Thermal Energy, Chemical Energy

IE350

Outline

- Thermal Energy
- Chemical Energy
- Electrolysis
- PV and electrolysis
- Fuel Cells

Thermal Energy

- We already know that in order to increase by 1°C the 1 gram of water we need 1 calorie.
- For any mass and any temperature difference we will have:

$$Q = C \cdot m \cdot \Delta t,$$

where C is the Specific Heat

Specific Heat

- The Specific Heat measurement unit, *c* naturally is:

$$\text{cal}/(\text{g}\cdot{}^\circ\text{C}) =$$

$$= 4.184\ \text{J}/(\text{g}\cdot{}^\circ\text{C}) \text{ or } \text{J}/(\text{g}\cdot{}^\circ\text{K})$$

- Water has a mass-specific heat capacity of about 4.184 joules per Kelvin per gram near 20 °C.
- … or 1 calorie per kelvin per gram near 20 °C (this is again the calorie definition).

Heat Storage

- Assume you have 1 ton of water at 94°C in a room. After some time the temperature decreases to 24°C. How much energy is released to the room?

$$Q = c \cdot m \cdot \Delta t$$

$$c = 4.184 \text{ MJ/(ton} \cdot {}^\circ\text{K)}$$

$$m = 1 \text{ t}$$

$$\Delta t = 70^\circ\text{C}$$

$$Q = 4.184 \cdot 70 \text{ MJ} = 292.88 \text{ MJ} = 81.35[5] \text{ kWh}$$

$$(1 \text{ kWh} = 3.6 \text{ MJ}).$$

Table of Specific Heat for Various Materials.

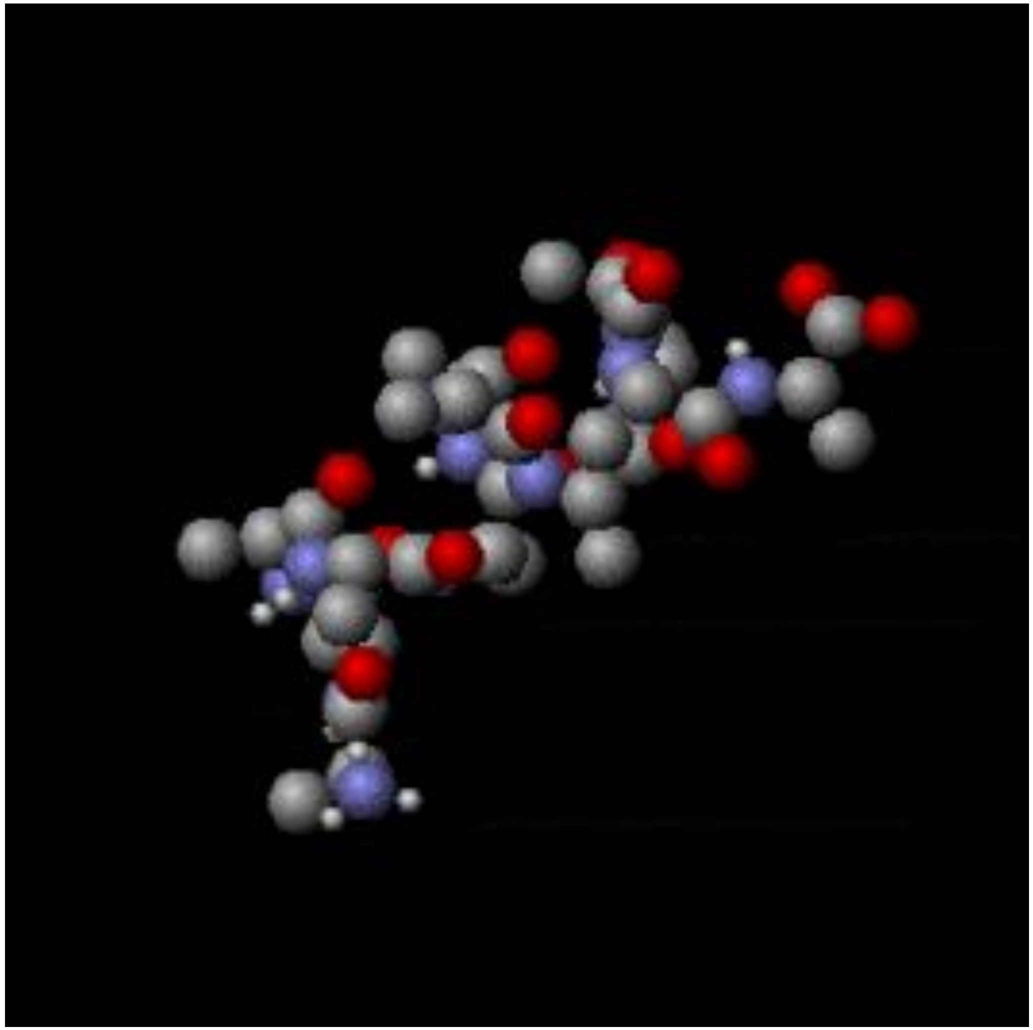
- Which material is best for heat storage?
- Remember that water is limited in Δt, e.g. bricks or granite – not so much.
- However losses at larger Δt-s are much higher.

Substance	**c_p J g^{-1} K^{-1}**
Asphalt	0.92
Brick	0.84
Concrete	**0.88**
Glass, pyrex	0.753
Granite	0.790
Gypsum	**1.09**
Marble, mica	0.880
Sand	**0.835**
Soil	**0.80**
Wood	0.42
Water	**4.1813**

Specific Heat (C) of H_2O

- **Water:** J/(g·°K)
  - gas,100 °C 2.08
  - liquid, 25 °C **4.1813**
  - solid, 0 °C 2.114

Specific Heat



Losses

Losses are linearly related to the temperature difference **Δt** (temperature gradient)!

Specific Heat of:
Fusion and Vaporization

- Specific Heat of Fusion:
  Amount of energy needed to turn solid into liquid.
- Specific Heat of Vaporization:
  Amount of energy needed to turn liquid into vapor.

H_2O: From Ice to Vapor

- How much Energy is needed to turn ***ice*** into ***vapor***?
- 5 steps of calculation:

1. Energy needed to reach the melting point;
2. Add energy needed to melt the ice;
3. Add energy needed to reach the vaporization point;
4. Add energy needed to vaporize the water;
5. Add energy needed to reach higher temperature of vapor (analogy with band gap in Si).

H_2O: From Ice to Vapor

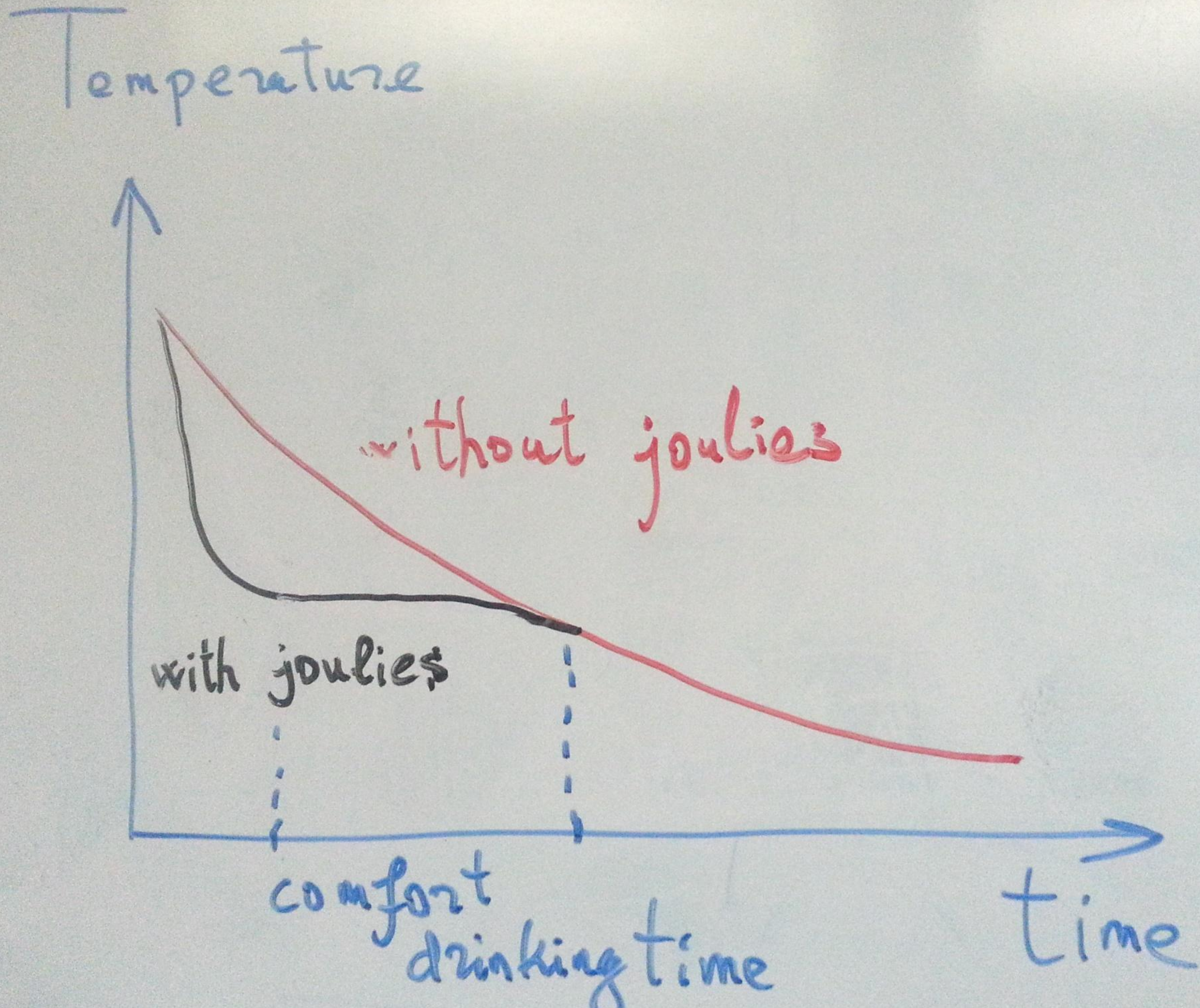
- Energy needed to melt the ice:
  333 J/g = specific heat of fusion
- Energy needed to vaporize the water:
  2260 J/g = specific heat of vaporization
- How this difference is explained?

Phase change storage!

Coffee Joulies

Coffee Joulies

- Coffee is HOT; Joulies are cool; Take the edge off your coffee so it is safe to sip sooner and stays in the perfect temperature range longer
- Polished 18/10 stainless steel shell - just like high end silverware
- Food-based and completely nontoxic phase change material sealed inside absorbs and releases heat from your coffee
- Keeps your coffee at 140°F (60°C) - the perfect drinking temperature
- Made in USA from 85% recycled stainless steel using hydro power from Niagara Falls


Temperature
without joulies
with joulies
comfort drinking time
time

Enthalpy

- Enthalpy or heat content (denoted as H or ΔH, or rarely as χ) is a quotient or description of thermodynamic potential of a system, which can be used to calculate the "useful" work obtainable from a closed thermodynamic system under constant pressure,
- Short definition: Enthalpy is the energy density in heat-mass transfer (transportation) phenomena.

Enthalpy

- Enthalpy,
  $H = \{\text{Energy content}\}/\text{mass} = E/m$
  measured in J/g or J/kg.
- Importantly, in many cases $\Delta H = \Delta Q/m$.

Humidity

- Absolute
- Relative
- Absolute Humidity = weight of water in the volume of air, g/m^3;
- … or weight of water in weight of air, g/kg.

Relative humidity

- Relative humidity is defined as the ratio of the partial pressure (or density) of water vapor in a gaseous mixture of air and water to the saturated vapor pressure (or density) of water at a given temperature. Relative humidity is expressed as a percentage and is calculated in the following manner:

- *RH* = 100% • [p(H_2O)]/[p*(H_2O)] $$RH = \frac{p_{(H_2O)}}{p^*_{(H_2O)}} \times 100\%$$

- where:
- *RH* is the relative humidity of the gas mixture being considered;
- $p_{(H_2O)}$ is the partial pressure of water vapor in the gas mixture; and
- $p^*_{(H_2O)}$ is the saturation vapor pressure of water at the temperature of the gas mixture.

Psychrometer

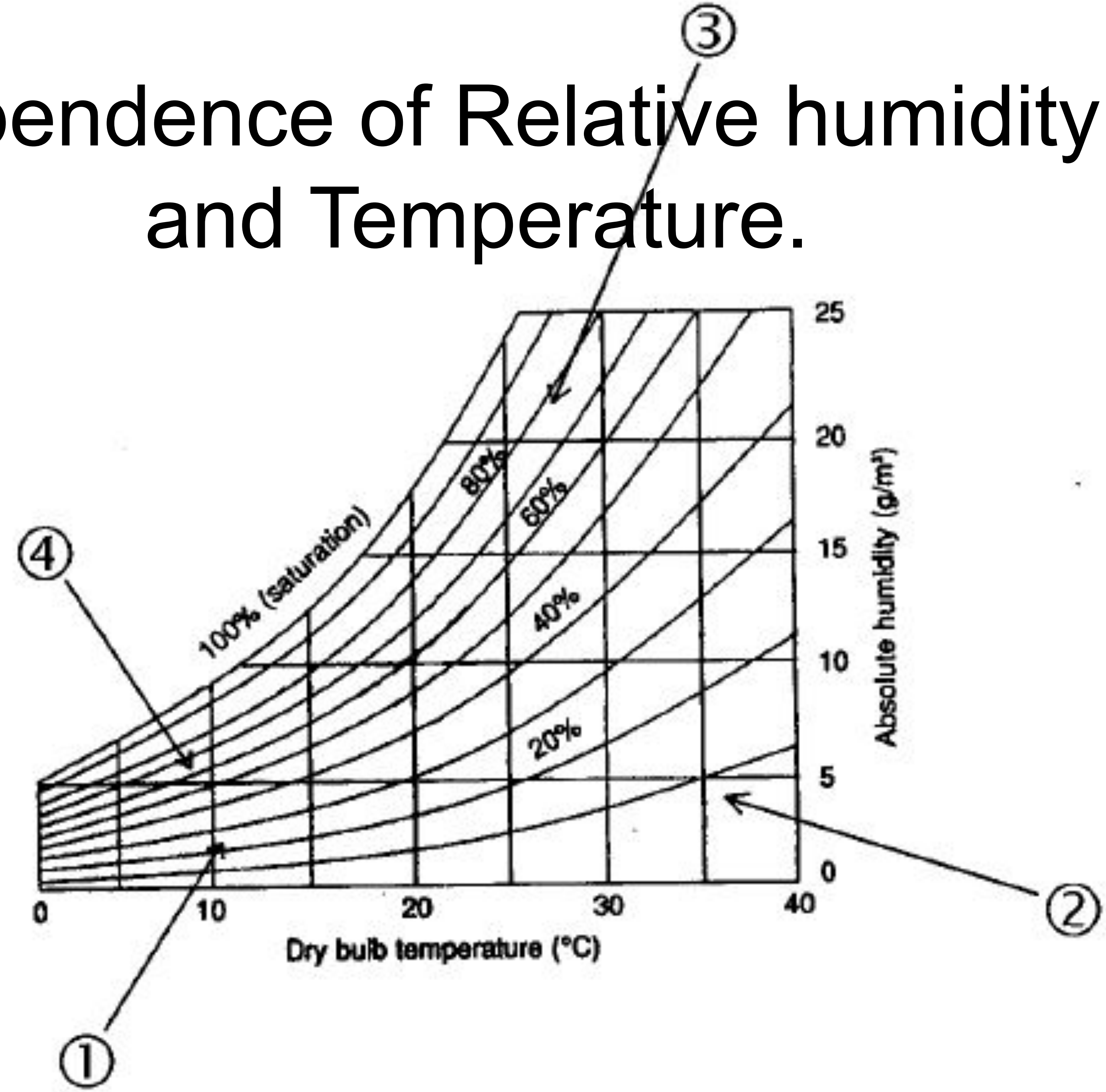
Relative Humidity %

Dry Bulb Temperature (Celsius)	Difference Between Wet-bulb and Dry-bulb Temperatures (ºC)															
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
-20	100	28														
-18	100	40														
-16	100	48														
-14	100	55	11													
-12	100	61	23													
-10	100	66	33													
-8	100	71	41	13												
-6	100	73	48	20												
-4	100	77	54	32	11											
-2	100	79	58	37	20	1										
0	100	81	63	45	28	11										
2	100	83	67	51	36	20	6									
4	100	85	70	56	42	27	14									
6	100	86	72	59	46	35	22	10								
8	100	87	74	62	51	39	28	17	6							
10	100	88	76	65	54	43	33	24	13	4						
12	100	88	78	67	57	48	38	28	19	10	2					
14	100	89	79	69	60	50	41	33	25	16	8	1				
16	100	90	80	71	62	54	45	37	29	21	14	7	1			
18	100	91	81	72	64	56	48	40	33	26	19	12	6			
20	100	91	82	74	66	58	51	44	36	30	23	17	11	5		
22	100	92	83	75	68	60	53	46	40	33	27	21	15	10	4	
24	100	92	84	76	69	62	55	49	42	36	30	25	20	14	9	4
26	100	92	85	77	70	64	57	51	45	39	34	28	23	18	13	9
28	100	93	86	78	71	65	59	53	47	42	36	31	26	21	17	12
30	100	93	86	79	72	66	61	55	49	44	39	34	29	25	20	16

DRY BULB

WET BULB

Dependence of Relative humidity and Temperature.



Anti-condensation bathroom mirror

Anti-condensation bathroom mirror

Chemical Energy

- The weight of a proton or neutron is $1.66 \cdot 10^{-24}$ g
- Since the electron weight is too small compared to proton, 1/1837 –th, the weight of atoms is defined by protons and neutrons.
- N_A, *Avogadro Number, = 6.022 ·10^{23}mol^{-1}* particles. The unit of amount of substance.
- number of atoms in 12g of the isotope carbon-12
- Interesting is that the volume of 1 mol of ideal gas is always the same. Precisely,

  22.414 $(dm)^3$/mol at 0 °C
  24.465 $(dm)^3$/mol at 25 °C

Avogadro Number’s Holiday

- October 23 is called Mole Day. It is an informal holiday in honor of the unit among chemists. The date is derived from Avogadro's constant, which is approximately 6.022×10^{23}. It starts at 6:02 a.m. and ends at 6:02 p.m.

Heat of Formation

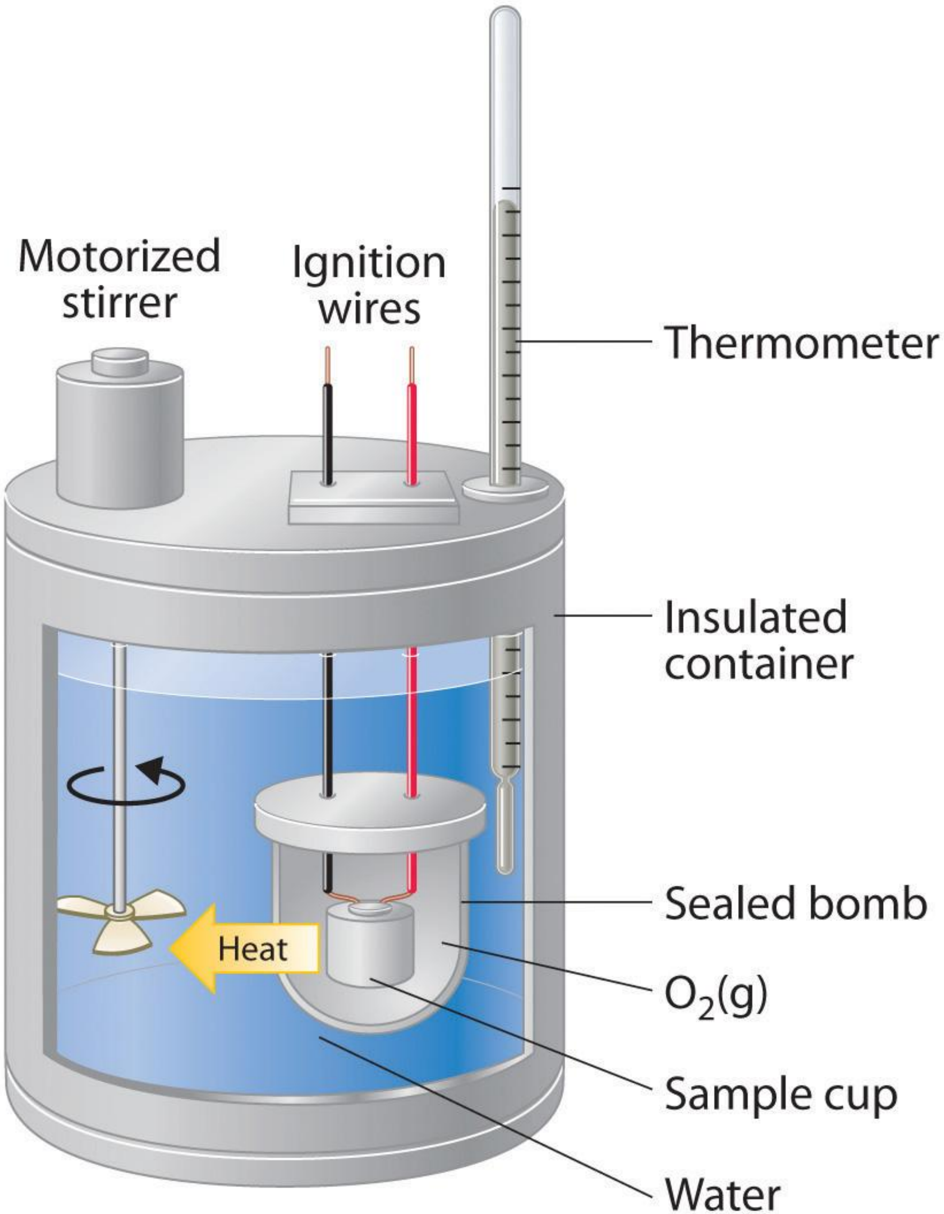
- Reactions can be endothermic – absorption of heat takes place, temperature of ambience is decreased;
- or exothermic – release of heat takes place, temperature of ambience is increased;
- Denoted by ΔH_f° - amount of energy per unit amount of substance, kcal/mol, released or absorbed by a reaction – is the reaction enthalpy.

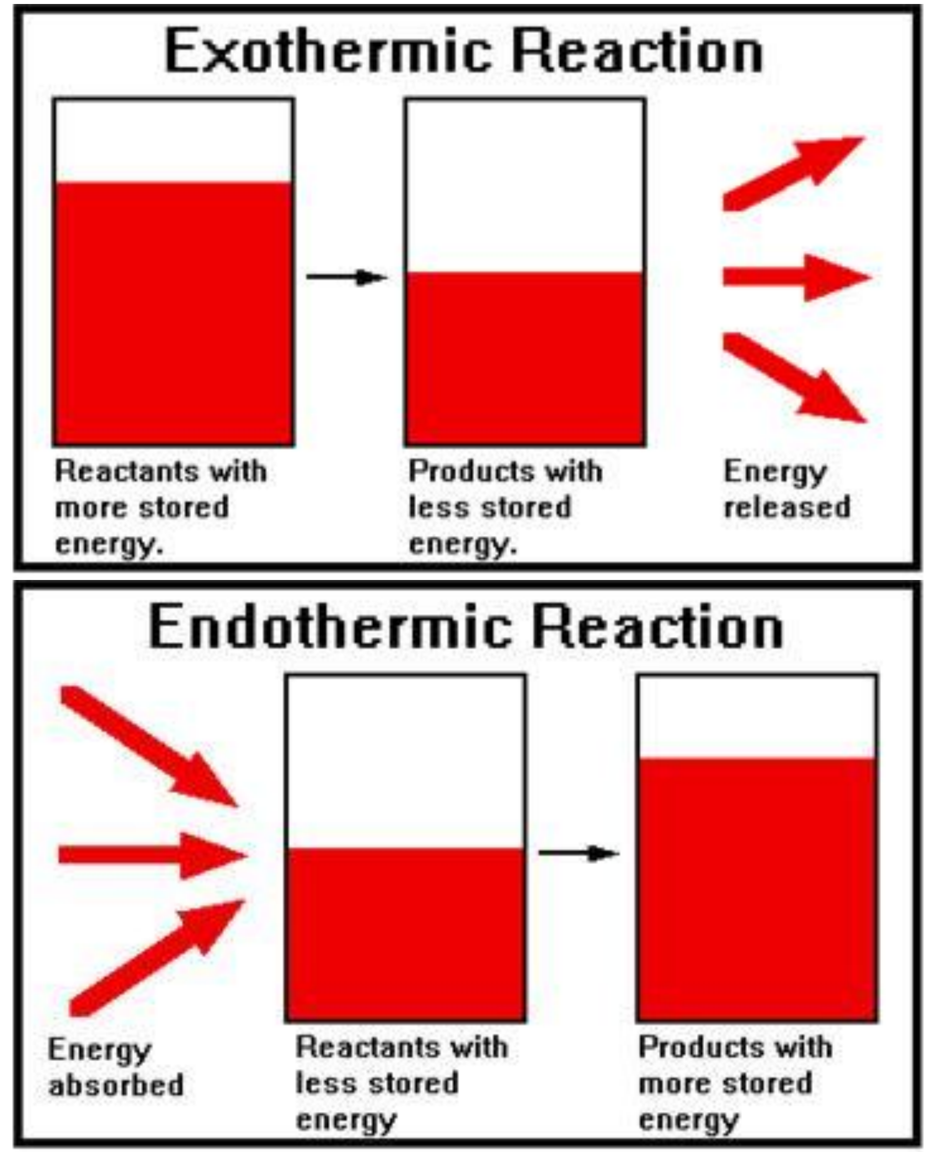
Exothermic   Endothermic

In an exothermic reaction, energy is released into the surroundings as heat. As a result, the temperature of the surroundings increases.

In an endothermic reaction, energy is absorbed from the surroundings. As a result, the temperature of the surroundings drops.

Exothermic & Endothermic reactions





Heats of Formation

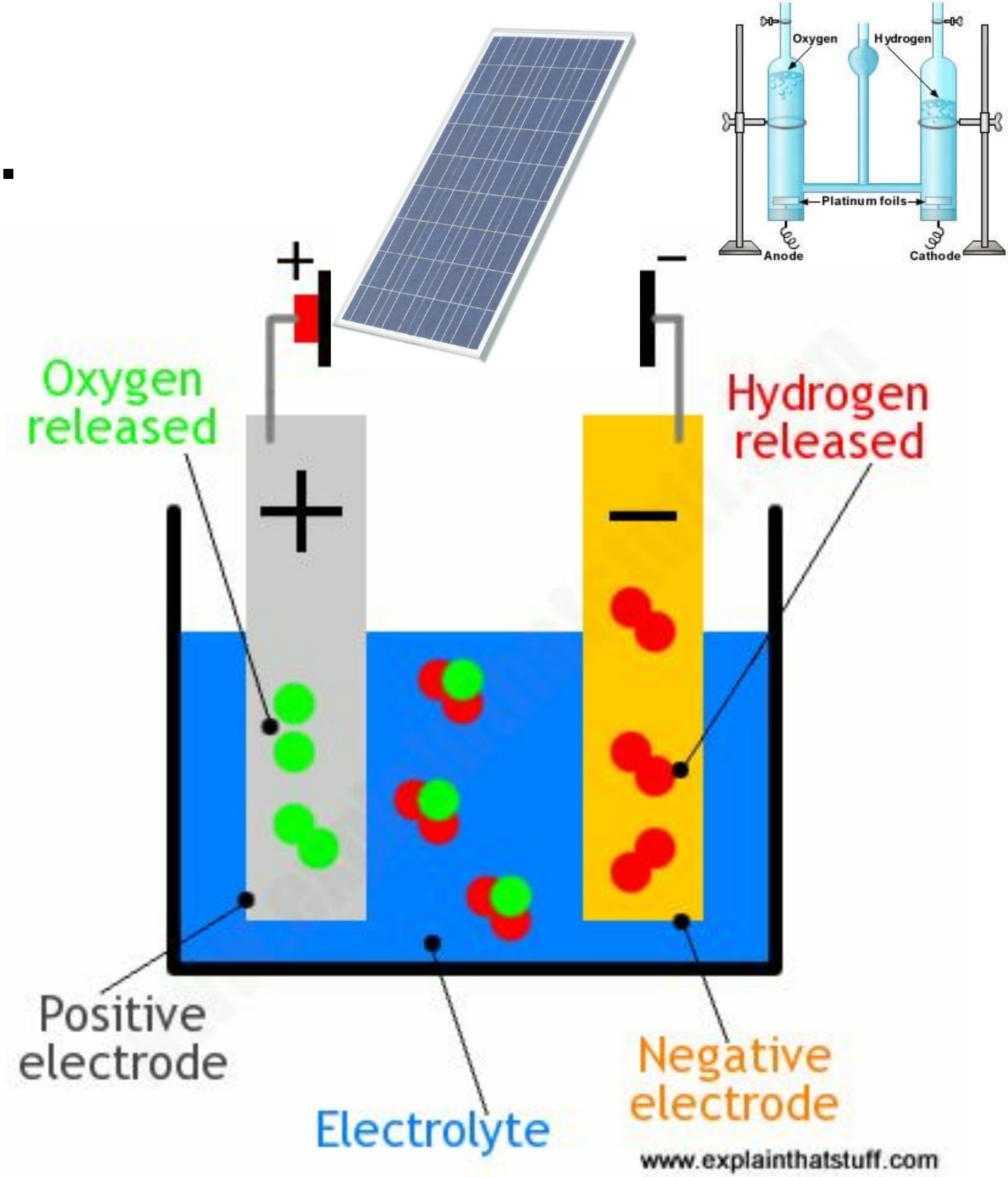
Compound	Notation	$\Delta H_f°$, kcal/mol
Carbon dioxide	CO_2	-94
Water	H_2O	-68
Methane	CH_4	-17.9
Gasoline	C_8H_{18}	-49.8
Diatomic gases	H_2, O_2, N_2, F_2, ..	0

Hydrogen and water

- We all know:
  $H_2 + O_2 \rightarrow H_2O$
- But the correct reaction formula is:
  $2H_2 + O_2 \rightarrow 2H_2O$
- This is stoichiometric reaction, and the result is **2 moles** of water, thus with energy balance the equation will be:
  $2H_2 + O_2 \rightarrow 2H_2O$ – **136 kcal**,
  since water $\mathbf{\Delta H_f°}$ **= - 68 kcal/mol**
  = - 286 kJ/mol.

Electrolysis.

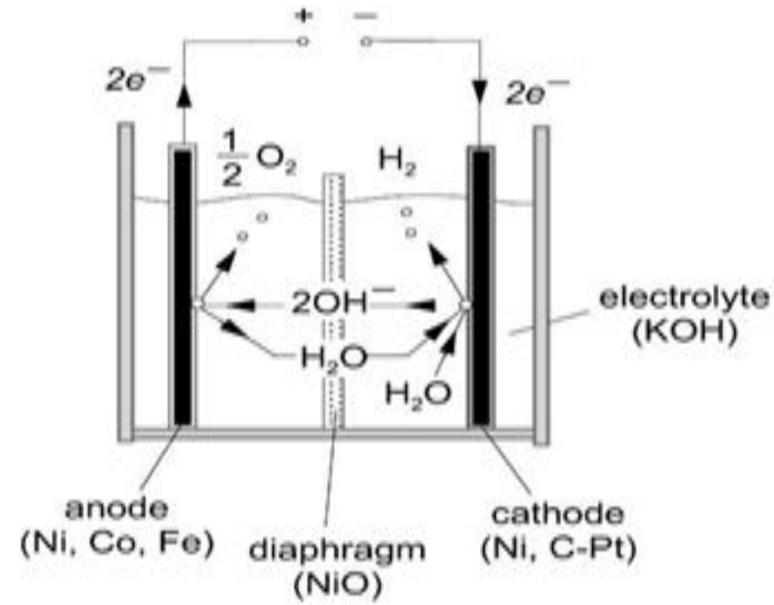
- However, what is the future?
- Hydrogen Combustion Engines?
- Hydrogen Fuel Cells?
- Large Ocean Solar Stations?



PV and electrolysis.

- Storage of solar energy is a problem yet to be solved.
- Hydrogen is one of the best solutions.
- Electrolysis efficiency is about 80%, with theoretical maximum of 94%.
- Safety problems: The enthalpy of combustion for hydrogen is 286 kJ/mol,
- Burning concentration starts from 4% (v)!
- However, as experience shows, it is safer than e.g. gasoline or methane!

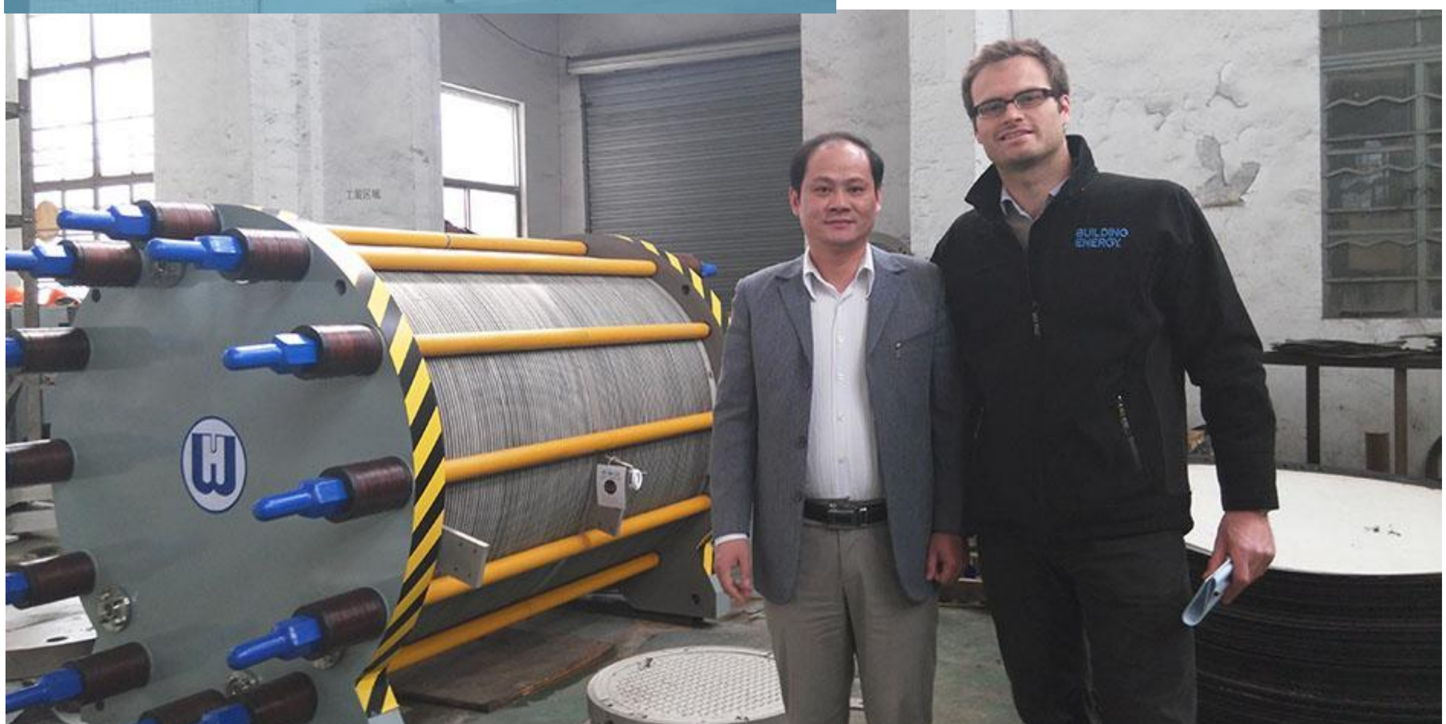
Electrolysers



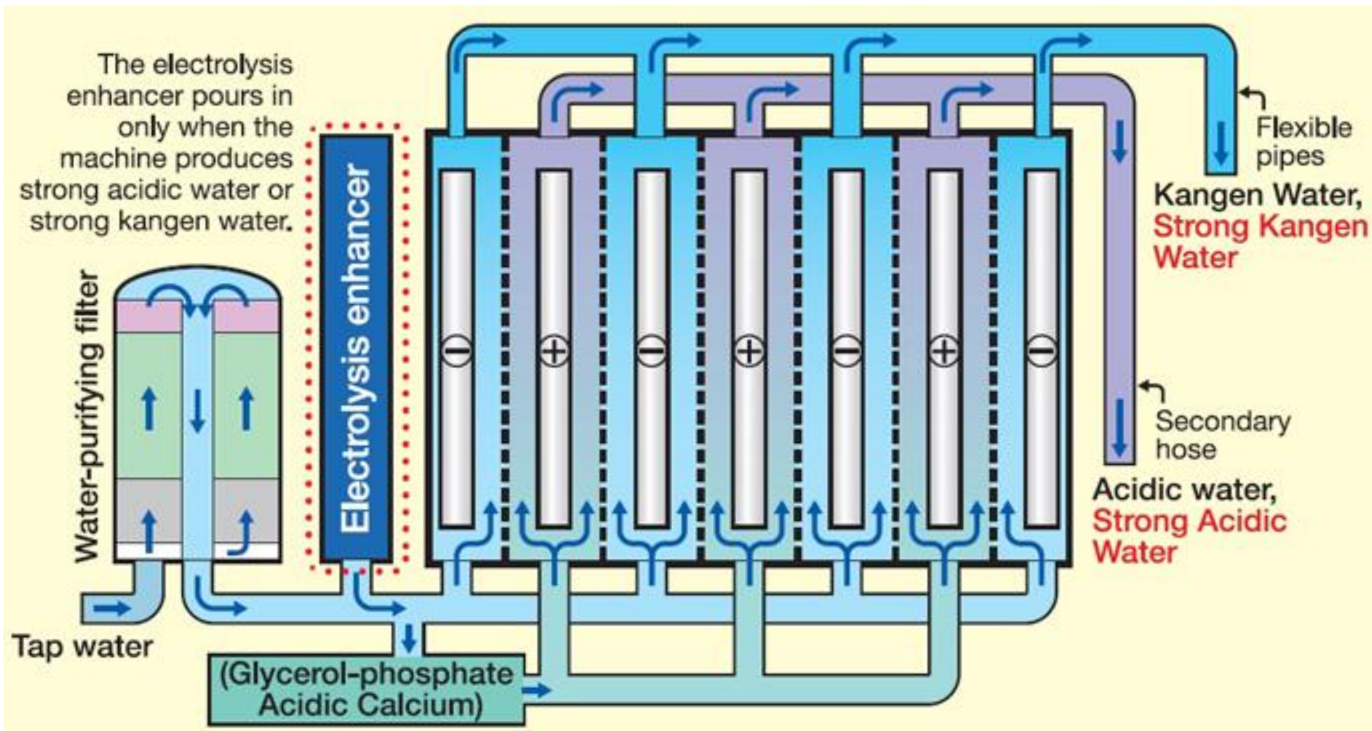
Type S–556 electrolyser

Electrolysers

Type S-556 electrolyser



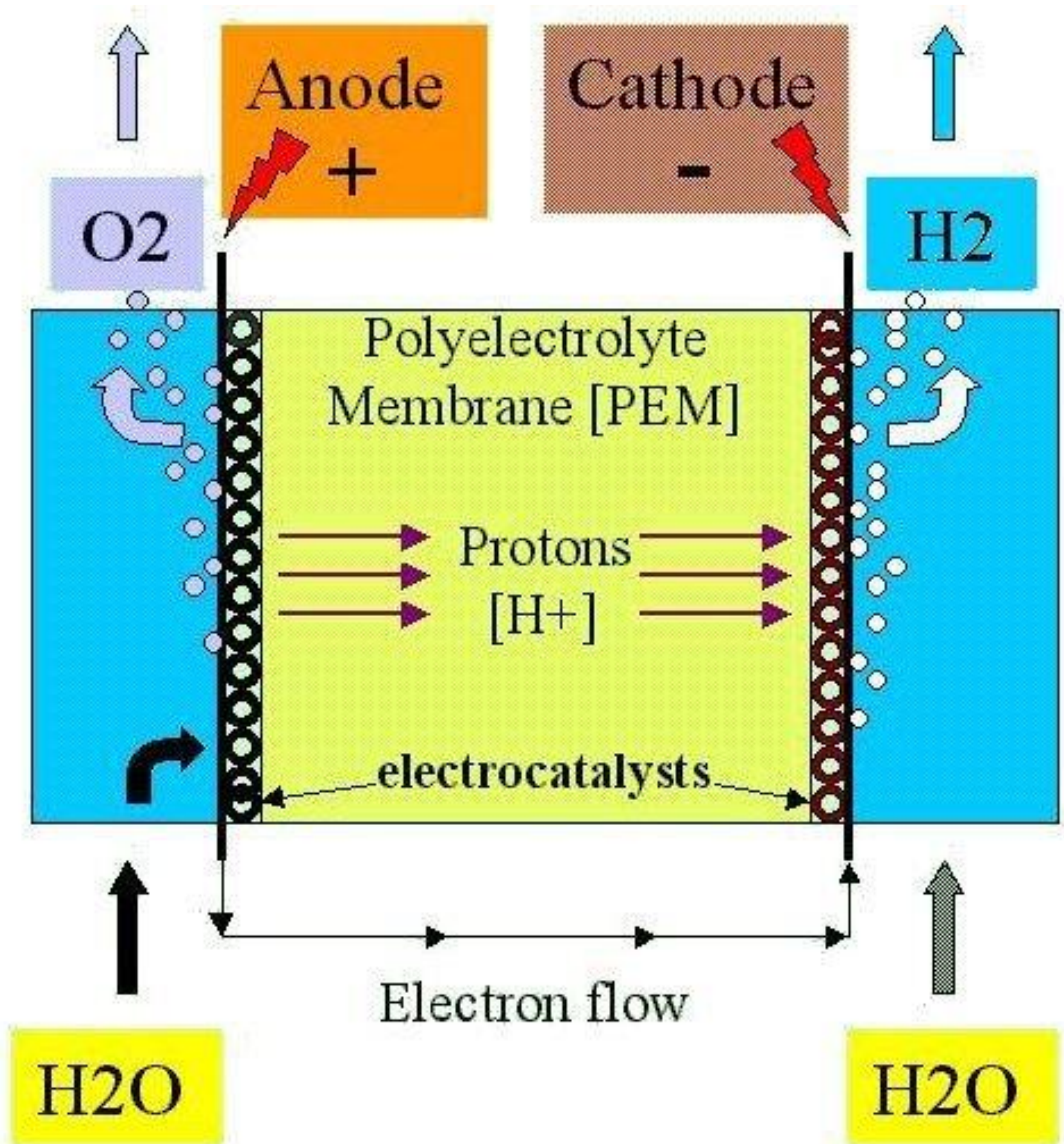
Electrolysers



Fuel cells

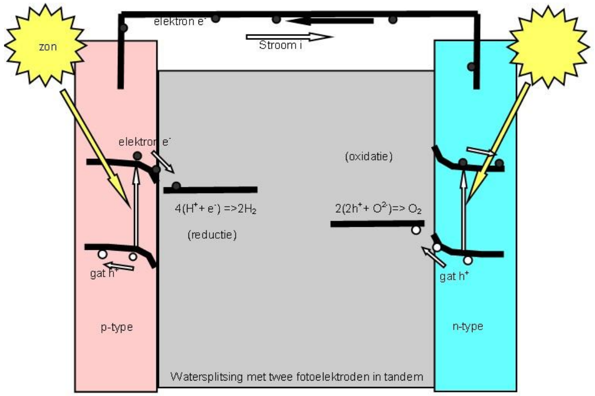
Its efficiency is a function primarily of *membrane* and *electrocatalyst* performance.

This becomes crucial under high-current operation, which is necessary for industrial-scale



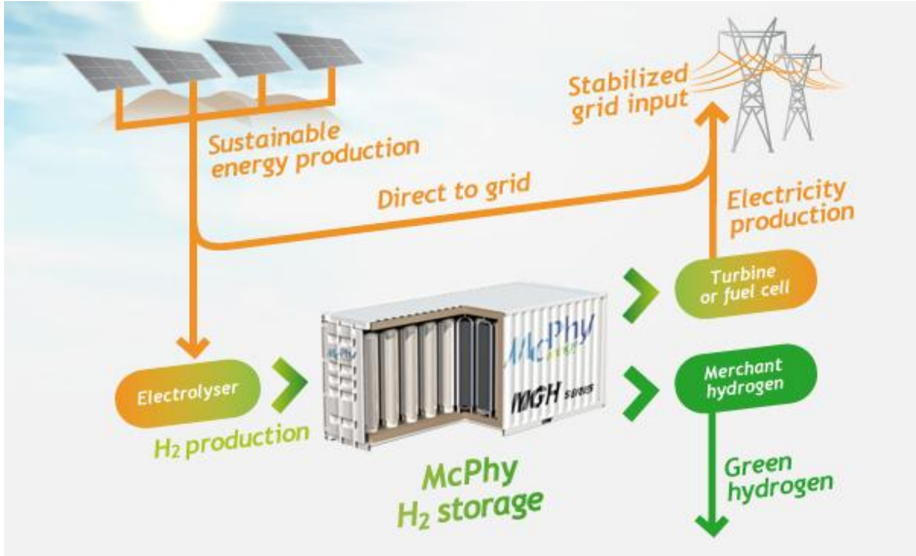
Photoelectrochemical cells

- In this type of photoelectrochemical cells, electrolysis of water to hydrogen and oxygen gas occurs when the anode is irradiated with electromagnetic radiation. This has been suggested as a way of converting solar energy into a transportable form, namely hydrogen. The photogeneration cells passed the 10 percent economic efficiency barrier.
- Lab tests confirmed the efficiency of the process. The main problem is the corrosion of the semiconductors which are in direct contact with water. Research is going on to meet the DOE requirement, a service life of 10000 hours.
- Photogeneration cells have passed the 10 percent economic efficiency barrier. Corrosion of the semiconductors remains an issue, given their direct contact with water.[5] Research is now ongoing to reach a service life of 10000 hours, a requirement established by the United States Department of Energy



How to store Hydrogen?

- Cylinders – compressed hydrogen
- Metal Hydrate Compounds
- Cryogenic storage
- Chemical Storage
- Carbon nanotube storage
- Glass Microspheres
- Liquid carrier storage



How is hydrogen stored?

Physical-based

- Compressed Gas

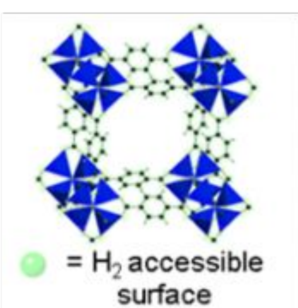
- Cold/Cryo Compressed

- Liquid H_2

Material-based

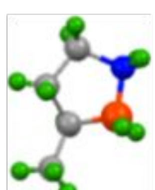
- Adsorbent

Ex. MOF-5



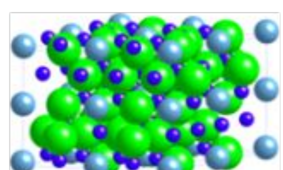
- Liquid organic

Ex. BN-methyl cyclopentane



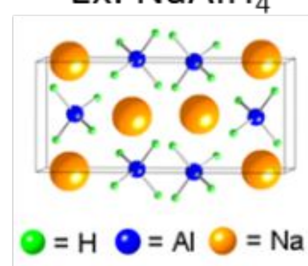
- Interstitial hydride

Ex. $LaNi_5H_6$



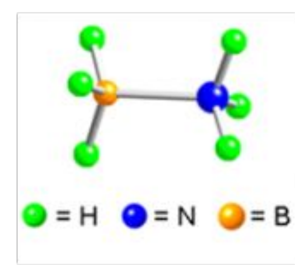
- Complex hydride

Ex. $NaAlH_4$



- Chemical hydrogen

Ex. NH_3BH_3

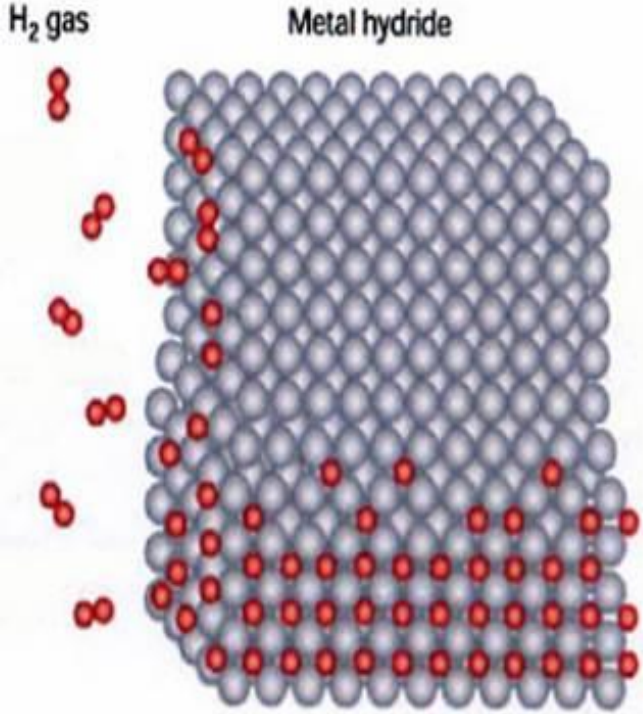


Cylinders – compressed hydrogen

- requires energy to acomplish
- lower energy density when compared to a traditional gasoline tank
- same energy content yields a tank that is 3,000 times bigger than the gasoline tank

Metal Hydrates

- MgH_2, $NaAlH_4$, $LiAlH_4$, LiH, $LaNi_5H_6$, $TiFeH_2$ and palladium hydride
- similar to a sponge, 1-2% of the weight.
- could reach to 5-7% if heated to 250°C
- delivering Hydrogen at a constant pressure.
- it also absorbs any impurities introduced into the tank by the hydrogen. The result is the hydrogen released from the tank is extremely pure, but the tank's lifetime and ability to store hydrogen is reduced as the impurities are left behind and fill the spaces in the metal that the hydrogen once occupied.

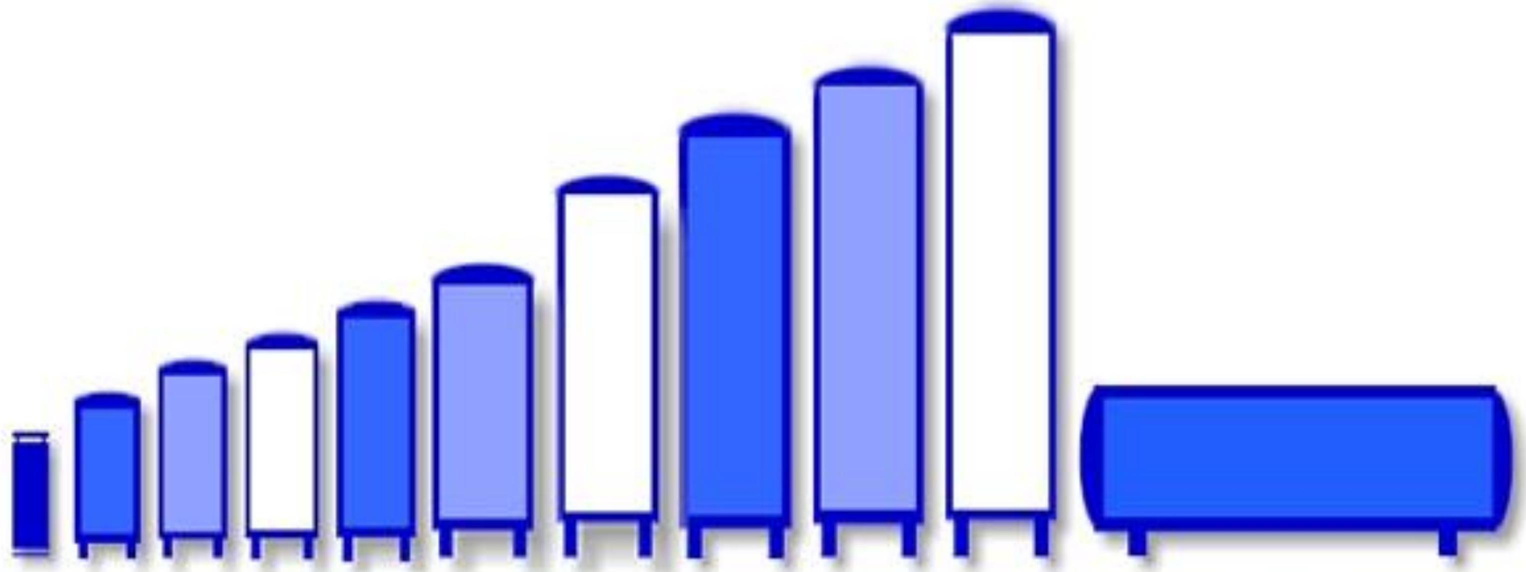


Cryogenic storage

- Liquid hydrogen typically has to be stored at 20º Kelvin or -253º C.
- again, necessitate spending energy to compress and chill the hydrogen into its liquid state, resulting in a net loss of about 30% of the energy that the liquid hydrogen is storing.
- a similar percentage will be due to the temperature gradient losses. Δt is usually > 270°C!
- Larger, composite material tanks would be beneficial.

Cryogenic storage

Typical Liquid (Cryogenic) Tank Size Storage Options (Liquid Phase Storage)



US Customary Units

(**typical values)											
Gallons	45	300	500	900	1,500	3,000	6,000	9,000	11,000	13,000	18,000
Diameter (inches)	20	48	48	60	60	96	96	120	120	120	144
Height (inches)	60	96	120	144	180	192	300	324	384	444	600 (Length)
Weight (Pounds, empty)	250	2,000	3,000	5,000	8,000	14,000	26,000	30,000	36,000	43,000	55,000
Design Pressure (PSIG)	200	200	200	200	200	200	200	200	200	200	200
Evaporation (%/day N2)	2.0	1.0	0.75	0.5	0.5	0.3	0.3	0.2	0.2	0.2	0.2

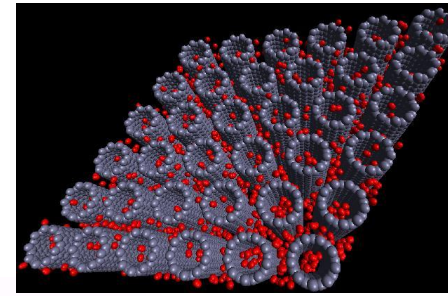
**Notes - Storage tank and size data are presented as "typical" for illustration purposes only. Users should refer to "actual" tank nameplates for design purposes.
- Free standing vaporizers are required to convert stored liquids to ambient temperature gases for gas phase applications.

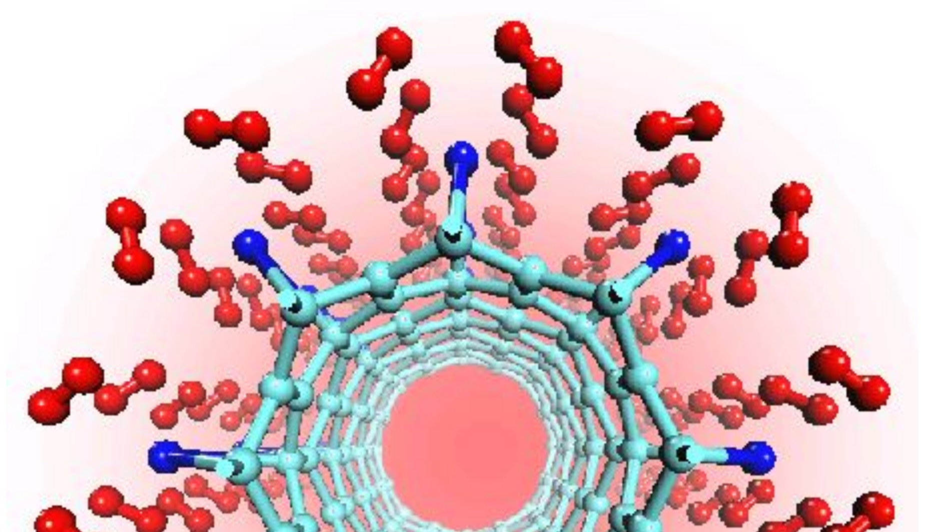
Chemical Storage

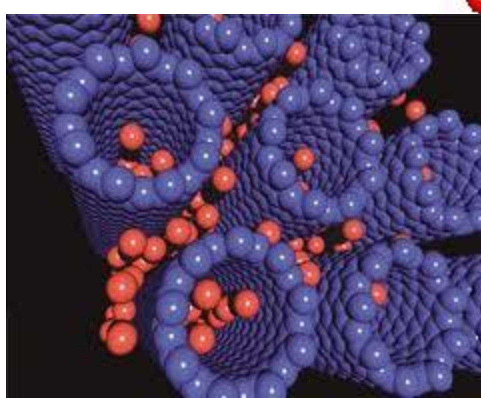
- Some examples of various techniques include ammonia cracking, partial oxidation, methanol cracking, etc. These methods eliminate the need for a storage unit for the hydrogen produced, where the hydrogen is produced on demand.
- Still in the research stage.

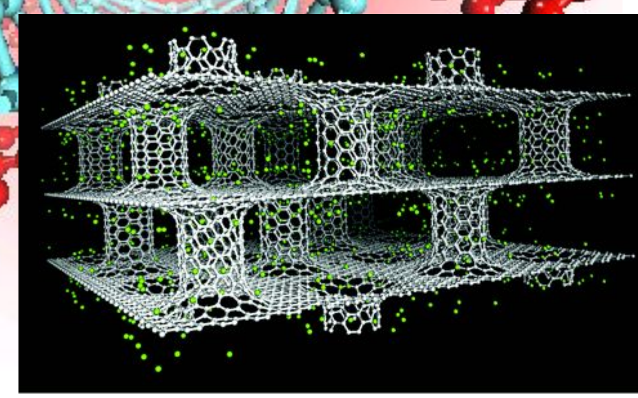
Carbon nanotube storage

- Carbon nanotubes are microscopic tubes of carbon, two nanometers (billionths of a meter) across, that store hydrogen in microscopic pores on the tubes and within the tube structures.
- 4.2% - to 65% of their own weight in hydrogen!



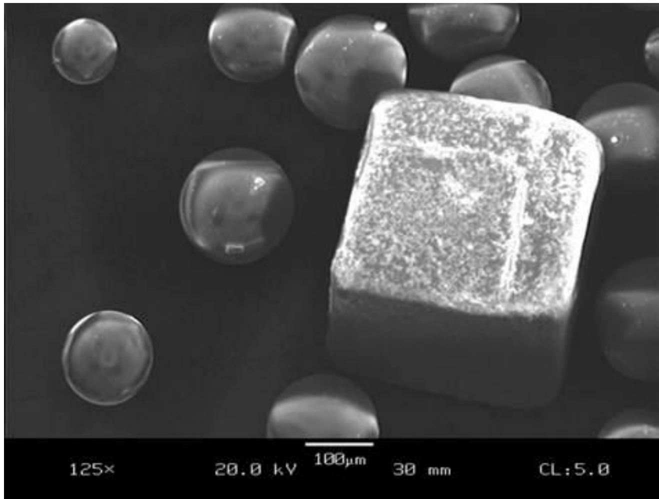






Glass Microspheres

- Tiny hollow glass spheres can be used to safely store hydrogen. The glass spheres are warmed, increasing the permeability of their walls, and filled by being immersed in high-pressure hydrogen gas.
- The spheres are then cooled, locking the hydrogen inside of the glass balls. A subsequent increase in temperature will release the hydrogen trapped in the spheres.
- Microspheres have the potential to be very safe, resist contamination, and contain hydrogen at a low pressure increasing the margin of safety.



Liquid Carrier (Carbohydrate) Storage

- This is the technical term for the hydrogen being stored in the fossil fuels that are common in today's society. Whenever gasoline, natural gas methanol, etc.. is utilized as the source for hydrogen, the fossil fuel requires reforming.
- The reforming process removes the hydrogen from the original fossil fuel.
- The reformed hydrogen is then cleaned of excess carbon monoxide, which can poison certain types of fuel cells, and utilized by the fuel cell.
- Reformers are currently in the beta stage of their testing with many companies having operating prototypes in the field.

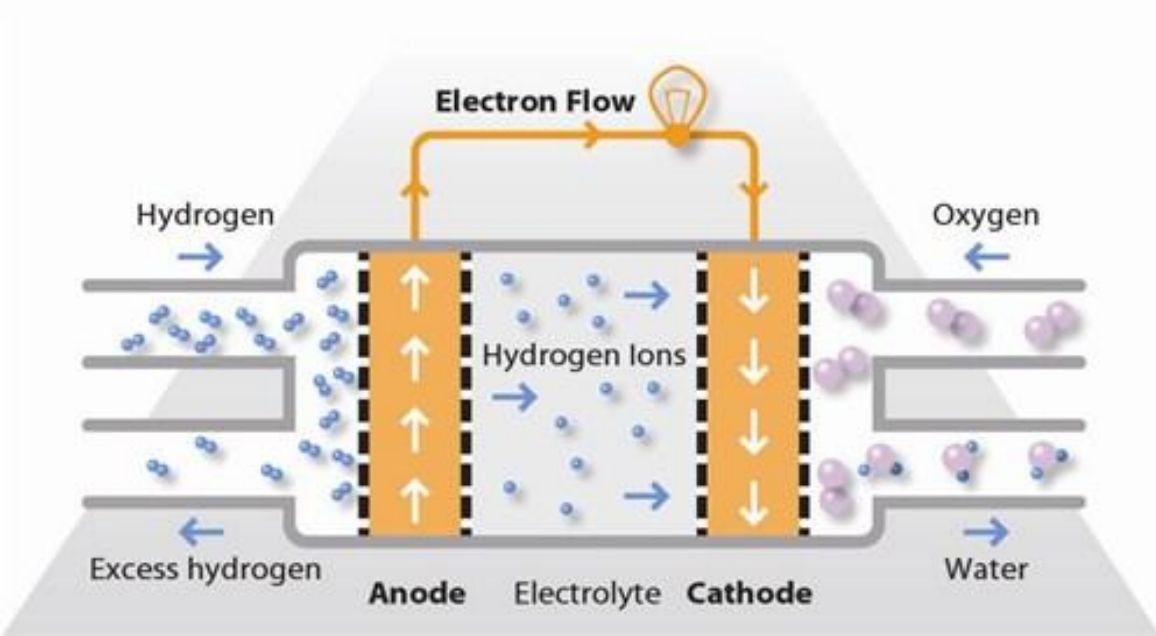
Hydrogen Safety

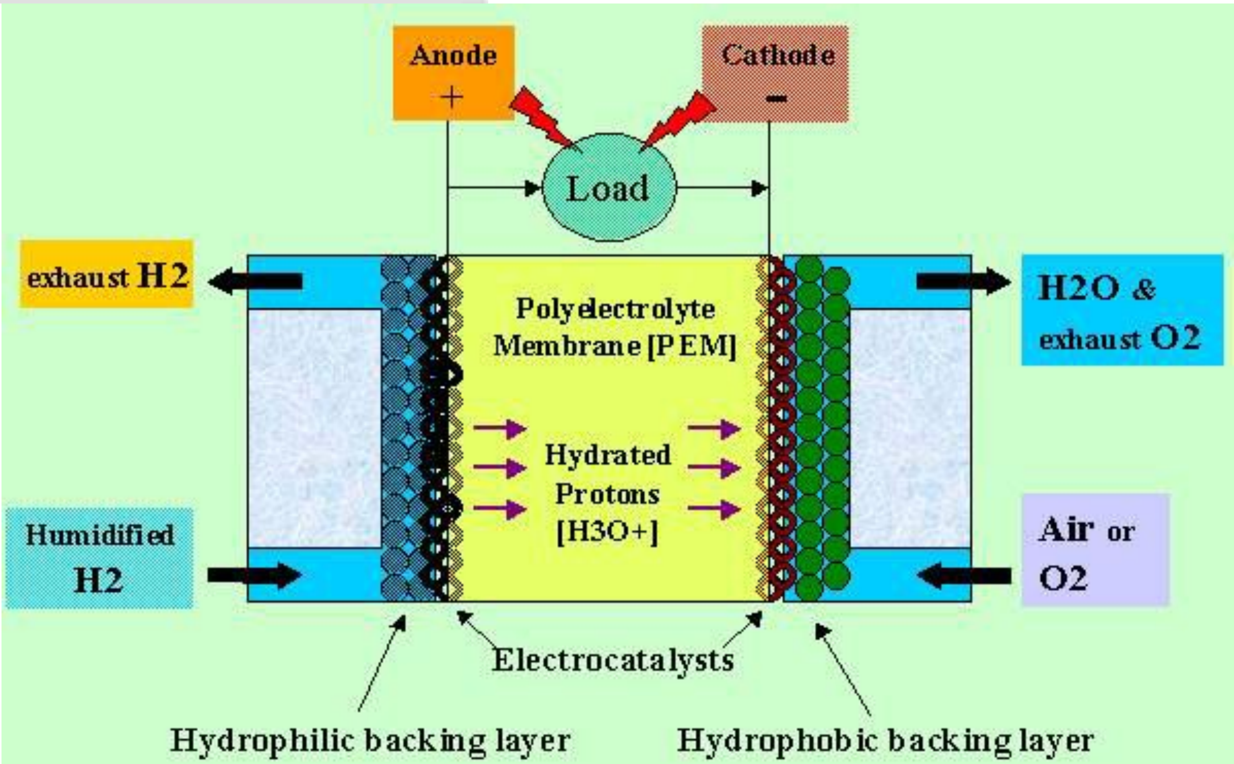
- The range of explosion proportion in air is rather wide, starting at 4%.
- Hydrogen is light – it goes up in atmosphere.
- Hydrogen molecules are small – they penetrate and escape from many situtations.

Hydrogen Use

- Internal Combustion Engines
- PEM Fuel Cells

PEM Fuel Cells

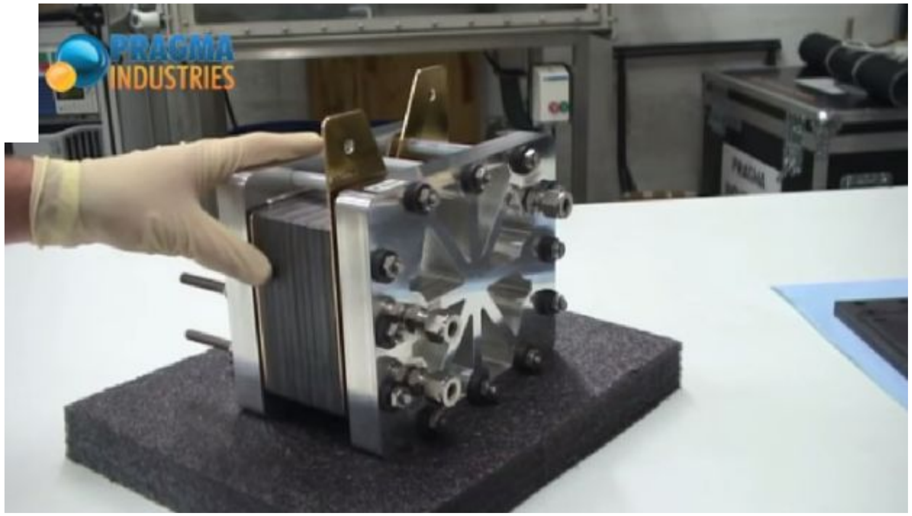


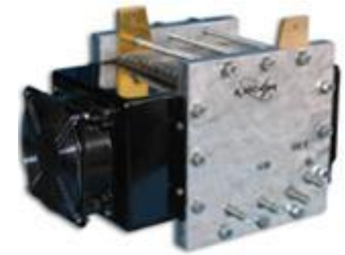


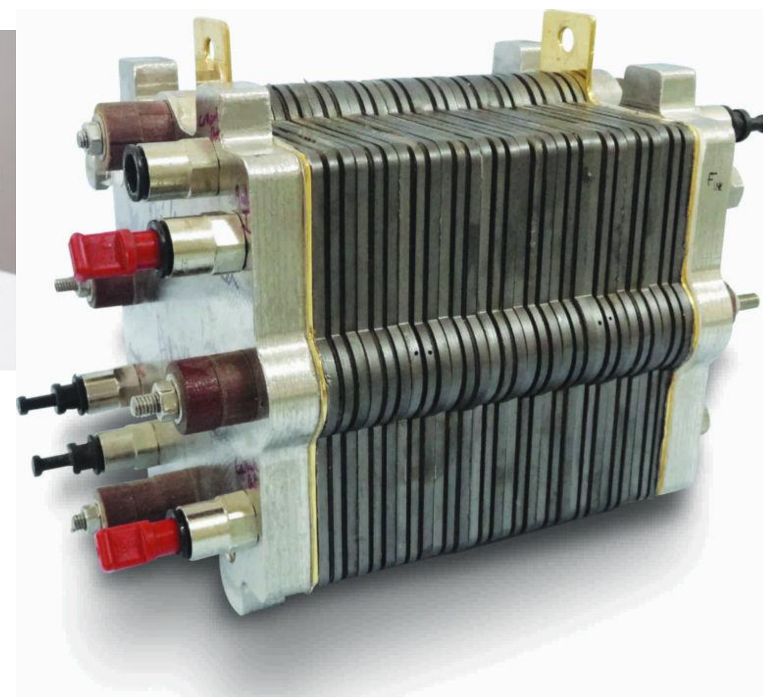
PEM Fuel Cells

- Acts like a battery, delivering electricity with efficiencies around 55%.
- This “battery” does not need to spend time on recharging! Whenever H_2 and O_2 (or humidified air) are supplied – it operates.
- The rest of the energy can theoretically be used – in a form of heat.
- Excellent way to provide distributed power and integrate with renewable sources.

PEM Fuel Cells







H2ECOnomy

Homework

1. Assume that a household needs 3 kW heating power on average of 24 hours during any day, during the 4.5 months of winter period. What kind of seasonal heat storage you may suggest (material, size, controllability, Δt, price)? Explain why and make the calculation.
2. Calculate the heat content **and** the daily amount of the hydrogen gas needed to power the daily need to run a fuel cell powered smartphone for 12 hours, 2.5W. Assume conversion efficiency of 43%.