Principles of Hydrogen Storage

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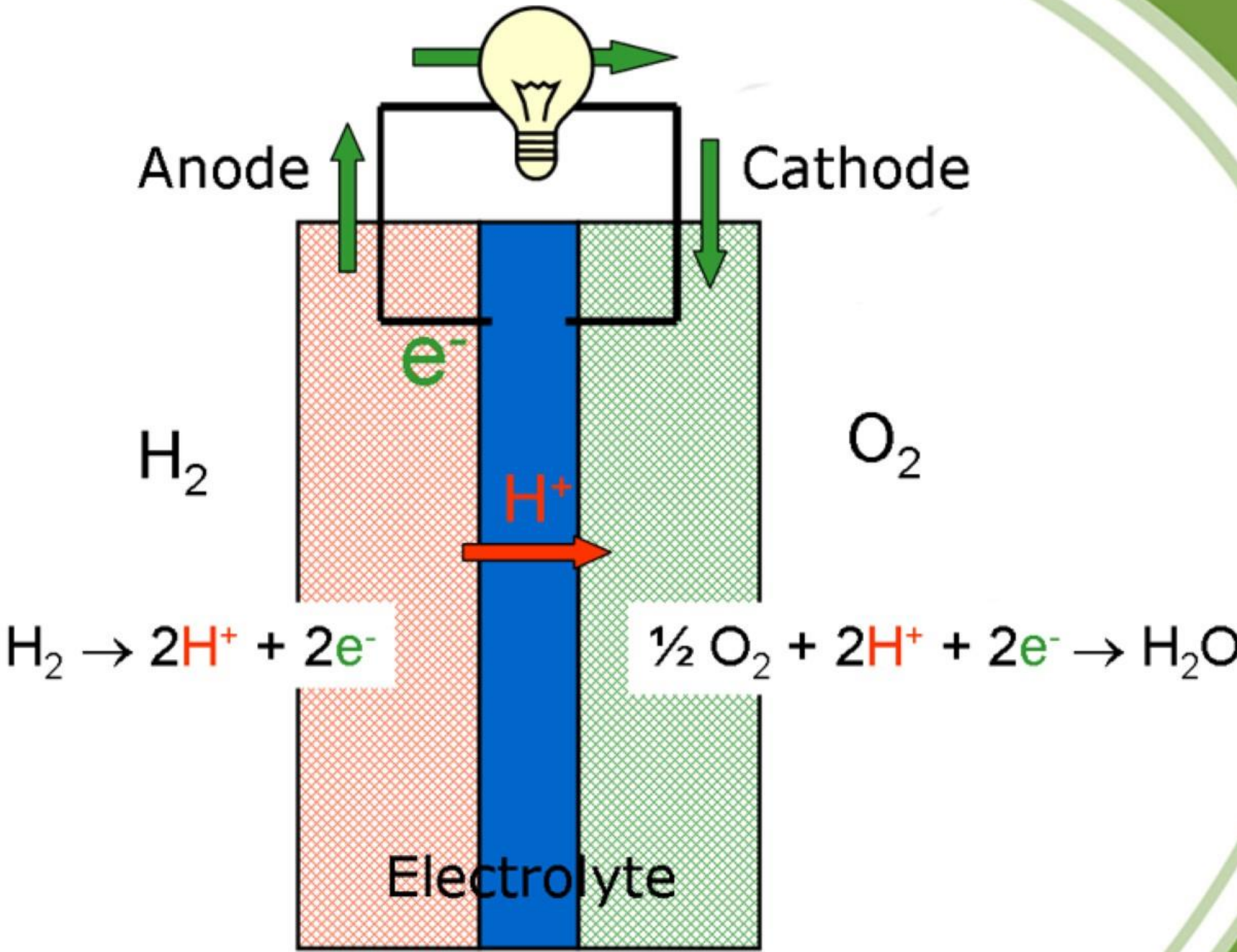
- Introduction
- Available Technologies

Hydrogen as a fuel

- It represents a environmentally clean energy source. The mass-related energy density of hydrogen is very high; 1 kg of hydrogen contains 120-133 MJ, which is approximately 2.5 times more energy than is contained in 1 kg of natural gas.
- Hydrogen is a promising energy carrier in future energy systems. However, storage of hydrogen is a substantial challenge, especially for applications in vehicles with fuel cells that use proton-exchange membranes (PEMs).



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

•Most abundant element in the universe representing 75 mass% or 90 vol%

•In the total water supply of the world is on the order of 10^{14} t

•In the atmosphere, only to the extent of less than 1 ppm (by volume).

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 **H** 1.00794(7)																	helium 2 **He** 4.002602(2)
lithium 3 **Li** 6.941(2)	beryllium 4 **Be** 9.012182(3)											boron 5 **B** 10.811(7)	carbon 6 **C** 12.0107(8)	nitrogen 7 **N** 14.0067(7)	oxygen 8 **O** 15.9994(3)	fluorine 9 **F** 18.9984032(5)	neon 10 **Ne** 20.1797(6)
sodium 11 **Na** 22.989770(2)	magnesium 12 **Mg** 24.3050(6)											aluminium 13 **Al** 26.981538(2)	silicon 14 **Si** 28.0855(3)	phosphorus 15 **P** 30.973761(2)	sulfur 16 **S** 32.065(5)	chlorine 17 **Cl** 35.453(2)	argon 18 **Ar** 39.948(1)
potassium 19 **K** 39.0983(1)	calcium 20 **Ca** 40.078(4)	scandium 21 **Sc** 44.955910(8)	titanium 22 **Ti** 47.867(1)	vanadium 23 **V** 50.9415(1)	chromium 24 **Cr** 51.9961(6)	manganese 25 **Mn** 54.938049(9)	iron 26 **Fe** 55.845(2)	cobalt 27 **Co** 58.933200(9)	nickel 28 **Ni** 58.6934(4)	copper 29 **Cu** 63.546(3)	zinc 30 **Zn** 65.38(2)	gallium 31 **Ga** 69.723(1)	germanium 32 **Ge** 72.64(1)	arsenic 33 **As** 74.92160(2)	selenium 34 **Se** 78.96(3)	bromine 35 **Br** 79.904(1)	krypton 36 **Kr** 83.798(2)
rubidium 37 **Rb** 85.4678(3)	strontium 38 **Sr** 87.62(1)	yttrium 39 **Y** 88.90585(2)	zirconium 40 **Zr** 91.224(2)	niobium 41 **Nb** 92.90638(2)	molybdenum 42 **Mo** 95.96(2)	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07(2)	rhodium 45 **Rh** 102.90550(2)	palladium 46 **Pd** 106.42(1)	silver 47 **Ag** 107.8682(2)	cadmium 48 **Cd** 112.411(8)	indium 49 **In** 114.818(3)	tin 50 **Sn** 118.710(7)	antimony 51 **Sb** 121.760(1)	tellurium 52 **Te** 127.60(3)	iodine 53 **I** 126.90447(3)	xenon 54 **Xe** 131.293(6)
caesium 55 **Cs** 132.90545(2)	barium 56 **Ba** 137.327(7)	lutetium 71 **Lu** 174.9668(1)	hafnium 72 **Hf** 178.49(2)	tantalum 73 **Ta** 180.9479(1)	tungsten 74 **W** 183.84(1)	rhenium 75 **Re** 186.207(1)	osmium 76 **Os** 190.23(3)	iridium 77 **Ir** 192.217(3)	platinum 78 **Pt** 195.078(2)	gold 79 **Au** 196.96655(2)	mercury 80 **Hg** 200.59(2)	thallium 81 **Tl** 204.3833(2)	lead 82 **Pb** 207.2(1)	bismuth 83 **Bi** 208.98038(2)	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [267]	dubnium 105 **Db** [268]	seaborgium 106 **Sg** [271]	bohrium 107 **Bh** [272]	hassium 108 **Hs** [270]	meitnerium 109 **Mt** [276]	darmstadtium 110 **Ds** [281]	roentgenium 111 **Rg** [280]	ununbium 112 **Uub** [285]	ununtrium 113 **Uut** [284]	ununquadium 114 **Uuq** [289]	ununpentium 115 **Uup** [288]	ununhexium 116 **Uuh** [293]	ununseptium 117 **Uus** —	ununoctium 118 **Uuo** [294]

Key:

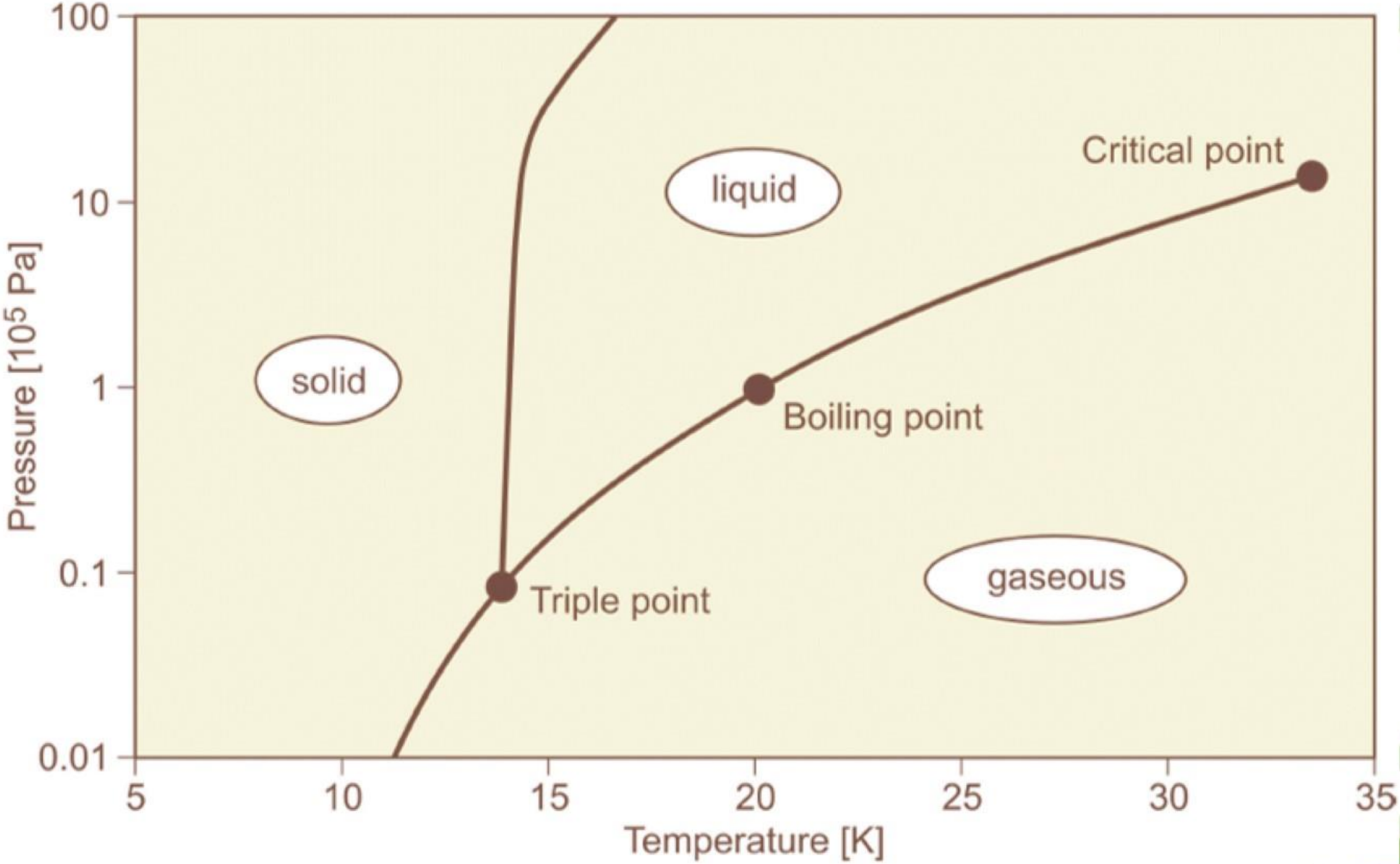
element name atomic number **symbol** 2003 atomic weight (mean relative mass)

Lanthanoids	lanthanum 57 **La** 138.9055(2)	cerium 58 **Ce** 140.116(1)	praseodymium 59 **Pr** 140.90765(2)	neodymium 60 **Nd** 144.24(3)	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36(3)	europium 63 **Eu** 151.964(1)	gadolinium 64 **Gd** 157.25(3)	terbium 65 **Tb** 158.92534(2)	dysprosium 66 **Dy** 162.500(1)	holmium 67 **Ho** 164.93032(2)	erbium 68 **Er** 167.259(3)	thulium 69 **Tm** 168.93421(2)	ytterbium 70 **Yb** 173.054(5)
Actinoids	actinium 89 **Ac** [illegible]	thorium 90 **Th** [illegible]	protactinium 91 **Pa** [illegible]	uranium 92 **U** [illegible]	neptunium 93 **Np** [illegible]	plutonium 94 **Pu** [illegible]	americium 95 **Am** [illegible]	curium 96 **Cm** [illegible]	berkelium 97 **Bk** [illegible]	californium 98 **Cf** [illegible]	einsteinium 99 **Es** [illegible]	fermium 100 **Fm** [illegible]	mendelevium 101 **Md** [illegible]	nobelium 102 **No** [illegible]

Physical properties

- At STP conditions, it is a colorless, odorless, tasteless, non-toxic, noncorrosive, non-metallic diatomic gas
- Most important characteristics is its low density
- Leakage rates are by a factor of 50 higher than for water and by a factor of 10 compared to Nitrogen.
- It is positively buoyant above a temperature of 22 K

Parameter	Hydrogen
Molecular weight [g/mol]	2.01594
Stoichiometric fraction in air [vol%]	29.53
Boiling point (BP) [K]	20.268
Melting point (MP) [K]	14.01
Triple point: Temperature [K]	13.8
Pressure [kPa]	7.2
Critical point: Temperature [K]	33.25
Pressure [MPa]	1.297
Density [kg/m^3]	31.4
Electronegativity [Pauling scale]	2.20
Density of gas @ NTP [2] [kg/m^3]	0.08345
gas @ STP [1] [kg/m^3]	0.08990
gas @ BP [kg/m^3]	1.338
liquid @ BP [kg/m^3]	70.78
solid @ 4 K [kg/m^3]	88.0
Expansion ratio liquid/ambient	845
Diffusion coefficient @ NTP [2] [m^2/s]	$0.61*10^{-4}$
Diffusion velocity @ NTP [2] [m/s]	< 0.02
Buoyant velocity [m/s]	1.2 - 9
Specific heat (constant p) of gas @ NTP [2] [kJ/(kg K)]	14.85
gas @ STP [1] [kJ/(kg K)]	14.304
gas @ BP [kJ/(kg K)]	12.15
liquid @ BP [kJ/(kg K)]	9.66


100
10
1
0.1
0.01
Pressure [10^5 Pa]
5
10
15
20
25
30
35
Temperature [K]
solid
liquid
gaseous
Critical point
Boiling point
Triple point

Available Technologies

- CGH_2 (compressed gaseous hydrogen), 35–70 MPa, room temperature

- LH_2 (liquid hydrogen), 0.1–1 MPa,- 253 ^0C

- Cryoadsorption on high-surface-area materials, 0.2– 0.5 MPa, -193 ^0C

Liquid hydrogen	Cryo-adsorption	Interstitial metal hydride	Compressed hydrogen	Alanate	Salt-like metal hydride	Water
LH2	Activated carbon	Laves Phase Comp./ $FeTiH_x$ / $LaNi_5H_x$	CGH2	$NaAlH_4$	MgH_2	H_2O
100 mat.wt%	6.5 mat.wt%	2 mat.wt%	100 mat.wt%	5.5 mat.wt%	7.5 mat.wt%	11 mat.wt%

Operating temperature

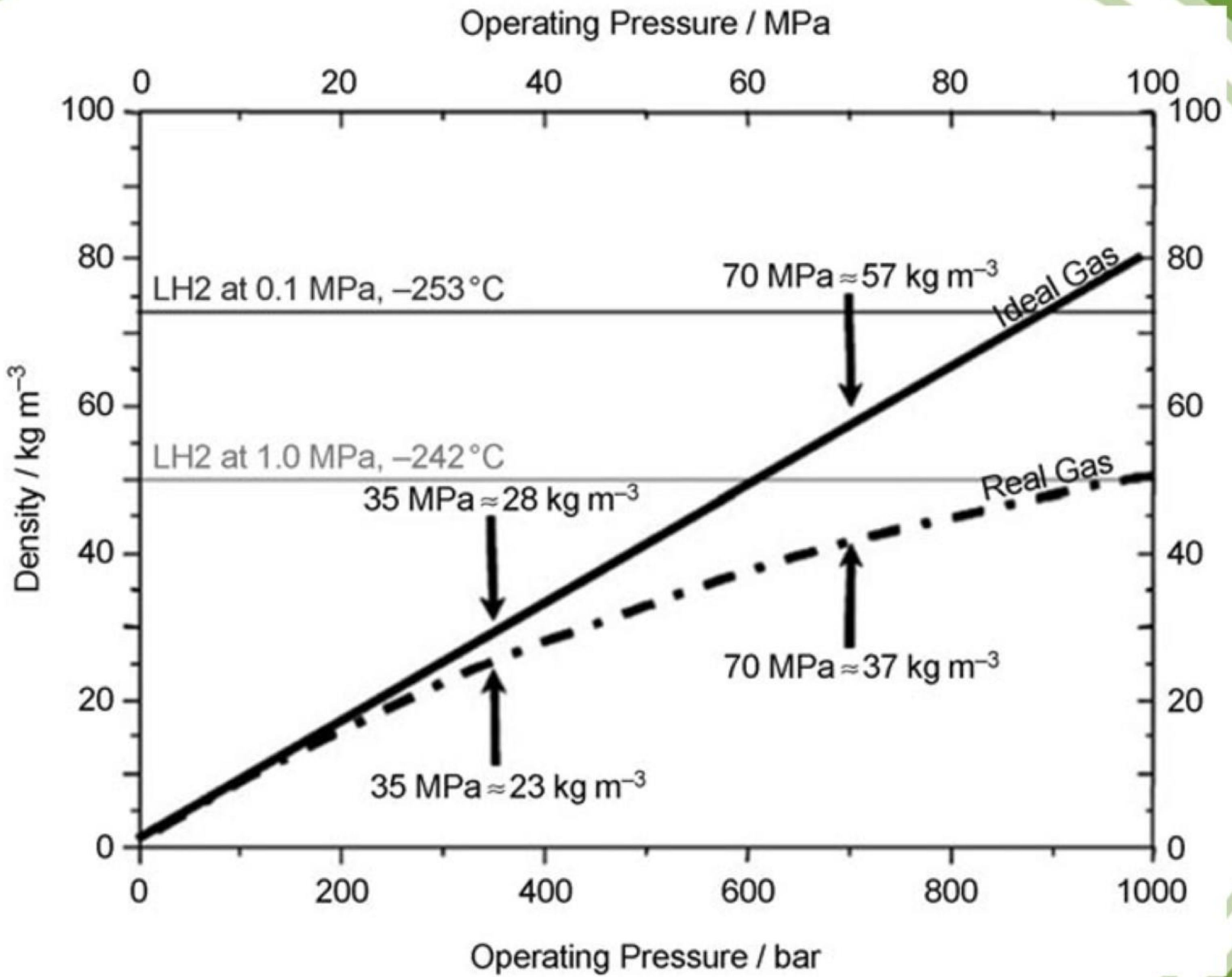
-253°C	› -200°C	0 - 30°C	25°C	70 - 170°C	330°C	›› 1000°C

Corresponding energy to release hydrogen in MJ per kg H_2

0.45	3.5	15	n/a	23	37	142

Compressed Gaseous Hydrogen

- To achieve vehicles with a range of about 500 km, it is necessary to store about 5–6 kg of hydrogen on board the car.
- Mechanical work to compress hydrogen is approximately 18 MJ per kg of hydrogen at 70 MPa, or 14.5 MJ per kg at 35 MPa.
- 0.048 kg H_2 per kg tank weight and 0.023 kg H_2 per liter tank volume. Together with the requirement of a cylindrical design (caused by the large operating pressures of about 35– 70 MPa), the integration of such a tank into existing car architectures remains an important challenge
- Three-vessel carbon composite unit to store 4.2 kg of hydrogen at 70 MPa weighs 135 kg (the weight of a similar steel system would be 600 kg)
- Refill an empty CGH2 system completely within three minutes.

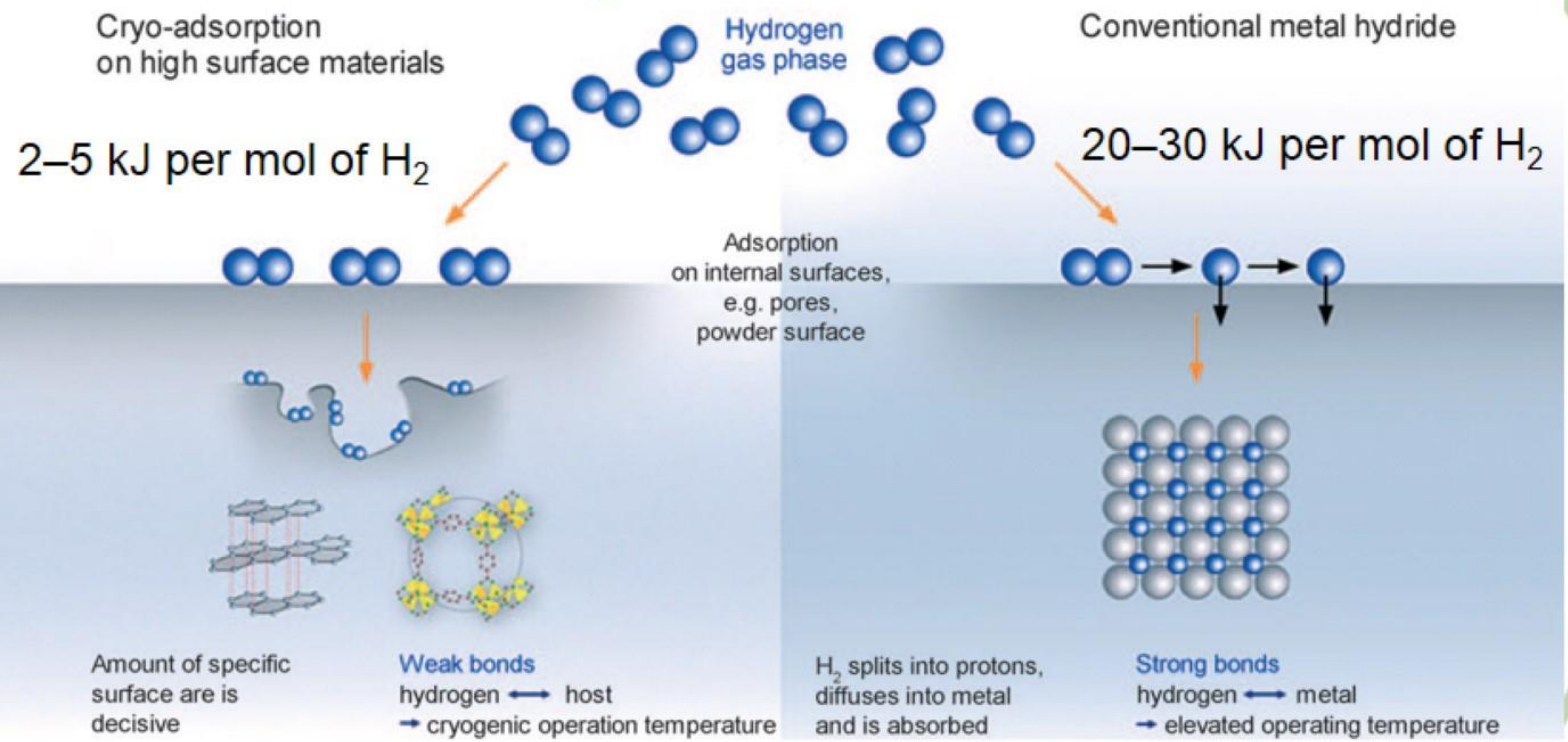

Operating Pressure / MPa
0
20
40
60
80
100
100
80
60
40
20
0
Density / kg m^{-3}
LH2 at 0.1 MPa, –253 °C
LH2 at 1.0 MPa, –242 °C
70 MPa ≈ 57 kg m^{-3}
Ideal Gas
Real Gas
35 MPa ≈ 28 kg m^{-3}
70 MPa ≈ 37 kg m^{-3}
35 MPa ≈ 23 kg m^{-3}
0
200
400
600
800
1000
Operating Pressure / bar

Liquid Hydrogen

- Potential advantage of LH_2 systems is the high mass density of hydrogen at -253 C and 0.1 MPa.
- The energy required to liquefy hydrogen already consumes 30% of the chemical energy stored
- Very low phase-change enthalpy of about 0.45 MJ per kg of H_2 between the liquid and gaseous state
- Heat flowing from the environment into the tank vessel leads to an evaporation of the hydrogen (boil- off) and increasing pressure within the tank
- On-board- and infrastructure-related, lead to unacceptable hydrogen losses.

(Cryo-)Adsorption

Adsorption is an exothermic reaction
Desorption is an endothermic reaction



General Considerations

- Typical adsorption enthalpies for hydrogen on adsorbents such as carbon or metal–organic frameworks are in the order of 2–5 kJ per mol of hydrogen.
- For Nitrogen, the heat of vaporization is 5.6 kJ per mol of N_2.
- Considering a heat of adsorption of 2 MJ per kg of H_2 , we would need 2200 moles of N_2 corresponding to 80 kg liquid nitrogen would be needed.
- About 200 kg of liquid nitrogen would be necessary if the heat of adsorption would be close to the higher values of 5 MJ per kg of H_2

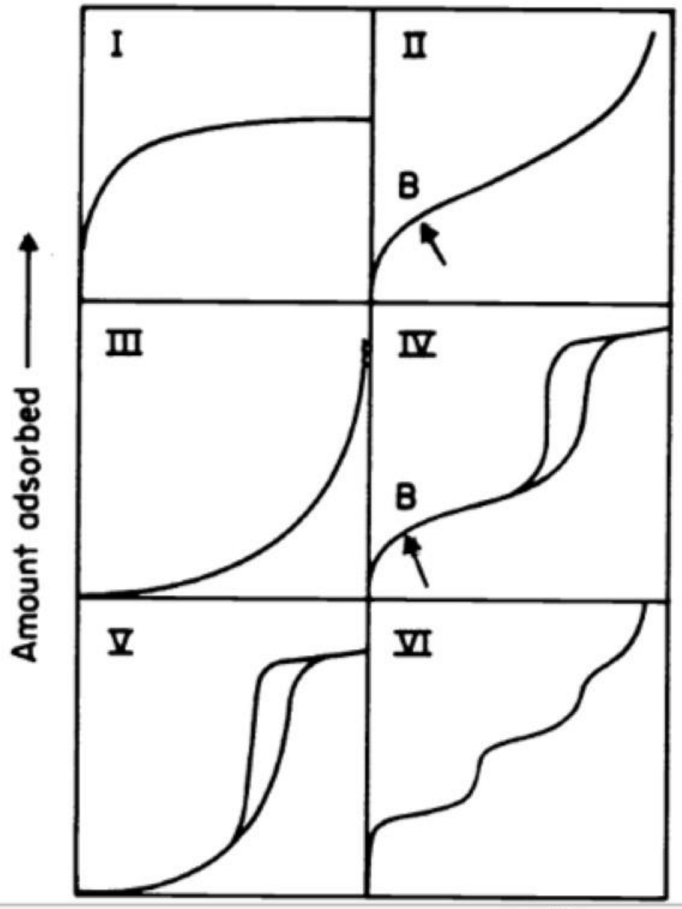
IUPAC (international union for pure and applied chemistry)classification on pores

- Macroporous (>50nm)
- Mesoporus (2-50nm)
- Microporus (<2nm)
- Generally, the hydrogen uptake is limited by both the specific surface area, with a proportionality constant of $1.9\text{x}10^{-2}$ wt % g m^{-2} , and by the pore structure and sizes of the adsorbents.
- Ideal materials have a high surface area and pores in the micropore range; ideally below 1 nm.

Adsorption Isotherms

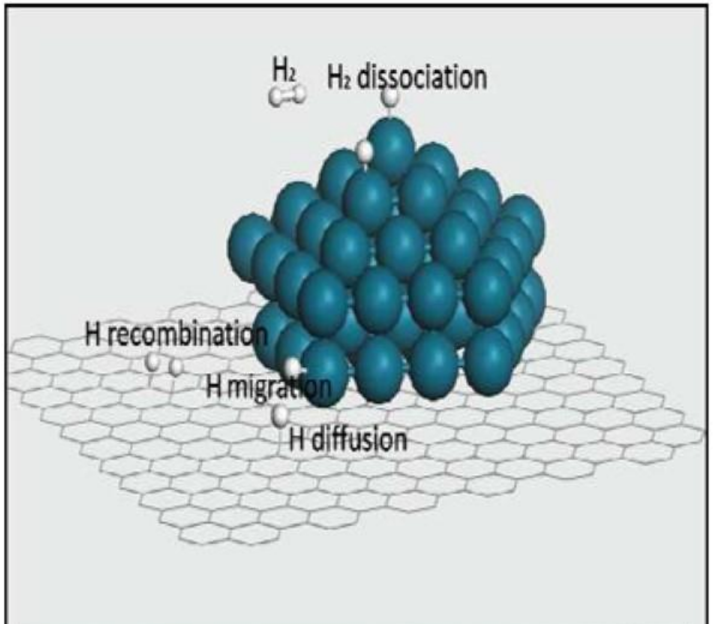
- An Adsorption Isotherm is obtained by measuring the amount of gas adsorbed across a wide range of relative pressures at a constant temperature (typically liquid N_2, 77K). Conversely desorption Isotherms are achieved by measuring gas removed as pressure is reduced
- 5 Classical Iostherm types described by Brunauer, Deming, Deming and Teller.

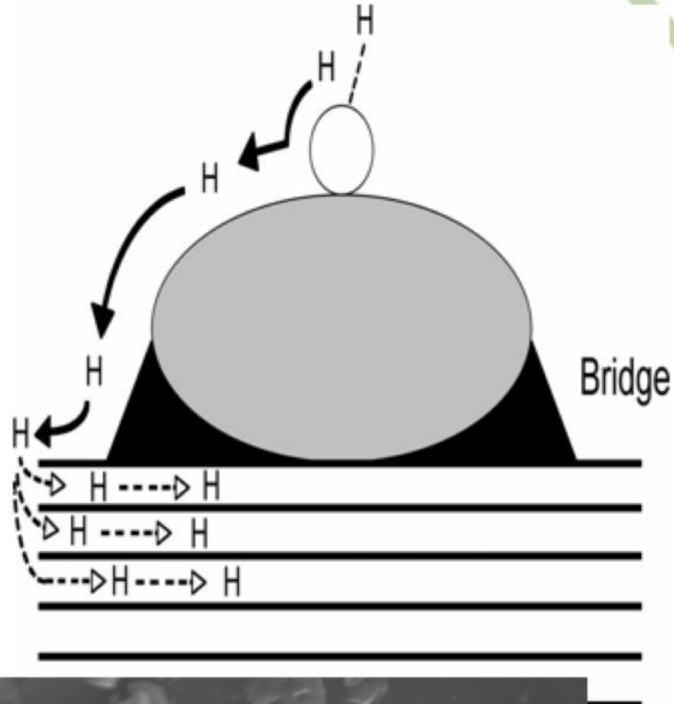
Different types of Adsorption Isotherms

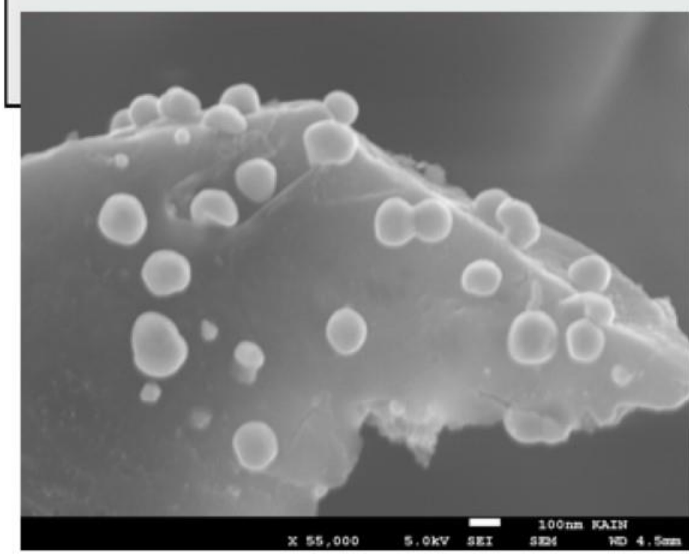


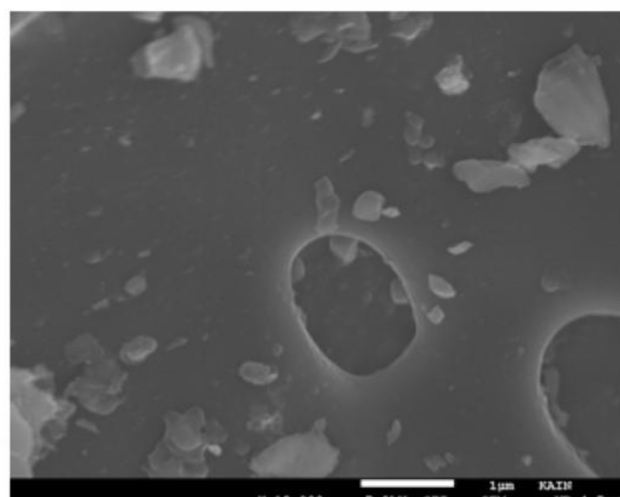
- Type I isotherms are given by microporous solids having relatively small external surfaces (e.g. activated carbons, molecular sieve zeolites and certain porous oxides), the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area.
- The Type II isotherm represents unrestricted monolayer-multilayer adsorption. Point B , the beginning of the almost linear middle section of the isotherm, is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption about to begin.
- Type III isotherm is convex over its entire range and therefore does not exhibit a Point B. In such cases , the adsorbent- adsorbate interactions play an important role.
- Type IV , its hysteresis loop is associated with capillary condensation taking place in mesopores
- The Type V isotherm is uncommon; it is related to the Type III isotherm in that the adsorbent- adsorbate interaction is weak
- The Type VI isotherm, in which the sharpness of the steps depends on the system and the temperature, represents stepwise multilayer adsorption on a uniform non-porous surface.

Promoting by Spillover









- cryoadsorption is still in the development phase, and significantly improved hydrogen adsorber materials are needed.
- it shows a way of tackling the drawbacks of LH_2 systems as the respective phase-change energy is an order of magnitude greater than that of liquid hydrogen.
- It can revolutionize hydrogen storage if adsorber materials are discovered in the near future with 10 wt% or more excess capacity at -196 C and approximately 2–3 MPa.

Many Thanks

- Questions ?