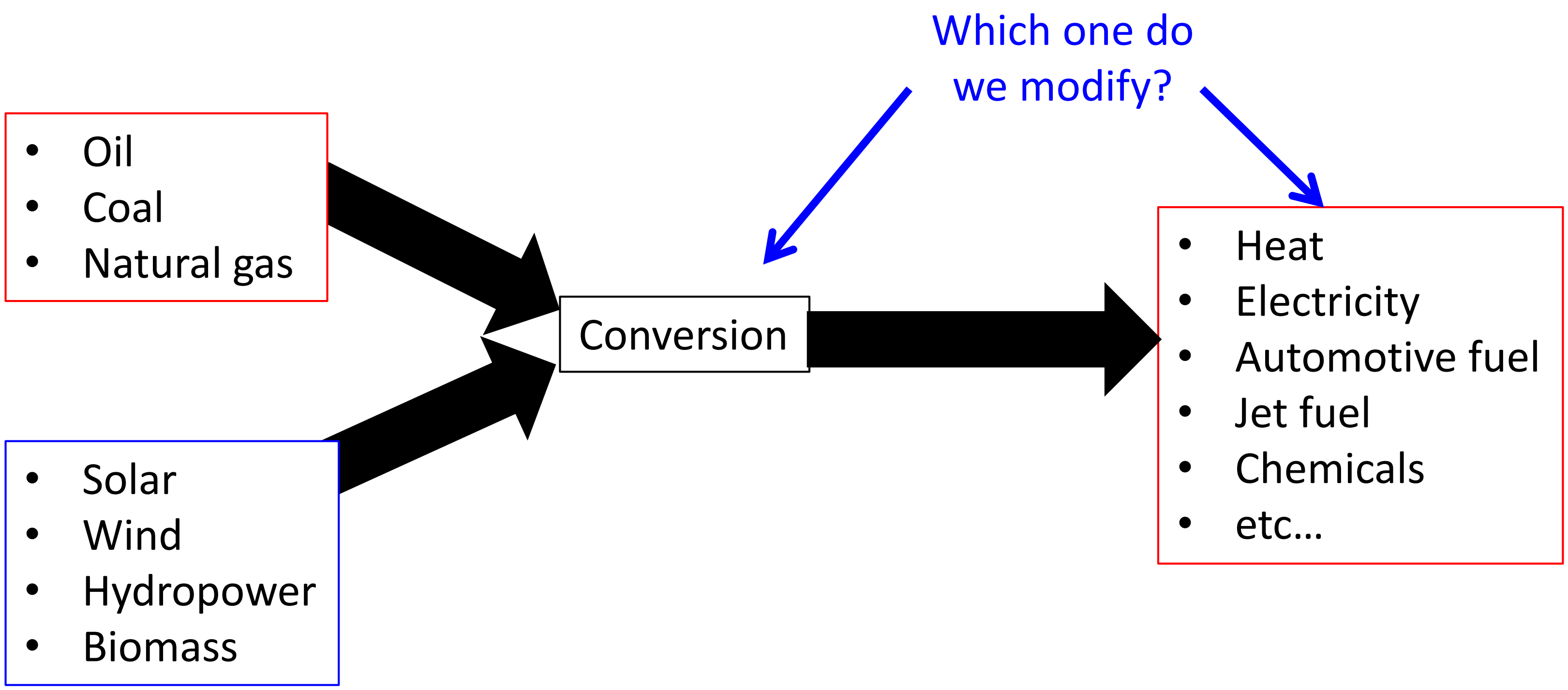
- Understand the difference between the heat engine and electrical engines.

- Understand the basic principles of electrochemistry.

- Understand the redox reactions related to battery technology

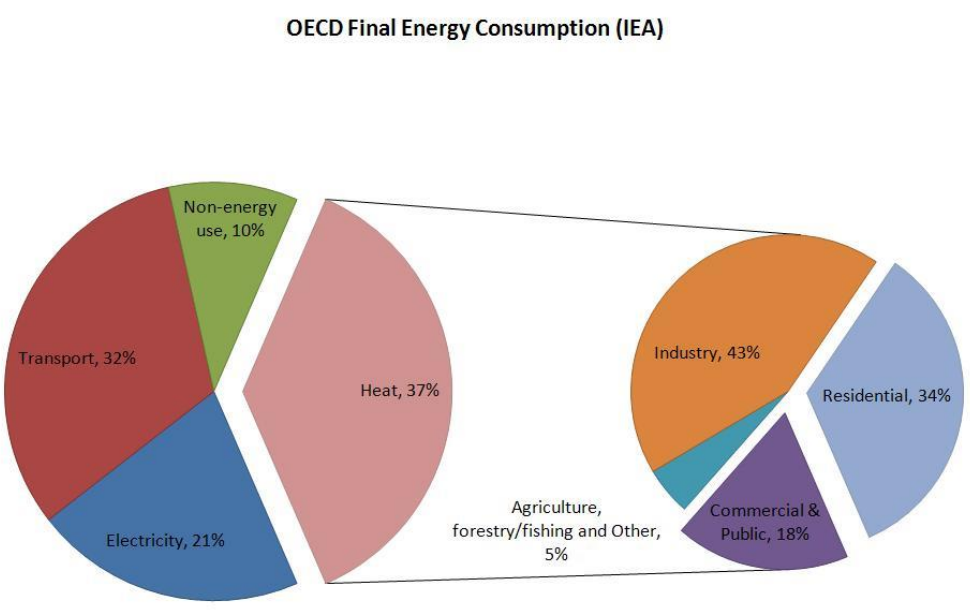
Energy Conversion

- We need 1 of 2 things to happen:
  - Convert all our sustainable energy sources to match the current energy sources we use.
  - Convert the current energy sources to match the sustainable energy we will produce.



Energy consumption for heat

- Heat corresponded to ~ 4.4 TW (assuming the % of the world's heating is the same as that as the OECD countries.)
- Industry uses slightly more energy than residential, with commercial a distant 3rd.
- For fertilizers natural gas is the dominant source (0.2 TW)

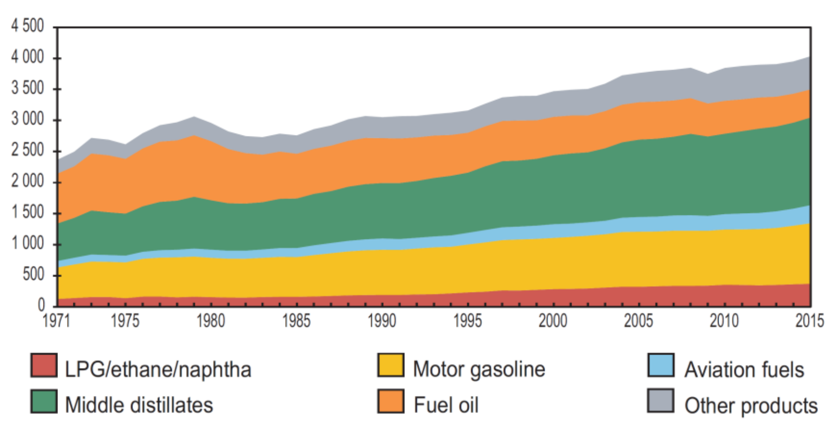


Fertilizer value from Energy Density, Vaclav Smil

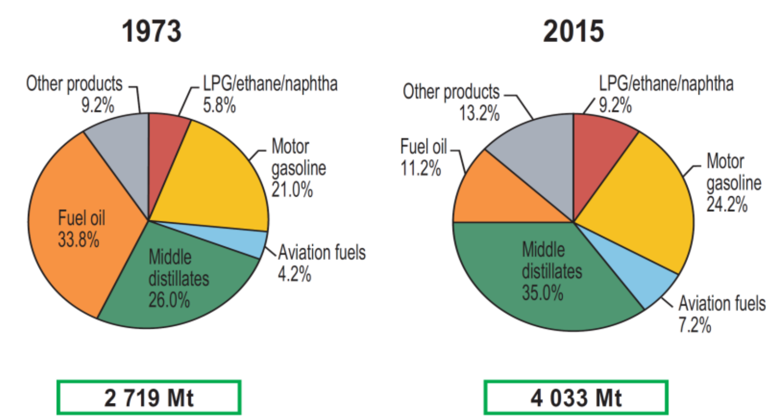
Oil energy consumption

- The world produces 4.8 TW of oil products. This is about 30% of the world's energy production (2012 data).
- Gasoline only corresponds to 23.3% of oil production.
- Three important areas to note are:
  - Fuel oil
  - Aviation fuel
  - Other products- (precursors for chemical industry)
  - Plastics (0.5 TW)

World refinery output from 1971 to 2015 by product (Mt)



1973 and 2015 shares of refinery output by product

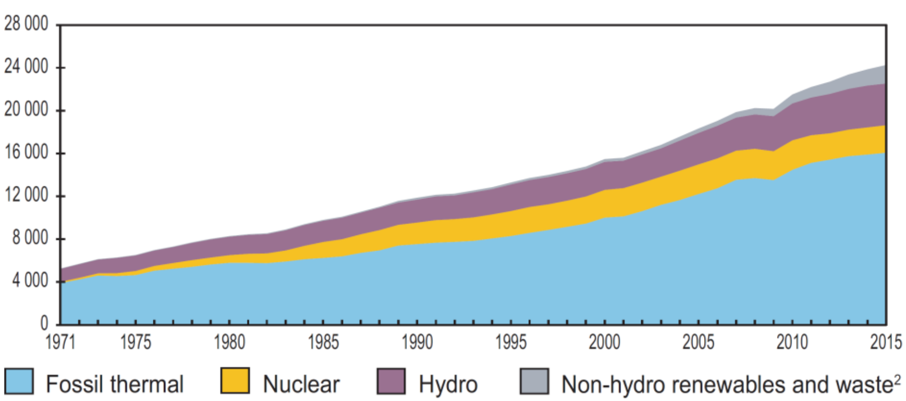


Key World Energy Statistics, 2017, IEA

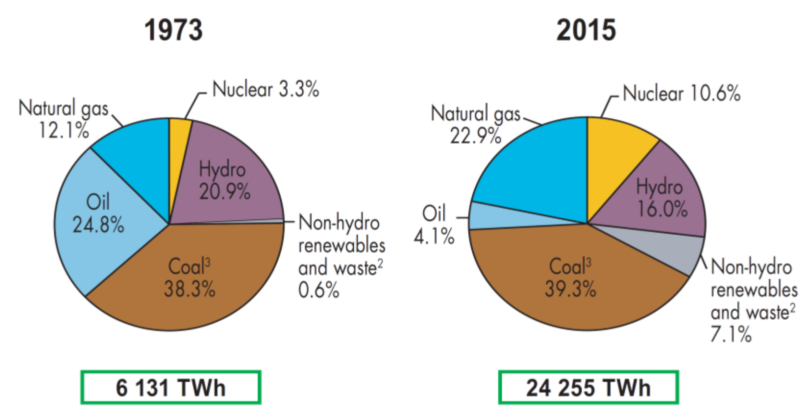
Electrical energy consumption

- The world produces 2.6 TW of electricity. This is about 14.6% of the world's energy production.
- Our increase in electrical usage over the last 30 years is much more than that of oil products.
- Coal and natural gas are the primary sources for electrical production.

World electricity generation[1] from 1971 to 2015 by fuel (TWh)

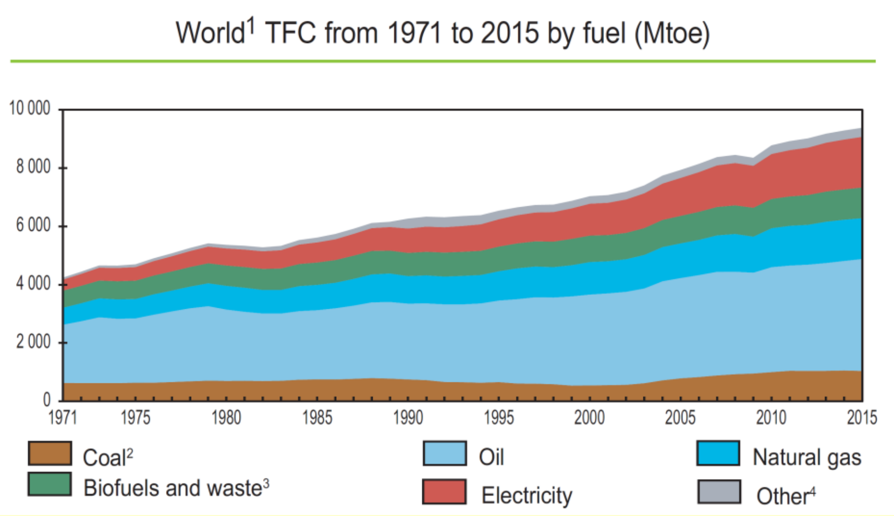


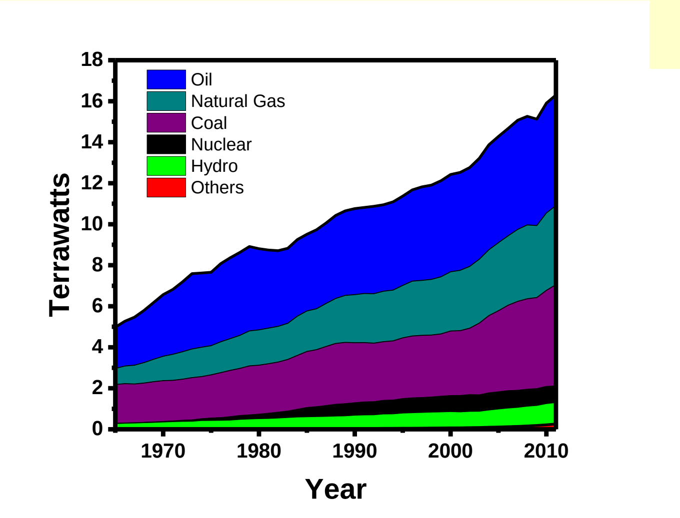
1973 and 2015 source shares of electricity generation[1]



Total energy consumption

- The world total energy consumption was 11.9 TW.
  - 4.8 TW for oil products (chemicals are a subgroup within here)
  - 4.4 TW from heating
  - 2.6 TW for electricity
- We say the world produces 17.7 TW. Where is the extra 5.8 TW?
- Why is oil dominant compared to coal in the left chart, but about the same in the right chart?





Production ≠ Consumption

- 17.7 TW is based off of energy production, whereas 11.8 TW is based off of energy consumption.

17.7 TW

- Oil
- Coal
- Natural gas

-5.8 TW

Conversion

11.9 TW

- Heat
- Electricity
- Automotive fuel
- Jet fuel
- Chemicals
- etc…

There will be even more losses here

- Inefficient light bulbs
- Inefficient motors

<u>Heat engines are a loss</u>

$$\eta_{Carnot} = \frac{T_{hot} - T_{cold}}{T_{hot}} \approx 30 - 40\%$$

An electrified approach does not have this limitation

Heat engine vs. electrical power

- Electrical power's (EP) efficiency is based on the following derivation:

1st law of thermodynamics: $\Delta H = Q - W$

If Q is zero, then we can take all the work (think windmill power) and convert it to internal energy (think electrical storage)

$$\eta_{EP} = \frac{-W}{\Delta H}$$

Thus our efficiency can be defined like this.

$$\eta_{EP} = \frac{\Delta H - Q}{\Delta H}$$

In reality W is not 100% efficient. From the 1st law…

2nd law of thermodynamics: $T\Delta S = Q$

$$\eta_{EP} = \frac{\Delta H - T\Delta S}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} = \frac{\Delta G}{\Delta H}$$

Electrical power production

$$\eta_{EP} = 1 - \frac{T\Delta S}{\Delta H} = \frac{\Delta G}{\Delta H}$$

- If you minimize your entropy or maximize your enthalpy you can greatly improve your efficiency.
- This relation scales the opposite way with temperature compared to the Carnot efficiency.
- Hydroelectric can theoretically get 99% energy conversion efficiency. In reality they get 85-90% due to mechanical losses.
- Electrifying all of society could probably cut our energy demands by ~50% - very rough estimate.

Quantitative advantage of Electrochemistry

- Take the reaction below:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

- We can:
  - Burn the hydrogen with oxygen to form water and get energy
  - Electrochemically convert (use ΔG) it water and get energy

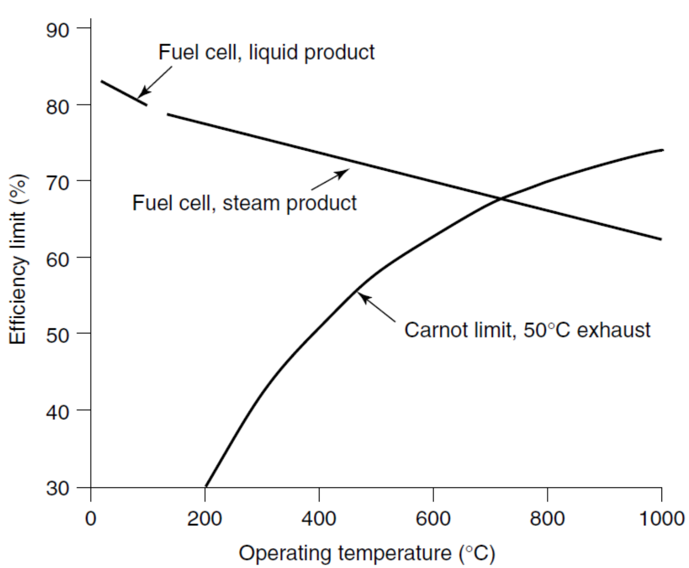


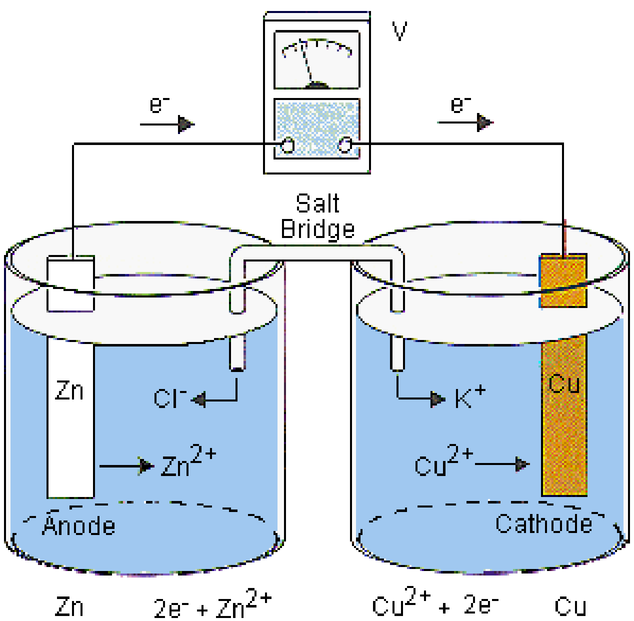
Figure 2.4 Maximum H_2 fuel cell efficiency at standard pressure, with reference to higher heating value. The Carnot limit is shown for comparison, with a 50°C exhaust temperature.

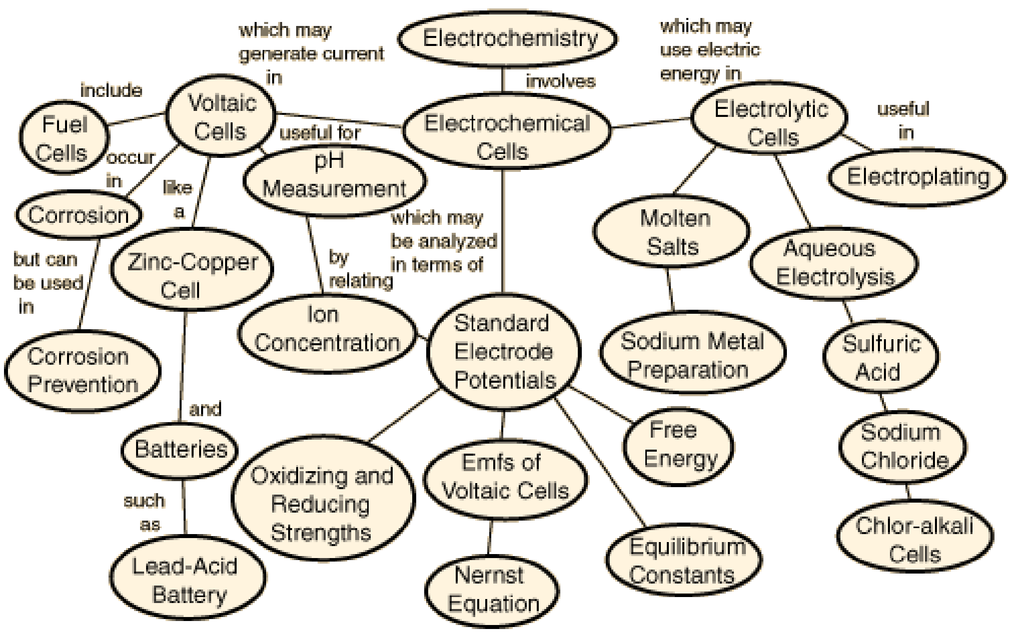
$$\eta_{Carnot} = \frac{T_h - T_c}{T_h}$$

$$\eta_{Fuel\ Cell} = \frac{\Delta G}{\Delta H}$$

Break

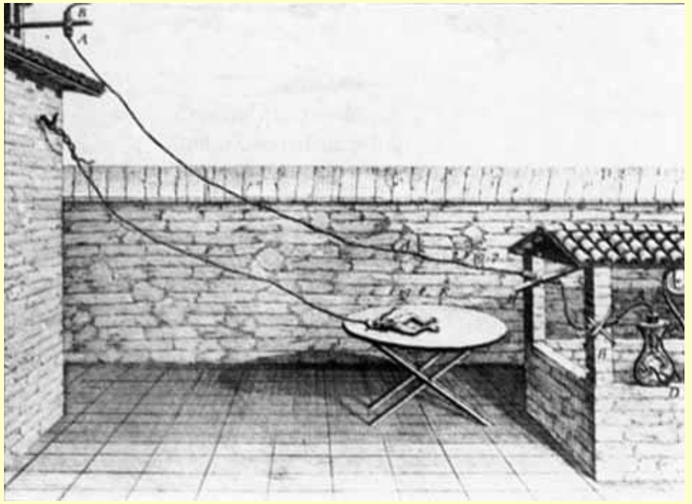
Electrochemistry





History of Electrochemistry

- In 1791 Luigi Galvani first linked chemical reactions with electrical current.
  - He was interested in biochemical reactions and discovered electrochemical reactions from animal tissue.



Galvani's test on frog legs

- In 1800 William Nicholson and John Ritter were able to electrolyze water into H_2 and O_2.

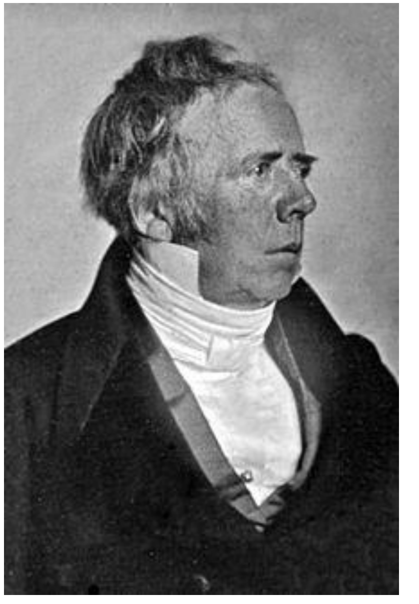
- In 1839 William Grove made a fuel cell in which he produced current by reacting H_2 with O_2 to make water.

- In the 1820's a famous Danish researcher studied electrochemistry. Does anybody know who?

Hans Christian Ørestad

- He is most famous for relating magnetic force with electrical current.
- He also was the first to synthesize aluminum metal.

$$AlCl_3 + 3K(Hg) \longrightarrow Al + 3KCl + Hg.$$

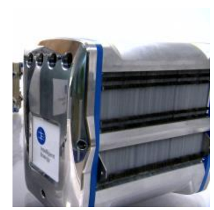


- He also founded DTU

Uses of Electrochemistry

- There are 2 major types of electrochemistry
  - Galvanic : This is where chemical reactions force an electrical current
  - Electrolytic: This is where electrical currents force a chemical reaction
- Batteries:
  - Run galvanicly when discharging
  - Run electrolytically when charging

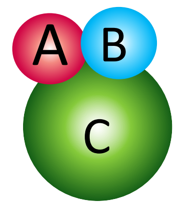
- Molecular fuels (such as hydrogen)
  - Fuel cells operate galvanically
  - Electrolyzers operate electrolytically



- Other uses
  - Galvanic- our nervous system, corrosion
  - Electrolytic- electroplating, electropolishing

Electrochemistry vs. Regular Reaction

- In a regular reaction both A and B are in intimate contact with each other (or contact with a catalyst C).

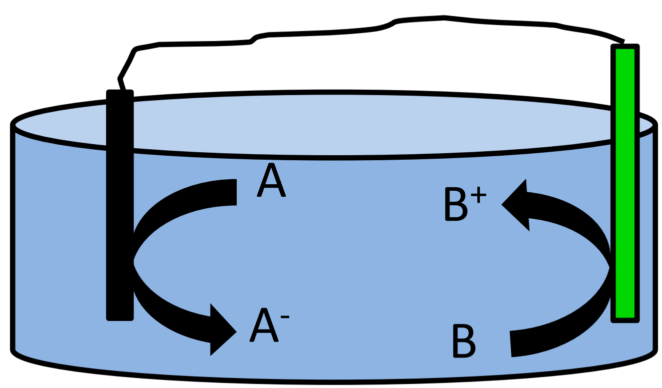


- Below is a generic electrochemcial reaction:

Charged Discharged

$$A + B \rightarrow A^{-} + B^{+}$$

- In an electrochemical reaction A and B can be very far apart, but connected by a wire.



Terminology

Oxidation reaction: The reaction in which an electron is removed.

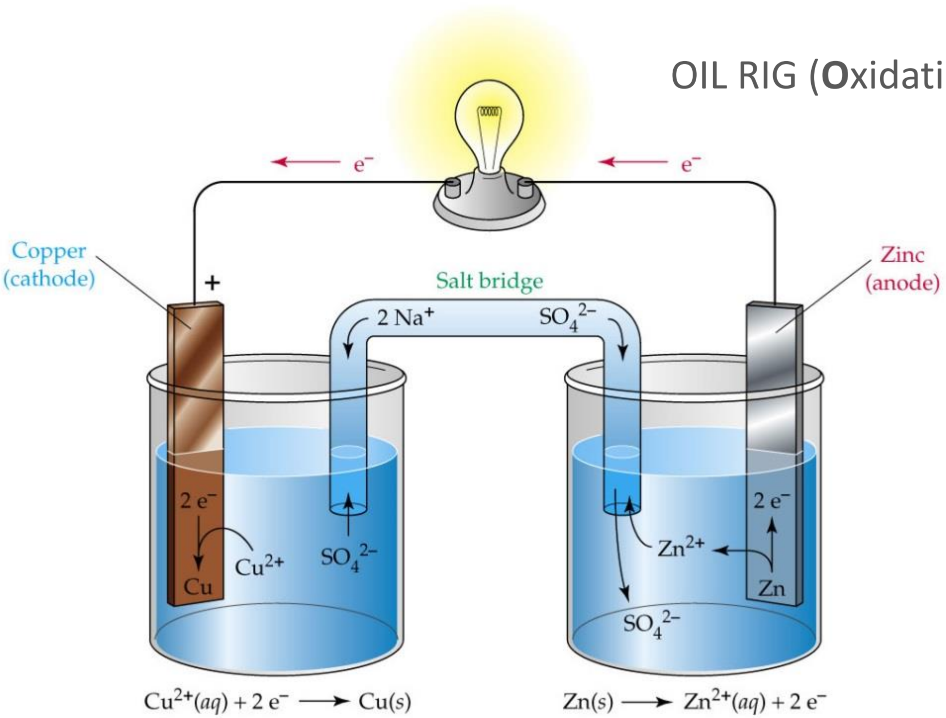
Reduction reaction: The reaction in which an electron is added

Anode: This is the electrode where oxidation occurs.

Cathode: This is the electrode where reduction occurs.

Useful Mnemonic:

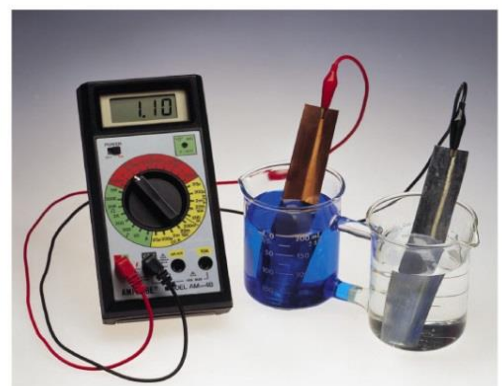
OIL RIG (**O**xidation **I**s **L**osing electrons; **R**eduction **I**s **G**aining electrons)



(a)

$E_{Cu2+/Cu}$=0.34 V

$E_{Zn/Zn2+}$=-0.76 V



(b)

Overall Reaction

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

Basics

- Most of electrochemistry is just thermodynamics divided by Faraday's constant.

$$\Delta E = \frac{\Delta G}{nF}$$

G = Gibbs Free Energy
F = Faraday's Constant (96,485 C/mol e^-)
E = Potential
n= # of electrons in the reaction

- Just like Gibbs free energy is a relative term, so is the potential.
- For our Cu/Zn reaction, we have the following.

This is useful since each 'half' reaction occurs at a different electrode.

$$\Delta E = \frac{\left({G_f}^{Cu} + {G_f}^{Zn^{2+}} - {G_f}^{Cu^{2+}} - {G_f}^{Zn}\right)}{nF}$$

$$\Delta E = \frac{\left({G_f}^{Cu} - {G_f}^{Cu^{2+}}\right) - \left({G_f}^{Zn} - {G_f}^{Zn^{2+}}\right)}{nF} = E^{Cu/Cu^{2+}} - E^{Zn/Zn^{2+}}$$

Exercise

- Assume you had the following reaction instead:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

- Theoretically how much energy could you get from 1 mol of H_2?
- How much hydrogen would you need to power an average laptop (60W) for 1 hour?
- What would be the theoretical potential of this reaction?

$$\Delta E = \frac{\Delta G}{nF}$$

F = Faraday's Constant (96,485 C/mol e^-)

Gibbs Free energy of H_2O is -237 kJ/mol

Exercise

- Assume you had the following reaction instead:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

H_2 Fuel cell reaction →

← Electrolysis

- Theoretically how much energy could you get from 1 mol of H_2?

Answer: 237 KJ (Since H_2 and O_2 both have G_f=0)

- How much hydrogen would you need to power an average laptop (60W) for 1 hour?

Answer: 60W for 1hour = 60 W for 3600S =216 kJ, thus 237 kJ/ 216 kJ = 0.9 mol H_2

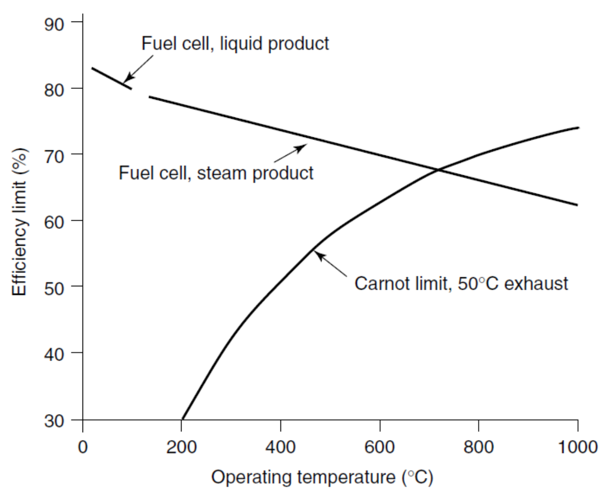
- What would be the theoretical potential of this reaction?

$$\Delta E = \frac{\Delta G}{nF} = \frac{G_f(H_2O) - G_f(O_2) - G_f(H_2)}{2 \times 96{,}485} = \frac{237{,}000 - 0 - 0}{2 \times 96{,}485} = 1.23\ V$$

Hydrogen fuel cell efficiency

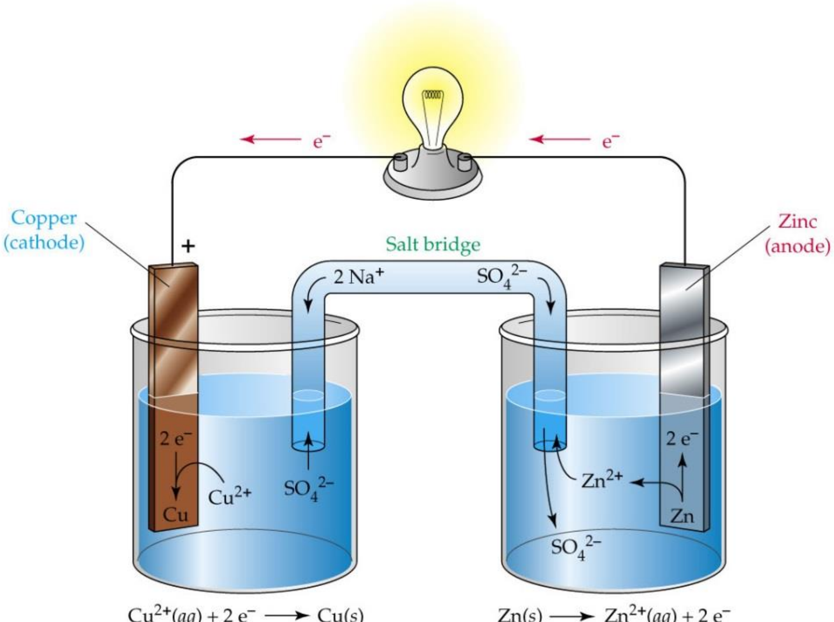
- From earlier we defined electrical efficiency as $\eta = \frac{\Delta G}{\Delta H}$
- Since H_2 and O_2 both are elements, there G_f, & H_f = 0 thus this is all about the H_2O. For H_2O:
  - G^f=-237 KJ/mol,
  - H^f=-286 KJ/mol (called Higher Heating Value- (HHV))

$$\eta_{Fuel\ Cell} = \frac{\Delta G}{\Delta H} = \frac{237\ kJ/mol}{286\ kJ/mol}\ or\ \frac{1.23\ V}{1.48\ V} = 83\%$$

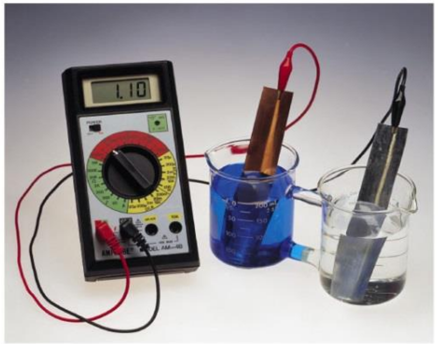


Basic Principles

- Batteries are any reaction where you get current and voltage out of an electrochemical reaction.
- A *good* battery is one that gets a large amount of energy, in minimal space, using cheap materials.



(a)



(b)

$E_{Cu2+/Cu}$=0.34 V

$E_{Zn/Zn2+}$=-0.76 V

Many of these values can be found here:
https://en.wikipedia.org/wiki/Standard_electrode_potential_%28data_page%29

<u>Overall Reaction</u>

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

Half Reactions

- Rather than have an entire reaction like this:

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

- We can write 2 equivalent 'half-reactions'. One for the reduction reaction and one for the oxidation reaction.

Reduction (Cathode): $Cu^{2+} + 2e^{-} \rightarrow Cu$ $\quad E^{Cu/Cu^{2+}} = 0.34\ V$

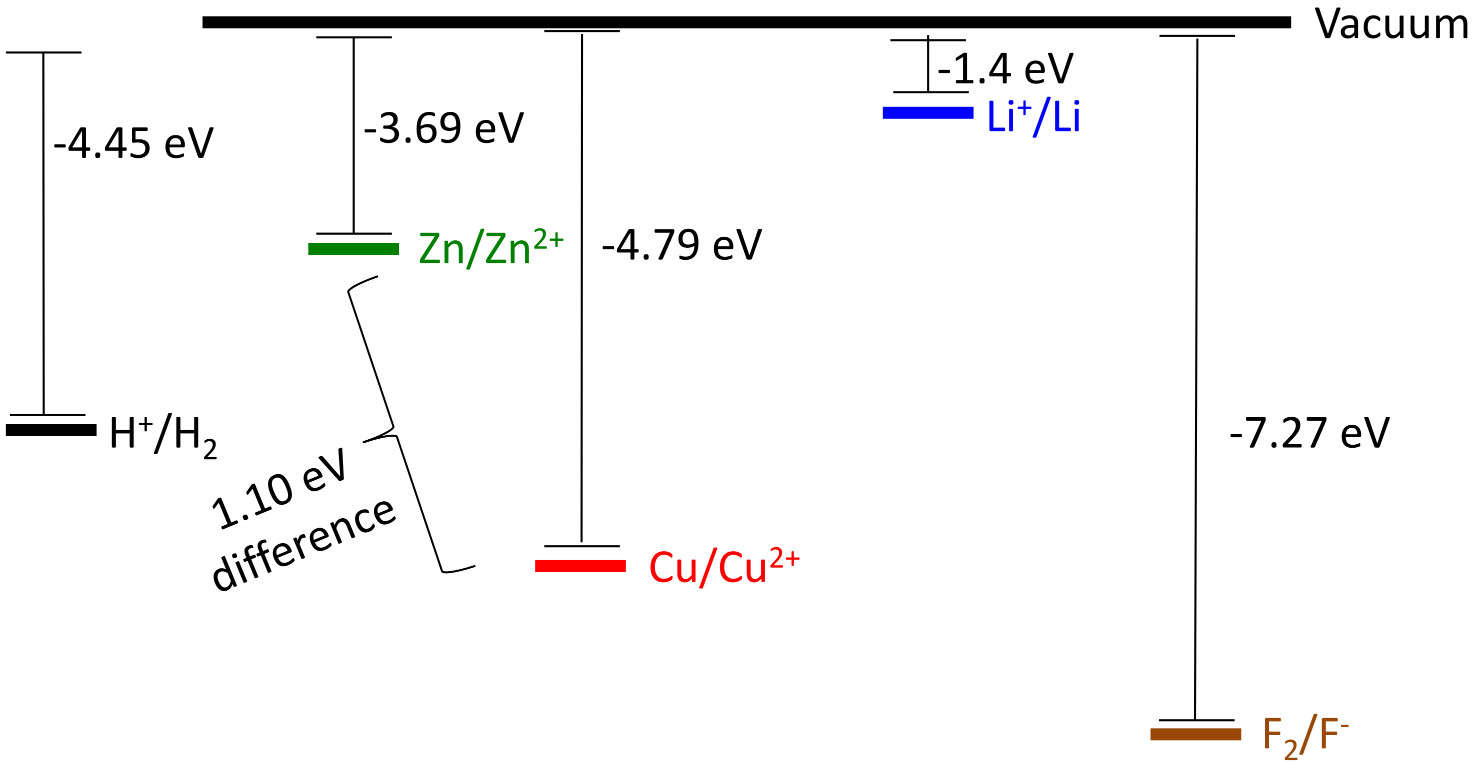
Oxidation (Anode): $Zn \rightarrow Zn^{2+} + 2e^{-}$ $\quad E^{Zn/Zn^{2+}} = -0.76\ V$

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

- In our half reactions we have electron and can also have protons (i.e. acid) or hydroxide ions (i.e. base)

Redox Potentials

- In electrochemistry we have 2 ‘half reactions’, which are completely seperate from each other from an energy standpoint.
- Thus it would be nice to relate each half reaction to a constant standard to easily switch out half reactions.



Reference electrode-NHE

- Our reference can be anything, but it should be something useful
- The hydrogen reaction is the most standard reference.

$$H_2 \rightarrow \ 2H^+ + 2e^-$$

- A standard hydrogen electrode (SHE) is defined when the hydrogen gas is at 1 bar and the acid is 1M H^+, whereas a normal hydrogen electrode (NHE) is at 1 atm. SHE differs from NHE by less than 0.2 mV.

- Due to platinum's efficiency for the H^+/H_2 reaction, the official NHE potential reference is measured on a Pt electrode.

- For reference 0 V vs. NHE = -4.45 V vs. Vacuum

Changing Concentrations

- The redox potential is the potential where we have 50% reactant and 50% product.

$$H_2 \rightarrow \ 2H^+ + 2e^-$$

- For the hydrogen reaction this means our equilibrium constant is 1 at the redox potential.

$$K = \frac{[H^+]^2}{[H_2]} = 1$$

- What if we change the concentration of H^+?

$$\Delta G = RTln(K)$$

$$nF\Delta E = RTln\left(\frac{(\Delta[H^+])^2}{\Delta[H_2]}\right)$$

Nernst Equation

$$\Delta E = \frac{RT}{nF} ln\left(\frac{Products}{Reactants}\right)$$

$$nF\Delta E = kTln\left(\frac{(\Delta[H^+])^2}{\Delta[H_2]}\right)$$

Goes to 0

$$E_{new} = E_{initial} + \frac{2kT}{nF}ln[\Delta H^+] - \frac{kT}{nF}ln[\Delta H_2]$$

n=2… This term will almost always match the power of the product (thus canceling out)

$$E_{new} = E_{initial} + \frac{kT}{2.303F}log[H^+]$$

59 mV at room temperature

$$E_{new} = E_{initial} - 59mV * pH$$

Called ‘Nerstian Shift’

Concept Check

Which one(s) of these half reactions is a function of pH:

a) . $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

b) . $4NaCl + O_2 + H_2O + 4e^- \rightarrow 4NaOH + 4Cl^-$

c) . $H_2SO_4 + 2e^- \rightarrow H_2 + 4SO_4{}^-$

d) . $AgCl + e^- \rightarrow Ag + Cl^-$

Break

Batteries

Basic Principles

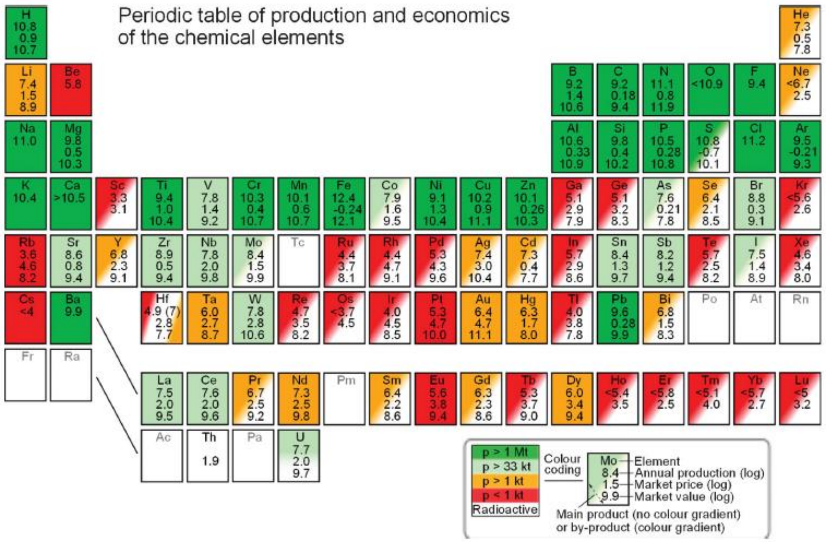
- Both energy and power are important.

$$E = P \times t$$

$$P = V \times i$$

E = Energy
P = Power
t = Time
V = Voltage
i = current

- We can use Peter Vesborg's paper to look at materials cost.



Maximize Voltage

- Find an oxidation and reduction reaction with a large difference in potential.

Conductivity issues

TABLE 18.1 Standard Reduction Potentials at 25°C

Stronger oxidizing agent / Weaker reducing agent

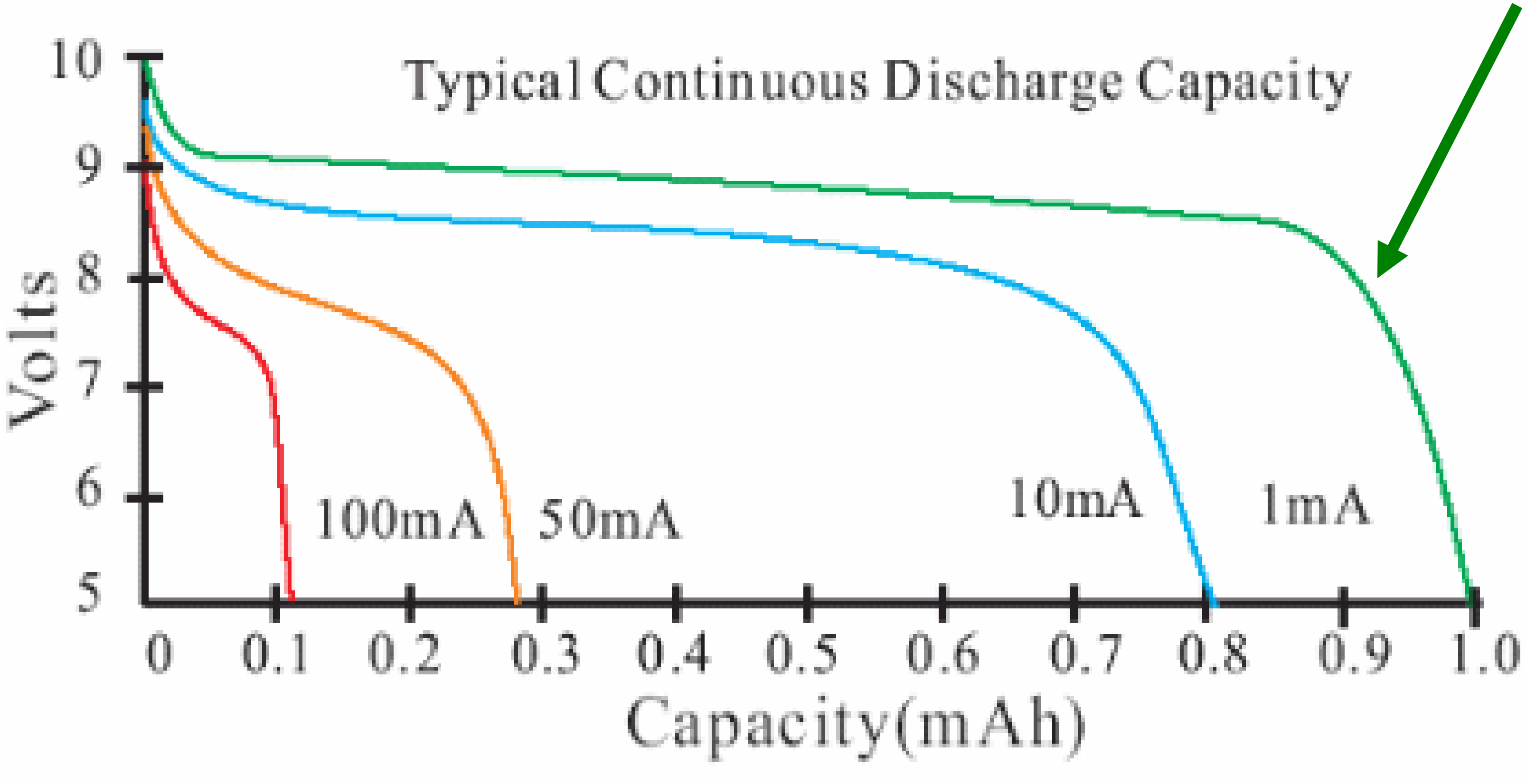
Reduction Half-Reaction		$E°$ (V)
$F_2(g) + 2e^-$	$\longrightarrow 2F\,(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Weaker oxidizing agent / Stronger reducing agent

Voltage vs. Current

- The key to a good battery is an easy redox reaction.
- This should lead to an i-V curve as followed:

Logarithmic decay due to Nerstian shift



Types of Batteries

- Batteries can be group into 2 types:

- **Primary Batteries** (non-rechargeable)- Examples are:
  - Typcially Alkaline batteries (typical 9V, AAA, AA, C, D)
  - Lithium batteries (FeS_2 type)
  - Carbon Fluoride batteries

- **Secondary Batteries** (rechargeable)- Examples are:
  - Lead-Acid Batteries
  - Nickel-Cadmium Batteries
  - Lithium ion batteries

- Since we are focused on sustainability we will only focus on secondary batteries.

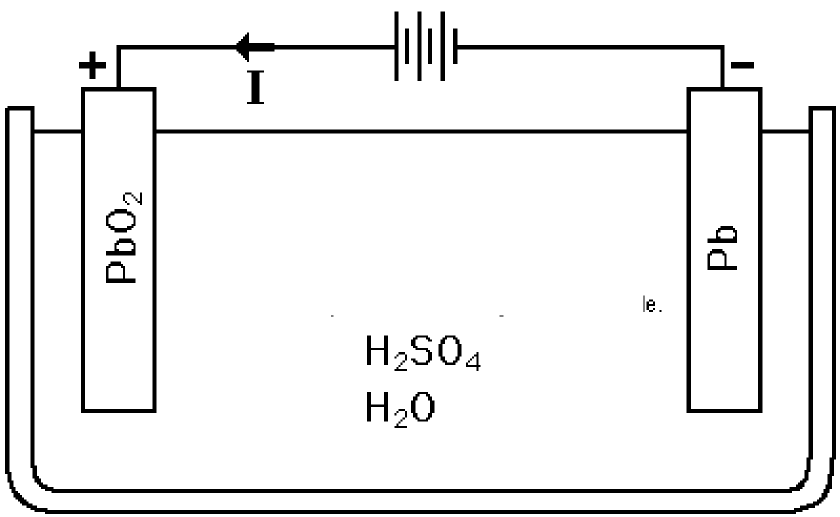
Lead Acid

- These are the typical car batteries.

Anode: $\mathrm{Pb} + H_2SO_4{}^{-} \rightarrow \mathrm{Pb}SO_4 + 2H^{+} + \color{red}{2e^{-}}$

Cathode: $\mathrm{Pb}O_2 + H_2SO_4{}^{-} + 2H^{+} + \color{red}{2e^{-}} \rightarrow \mathrm{Pb}SO_4 + 2H_2O$

$$\mathrm{Pb} + \mathrm{Pb}O_2 + 2H_2SO_4 \rightarrow 2\mathrm{Pb}SO_4 + 2H_2O$$



Lead Acid

- How much charge/kg of Lead can you obtain from these devices?
- Given these devices have an open circuit voltage of 2.1 V, how much Energy/kg can these devices theoretically hold?

Anode: $\mathrm{Pb} + H_2SO_4{}^{-} \rightarrow \mathrm{Pb}SO_4 + 2H^{+} + 2e^{-}$

Cathode: $\mathrm{Pb}O_2 + H_2SO_4{}^{-} + 2H^{+} + 2e^{-} \rightarrow \mathrm{Pb}SO_4 + 2H_2O$

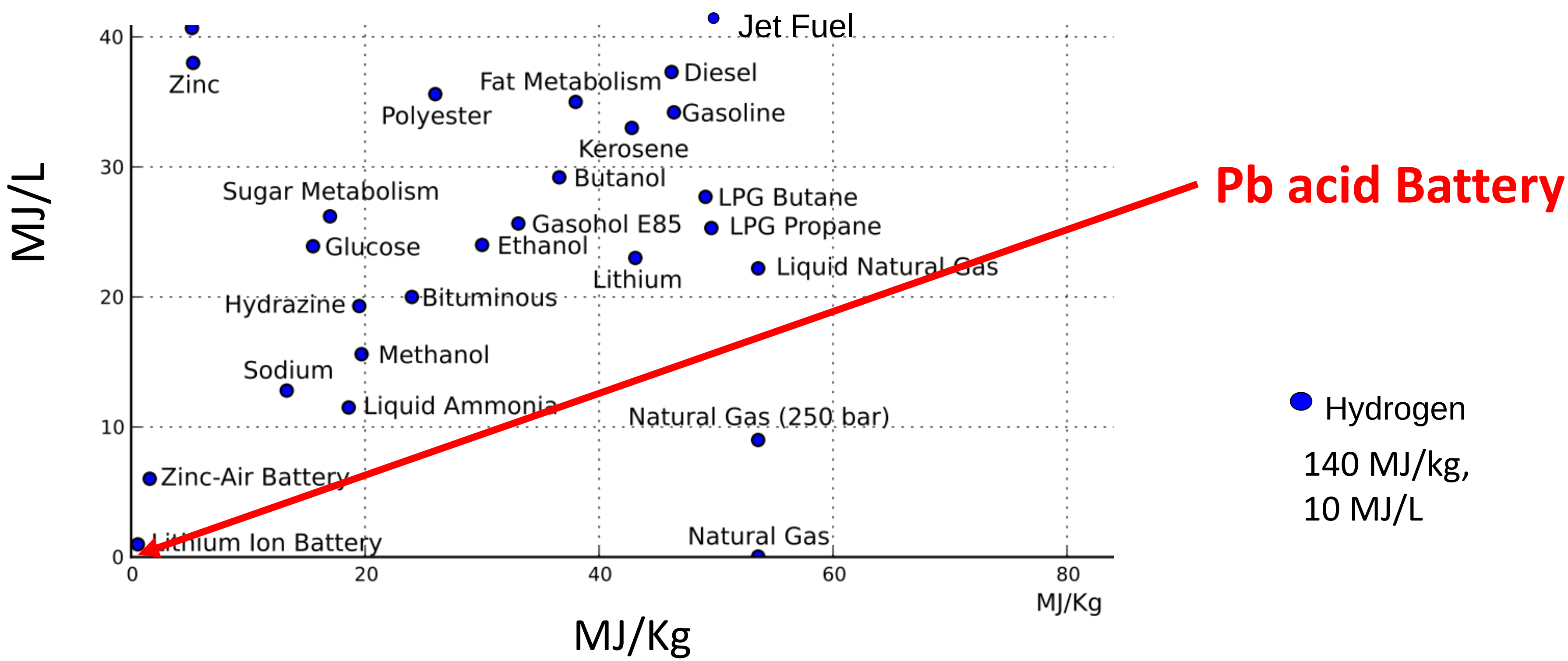
$$\mathrm{Pb} + \mathrm{Pb}O_2 + 2H_2SO_4 \rightarrow 2\mathrm{Pb}SO_4 + 2H_2O$$

Lead Acid

- How much charge/kg of lead can you obtain from these devices?
  - Mol. Weight of Pb= 207 g/mol
  - 1kg Pb = 4.83 mol Pb
  - You need 2 atoms of Pb for every 2 e- transferred,
  - 4.83 mol Pb = 4.83 mol e-
  - 1 mol e- = 96,485 C (Faraday's constant.)
  - Thus we have 466,000 Coulumbs/Kg. (Or 129.4 Ah/kg)
- Given these devices have an open circuit voltage of 2.1 V, how much Energy/Kg can these devices theoretically hold?
  - Energy= Columbs x Voltage = 466,000x 2.1 = 979 KJ/Kg of Pb.
  - or 207/(130+207) =61% *979 =601 KJ/Kg if we include acid and oxygen from PbO_2.
- Dillution of the acid makes this value lower for real devices (typically about 140 kJ/kg).

Will we burn things in a sustainable society?

- Airplanes and boats almost certainly will need the energy density from molecules not batteries.
- Hydrogen and Hydrazine are both used in rockets and both can be done sustainably.



Lead Acid

- The open circuit voltage is about 2.1 V.
- Durability- 800 cycles (3 years in a car).
- Auto industry uses 1 million tons of lead for batteries and an extra ~7% is used/lost in the mining/manufacturing process of batteries.
- Deactivation mechanism- $PbSO_4$ crystallizes and becomes compact preventing it's ability to react.
- Corrosion issues from the acid, and potential explosions from electrolysis (H_2 + O_2) are other issues with this.

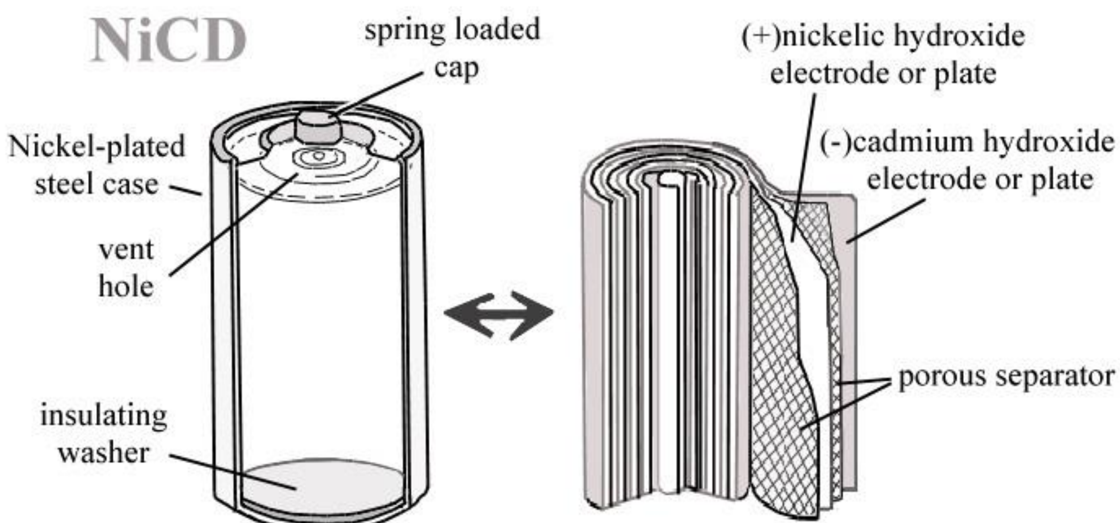
NiCd

- NiCd was traditionally used as rechargeable batteries

Anode: $\mathrm{Cd} + OH^- \rightarrow \mathrm{Cd}(OH)_2 + 2e^-$

Cathode: $2\mathrm{NiO}(OH) + 2H_2O + 2e^- \rightarrow 2\mathrm{Ni}(OH)_2 + 2OH^-$

$$2\mathrm{NiO}(OH) + \mathrm{Cd} + 2H_2O \rightarrow 2Ni(OH)_2 + \mathrm{Cd}(OH)_2$$



Nickel Cadmium

- The open circuit voltage is about 1.2 V.
- The practical energy density is 140 kJ/kg.
- Durability- 2000 cycles.
- The biggest issue with these is disposal of cadmium since it is toxic.
- For toxicity reasons these batteries have basically been banned in the EU.

Ni Metal Hydride

- These are replacing NiCd electrodes becuase the reactions are quite similar.

Cathode: $H_2O + M + e^{-} \rightarrow OH^{-} + \mathrm{MH}$

Anode: $\mathrm{Ni}(OH)_2 + 2OH^{-} \rightarrow 2\mathrm{NiO}(OH) + H_2O + e^{-}$

$$\mathrm{Ni}(OH)_2 + \mathrm{M} \rightarrow \mathrm{NiO}(OH) + \mathrm{MH}$$

M = Metals (or Metal Composites)

$\underline{AB_5}$

Lanthanum	Nickel
Cerium	Cobalt
Neodymium	Manganese
Praseodymium	Aluminum

$\underline{AB_2}$

Titatnium	Ziconium
Vanadium	Nickel

Nickel Metal Hydride

- The specific energy is 360 kJ/kg. This is 3 times higher than NiCd.
- The open circuit voltage is about 1.2 V.
- Durability- 500- 2000 cycles.
- These are used in many of the older electric cars.
- Cells can retain 70-85% of their capacity after 1 year.
- Too fast charging or allowing the battery to discharge completely can lead to permanent damage.

Toyota Prius Battery

Lithium Ion batteries

- John Goodenough (professor , U. of Texas) basically opened up the lithium ion battery field.

- The open circuit voltage is about 3.5 V.

John Goodenough

Cathode: $$FePO_4 + xLi^+ + xe^- \leftrightarrow xLiFePO_4 + (1-\mathrm{x})FePO_4$$

Anode: $$x\mathrm{Li}C_6 \leftrightarrow xLi^+ + xe^- + xC_6$$

$$\mathrm{Li}C_6 + FePO_4 + x\mathrm{Li}C_6 \leftrightarrow xLiFePO_4 + (1-\mathrm{x})FePO_4 + xC_6$$

Where $x_{maximum} = 0.6$

- These are what is in your laptop and cellphone.

Li-ion Batteries

- There are other ways to do lithium ion batteries as well.

Cathode: $Li_{1-x}NiMnCoO_2 + xLi^+ + xe^- \leftrightarrow LiNiMnCoO_2$

Anode: $x\mathrm{Li}C_6 \leftrightarrow xLi^+ + xe^- + xC_6$

$$\mathrm{Li}C_6 + Li_{1-x}NiMnCoO_2 \leftrightarrow LiNiMnCoO_2 + xC_6$$

- C_6 is typically graphite.
- Tesla uses a nickel-cobalt-aluminum alloy for their cars and a nickel-magnesium-cobalt alloy for their battery packs.

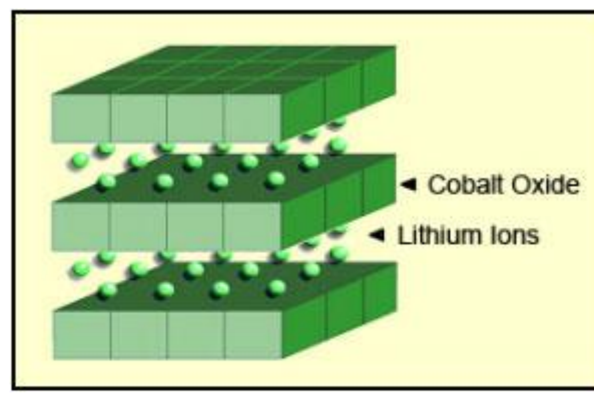


Image from BatteryUniversity.com

Electrolytes

- The high voltage from batteries will split water into H_2 and O_2 so another electrolyte is needed

- Often a propylene carbonate with dimethoxy ethane with 1M $LiClO_4$ is used.

Can be explosive when mixed with organics

Flammable

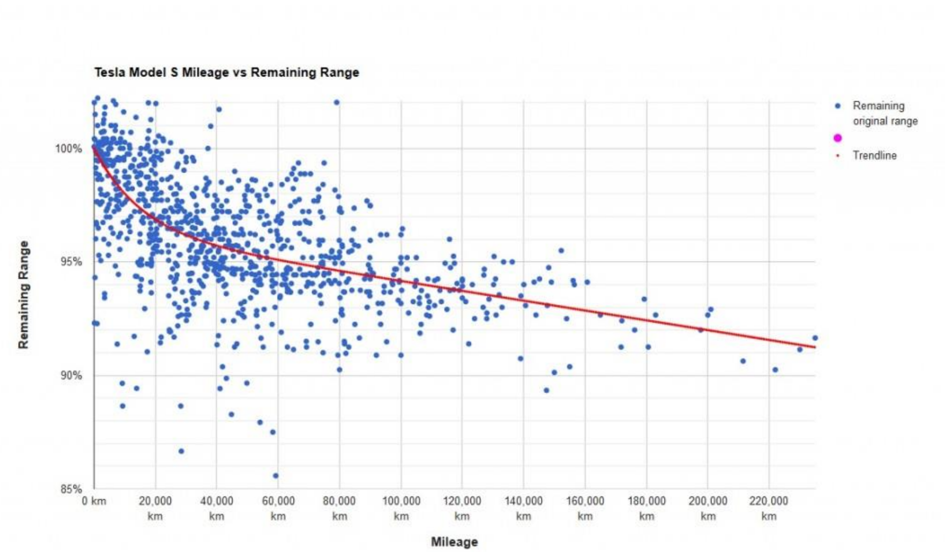
Flammable

- The quest now is to look for a solid state electrolyte.
- Goodenough has one that looks promising.

Lithium Ion Battery

- The specific energy is 460 kJ/kg. This is the highest of all major batteries
- The open circuit voltage is about 3.6 V.
- Durability- 400- 1000 cycles (or even more).
- These are used in Tesla's cars.

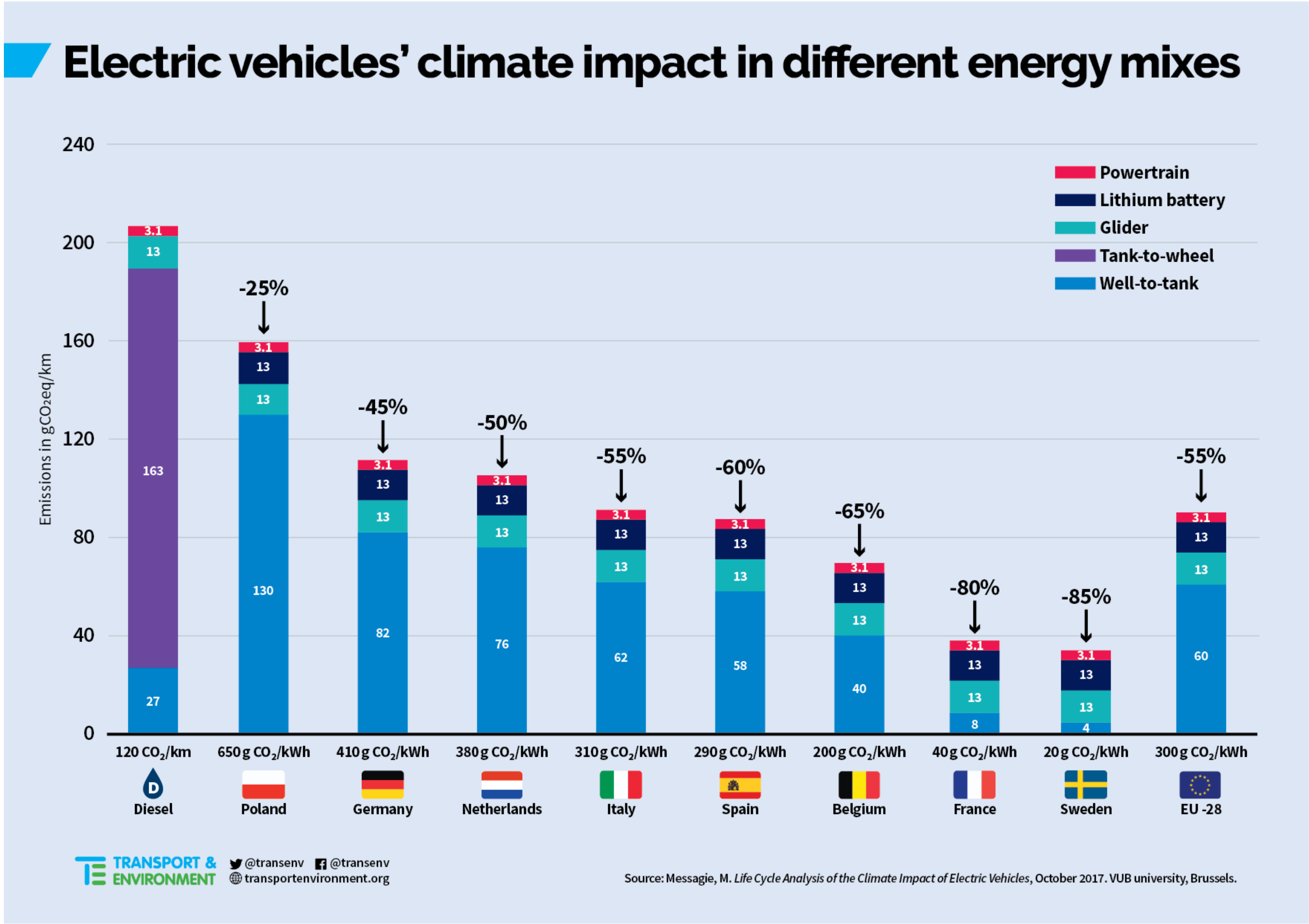
[Tesla Model S Battery]



[Battery performance of Tesla S]

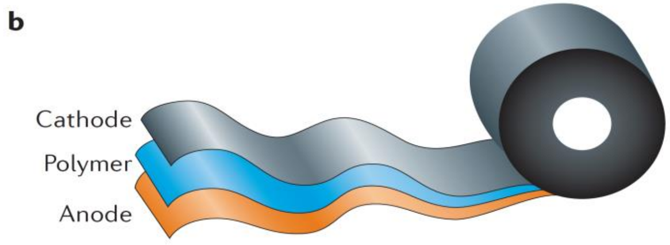
Climate impact

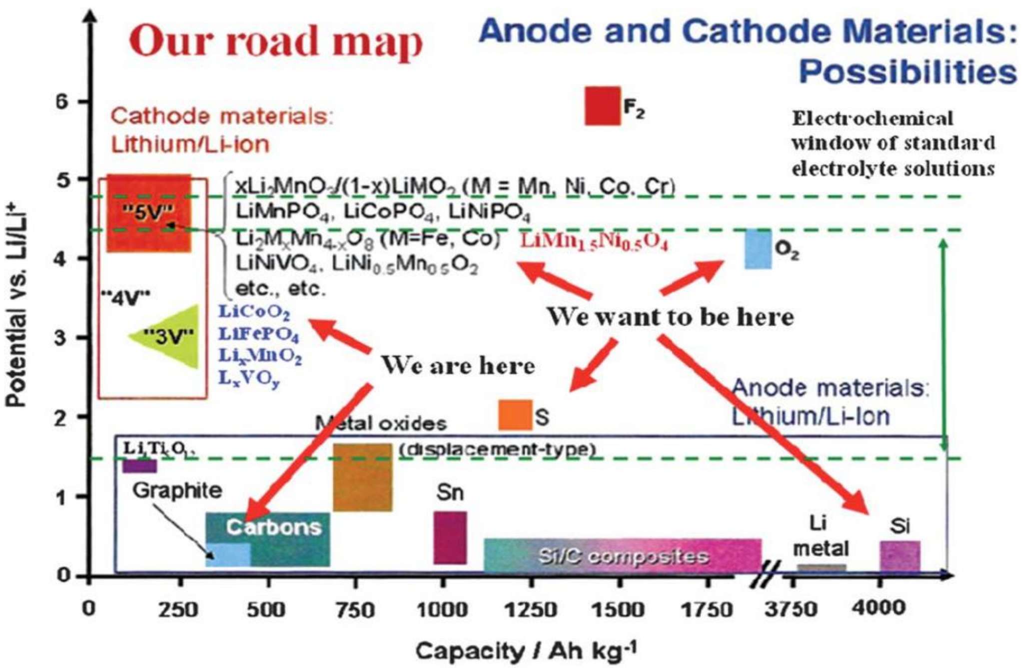
- Even with today's electricity make-up, electric vehicles are still more environmentally friendly than internal combustion cars.



Li-ion Batteries

- Li has a low molecular weight helping its energy density.
- Different redox couples are being investigated to improve performance and safety





Marom, et al., J.Mater.Chem., 2011,21, 9938–9954

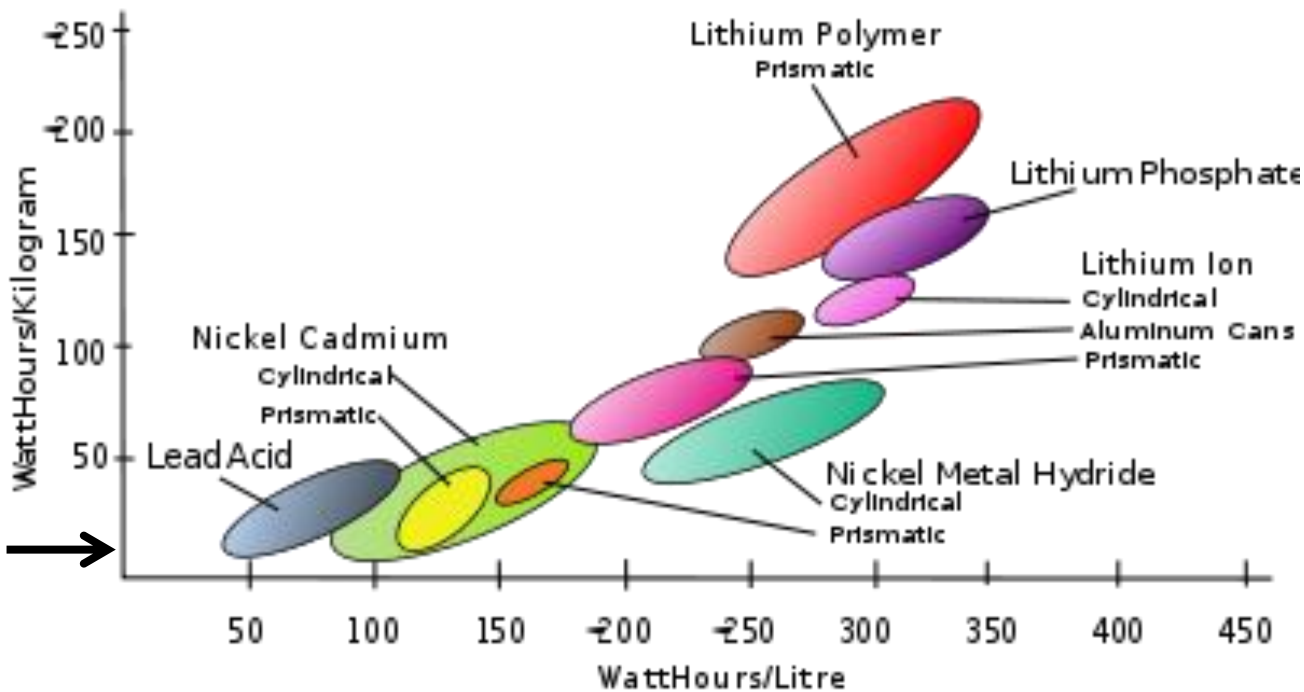
Table 1 | **Summary of lithium-ion solid electrolyte materials**

Type	Materials	Conductivity ($S\,cm^{-1}$)	Advantages	Disadvantages
Oxide	Perovskite $Li_{3.3}La_{0.56}TiO_3$, NASICON $LiTi_2(PO_4)_3$, LISICON $Li_{14}Zn(GeO_4)_4$ and garnet $Li_7La_3Zr_2O_{12}$	10^{-5}–10^{-3}	• High chemical and electrochemical stability • High mechanical strength • High electrochemical oxidation voltage	• Non-flexible • Expensive large-scale production
Sulfide	Li_2S–P_2S_5, Li_2S–P_2S_5–MS_x	10^{-7}–10^{-3}	• High conductivity • Good mechanical strength and mechanical flexibility • Low grain-boundary resistance	• Low oxidation stability • Sensitive to moisture • Poor compatibility with cathode materials
Hydride	$LiBH_4$, $LiBH_4$–LiX (X = Cl, Br or I), $LiBH_4$–$LiNH_2$, $LiNH_2$, Li_3AlH_6 and Li_2NH	10^{-7}–10^{-4}	• Low grain-boundary resistance • Stable with lithium metal • Good mechanical strength and mechanical flexibility	• Sensitive to moisture • Poor compatibility with cathode materials
Halide	LiI, spinel Li_2ZnI_4 and anti-perovskite Li_3OCl	10^{-8}–10^{-5}	• Stable with lithium metal • Good mechanical strength and mechanical flexibility	• Sensitive to moisture • Low oxidation voltage • Low conductivity
Borate or phosphate	$Li_2B_4O_7$, Li_3PO_4 and Li_2O–B_2O_3–P_2O_5	10^{-7}–10^{-6}	• Facile manufacturing process • Good manufacturing reproducibility • Good durability	• Relatively low conductivity
Thin film	LiPON	10^{-6}	• Stable with lithium metal • Stable with cathode materials	• Expensive large-scale production
Polymer	PEO	10^{-4} (65–78 °C)	• Stable with lithium metal • Flexible • Easy to produce a large-area membrane • Low shear modulus	• Limited thermal stability • Low oxidation voltage (<4 V)

Manthiram, A., NATURE REVIEWS MATERIALS, 2017

Comparison of Batteries

- Efficiencywise lead acid is not good whereas Li-ion is the best.
- Lead-Acid are still more reliable, which is why they are used in automotive applications.



Supercapacitors →

Lecture - Learning Objectives

At the end of this lecture you should be able to:

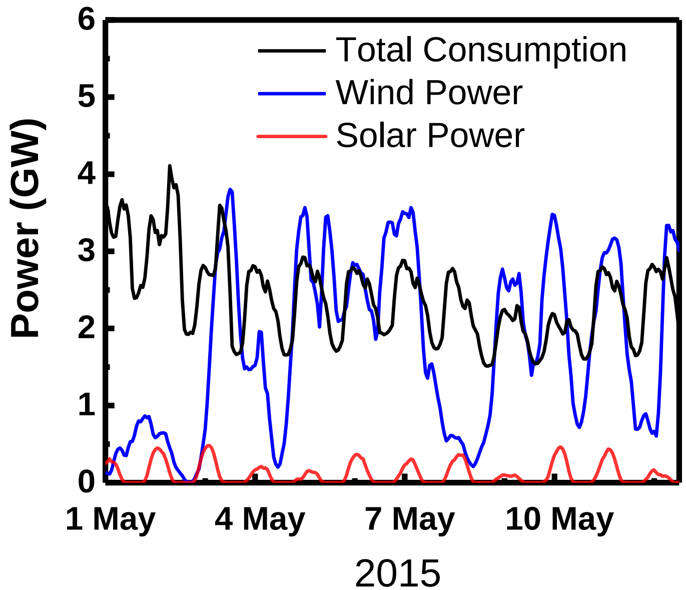
- Understand the difference between the heat engine and electrical engines.

- Understand the basic principles of electrochemistry.

- Understand the redox reactions related to battery technology

Energy Storage

- How much do we need to store ?
  - No one really knows
  - We will try to get an order of magnitude estimate
- Denmark's electricity consumption and production can be found at energinet.dk (specifically this website)
- By using this data you can make cool data like this shown below.



Energy Storage

- Take the data for the last year and increase the overall wind production by a factor X and the solar by a factor of Y such that the total energy consumption is met.
- When wind+solar exceeds consumption this will need to be stored , and when it is less than consumption it will need to be used from storage.
- How much storage will you need in an optimized case?
- If we assume the rest of the world is like Denmark, and only 1/6th of the total energy is electricity, we can multiply our electrical storage needs by 6 to get total energy storage needed.
- What would this

A battery storage society

- Currently batteries cost 300$/kwh but are expected to drop to 100$/kwh in 5 years.
- How much would it cost to store 24 hours worth of the world's energy usage assuming 100$/kwh ?
- How does this compare to the gross world product (8×10^{12} $/year)

Excercises

- Review the Zn/Cu electrochemical reaction (slide 7). If you have 10g of Zn
  - A) What is the theoretical maximum amount of Cu you could deposit (assuming you had enough Cu^{2+})
  - B) What is the maximum theoretical amount of energy you could extract from this electrochemical reaction.

Concept Check

What battery will have the highest potential? (Refer to standard reduction potential of species graph):

a) . $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

b) . $2Ag^{+} + Pb \leftrightarrow Ag + Pb^{2+}$

c) . $2NaCl \leftrightarrow Na + Cl_2$

d) . $O_2 + H_2 \leftrightarrow H_2O$

Concept Check

The most important thing to get a high voltage in a battery is :

a) Charge transferred per reaction

b) Molecular weight of battery redox materials

c) Having easy reaction kinetics.

d) Redox potential difference between half-reactions

A battery storage society

- We use 17.6 TW for 24 hours (or 86400 s)

$$Energy\ Needed = 17.6 \times 10^{12}\frac{J}{s} \times 86400\ s = 1.52\ \times 10^{18} J$$

$$1.52\ \times 10^{18} J = 1.52\ \times 10^{18} J \times \frac{1hr}{3600s} \times \frac{1kW}{1000^{J}/_{s}} = 0.422 \times 10^{12} kW * hr$$

$$Cost\ = 0.422 \times 10^{12} kW * hr \times 100 \frac{\$}{kW*hr} = 4.22 \times 10^{13} \$$$

World Gross Product is 8.7 x 10^{13} $/year

- Review the Zn/Cu electrochemical reaction (slide 7). If you have 10g of Zn
  - A) What is the theoretical maximum amount of Cu you could deposit (assuming you had enough Cu^{2+})

Answer:10 g Zn / 65 g/mol = 0.15 mol Zn. Since we lose 2 e- from Zn and gain 2e- on Cu, we need 0.15 mol Cu. 0.15mol x 63.5 g/mol =9.8 g.

  - B) What is the maximum theoretical amount of energy you could extract from this electrochemical reaction.
  - Answer: Energy= V x charge. From Slide 7 Voltage =1.1 V. We will transfer 2e- per Zn and we have 0.15 mol, thus we will have 0.3 mol. We need to multiply this by Faraday's constant(96, 485 C/mol) to get 29,000 C. V x I = 1.1 V x 29,000 C = 31,900 V x C = 31.9 kJ