UNIVERSITÀ
DEGLI STUDI
DI TRIESTE

Dipartimento di
Ingegneria
e Architettura

HYDROGEN STORAGE

– PART 3 –

SOLID-STATE HYDROGEN STORAGE

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A.A. 2023-2024

OUTLINE

1. Solid State Hydrogen Storage
2. Hydrogen Physisorption
3. Hydrogen Chemisorption
4. Tanks for Solid Hydrogen Storage

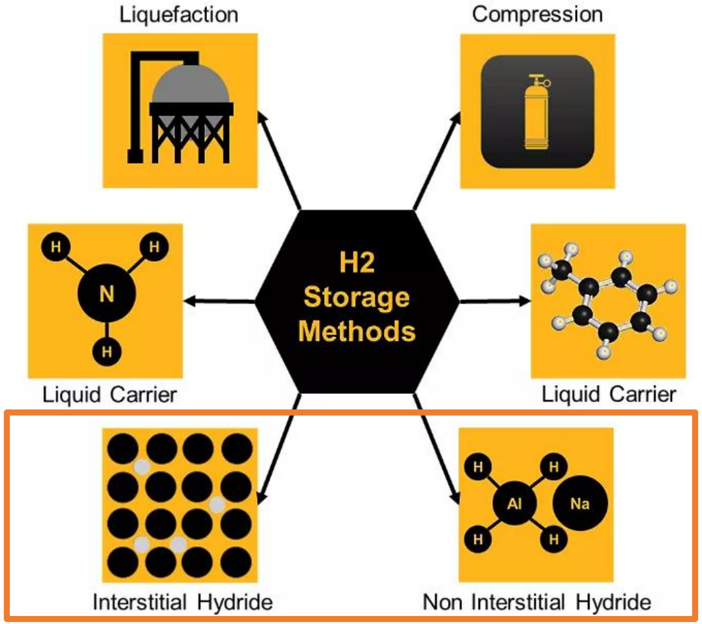
BIBLIOGRAPHY

Reference	Paragraph/Pages
Handbook of Hydrogen Storage, Michael Hirscher, 2010 Wiley	Ch. 2 and 4

Insights	
R1	Zhou W. et al., Hydrogen and Methane Adsorption in Metal-Organic Frameworks: A High-Pressure Volumetric Study, J. Phys. Chem. C 2007, 111, 16131-16137; DOI: https://doi.org/10.1039/D2SE00618A
R2	Swenson H., Stadie N., Langmuir's Theory of Adsorption: A Centennial Review, Langmuir 2019, 35, 5409−5426. DOI: https://doi.org/10.1021/acs.langmuir.9b00154
R3	Majid N., Progress in filtration and separation - ch14 - surface area: BET, 585-608, Academic Press, (2015); DOI: https://doi.org/10.1016/B978-0-12-384746-1.00014-8
R4	Lototskyy M.V. et al., Metal hydride systems for hydrogen storage and supply for stationary and automotive low temperature PEM fuel cell power modules, International Journal of Hydrogen Energy, 40, 35, (2015), 11491-11497; DOI: https://doi.org/10.1016/j.ijhydene.2015.01.095
R5	Afzal M. et al., Heat transfer techniques in metal hydride hydrogen storage: A review, International Journal of Hydrogen Energy, 42, 52, (2017), 30661-30682; DOI: https://doi.org/10.1016/j.ijhydene.2017.10.166

0. HYDROGEN STORAGE

HYDROGEN STORAGE METHODS

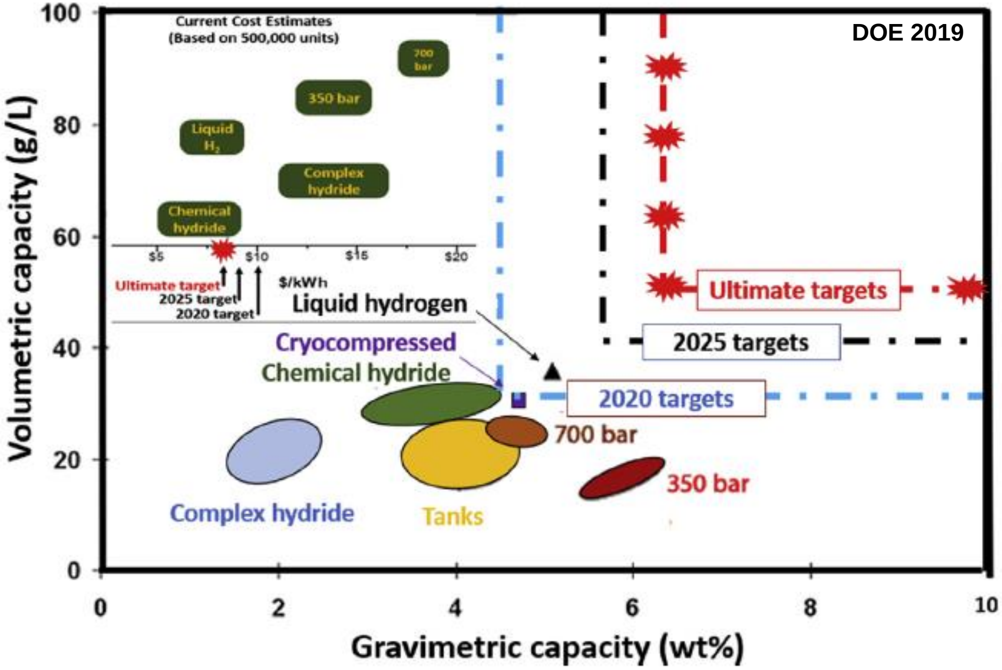


https://wildeanalysis.co.uk/resource/time-right-for-hydrogen/

1. SOLID-STATE HYDROGEN STORAGE

INTRODUCTION

In principle, solid-state hydrogen storage can be potentially superior to its compression or liquefaction. The interest in storing hydrogen as a metal hydride is particularly attracting for the automotive sector and mobile applications, where high gravimetric and volumetric storage capacities are particularly critical.



E. Boateng, A. Chen / Materials Today Advances 6 (2020) 100022

INTRODUCTION

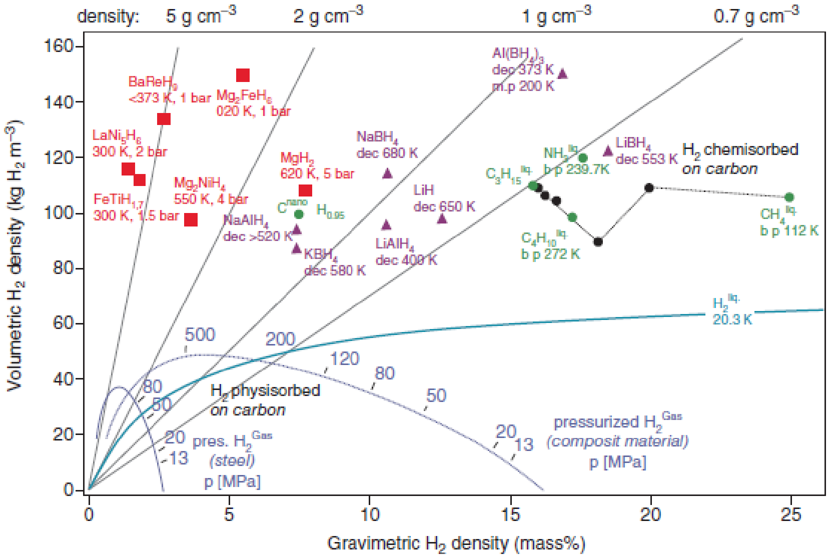
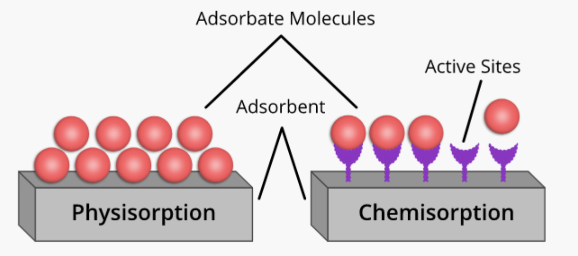


Figure 7.10 Volumetric and gravimetric hydrogen density of some selected hydrides [2].

Although several compounds can be theorized being competitive in terms of gravimetric and volumetric hydrogen storage densities, their potential fades out when widening the view to a system level. In addition, there are several other factors that severely limit or prevent their practical application, such as non-reversibility / cyclability, thermodynamic barriers and slow kinetics of hydrogen uptake/release

CHEMI-PHYSICAL PROCESSES FOR HYDROGEN BOUNDING



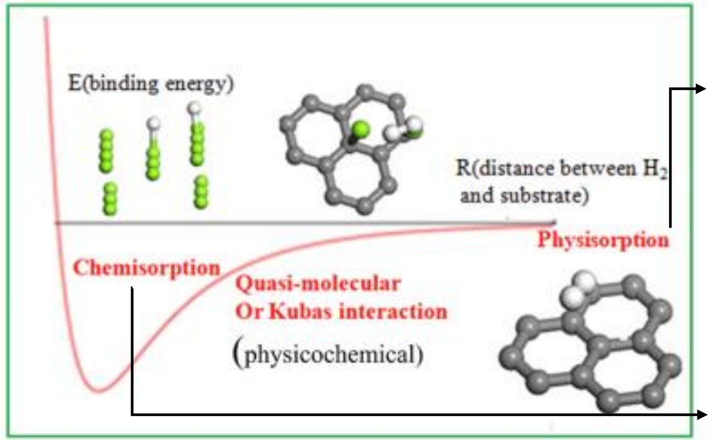
Physisorption	Chemisorption
H_2 is adsorbed at the surface by Van der Waals interactions	H_2 is chemically held into reaction sites by chemical (covalent) bonds
In order to get adsorbed, the hydrogen molecule needs to be displaced in close contact with the surface (around one molecular radius)	Storing and release requires bond formation or breaking energy
It takes place (significantly) below 0°C (273 K) and/or at high pressures	It takes place at high temperatures
Completely reversible; no activation energy is needed	Activation energy is required
Hydrogen can be stored in multilayers	Monolayer phenomenon
Hydrogen molecules are not dissociated	

CHEMI-PHYSICAL PROCESSES FOR HYDROGEN BOUNDING

It is possible to discriminate among these three methods of hydrogen bonding depending on the energy of interaction involved:

$$E = \frac{\beta_{H_2}\beta_S}{R^6}$$

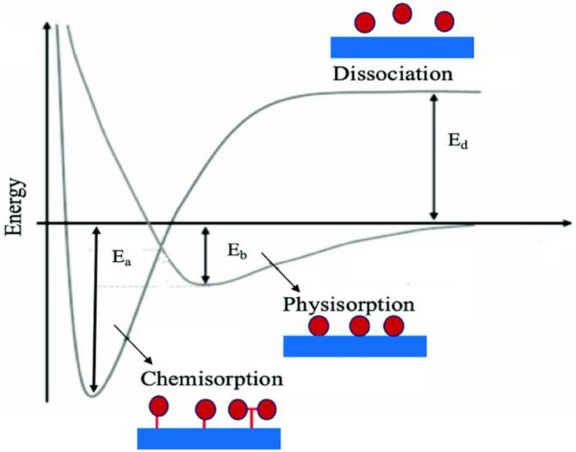
Where β_{H_2} is the polarizability of the hydrogen molecule, β_S is the polarizability of the sorbent, and R is the interaction distance.



Long-range interaction
H_2 in gas form
$E \sim 0.04 - 0.11\ eV$
$\bar{R}_{H_2-subst.} \geq 2.5$ Å
$L_{H_2\ bond} = 0.76$ Å

Short-range interaction
H_2 is dissociated
$E \sim 0.52 - 1.04\ eV$
$\bar{R}_{H_2-subst.} \leq 2.5$ Å
$L_{H_2\ bond} = 0.76$ Å

Faye O., et al., International Journal of Hydrogen Energy, 47, 29, (2022), 13771-13802



Farrukh S., et al., Nanotechnology and the generation of sustainable hydrogen. green energy and technology, (2021), Springer

2. HYDROGEN PHYSISORPTION

PHYSISORPTION

Hydrogen is bound to the sorbent material in molecular form without being dissociated, and by means of van der Waal forces developing between the gas molecules and the atoms on the surface of the solid. These intermolecular forces derive from the interaction between temporary dipoles which are formed due to the fluctuations in the charge distribution in molecules and atoms.

The potential of interaction is described by means of the Lennard-Jones equation:

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

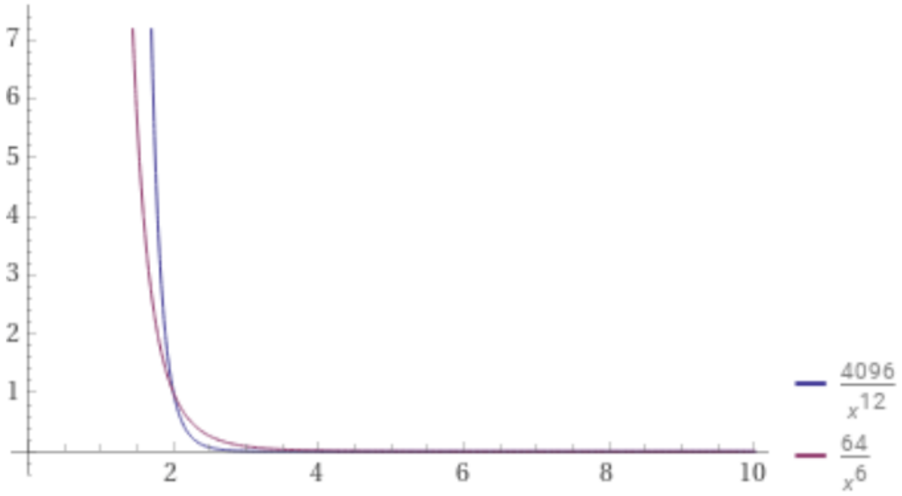
Where ε is the depth of the energy well, r, the surface-to-molecule distance, σ is the value of r at which the potential is null (no more interaction).

PHYSISORPTION

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The Lennar-Jones relation is formed by two terms:

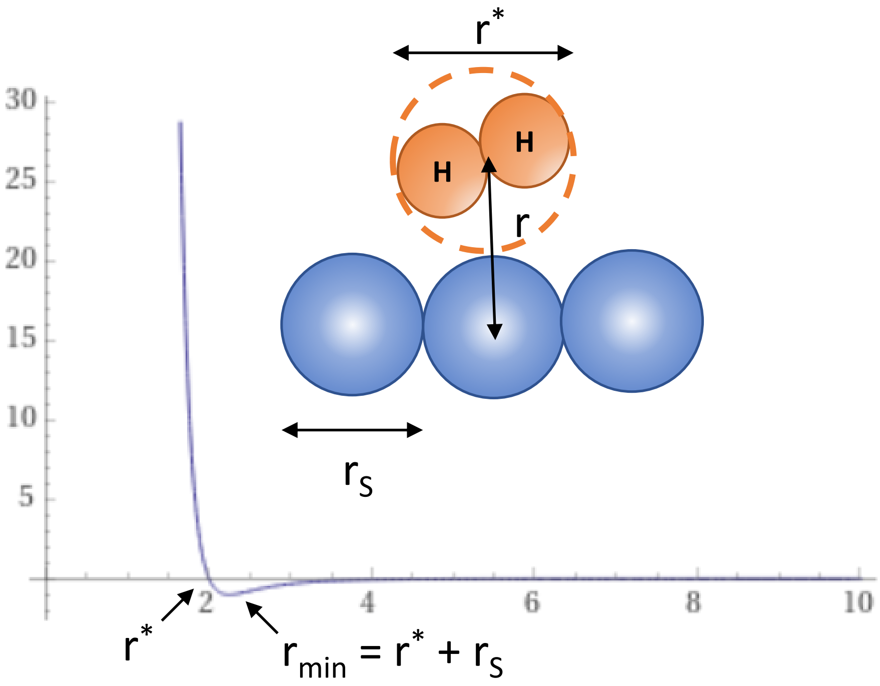
- an attractive term that diminishes with the distance between the molecule and the surface to the power of −6
- and a repulsive term that diminishes with the distance to the power of −12



PHYSISORPTION

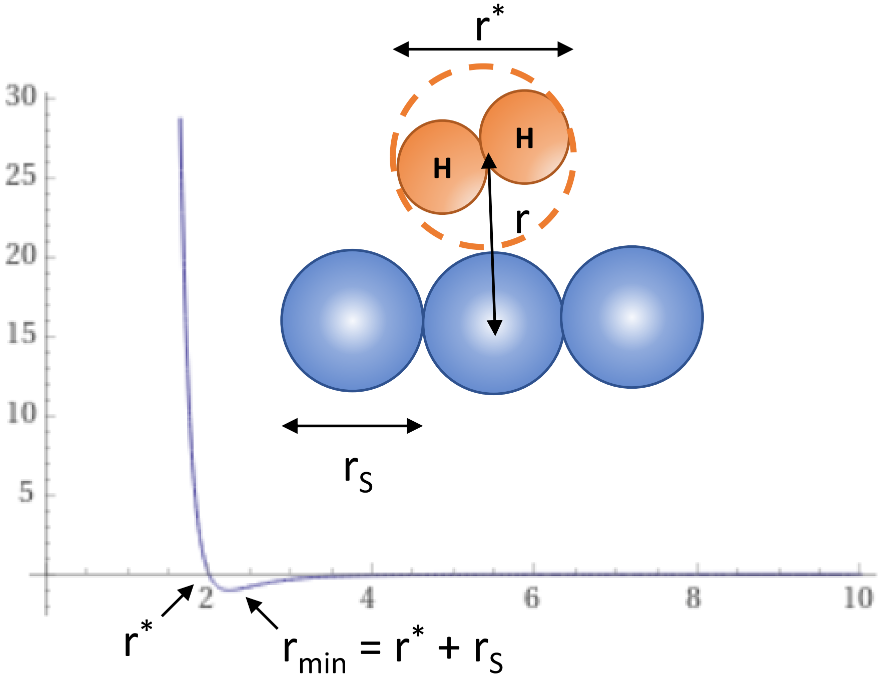
As a result:

1. the potential energy of the molecule shows a minimum at a distance of approximately equal one hydrogen molecule radius (≈ 0.2 nm).



PHYSISORPTION

2. The energy minimum (in the order of 0.01–0.1 eV, corresponding to 1–10 kJ·mol^{-1}, which is also the heat of adsorption required by the process) can be usually found at a distance from the surface which is approximately equal to the so-called van der Waals radii of the adsorbent atom and the adsorbate molecule. The design of the sorbent materials can be thus optimized as it is possible to directly tune the interaction potential by changing the properties of the host material.



HYDROGEN PHYSISORPTION

In order to determine the most proper materials to be used for hydrogen physisorption, the optimum enthalpy of adsorption (ΔH^0_{opt}) needs to be compared.

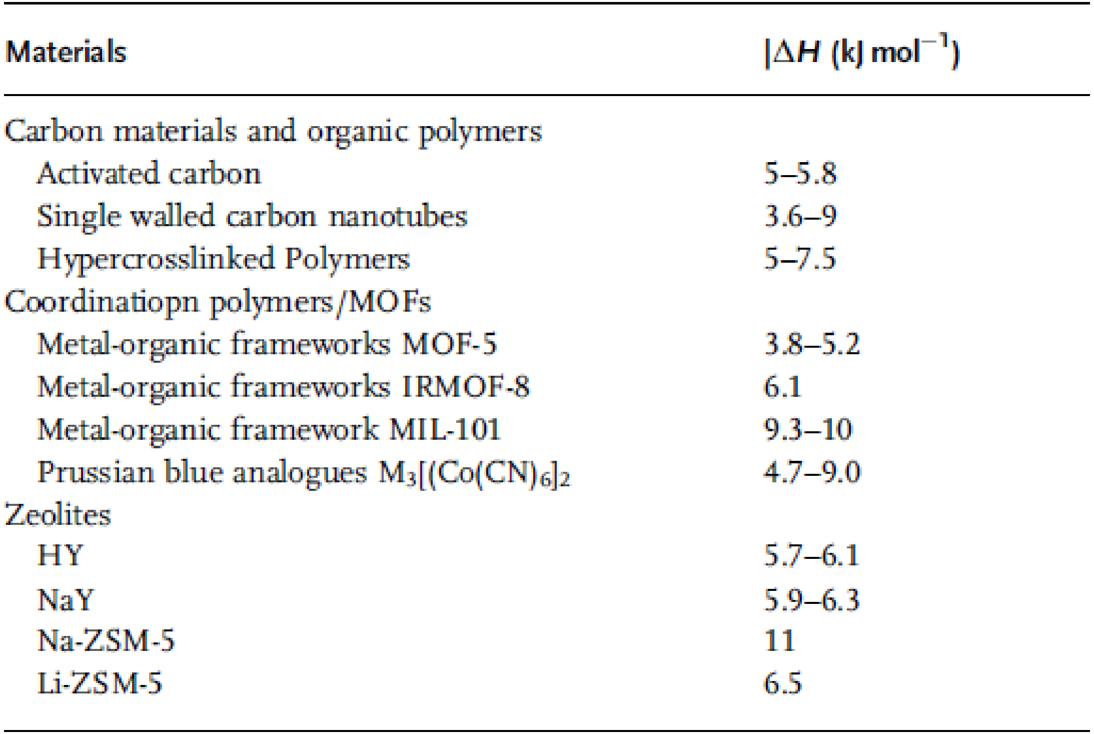
In standard conditions, $\Delta H^0_{opt} = 15.1\ kJ\ mol^{-1}$. This results is obtained by means of the Langmuir adsorption model, in which ideal gas at isothermal conditions are assumed (despite such a model is quite imprecise it works well for a light and low-interacting gas as hydrogen molecule is), where:

$$\Delta H^0_{opt} = T\Delta S^0 + \frac{RT}{2}\ln\left(\frac{P_1 P_2}{P_0^2}\right)$$

Where P_1 and P_2 are respectively the storage (3 MPa) and exhaustion (0.15 MPa) pressures, P_0 the standard pressure (0.1 MPa), and where the enthalpy change on adsorption can be considered being $\Delta S^0 \cong -8R$ (as for a variety number of adsorbents).

1- https://www.seas.upenn.edu/~amyers/LangmuirStg.pdf

HYDROGEN PHYSISORPTION



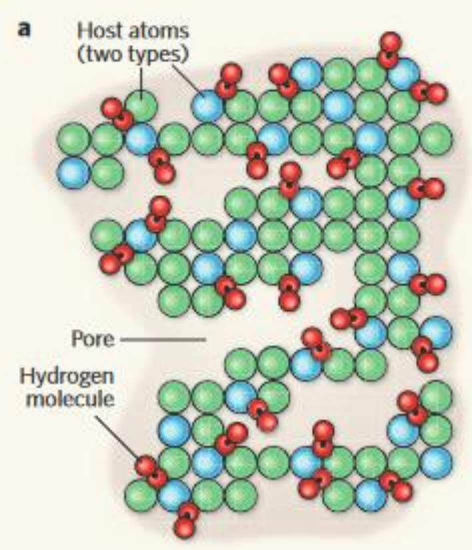
Materials	$\|\Delta H$ (kJ mol^{-1})
Carbon materials and organic polymers	
Activated carbon	5–5.8
Single walled carbon nanotubes	3.6–9
Hypercrosslinked Polymers	5–7.5
Coordinatiopn polymers/MOFs	
Metal-organic frameworks MOF-5	3.8–5.2
Metal-organic frameworks IRMOF-8	6.1
Metal-organic framework MIL-101	9.3–10
Prussian blue analogues $M_3[(Co(CN)_6]_2$	4.7–9.0
Zeolites	
HY	5.7–6.1
NaY	5.9–6.3
Na-ZSM-5	11
Li-ZSM-5	6.5

MATERIAL POROSITY AND STORAGE CAPACITY

Because physisorption stores hydrogen on the surface and not in the bulk of materials, material porosity becomes one of the key factors in evaluating their performances as storage materials. The adsorption capacity of a porous material is best described through its adsorption isotherm, where the hydrogen uptake is display versus the hydrogen pressure. Hydrogen uptake is typically expressed as gravimetric storage capacity, wt%, or as volumetric storage capacity, where the volume occupied by the solid material (V_S) is used as a reference point :

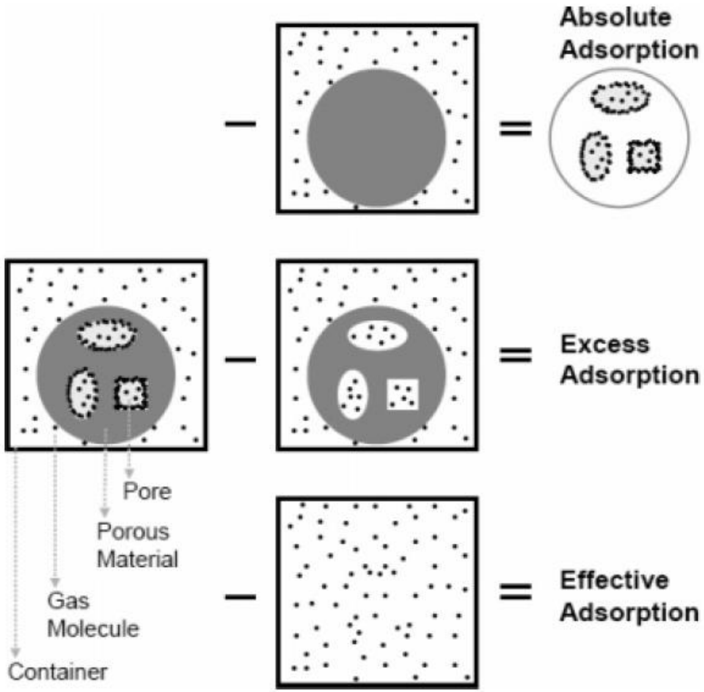
$$wt\% = \frac{m_{H_2}}{m_{H_2}+m_S}\% \qquad vol\% = \frac{m_{H_2}}{V_S}\%$$

Where m_{H_2} is the mass of adsorbed hydrogen and m_s is the mass of the adsorbent.



Schlapbach L., Nature, 460, (2009)

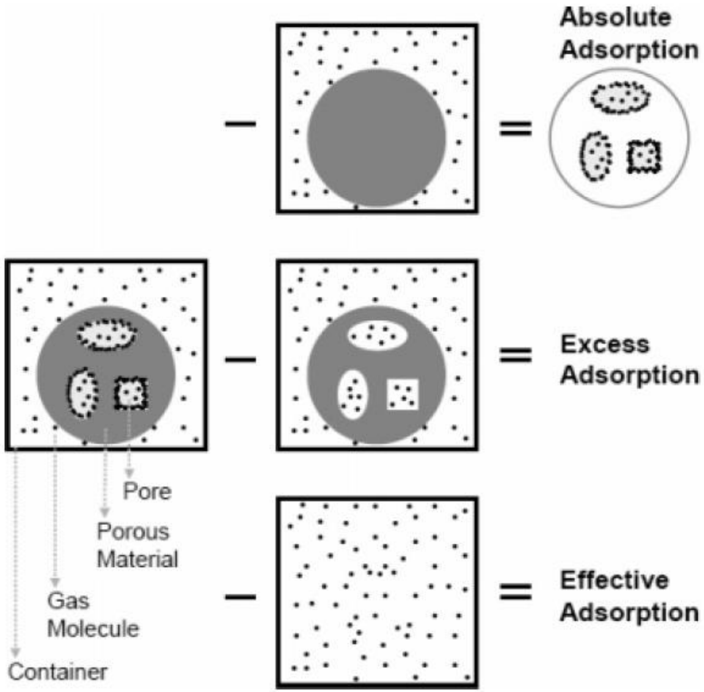
ABSOLUTE, EXCESS, AND EFFECTIVE ADSORPTION



Zhou W. et al., *J. Phys. Chem. C, Vol. 111, No. 44, 2007* R.1

It worth to point out as theoretical calculations and experimental data can differ if some specifications are not taken into account. In this extent, it is fundamental distinguishing in between absolute storage capacity, excess storage capacity, and effective one.

ABSOLUTE, EXCESS, AND EFFECTIVE ADSORPTION

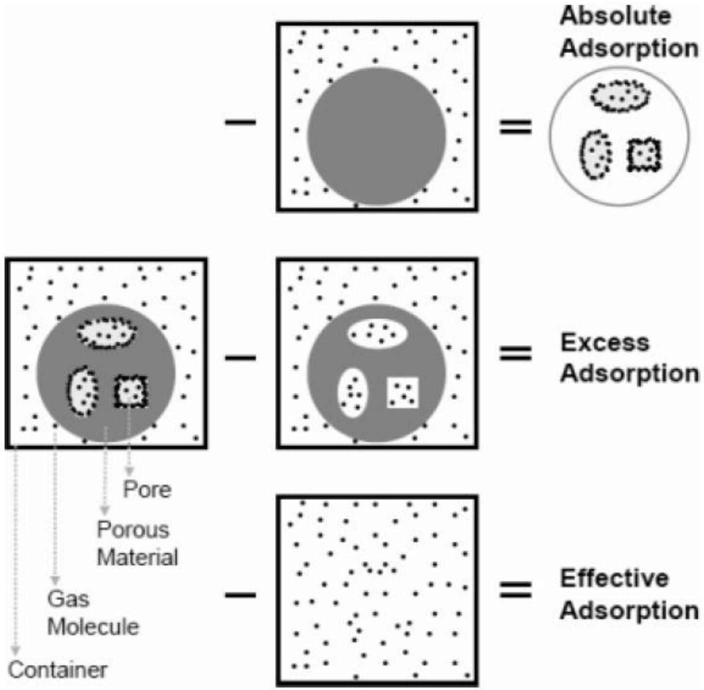


Effective adsorption.

amount of gas stored in a container with the adsorbent minus the amount of gas that can be stored in the same container without any adsorbent. While the excess adsorption accounts for the pore volume, the effective adsorption also evaluates the sample skeleton volume in the gas container.

Therefore, it is the most proper parameter to tell which pressure range is optimal at a certain temperature and is a very useful characteristic for a material in practical gas storage applications, quantifying the net gain of the amount of gas stored with the help of the adsorbent material.

ABSOLUTE, EXCESS, AND EFFECTIVE ADSORPTION



Zhou W. et al., *J. Phys. Chem. C, Vol. 111, No. 44, 2007* R.1

Absolute adsorption.

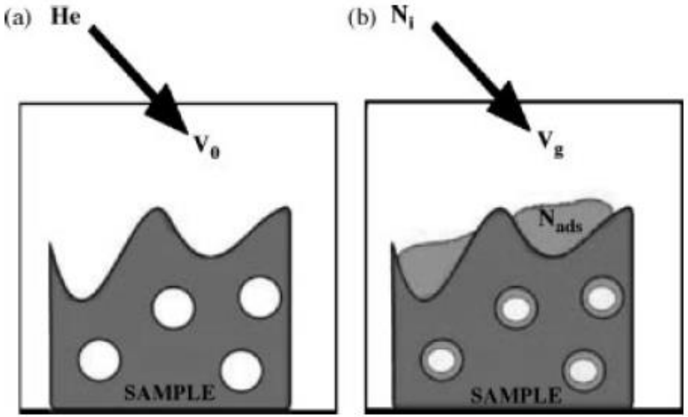
It represents the total amount of gas introduced to the sample cell without considering the amount of gas (outside of the adsorbent) in the gas phase. Thus, it accounts for the total amount of adsorbed molecules in the pores, and it is usually retrieved computationally.

It is predicted from theoretical calculations, and it can be evaluated as:

$$N_{ads} = N_i - V_g \rho_g$$

Where N_i is the amount of gas introduced, V_g is the free volume occupied by the gas (including the pore volume), and ρ_g is the gas density.

ABSOLUTE, EXCESS, AND EFFECTIVE ADSORPTION



Excess adsorption.

Nonetheless, determining the volume Vg is hard (if not impossible), its value can be estimated by measuring the volume of expansion of an inert (or poorly interacting) gas (V_0), as helium.

In this framework, the excess adsorption can be accounted analogously to the absolute adsorption by replacing the free volume occupied by the gas (V_g), with V_0:

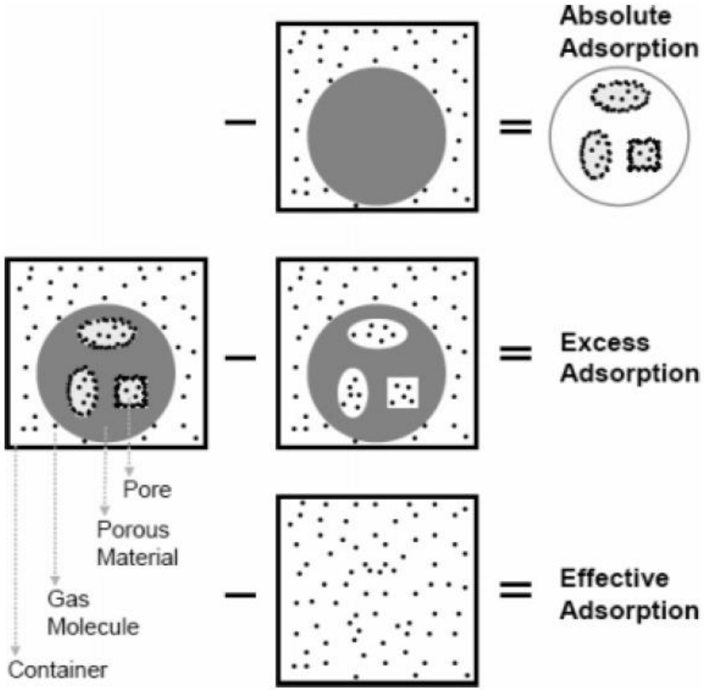
$$N_{ex} = N_i - V_0\rho_g$$

And:

$$N_{ex} = N_{ads} - \rho_g\left(V_0 - V_g\right) = N_{ads} - \rho_g V_a$$

Where V_a is the difference among volume occupied by the adsorbed phase and the pore volume. At low pressures it can be approximated with V_0.

ABSOLUTE, EXCESS, AND EFFECTIVE ADSORPTION



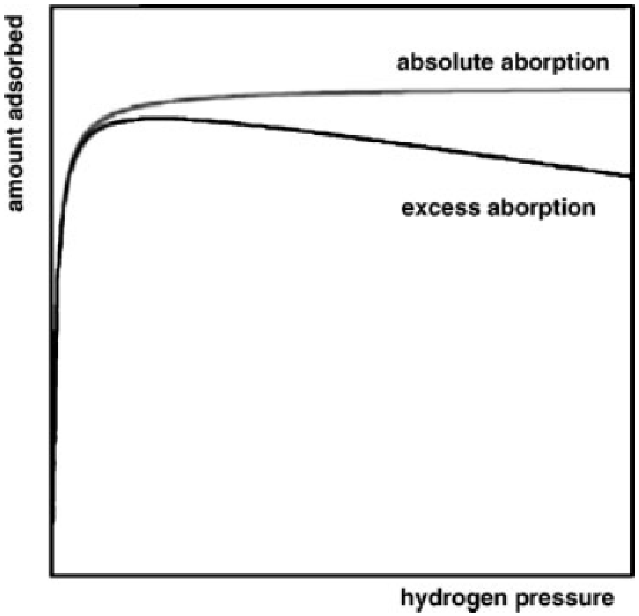
Zhou W. et al., *J. Phys. Chem. C, Vol. 111, No. 44, 2007* R.1

In this context, by defining ρ_a as the density of the adsorbed phase:

$$N_{ex} = N_{ads}\left(1 - \frac{\rho_g}{\rho_a}\right)$$

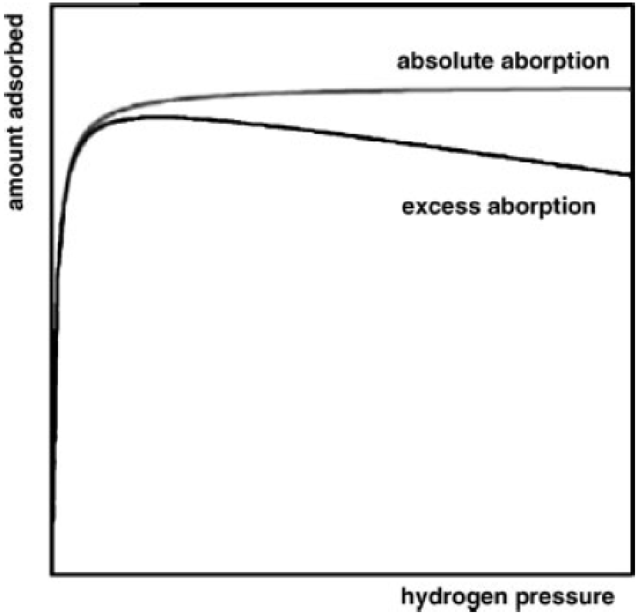
The amount of adsorbed hydrogen can be estimated from the measurement of the excess adsorption and the ratio among the adsorbent-to-gas densities.

ABSOLUTE, EXCESS, AND EFFECTIVE ADSORPTION



Typical absolute adsorption evolution of hydrogen at 77 K is represented via the so-called type-I Langmuir isotherm (IUPAC classification): after a steep increase of stored gas, depicting the formation of a monolayer, the adsorption of additional hydrogen stabilises to a plateau, does not allow further increase in storage performances, indicating the difficulty for the system in promoting multilayer formation.

ABSOLUTE, EXCESS, AND EFFECTIVE ADSORPTION



The same trend is also described by the excess adsorption evolution reaches a maximum and then decreases by increasing pressure, corresponding to saturated pore adsorption, but increasing density of the gas phase. It worth to notice as this decreasing trend does not correspond to a reduced adsorption properties of the material.

IUPAC ADSORPTION PROFILES

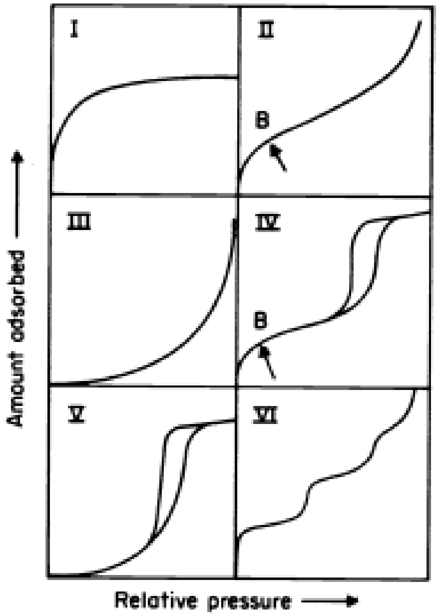


Fig. 2. Types of physisorption isotherms

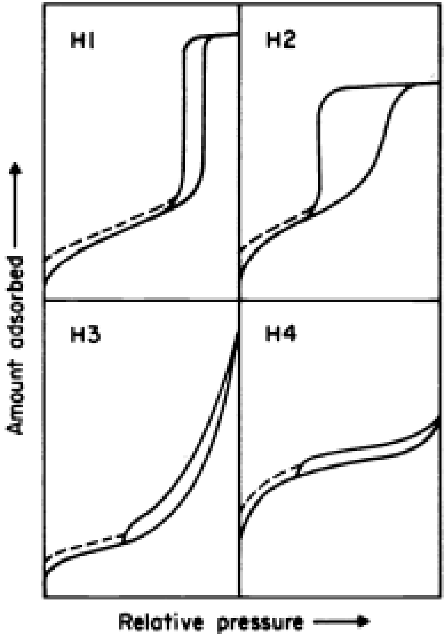
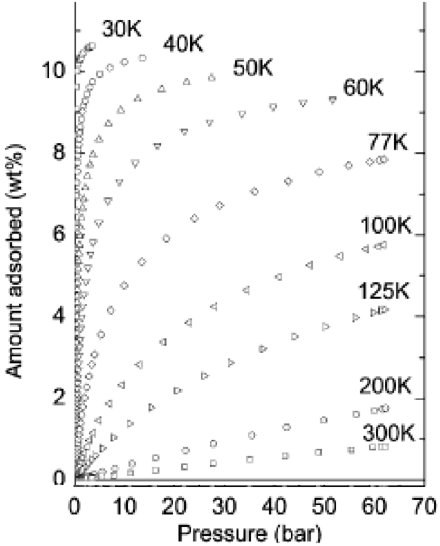


Fig. 3. Types of hysteresis loops

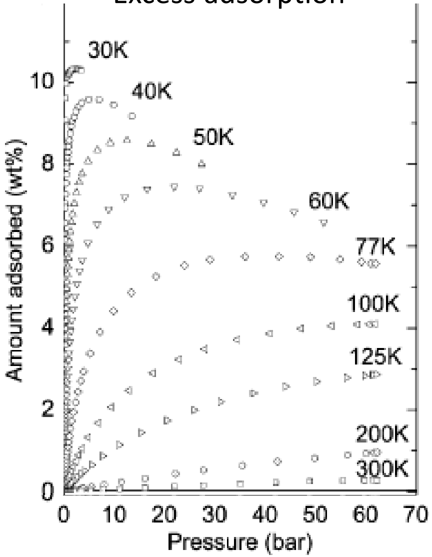
Sing K.S.W. et al., Pure&Appl.Chem.,57,4,(1985),603—619

ABSOLUTE, EXCESS, AND EFFECTIVE ADSORPTION

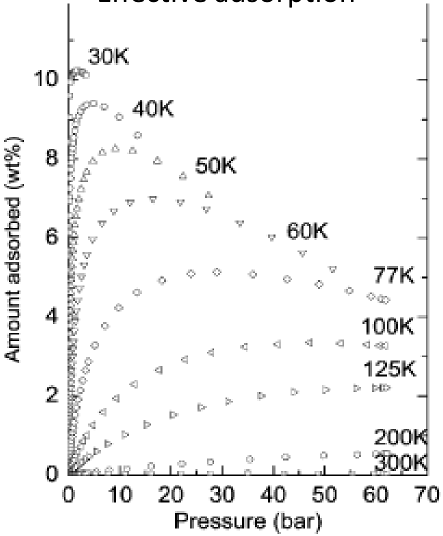
Absolute adsorption



Excess adsorption

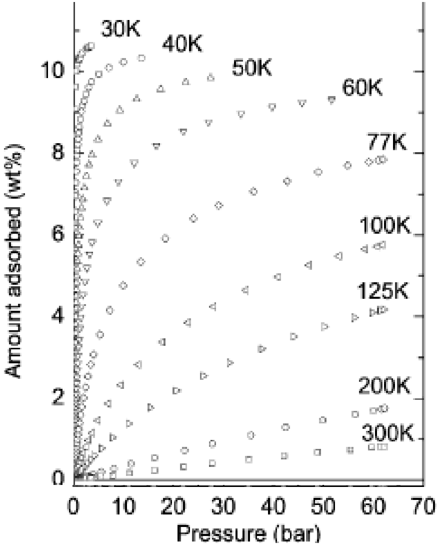


Effective adsorption

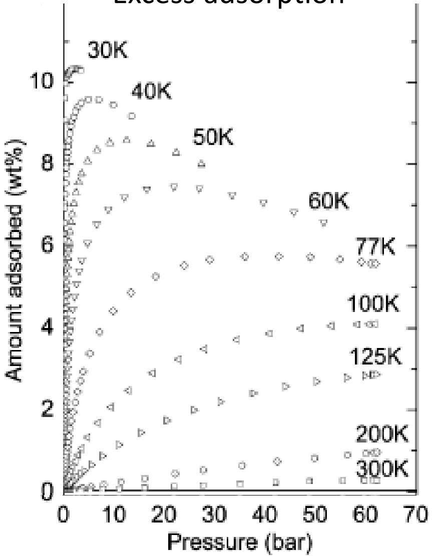


- at low pressure and high temperature, the difference between the three adsorptions is negligible
- at high pressure or low temperature the difference becomes substantial
- With increasing pressure, the absolute adsorption approaches a saturation value but the excess and effective adsorption isotherms reach a maximum and then start to decrease. This significant difference is proportional to the pore volume and the pressure

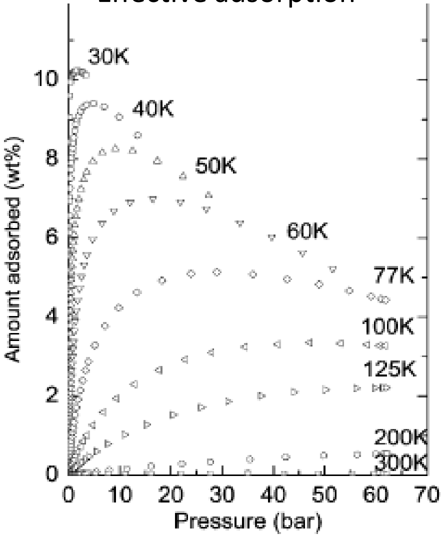
ABSOLUTE, EXCESS, AND EFFECTIVE ADSORPTION



Absolute adsorption



Excess adsorption



Effective adsorption

- The maximum in the excess adsorption isotherm occurs at the point where the gas densities in the sample pore and the bulk gas are increasing at the same rate with respect to pressure, so that an increase in pressure has no effect upon the amount adsorbed. At higher pressure, the gas density in the sample pore starts to saturate while the bulk gas density keeps increasing, resulting in a negative gain in the excess amount adsorbed

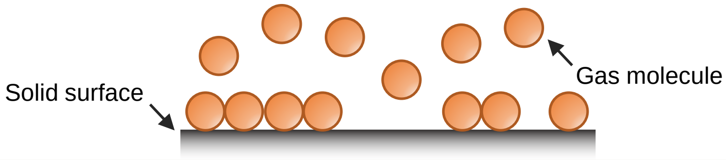
HYDROGEN PHYSISORPTION – SPECIFIC SURFACE AREA

The capacity of adsorption of a material is described by the estimation of its specific surface area, which is used for comparing material performances.

Due to the fact that such amount is hard (if not impossible) to be measured, it is usually estimated. In this extent two models can be used:

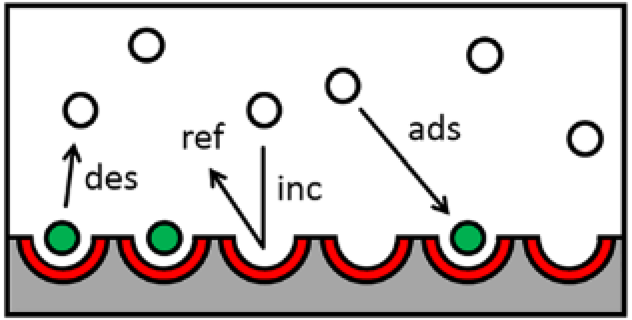
1. Langmuir model

Established for the specific case of chemisorption in a single layer in free contact with the gas phase. Adapted to physisorption it provides a simplified result, corresponding to micropore capacity.



HYDROGEN PHYSISORPTION – SPECIFIC SURFACE AREA

The Langmuir model acknowledges four processes occurring between a gas in equilibrium with a surface (consisting of discretized adsorption sites): incidence, reflection, adsorption, and desorption. It was developed under the assumption that intermolecular interactions can be neglected.

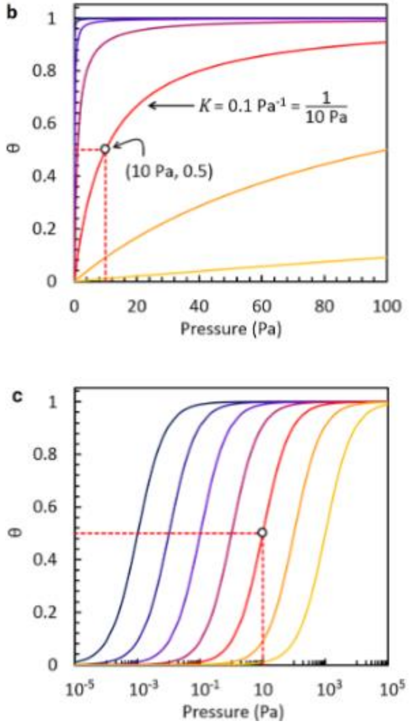


HYDROGEN PHYSISORPTION – SPECIFIC SURFACE AREA

Within the Langmuir model the fractional occupancy of the surface sites by adsorbed molecules, θ, can be expressed as:

$$\theta = \frac{r_{inc} p_{ads}}{r_{des,sat} + r_{inc} p_{ads}} = \frac{KP}{1 + KP}$$

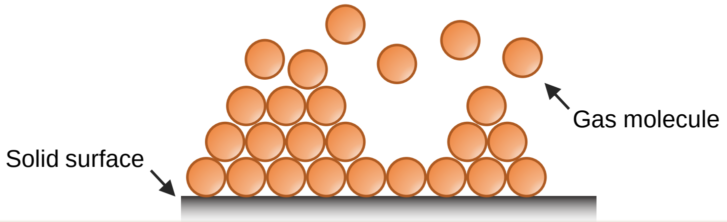
Where K is the Langmuir constant (pressure independent, temperature dependant) characterizing the isotherms of adsorption of a material.



HYDROGEN PHYSISORPTION – SPECIFIC SURFACE AREA

2. Brunauer, Emmet, and Teller (BET) model

Used to take into account multilayer formation, is the most popular approach for calculating the specific surface area. It stipulates that adsorption in the first layer occurs with a constant binding energy (adsorption is homogeneous), there are no interactions among the adsorbed molecules, each adsorbed molecule is an adsorption site for the next layer and adsorbate layers are in equilibrium. Moreover, the number of adsorption layers can be unlimited, and that the adsorption energy of the first layer corresponds with the enthalpy of adsorption, while for the second and subsequent layers with the enthalpy of condensation.



POROUS MATERIALS FOR HYDROGEN PHYSISORPTION

Hydrogen storage via physisorption is achieved by means of porous materials which porosity extends from the meso to the nanoscale. The capacity of a material to adsorb hydrogen molecules can be expressed in terms of percentage of carried hydrogen weight, referred to the total weight of the storing device.

The capability of a material in storing hydrogen is expressed by means of its specific surface area (as a standard, in the order of 2000 $m^2\ g^{-1}$).

In order to improve specific surface area, available surface for adsorption, bulk density of the adsorbent and characteristic binding energy of the hydrogen molecule within the material are needed to be optimized.

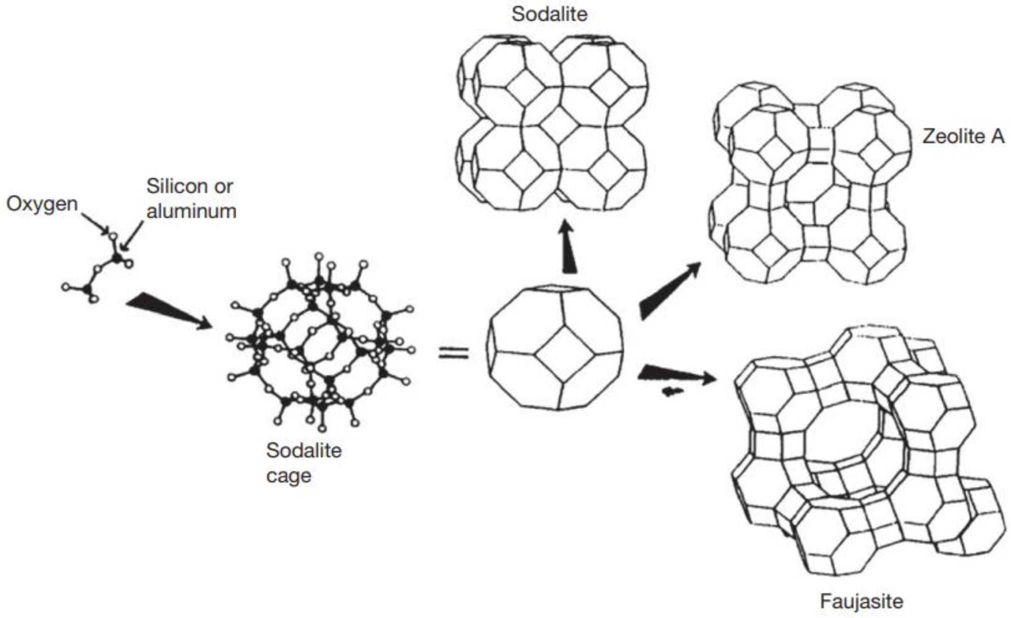
POROUS MATERIALS FOR HYDROGEN PHYSISORPTION

Zeolites

Synthetic compounds mainly composed by Si or Al, which are made by crystallization of a gel precursor.

During the synthesis process they host metal ions to the structure which are able to induce local electrostatic forces able to induce hydrogen adsorption.

They are characterized by a very open microporous structure. Because they are no able to exposed all the cations they don't overcome carbon-based storage technology



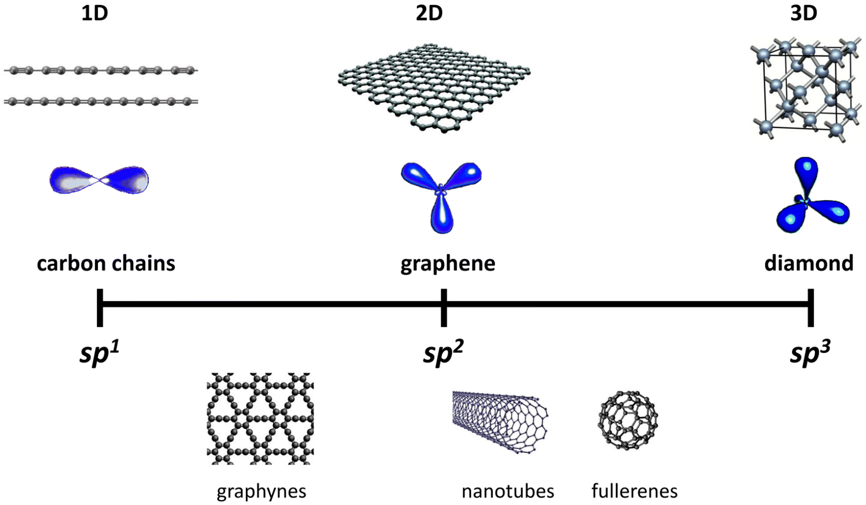
Martínez C., Corma A., 5.05 - Zeolites, Comprehensive Inorganic Chemistry II (Second Edition), Elsevier, 2013,

POROUS MATERIALS FOR HYDROGEN PHYSISORPTION

Carbon materials

a great variety of porous carbon nanostructures exist, mainly consisting of carbon atoms locally ordered (i.e. hexagon), in order to promote the sp2-hybridization of atomic orbitals.

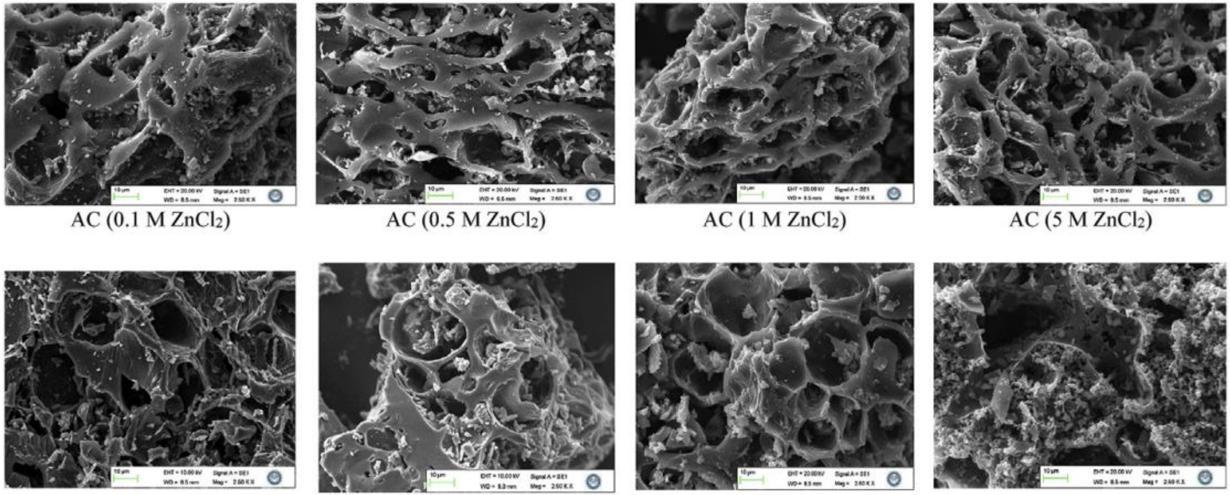
In principle, these materials can be divided into two main classes: those which possess a long-range order of the elementary cell, like carbon nanotubes or nanofibers, and those which have irregular structures, like activated carbon. Most of the carbon nanostructures possess an ordered array, typically of short range, surrounded by disordered parts.



Banhart F., *ChemTexts* 6, 3 (2020)

POROUS MATERIALS FOR HYDROGEN PHYSISORPTION

Activated carbons are amorphous materials possessing a high degree of porosity and a high specific surface area. They are mainly prepared by pyrolysis of carbonaceous raw materials previously processed. According to the production process used, specific surface area can vary from 700 to 3000 m^2 g^{-1}.



AC (0.1 M $ZnCl_2$) AC (0.5 M $ZnCl_2$) AC (1 M $ZnCl_2$) AC (5 M $ZnCl_2$)

AC (0.1 M KOH) AC (0.5 M KOH) AC (1 M KOH) AC (5 M KOH)

Dogan M. et al, Journal of the Energy Institute, 93, 6, (2020), 2176-2185

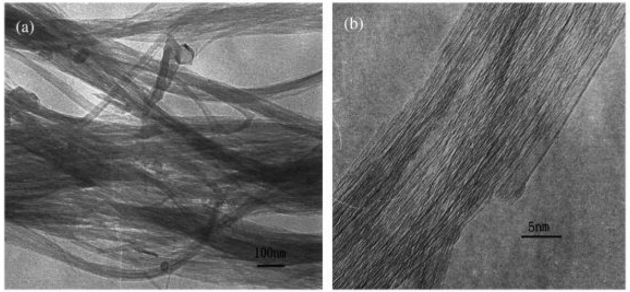
POROUS MATERIALS FOR HYDROGEN PHYSISORPTION

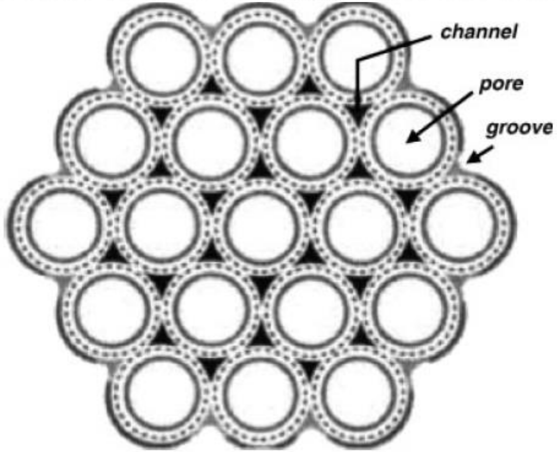
Among all carbon materials, high grade activated carbon and porous carbons are the best adsorbents for hydrogen at 77 K, because they possess the highest specific surface area.

However, however, they are a disordered structure with a broad pore size distribution, which cannot be precisely controlled during the synthesis.

Conversely, (bare or functionalized) carbon nanotubes demonstrated not to be so effective, showing performances in the order of wg%=1% (at room temperature) far away from international standards (wg% = 1.8% minimum for 2025). To date they have mostly being studied for understanding the adsorption processes, due to their long-range ordered structure and the large availability of adsorption sites.

To date is believed as the biggest issue might be related to difficulties in hydrogen molecule in reaching the adsorption sites.





Liu C., et al., Carbon, 48, 2, (2010), 452-455

POROUS MATERIALS FOR HYDROGEN PHYSISORPTION

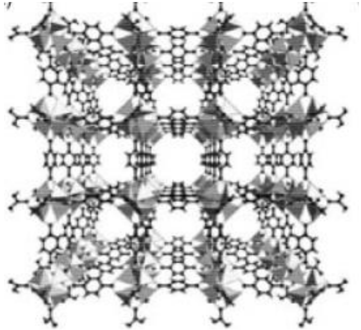
Organic Polymers

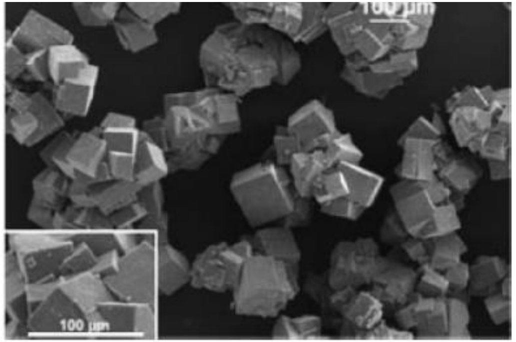
In synthetizing and developing new materials for hydrogen storage, the main approach was based on forming materials with intrinsic micro-porosity. The advantage of such materials rely in the fact that are composed by light atoms (such as C, H, N, O), and posses high specific surface areas. Nonetheless, the resulting hydrogen storage values revealed worse than many porous carbon samples.

POROUS MATERIALS FOR HYDROGEN PHYSISORPTION

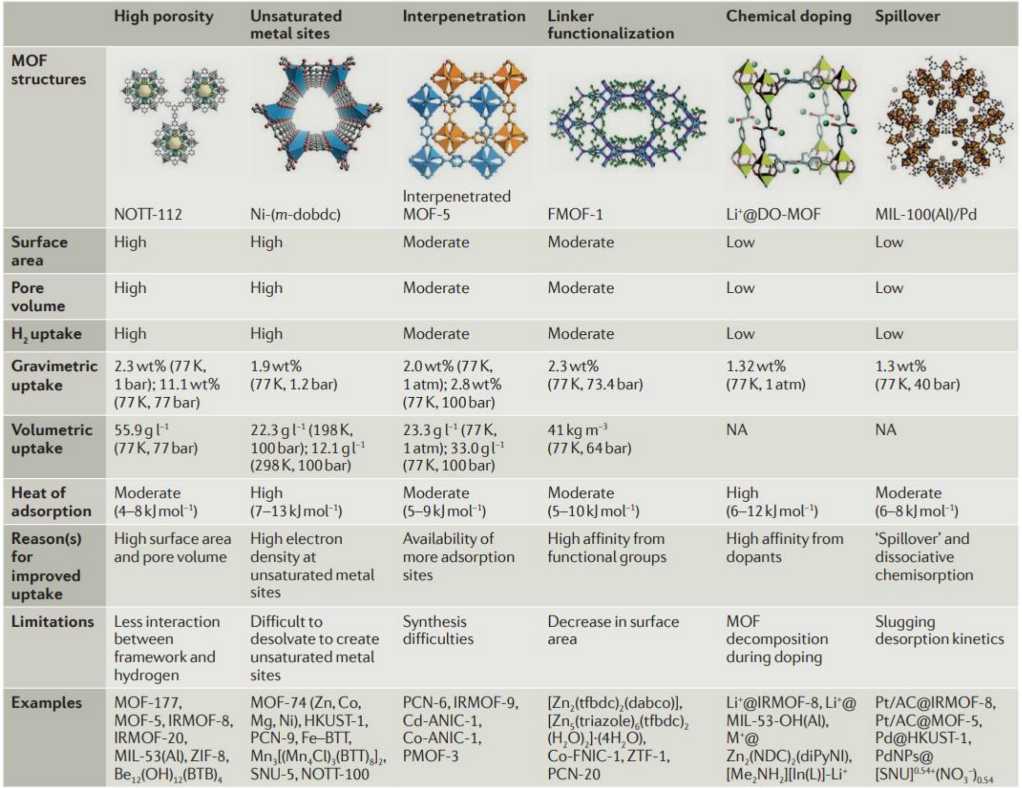
Metal Organic Frameworks

Composed by metal ions, metal oxide clusters (or inorganic parts) of larger dimensionality coordinated by organic ligands in a rigid three dimensional lattice, forming highly ordered structures, characterized by very high specific surface areas (from 3000, up to 7000 $m^2\ g^{-1}$), and high gravimetric uptakes at 77 K (in general around 2%; even higher when pressure is risen). It was demonstrated as their high specific surface are is corelated to their adsorption capabilities





POROUS MATERIALS FOR HYDROGEN PHYSISORPTION



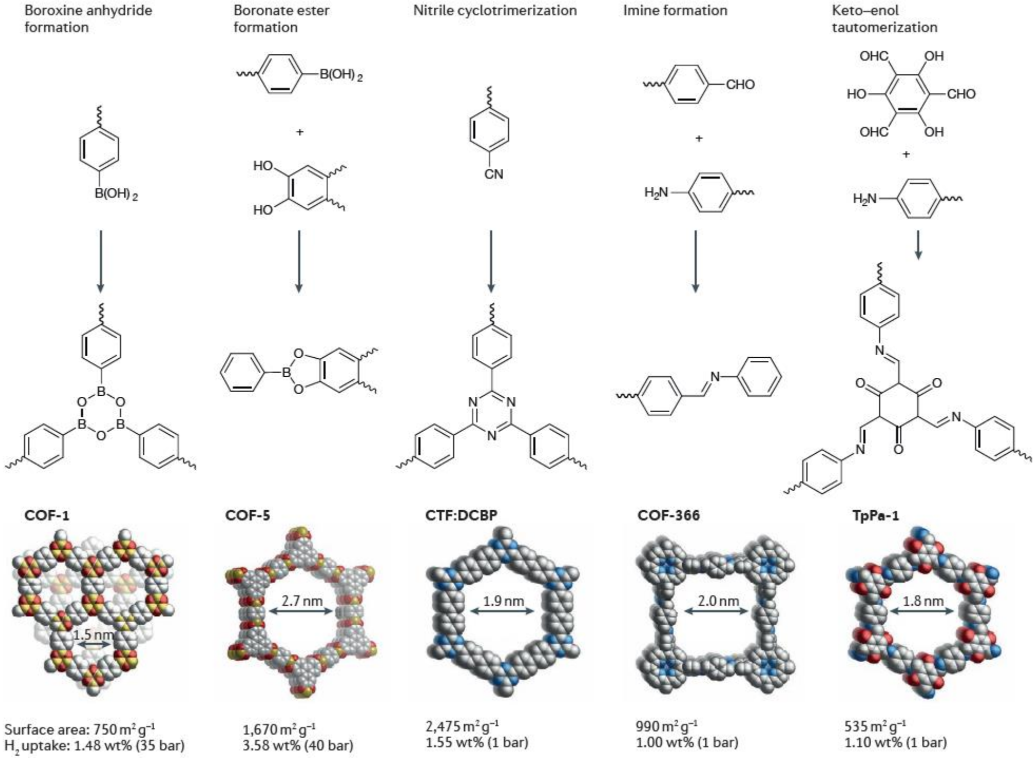
	High porosity	Unsaturated metal sites	Interpenetration	Linker functionalization	Chemical doping	Spillover
MOF structures	NOTT-112	Ni-(*m*-dobdc)	Interpenetrated MOF-5	FMOF-1	Li^+@DO-MOF	MIL-100(Al)/Pd
Surface area	High	High	Moderate	Moderate	Low	Low
Pore volume	High	High	Moderate	Moderate	Low	Low
H_2 uptake	High	High	Moderate	Moderate	Low	Low
Gravimetric uptake	2.3 wt% (77 K, 1 bar); 11.1 wt% (77 K, 77 bar)	1.9 wt% (77 K, 1.2 bar)	2.0 wt% (77 K, 1 atm); 2.8 wt% (77 K, 100 bar)	2.3 wt% (77 K, 73.4 bar)	1.32 wt% (77 K, 1 atm)	1.3 wt% (77 K, 40 bar)
Volumetric uptake	55.9 g l^{-1} (77 K, 77 bar)	22.3 g l^{-1} (198 K, 100 bar); 12.1 g l^{-1} (298 K, 100 bar)	23.3 g l^{-1} (77 K, 1 atm); 33.0 g l^{-1} (77 K, 100 bar)	41 kg m^{-3} (77 K, 64 bar)	NA	NA
Heat of adsorption	Moderate (4–8 kJ mol^{-1})	High (7–13 kJ mol^{-1})	Moderate (5–9 kJ mol^{-1})	Moderate (5–10 kJ mol^{-1})	High (6–12 kJ mol^{-1})	Moderate (6–8 kJ mol^{-1})
Reason(s) for improved uptake	High surface area and pore volume	High electron density at unsaturated metal sites	Availability of more adsorption sites	High affinity from functional groups	High affinity from dopants	'Spillover' and dissociative chemisorption
Limitations	Less interaction between framework and hydrogen	Difficult to desolvate to create unsaturated metal sites	Synthesis difficulties	Decrease in surface area	MOF decomposition during doping	Slugging desorption kinetics
Examples	MOF-177, MOF-5, IRMOF-8, IRMOF-20, MIL-53(Al), ZIF-8, $Be_{12}(OH)_{12}(BTB)_4$	MOF-74 (Zn, Co, Mg, Ni), HKUST-1, PCN-9, Fe–BTT, $Mn_3[(Mn_4Cl)_3(BTT)_8]_2$, SNU-5, NOTT-100	PCN-6, IRMOF-9, Cd-ANIC-1, Co-ANIC-1, PMOF-3	$[Zn_2(tfbdc)_2(dabco)]$, $[Zn_5(triazole)_6(tfbdc)_2(H_2O)_2]\cdot(4H_2O)$, Co-FNIC-1, ZTF-1, PCN-20	Li^+@IRMOF-8, Li^+@MIL-53-OH(Al), M^+@$Zn_2(NDC)_2(diPyNI)$, $[Me_2NH_2][In(L)]$-Li^+	Pt/AC@IRMOF-8, Pt/AC@MOF-5, Pd@HKUST-1, PdNPs@$[SNU]^{0.54+}(NO_3^-)_{0.54}$

Teng H. et al, *Nature Reviews Materials, 1,* (2016), *16059*

POROUS MATERIALS FOR HYDROGEN PHYSISORPTION

Covalent Organic Frameworks

Made by organic structural building units are held together by strong covalent bonds. They are characterized by low density, high surface area, and tuneable pore size, which allowed to exhibit 1-8% of wt% hydrogen at 77 K (at pressure value ranging from 15 to 50 bar). They are currently under study and have demonstrated to be able to be functionalized via doping with cations (for example Li^+) or metal nanoparticles (made for example by Pd) to enhance their hydrogen storage at room temperature.



Teng H. et al, Nature Reviews Materials, 1, (2016), 16059

FINAL OUTLOOK AND FUTURE PERSPECTIVES

Due to the weak interaction between hydrogen molecules and the adsorbents, **high storage capacities are found at low temperatures only**. In average, it was found that 77 K is the optimal temperature at which maximum hydrogen uptake is achieved.

Physisorption is then characterized by **fast kinetics, complete reversibility, producing small heat during refueling**, when compared to chemisorption, making this storage method suitable for on-board refueling.

For a long time, zeolites were the best crystalline materials and activated carbons the best disordered materials for gas storage by physisorption. Recently, the new classes of crystalline metal organic frameworks and novel templated porous carbons have been developed which possess specific surface areas exceeding those of activated carbons, but they are still far form the targets set in terms of gravimetric capacity.

3. HYDROGEN CHEMISORPTION

HYDROGEN CHEMISORPTION

In chemisorption, hydrogen is chemically bound to other solid compounds via formation (and breaking) of covalent bonds.

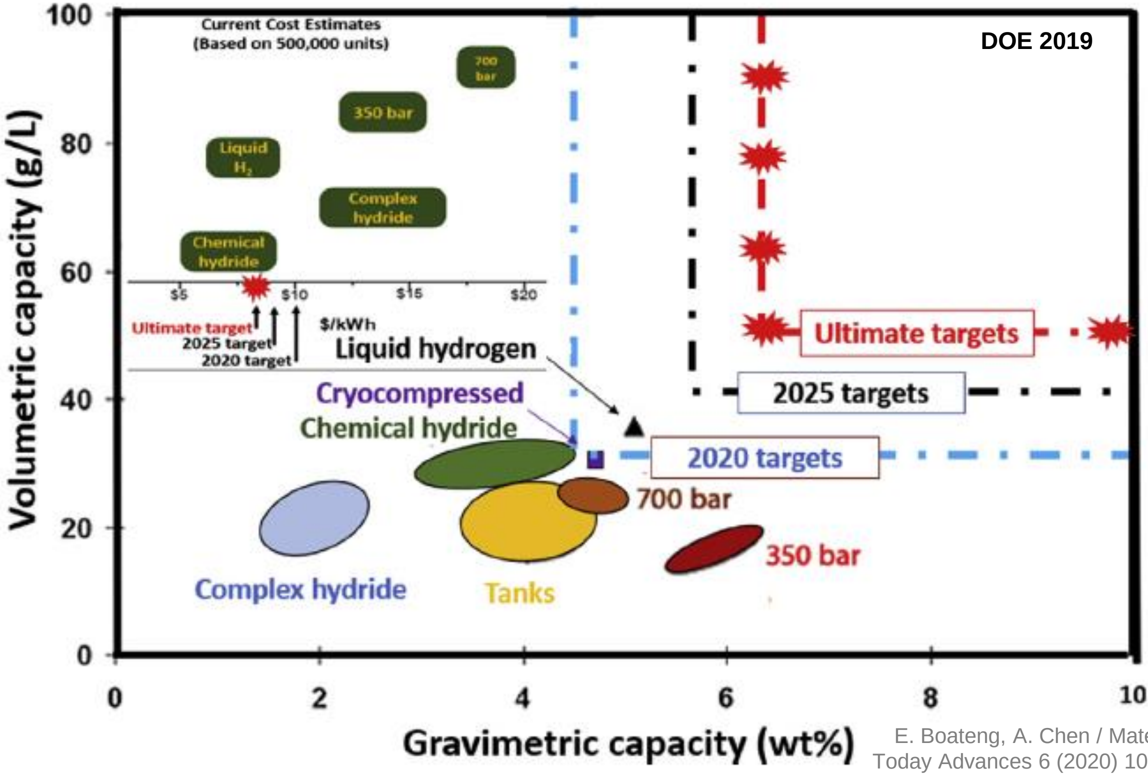
As a result, many of the challenges involving such a storage method are related to the thermodynamics and kinetics of dehydrogenation.

In chemisorption, hydrogen can be bound to metals, intermetallic compounds, and alloys to form metal hydrides, and by releasing heat during absorption. Consequently, hydrogen desorption requires heat to be delivered to the compound. Hydrogen chemisorption to a metal (M) can be expressed as:

$$M + \frac{x}{2} H_2 \leftrightarrow MH_x$$

HYDROGEN CHEMISORPTION

The main advantages of storing hydrogen in a metal hydride are the high hydrogen volumetric densities and the possibility to absorb and desorb hydrogen with a small change in hydrogen pressure, making it interesting for on-board applications.



E. Boateng, A. Chen / Materials Today Advances 6 (2020) 100022

METAL HYDRIDES

Another feature related to the use of metal hydrides is that such a class of compounds is well known in industrial processing (in example they are used as anode materials in commercial nickel-metal-hydrides (Ni-MH) rechargeable batteries). In relation to hydrogen technologies, metal hydrides can be also found in process of hydrogen purification, separation from gas mixtures (such as H_2-CH_4), or hydrogen getters (detectors), among the others.

Depending on the elements used for hosting hydrogen, and depending on the type of bond created, three types of metal hydrides can be identified

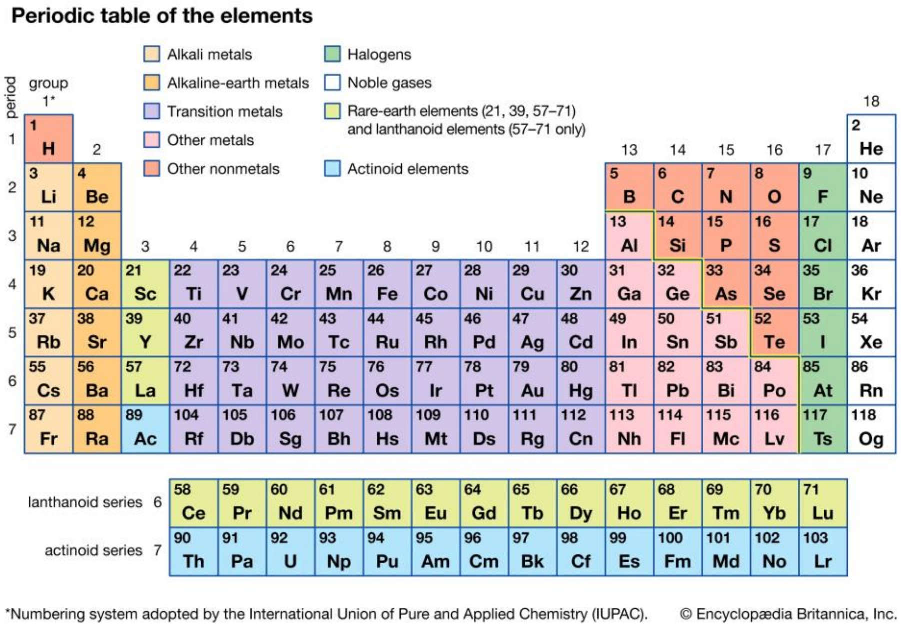
1. Ionic (or saline) hydrides
2. Covalent hydrides
3. Metallic hydrides

METAL HYDRIDES CLASSIFICATION

Ionic or saline hydrides.

Binary hydrides of all alkali metals and of alkaline earth metals, from calcium through barium. In these compounds, hydrogen exists as a negatively charged ion (H^-). Such class of compounds is characterized by similar properties as the halides.

Typical binary ionic hydrides are sodium or calcium hydrides (NaH, CaH_2). In general, the binary ionic hydrides are too stable for hydrogen storage application with the exception of magnesium. In this case, however, the interaction between hydrogen and magnesium is partly ionic and partly covalent, and MgH should be considered a transition hydride between ionic and covalent hydrides.



Periodic table of the elements

- Alkali metals
- Alkaline-earth metals
- Transition metals
- Other metals
- Other nonmetals
- Halogens
- Noble gases
- Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)
- Actinoid elements

period	group 1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
actinoid series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

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METAL HYDRIDES CLASSIFICATION

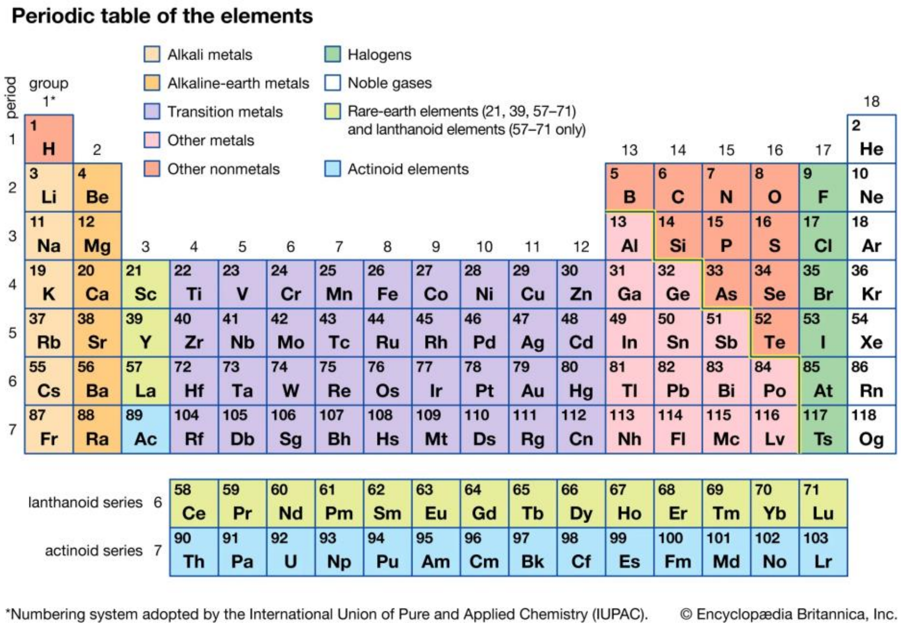
Covalent hydrides

Compounds composed by hydrogen and non-metals. Here atoms of similar electronegativities share electron pairs.

Most of the covalent hydrides are liquid or gaseous at room temperature and those that are solid are thermally unstable.

Some examples are provided by: hydrogen sulfide (H_2S), silane (SiH_4), aluminum borohydride ($Al(BH_4)_3$), and methane (CH_4).

Unfortunately, covalent hydrides have to be synthetized, and cannot be formed by direct reaction of hydrogen gas and the element, thus limiting their use as good candidates for hydrogen storage applications.



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3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
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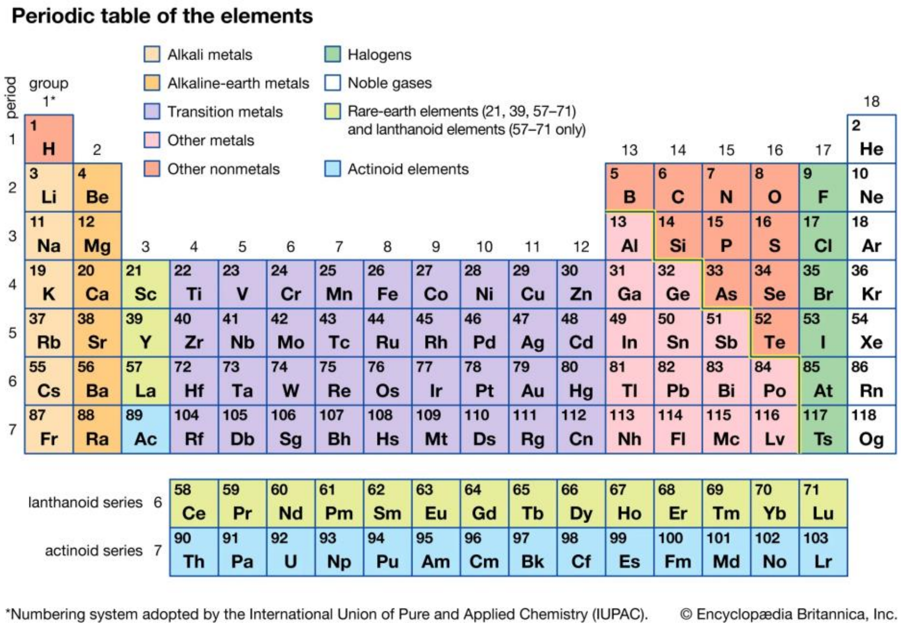
METAL HYDRIDES CLASSIFICATION

Metallic hydrides

Formed together with transition metals, including the rare earth elements and the actinide series. Here, hydrogen acts as a metal and forms a metallic bond. They have high thermal and electrical conductivities. However, unlike metals, they are quite brittle. The prevailing explanation is that in the metallic hydrides the 1s electron on the hydrogen atom participates in the conduction band of the metal to generate new M–H bonding states. Metallic hydrides have a wide variety of stoichiometric and non-stoichiometric compounds and are formed by direct reaction of hydrogen with the metal or by electrochemical reaction and they are characterized by a mixture of different types of bonding.



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*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

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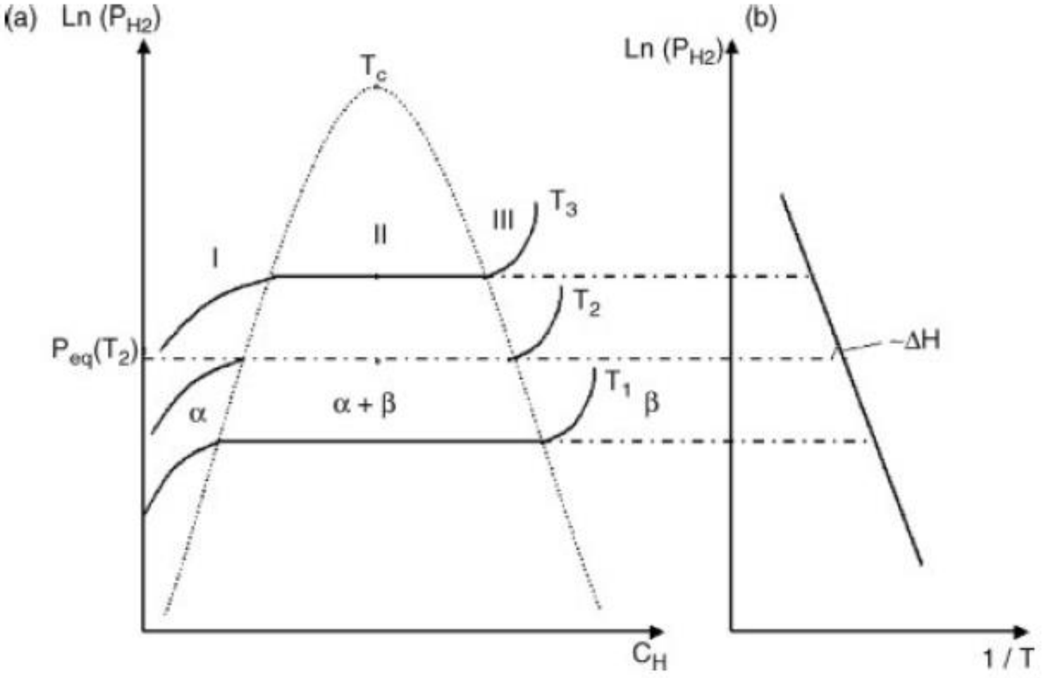
THERMODYNAMICS OF METAL HYDRIDES

One investigating thermodynamics of metal hydride formation via chemisorption, the heat of formation for the reaction (Q) needs to be considered:

$$M + \frac{x}{2} H_2 \leftrightarrow MH_x + Q$$

Moreover, by means of the pressure-composition isotherms needs to be evaluated.



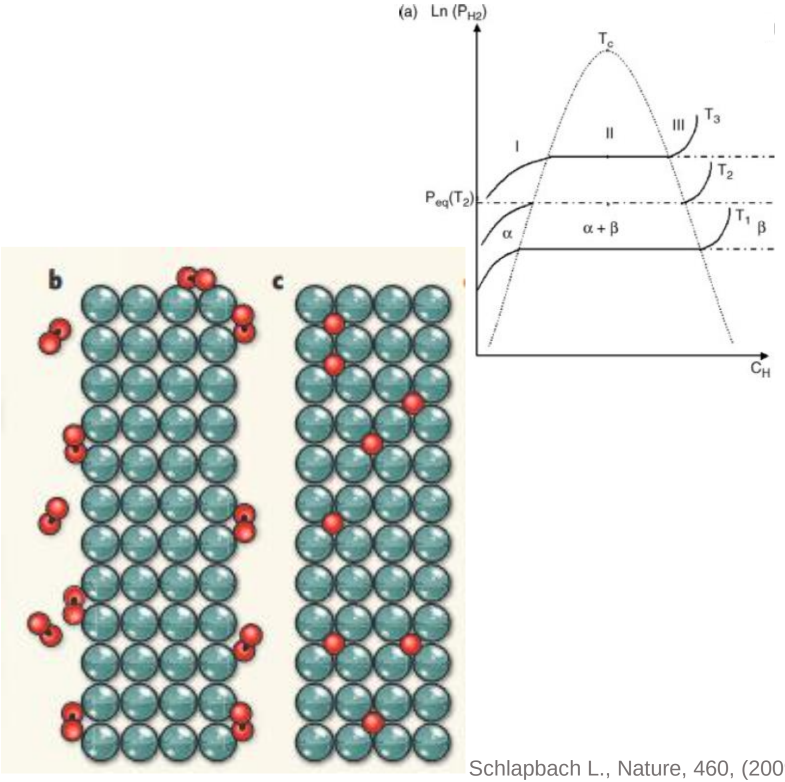
THERMODYNAMICS OF METAL HYDRIDES

Here, three regimes can be highlighted.

$$M + \frac{x}{2} H_2 \leftrightarrow MH_x + Q$$

Low hydrogen concentrations (x<<1)

Hydrogen molecule is split and single hydrogen atoms dissolve in the metal lattice and forms a solid phase (named α), having the same crystal structure as the bare metal.



Schlapbach L., Nature, 460, (2009)

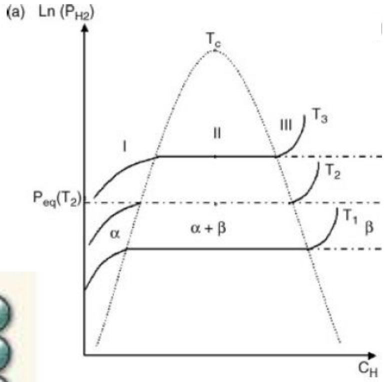
THERMODYNAMICS OF METAL HYDRIDES

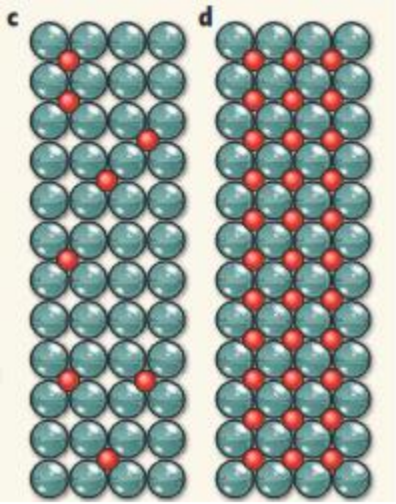
$$M + \frac{x}{2} H_2 \leftrightarrow MH_x + Q$$

Intermediate and high hydrogen concentrations (x > 0.1)

By increasing hydrogen concentration, the formation of H–H bond promotes hydrogen nucleation and the so-called β phase starts to form. At this stage hydrogen gas, solid α and β phases coexist forming metallic compound mixed to gaseous hydrogen.

At higher concentrations, all of the hydrogen is entered in the solid β phase which becomes predominant.





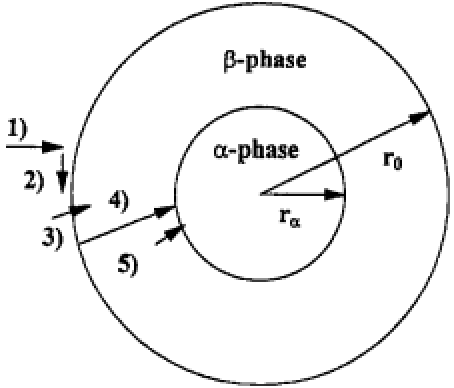
Schlapbach L., Nature, 460, (2009)

REACTION STEPS FOR ABSORPTION AND DESORPTION

Hydride formation starts at the metal/gas interface and grows towards the bulk, under the establishment of a concentration gradient of the α phase.

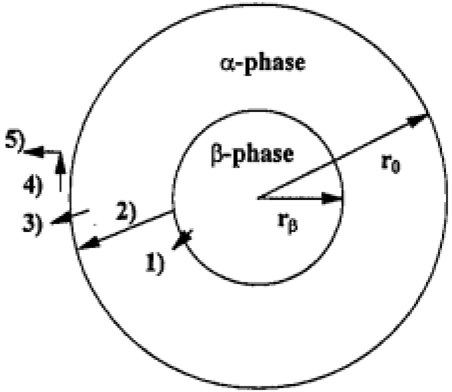
Also the transition to the β phase follows the same dynamics, as at the interface the energetic cost of the lattice expansion sustaining the formation of the β phase requires less energy.

Absorption



1) physisorption
2) chemisorption
3) surface penetration
4) diffusion
5) hydride formation

Desorption



1) hydride decomposition
2) diffusion
3) surface penetration
4) recombination
5) desorption to gas phase

Martin M., et al., Journal of Alloys and Compounds 238 (1996) 193-201

THERMODYNAMICS OF METAL HYDRIDES

Thermodynamic equilibrium is given once the chemical potential of molecular (μ_{H_2}) and atomic hydrogen in solution in the metal (μ_H) are balanced: $\frac{1}{2}\mu_{H_2}(P,T) = \mu_H(P,T,c_H)$

With c_H being the hydrogen concentration. In the **low pressure regime** (P < 100 bar) hydrogen can be considered as an ideal gas and its chemical potential can be related to the gas pressure as:

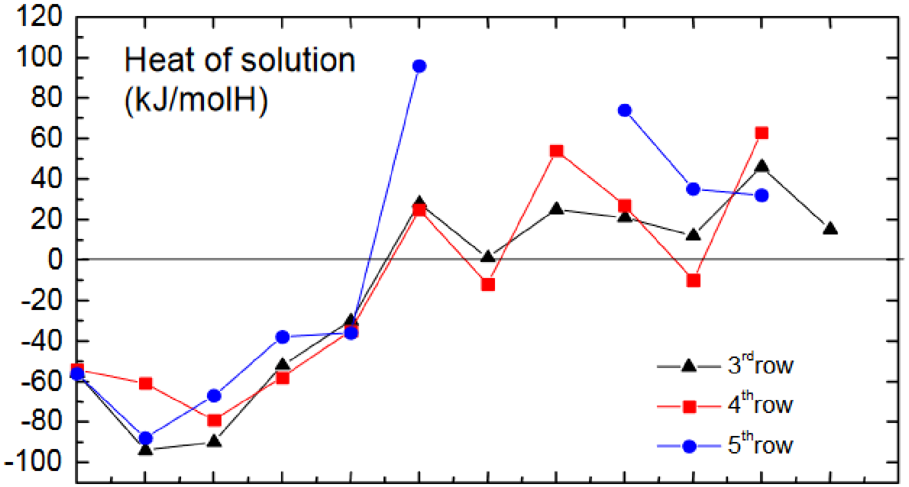
$$\frac{1}{2}\mu_{H_2} = \frac{1}{2}H_{H_2}^0 - \frac{1}{2}TS_{H_2}^0 + RT\ln P_{H_2}^{1/2}$$

Where $H_{H_2}^0$ and $S_{H_2}^0$ are the standard state enthalpy and entropy, respectively. Once evaluating the chemical potential of the hydrogen atoms inside the metal, three contributions need to be considered: the enthalpy of solution H_S, one describing the atomic displacement of the hydrogen atoms in the lattice (configurational contribution, TS_S^{conf}), and another describing the disorder introduced by temperature (vibrational contribution, TS_S^{vib}):

$$\mu_H = H_S - TS_S^{vib} + TS_S^{conf}$$

Where: *b* is the number of interstitial sites per metal atoms, and *c* is the number of sites occupied by hydrogen atoms.

THERMODYNAMICS OF METAL HYDRIDES



K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Griessen R., Zuttel A., Science and technology of hydrogen in metals, Vrije Universiteit, 2003

At the equilibrium $\frac{1}{2}\mu_{H_2} = \mu_H$; for low H_2 concentration, $c \ll b$, and:

$$\boxed{\Delta H_S = T\Delta S_S + RT\ln P^{1/2} + RT\ln b}$$

Where ΔH_S is the heat of solution (also named as heat of formation) of the chemisorption process.

The heat of solution is periodic according to the elemental position in the periodic table.

Moreover, for the early-transition metal hydrides ΔH<0 (endothermic), while for late-transition metals and metals it is ΔH>0 (exothermic)

This leads to the conclusion that heat of solution is mainly determined by the (electronic) structure of the metal.

The heat of solution defines also the stability of metal hydrides because is also related to the thermodynamic conditions at which dissociation takes place.

THERMODYNAMICS OF METAL HYDRIDES

The transition from the α- to the β-phase takes place in the **high pressure regime** (region *II*). The equilibrium pressure (P_{eq}) for the transition can be thus related by the van't Hoff's relation to the variations both of H_S and reaction entropy:

$$\ln P_{eq} = -\frac{\Delta S}{R} + \frac{\Delta H}{RT}$$

The equation can be simplified under these two assumptions: (i) the term ΔS can be considered constant, and (ii) the enthalpy of formation of the β-phase varies linearly with the hydrogen concentration (x):

Elastic contribution

Electronic contribution

$$\frac{\partial \Delta H}{\partial x} \cong -\gamma K_0 \frac{v_H^2}{v_0} + \left(\frac{\partial \Delta H}{\partial x}\right)_V$$

Where v_0 is the atomic volume of the host specimen, v_H is the volume increase per hydrogen atom, K_0 is called bulk modulus, which is nearly constant with hydrogen concentration, and $\gamma = \frac{2(1-2\sigma)}{3(1-\sigma)}$, dependant on Poisson's ratio, σ.

MATERIALS FOR HYDROGEN CHEMISORPTION

Hydrogen chemisorption is usually carried out via intermetallic compounds, that is, metallic alloys forming an ordered solid-state compound between two or more metallic elements whose crystal structure differs from that of the other constituents. In most cases, intermetallic compounds are built by alloying:

- a metal which easily forms stable hydrides (A)
- and another element which does not form stable hydrides (B)

The intermetallic compounds thus formed could then be grouped according to their stoichiometry, such as:

- AB_5 ($LaNi_5$, $CaNi_5$)
- AB_2 ($ZrMn_2$, ZrV_2)
- AB ($TiFe$)
- A_2B (Mg_2Ni)

MATERIALS FOR HYDROGEN CHEMISORPTION

Stoichiometry thus provides a first classification method for comparing intermetallic compounds. Within some stoichiometric groups, some approximations can be introduced (as in example linear correlation among pressure and cell volume for AB_5, in example).

One common feature of intermetallic compounds for hydrogen chemisorption is that entropy variation for them is for them constant. Thus, from the van’t Hoff’s relation:

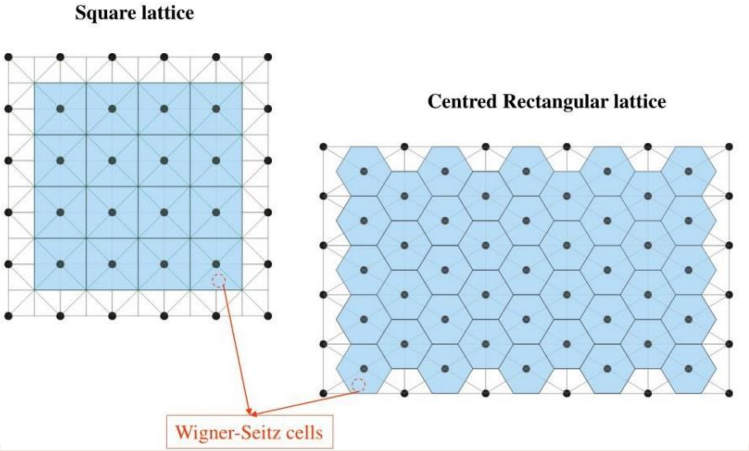
$$\ln P_{eq} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

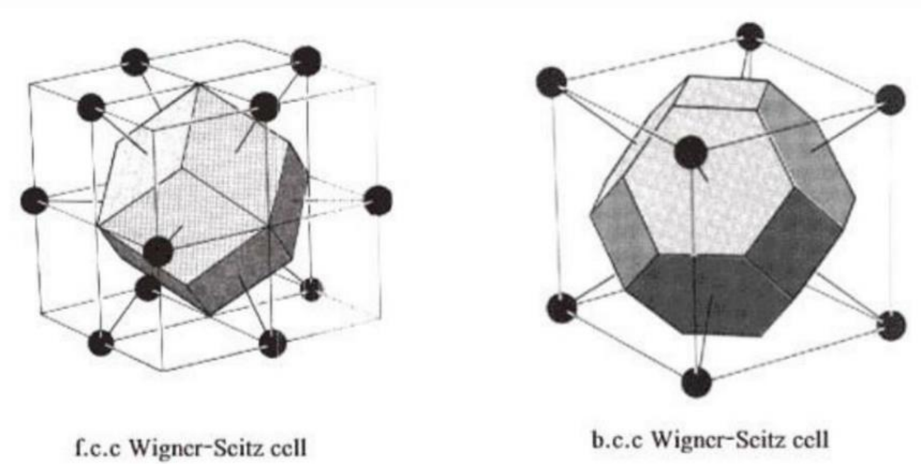
Is clear as temperature and pressure are the main thermodynamic parameters influencing the heat of formation (ΔH). In this extent, semi-empirical models can be applied for some systems and give useful physical insight on the hydride formation and stability. To better evaluate the performances of different hydrides, two empirical models will be presented: the *Miadema’s model* and the *Semi-empirical band structure* one.

MIEDEMA’S MODEL

It’s a thermodynamic model (developed in the 1970s) for estimating the heat of solution of metal alloys, which was found to give reasonably good agreement between with experimental data.

Within the Miedema’s model, metals are not modelled as a lattice of positive ions surrounded by a “sea” of electrons, but at each lattice point it is assigned the so-called Wigner-Seitz cell having the same symmetry properties of the crystalline network filling the entire space of analysis.

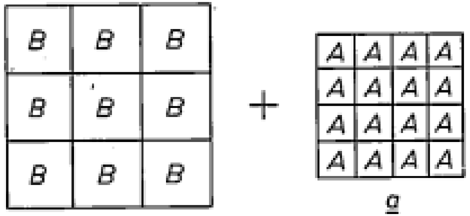



f.c.c Wigner-Seitz cell

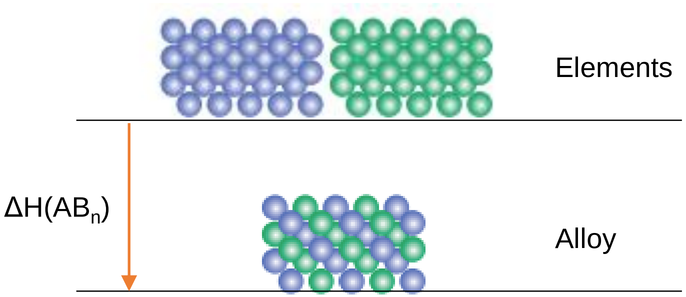
b.c.c Wigner-Seitz cell

MIEDEMA'S MODEL

In equilibrium conditions, the analysed space is represented by the sum of the volumes of the A and B phases, defining the equilibrium condition in which energy is minimised.



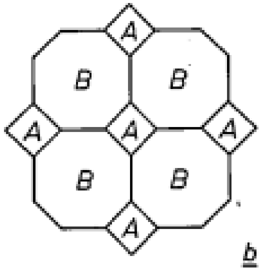
Miedema, Philips tech. Rev., (1973), 33, 6, 149 - 161

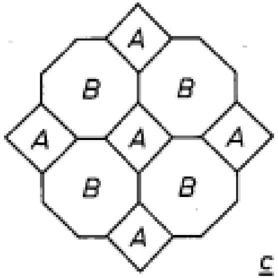


Züttel A., Encyclopedia of Electrochemical Power Sources – Fuels – hydrogen storage – hydrides, Elsevier (2009), 440-458

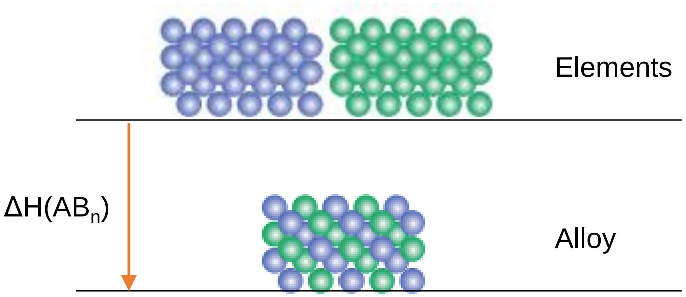
MIEDEMA’S MODEL

At the alloy formation, electron transfer process taking place among the metal with bigger chemical potential (B) to the metal having lower chemical potential (B), induces a re-organization of the volume of the Wigner-Seitz cell, and a consequent increase of enthalpy of formation of the alloy from the energy minimum.





Miedema, Philips tech. Rev., (1973), 33, 6, 149 - 161



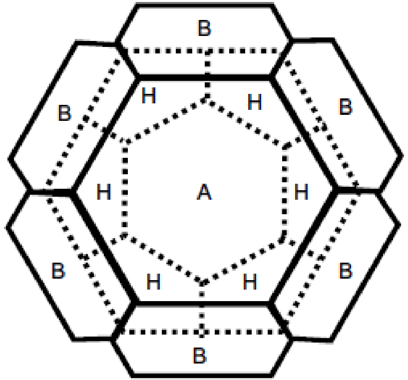
Züttel A., Encyclopedia of Electrochemical Power Sources – Fuels – hydrogen storage – hydrides, Elsevier (2009), 440-458

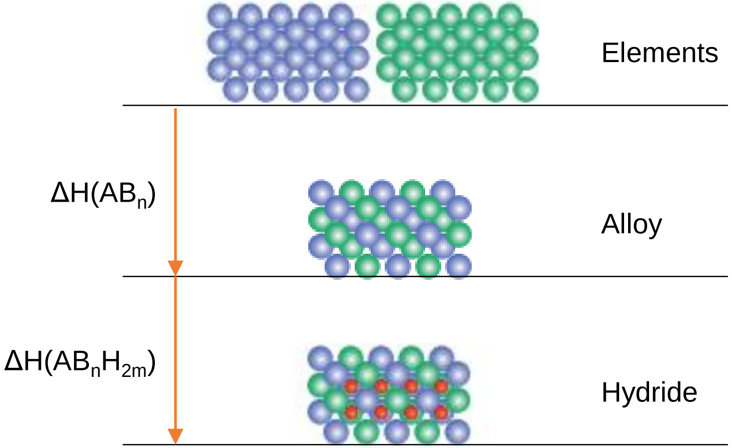
MIEDEMA’S MODEL

Thus, under the assumption of constant electron density, hydrogen absorption can be modelled as a transition from a binary alloy to a ternary alloy (representing the hydride)

$$AB_n + xH_2 \leftrightarrow AB_nH_{2x}$$

And the absorption process can be represented as a variation in the relative volume of the Wigner-Seitz cell within the lattice, which allows to calculate heat of solution.



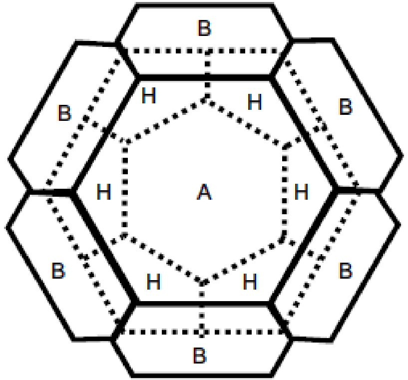


Züttel A., Encyclopedia of Electrochemical Power Sources – Fuels – hydrogen storage – hydrides, Elsevier (2009), 440-458

MIEDEMA'S MODEL

By assuming that hydrogen atoms have a stronger affinity with atoms of metal *A*, than ones of metal *B*, upon hydrogenation, hydrogen atoms are going to be bound to metal A, but they are in contact with metal B too. In order to be able to bound to the host metal, during hydrogenation, some bonds between A and B must thus break. This change in bond distribution is at the basics of the variation in heat of formation of the hydride, which can be assumed to energetically equivalent to a mechanical mixture of AH_m and B_nH_m, once the contact surface of A-H and B-H Wigner-Seitz cells can be considered equivalent. Thus:

$$\Delta H(AB_nH_{2m}) = \Delta H(AH_m) + \Delta H(B_nH_m) - \Delta H(AB_m)$$



The heat of formation of the hydride can be calculated as the sum of the heat of formation of the elemental hydrides and the heat of formation for the alloy. This equation is knowns as *Miedema's rule of reversed stability.* Due to the minus sign :

- more stable (lower H) alloys produce more unstable hydrides
- more unstable alloys produce more stable hydrides.

SEMI-EMPIRICAL BAND STRUCTURE MODEL

In the Semi-empirical Band Structure Model, the heat of formation calculation is performed thanks to the linear proportionality among heat of formation and electron binding energy (ΔE) of the metal binding to hydrogen:

$$\Delta H = \frac{n_S}{2}[\alpha \Delta E - \beta]$$

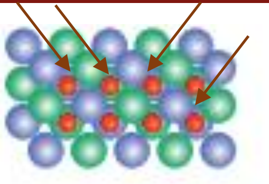
Where α and β are parameters determined empirically, and n_S is the number of electrons per atom in the lowest conduction band of the metal. The binding energy can be expressed as the difference among the energy of the s-th conduction band and the Fermi level:

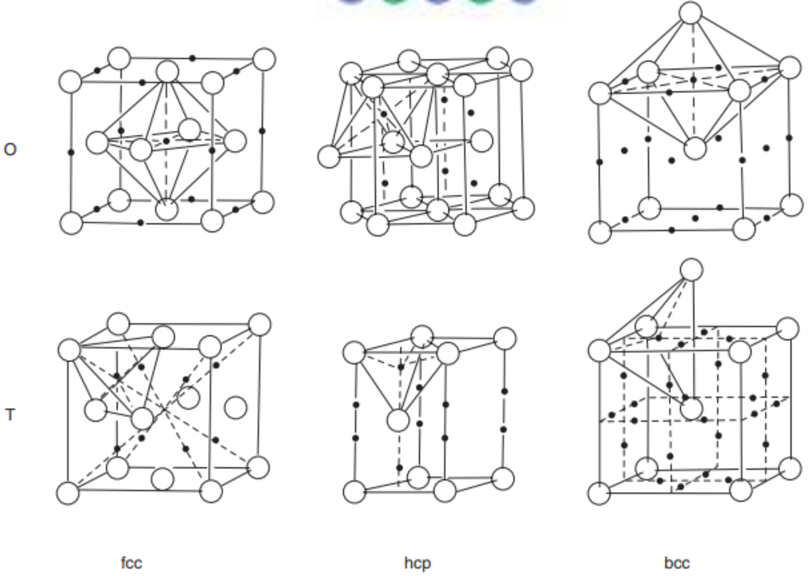
$$\Delta E = E_F - E_S$$

Where the Fermi level is the energy of the highest conduction band, above which electrons are not considered bounded to atoms.

It allows to obtain more precise results than the Miedema's one.

EFFECTS ON HYDROGENATION ON THE ELECTRONIC STRUCTURE





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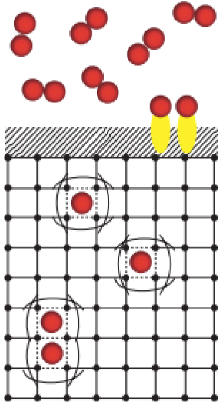
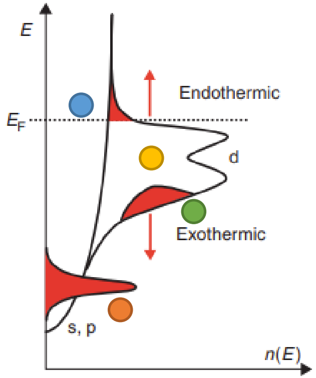




🟡 1. Reduction of symmetry and width of the conduction band.
🟠 2. Appearance of a metal–hydrogen bonding band below the metal d-band, where electrons move lowering the Fermi level.
🟢 3. The H–H interaction produces new attributes in the lower portion of the density of states.
🔵 4. Inequality between the additional electrons brought by hydrogen and the number of new electron states leads to rise of the Fermi level.

MATERIALS SUITABLE FOR HYDROGEN CHEMISORPTION

When evaluating suitability of a material to be used as host for chemisorption, the following aspects have to be considered:

1. The **synthesis methods** usable for its production need to be adapted to industrial scaling up. In fact, while a fine control over material synthesis can be obtained at laboratory grade, during industrial scaling up to large production techniques, performances can be limited.
2. **Material activation** is often required to brake the passivating oxide layer which would reduce the storage efficiency. Activation is performed by injecting hydrogen at higher pressures and temperatures than usual operative condition to force hydrogen molecules to permeate through the oxide layer. After dehydrogenation, the lattice expansion and contraction induces some breakings within the hosting material which allow to expose un-oxidized absorption sites.

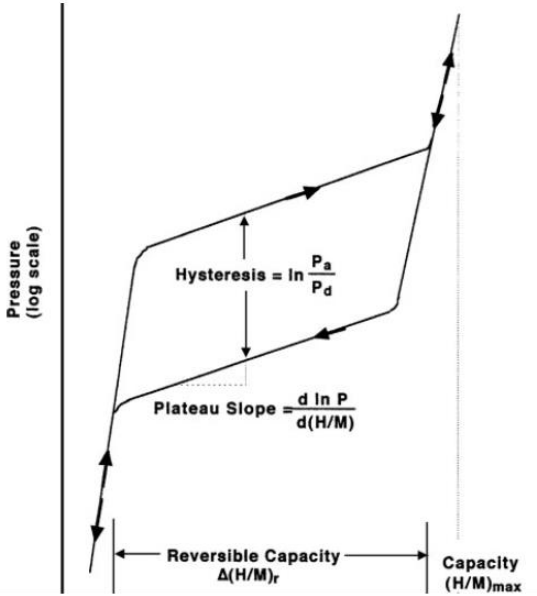
MATERIALS SUITABLE FOR HYDROGEN CHEMISORPTION

3. **Hysteresis** is a common phenomena usually characterizing materials which are related to some “memory effect” (as an example: magnetism). In hydrogen chemisorption hysteresis develops in form of different “pressure paths” occurring during hydrogenation and dehydrogenation.

The importance in characterizing hysteresis is relied to the fact that it could cause a general loss of efficiency due to irreversible deformations of the structure host material during hydrogen absorption and desorption.

In most applications it should be as small as possible.

For chemisorption, hysteresis is characterized by four different features.



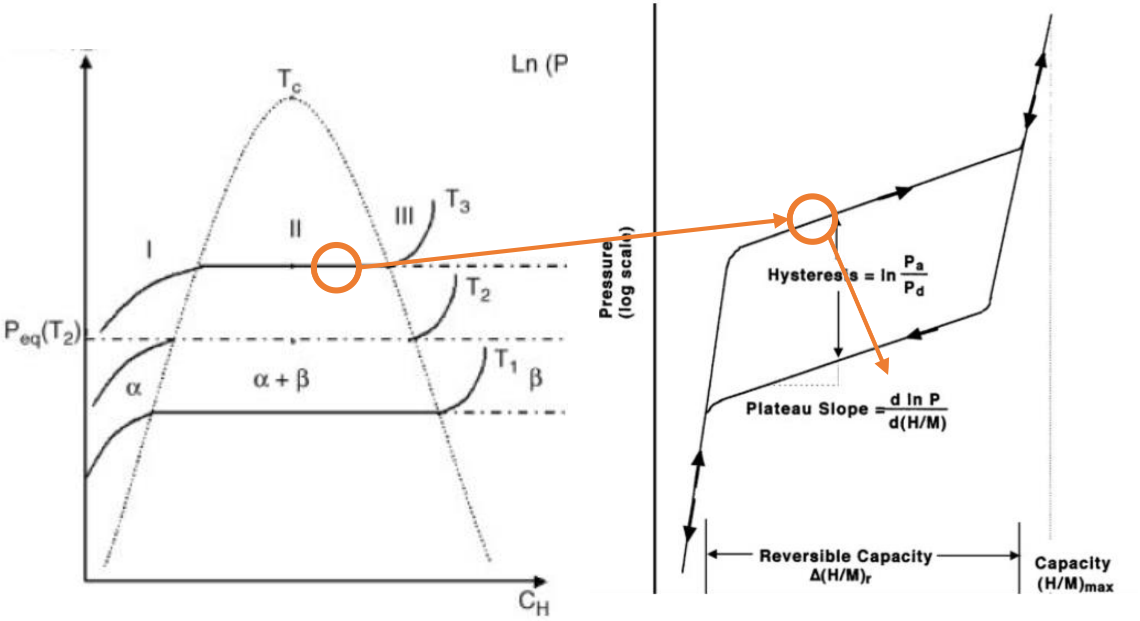
MATERIALS SUITABLE FOR HYDROGEN CHEMISORPTION

I. The plateau slope.

During hydrogenation, pressure should stay constant until all of the matter in the α phase have been converted into the β one.

However, in real conditions, inhomogeneities into the hosting materials constitute a resistance for the process and additional pressure is required to promote hydrogenation, giving rise to the positive slope of the rising path:

$$\nu = \frac{d \ln P}{d(H/M)}$$



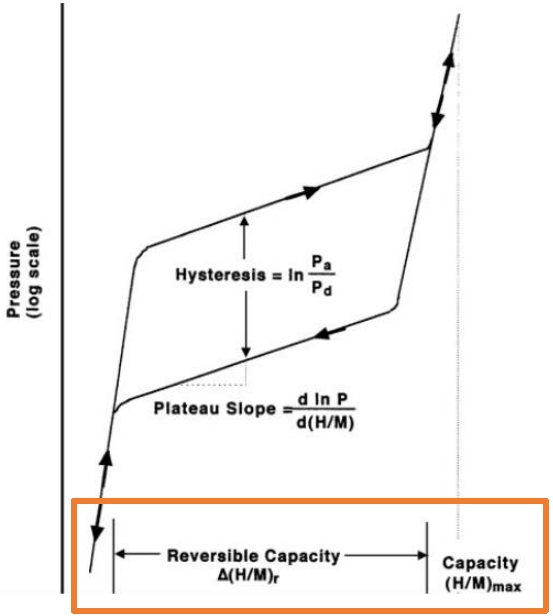
MATERIALS SUITABLE FOR HYDROGEN CHEMISORPTION

II. The reversible capacity.

It is defined as the width of the plateau region and is the most important factor for practical applications.

It can be reported either in terms of atomic ratio (H/M), thus the number of hydrogen atoms stored with respect to the number of metal atoms, or in weight percent (wt.%), that is the percentage of the weight of hydrogen stored over the weight of the hydride phase.

Sometimes the volumetric capacity can be also used.



MATERIALS SUITABLE FOR HYDROGEN CHEMISORPTION

4. **Hydrogenation kinetics.** Theoretically, and at a laboratory scale, hydrogenation kinetics aim to investigate physical and chemical processes at in order to enhance the reaction rate of chemisorption, as chemisorption needs the hydrogen molecule bond to be broken before hydrogen atoms can diffuse into the material lattice.

Nonetheless, it worth to pay attention that real applications are often limited by apparently simpler aspects. In example, let's focus on the hydrogenation process forming MgH_2, where the hosting material is doped with Nb_2O_5 (1 mol%), which is characterized by particularly fast reaction kinetics.

Capacity ≈ 5 wt.%

$T_{operation}$: 150 ÷ 250 °C

For 30 s of operation 2kW / mol_{H2} need to be removed from the alloy to keep it working at constant temperature.

By scaling up to industrial needs it turns out as by filling a tank of 5 kg of hydrogen within 300 s, 500 kW of heat need to be removed from the tank.

MATERIALS SUITABLE FOR HYDROGEN CHEMISORPTION

5. Cycle life. For industrial applications, effective cycling over hundreds or thousands of cycles needs to be guaranteed without significant performance losses. Life cycling can be reduced because of:

- Metastable behavior with respect to disproportionation, a reaction leading to the formation of a hydride with lower energy than the original alloy at standard conditions (i.e. the disproportionation reaction for $LaNi_5$: $LaNi_5 + H_2 \rightarrow LaH_2 + 5Ni$, has a lower free energy than the hydration reaction: $LaNi_5 + 3H_2 \leftrightarrow LaNi_5H_6$. One drawback of the disproportionation reaction is that requires a deeper atomic rearrangement)
- Poisoning due to impurities in the hydrogen gas (screening effect, occupation of reaction sites)
- Particles agglomeration (less favorable S/V ratio)
- Structural relaxation, crystalline growth, phase change and/or formation of non-hydride phases

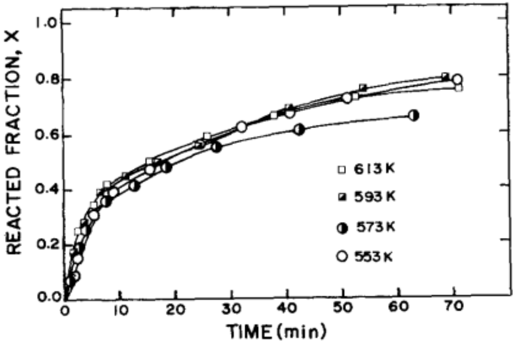
To date, magnesium and Mg-based compounds could sustain up to a few thousand cycles without drastic changes in hydrogen sorption properties.

FINAL CONSIDERATIONS

6. Decrepitation. It is the self-pulverization of alloy particles into smaller-size powder because of volume change upon hydrogenation and the brittle nature of hydriding alloys. This could change the packing of a material which in turn will change the heat transfer and gas flow inside the storage tank. This effect is amplified by the fact that the intrinsic heat conductivity is usually different for the hydrided and dehydrided state. Decrepitation could be a serious problem because the small particles will fall to the lower part of the tank and, upon hydrogenation, could expand to such an extent as to lead to tank rupture.

SUMMARY AND FINAL CONSIDERATIONS

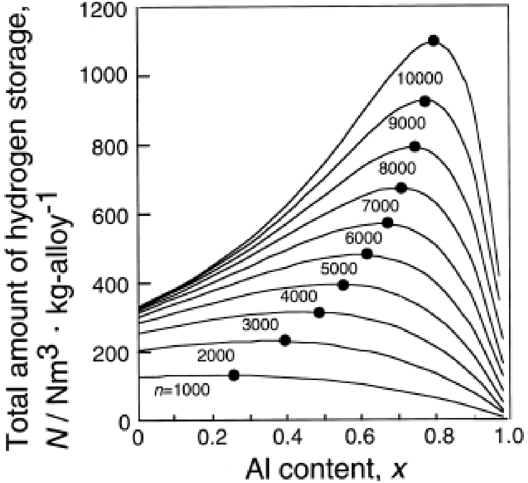
To better highlight the most performing operational conditions and/or material for metal hydride, the plot of curves showing the amount of reacted hydrogen versus time can be analysed. They are a tool for



Jung W.B. et al., Int. J. Hydrogen Energy, *15, (9)*, (1990), *641–648*

for highlighting the presence of rate-limiting steps of the reaction.

Another way to improve cycling stability is given by element substitution, consisting of doping the host material with other elements.



Nishimura K. et al., J. Alloys&Comp, *268, (1-2)*, (1998), *207-210*

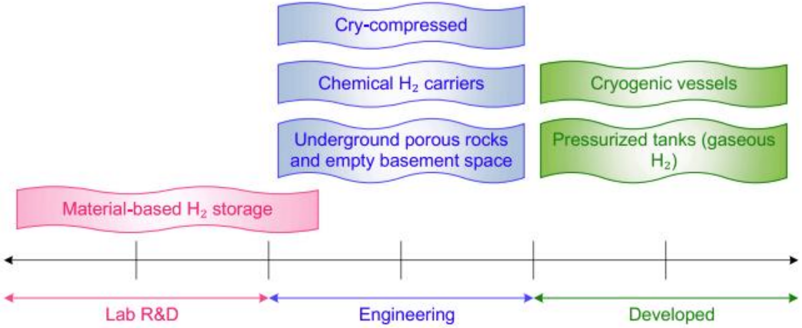
STATE OF THE ART

Alloy classification	Max storage capacity (wt.%)	Costs (€/g_{H2})	Notes
AB	1 – 2	0.34 – 0.35	Severe activation conditions required oxide film formation is easy to form.
AB_2	1.5 – 2 (up to 3.4 recorded)	0.5 – 1.3	Long life cycle and low cost, but sensitive o gas impurities
A_2B	Up to 3.6		Hydrogen needs to be released above 250-300 °C
AB_5	Up to 1.5	0.7 – 2	Low hysteresis, low capacity, operation temperature: about 100 °C, ease of activation, not cheap
Borohydride complex	8 – 18		Light, high storage capacity, difficult hydrogen release, operating temperature: 300 – 400 °C
Alanates	4 – 10		Light, high storage capacity, operative temperature: 100 – 400 °C

Ghorbani B. et al., J. Env. Chem. Eng, 11, (3), (2023), 109957

SUMMARY AND FINAL CONSIDERATIONS

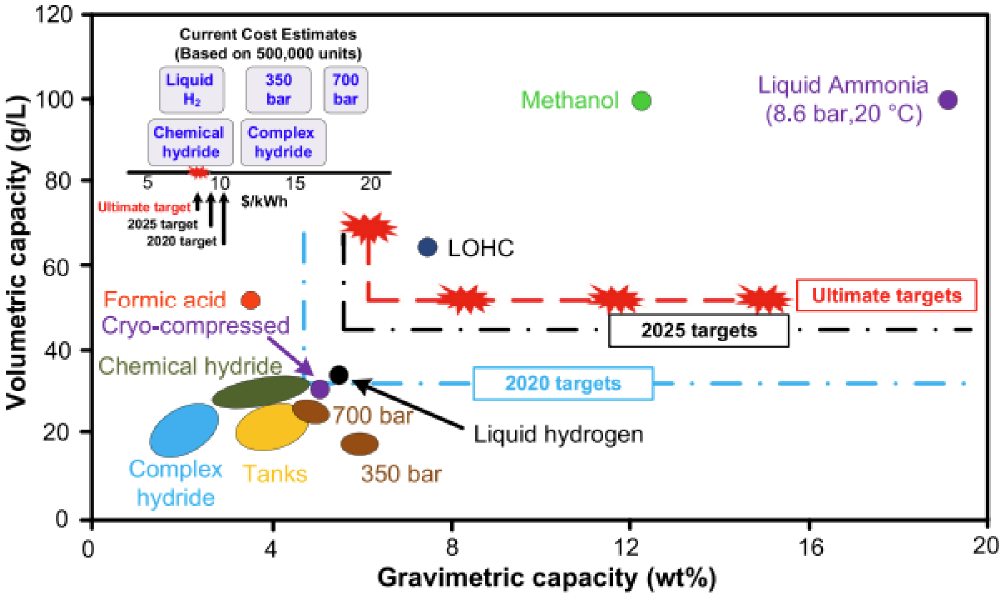
- Kinetics of hydrogen absorption and release are influenced by a plethora of aspects, but in general it can be summarised that hydrogen absorption is characterised by fast reaction rates and a heat of reaction which is specific of the host material. Reaction kinetics depend on the chemistry of the system, but also on the size, surface properties, degree of purity of both the solid and the gas phases.
- The main limitations are due to poor mass and heat transfer, which are increasing the loading operation, but also to the embrittlement of the hydride phase, constituting the main aging phenomenon.



Ghorbani B. et al., J. Env. Chem. Eng, 11, (3), (2023), 109957

SUMMARY AND FINAL CONSIDERATIONS

- Chemisorption is a very attractive method for hydrogen storage in form of metal hydrides.



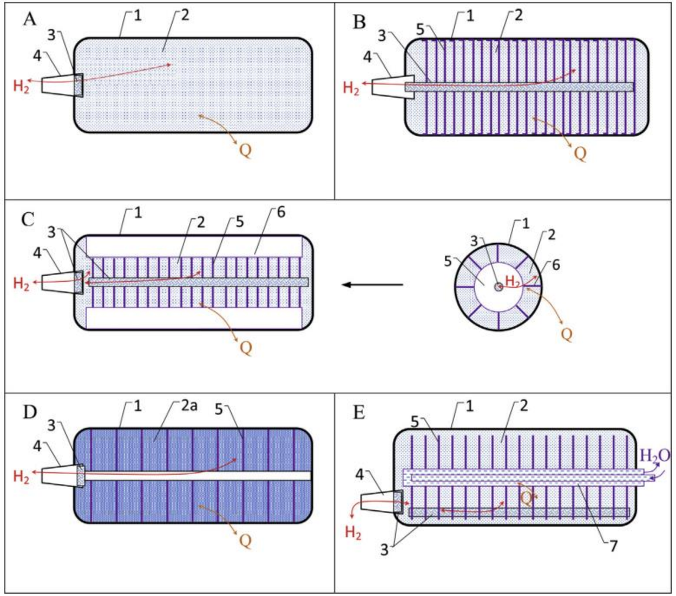
Ghorbani B. et al., J. Env. Chem. Eng, 11, (3), (2023), 109957

4. METAL HYDRIDE SYSTEMS FOR SOLID HYDROGEN STORAGE

TANKS FOR SOLID HYDROGEN STORAGE

It was presented as temperature management is one of the biggest problems to be handled if large storage capacities are wanted to be achieved, as tanks operating at low temperature (around or below 100 °C) are characterized by capacities of about one to few wt.% values.

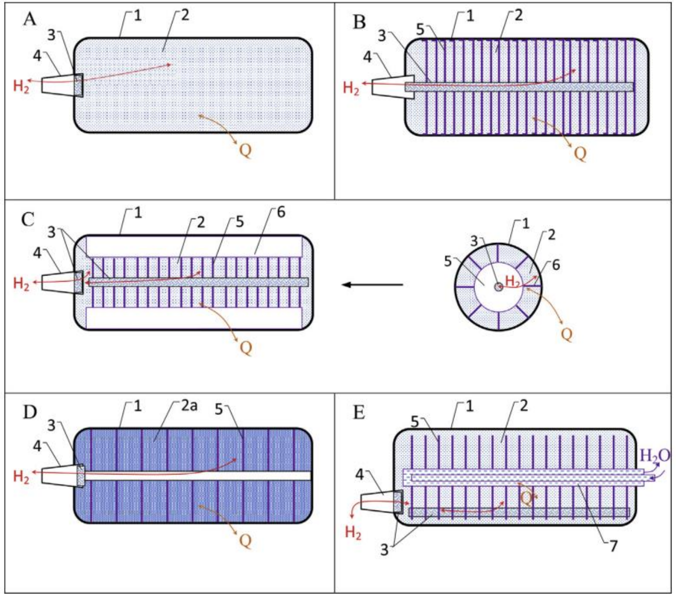
Tanks are classified according to the factors governing the heat transfer. Longitudinal or traversal fins are used in combination with pipes to homogeneously diffuse and gather hydrogen gas.



Lototskyy M.V. et al., Int. J. Hydr. En., 40, 35, (2015), 11491-11497

TANKS FOR SOLID HYDROGEN STORAGE

- Layout A – powder (2) is directly loaded in the compartment (1). Hydrogen flows across a filter(3), tanks to a gas connector (4).
- Layout B – transversal aluminium-copper fins are used form metal-hydride beds with (5) improved heat transport.
- Layout C – Longitudinal fins (6) are added to the tank.
- Layout D – thermally-expanded graphite is added to metal-hydride beds composition to improve heat transfer
- Layout E – liquid heating-cooling fluid circulation is added to the tank.



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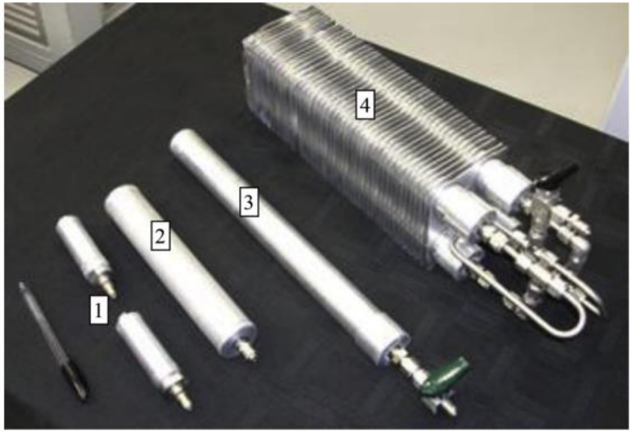
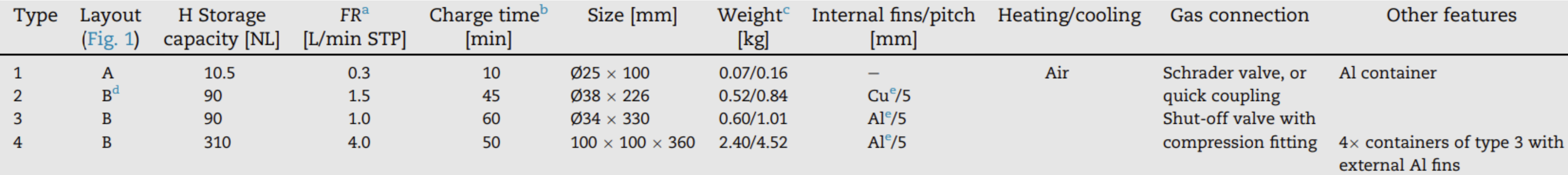
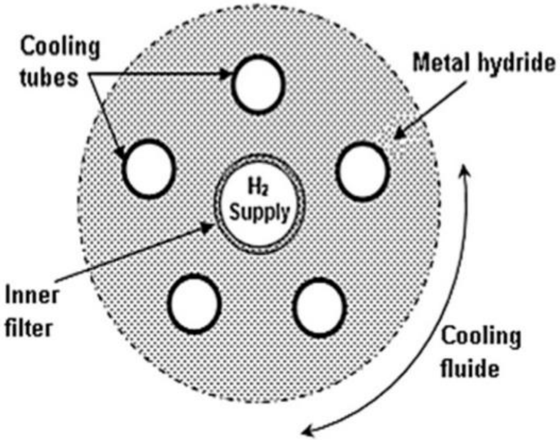
TANKS FOR SOLID HYDROGEN STORAGE

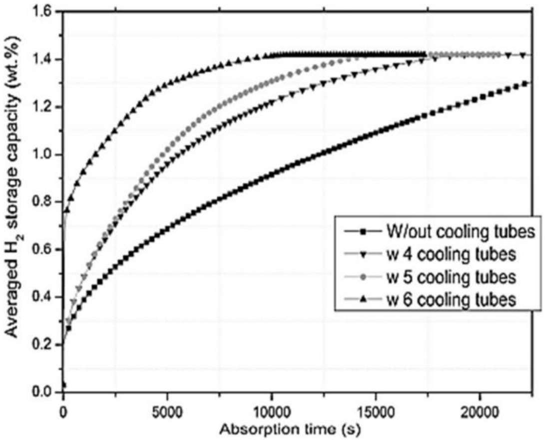




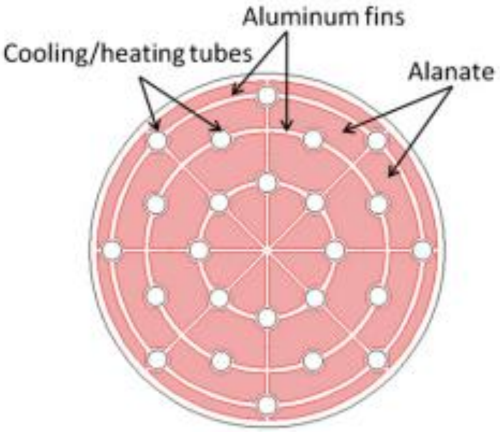
Type	Layout (Fig. 1)	H Storage capacity [NL]	FR[a] [L/min STP]	Charge time[b] [min]	Size [mm]	Weight[c] [kg]	Internal fins/pitch [mm]	Heating/cooling	Gas connection	Other features
1	A	10.5	0.3	10	Ø25 × 100	0.07/0.16	–	Air	Schrader valve, or quick coupling	Al container
2	B[d]	90	1.5	45	Ø38 × 226	0.52/0.84	Cu[e]/5			
3	B	90	1.0	60	Ø34 × 330	0.60/1.01	Al[e]/5		Shut-off valve with compression fitting	
4	B	310	4.0	50	100 × 100 × 360	2.40/4.52	Al[e]/5			4× containers of type 3 with external Al fins

TANKS FOR SOLID HYDROGEN STORAGE





Azfal M. et al., Int. J. Hydr. En., 42, (2017), 30661-30682



Raju M., Kumar S., Int. J. Hydr. En., 36, (2011), 1578-1591

TANKS FOR SOLID HYDROGEN STORAGE – HEAT TRANSFER

Thermal conduction under a temperature gradient is described by the Fourier’s law:

$$q = k\nabla T$$

where q is the heat flux density, and k the thermal conductivity of the (host) material.

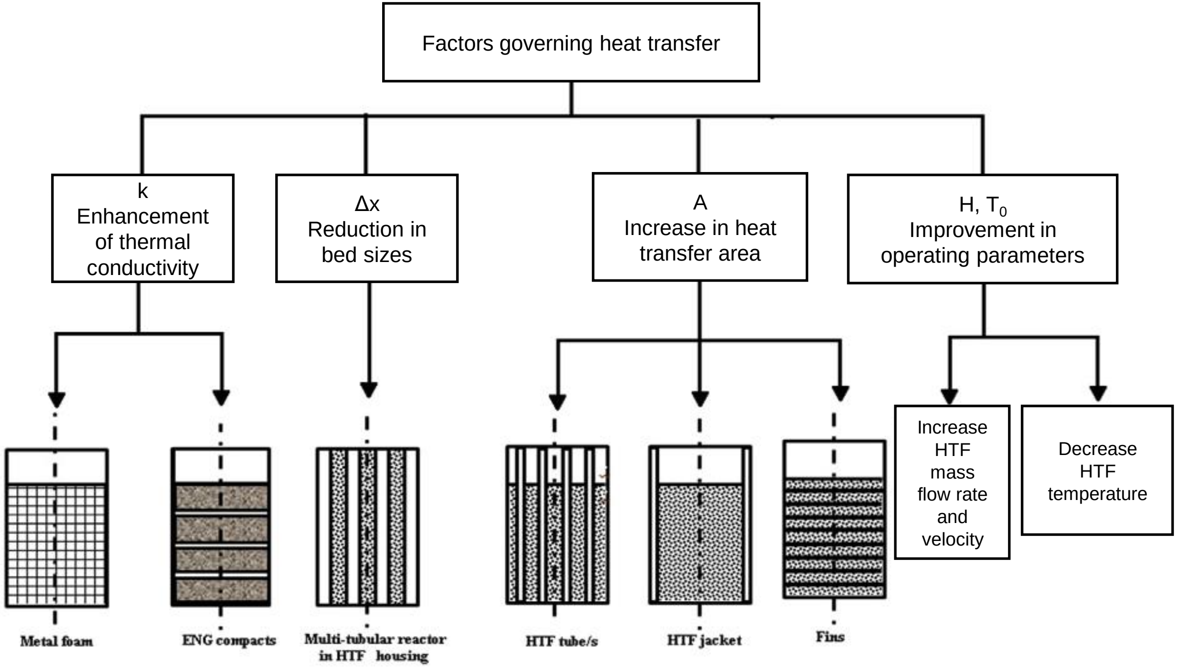
For a homogeneous material, and simplifying the equation in the 1D case, and considering the heat transfer surface area (A):

$$q = kA\frac{\Delta T}{\Delta x}$$

In addition, the relationship for heat transfer by convection is:

$$q = hA(T - T_0)$$

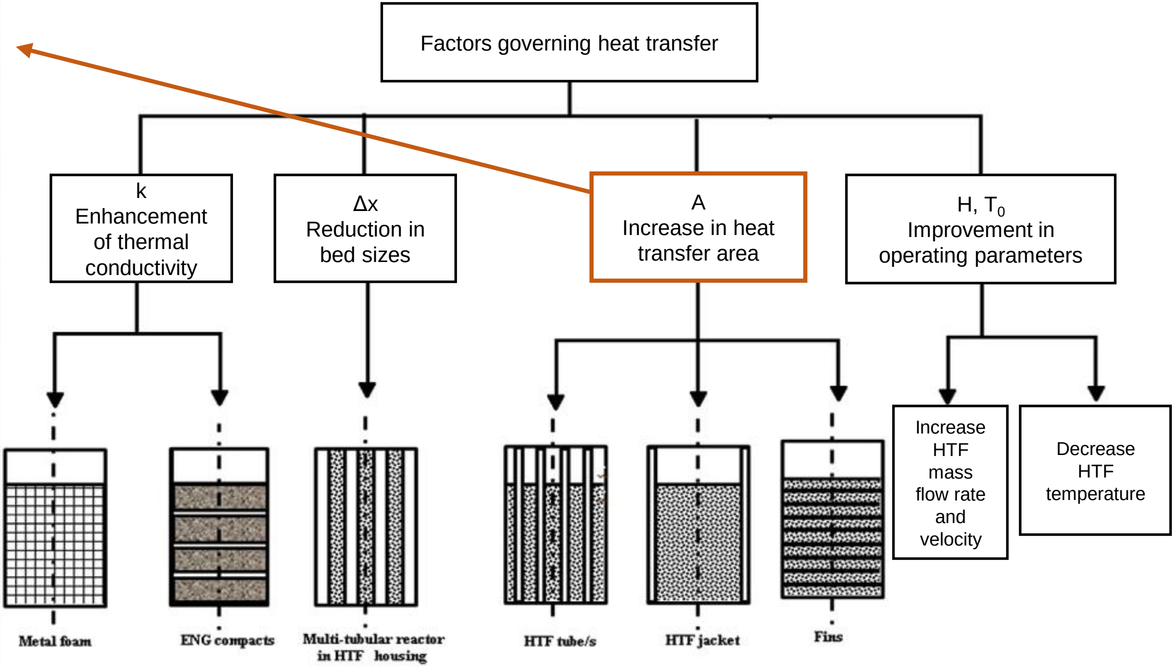
Where h is the heat transfer coefficient, and T_0 the temperature of the cooling fluid.



Azfal M. et al., Int. J. Hydr. En., 42, (2017), 30661-30682

TANKS FOR SOLID HYDROGEN STORAGE – HEAT TRANSFER

- Optimising hydride arrangement
  Fins → Flakes → Foam
- Optimising particle and pore size distributions.
- Reducing the loss of contact area with the thermal management system upon hydride expansion/contraction due to hydrogen absorption/desorption.



Factors governing heat transfer

k
Enhancement of thermal conductivity

Δx
Reduction in bed sizes

A
Increase in heat transfer area

H, T_0
Improvement in operating parameters

Increase HTF mass flow rate and velocity

Decrease HTF temperature

Azfal M. et al., Int. J. Hydr. En., 42, (2017), 30661-30682

TANKS FOR SOLID HYDROGEN STORAGE – HEAT TRANSFER

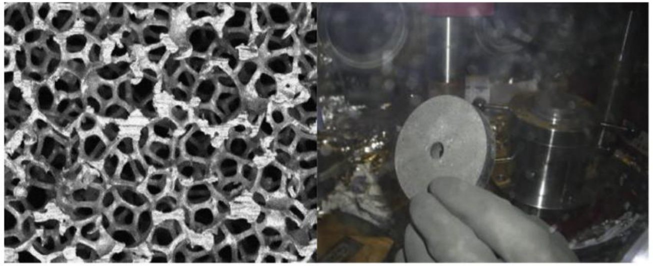
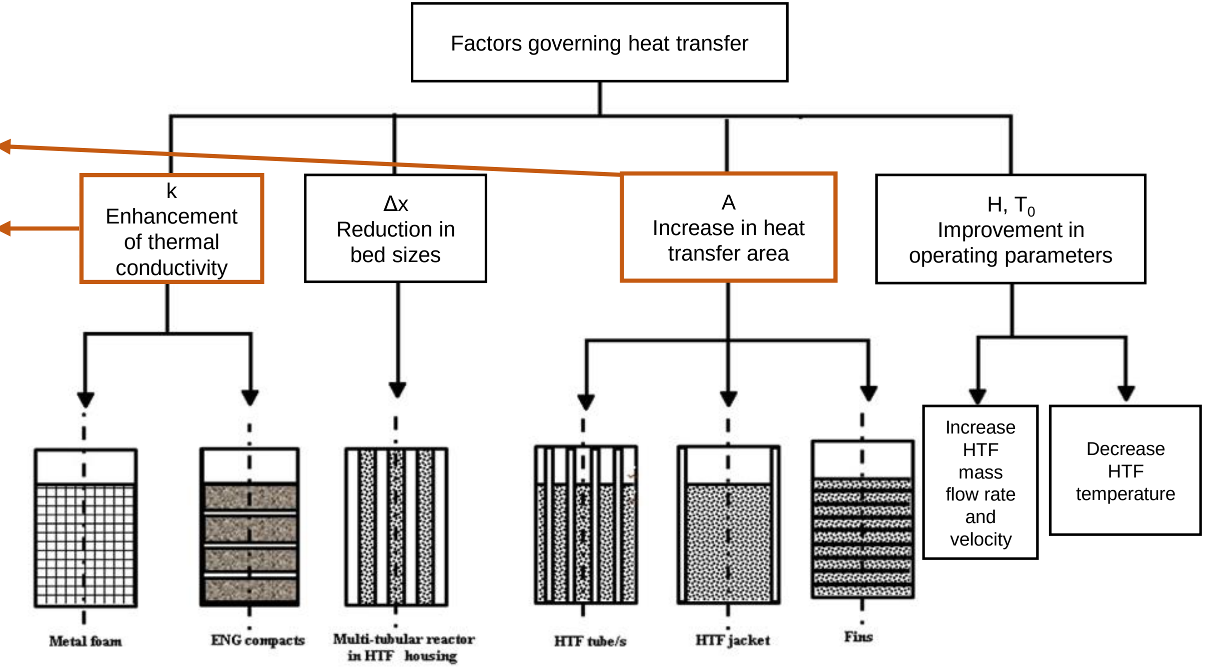


Fig. 4 – **a) Aluminum mesh for improvement of thermal conductivity [22] b) $NaAlH_4$ compacts [34].**



Factors governing heat transfer

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Increase HTF mass flow rate and velocity

Decrease HTF temperature

Azfal M. et al., Int. J. Hydr. En., 42, (2017), 30661-30682

TANKS FOR SOLID HYDROGEN STORAGE – CONCLUSIONS

Tanks for solid hydrogen storage still need to be improved in terms of:

- Volumetric and gravimetric energy density
- Costs and refuelling times
- hydrogen discharge kinetics needs to be speeded up
- Integration with FC plant in order to maximise the wasted heat recovery

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Dipartimento di
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