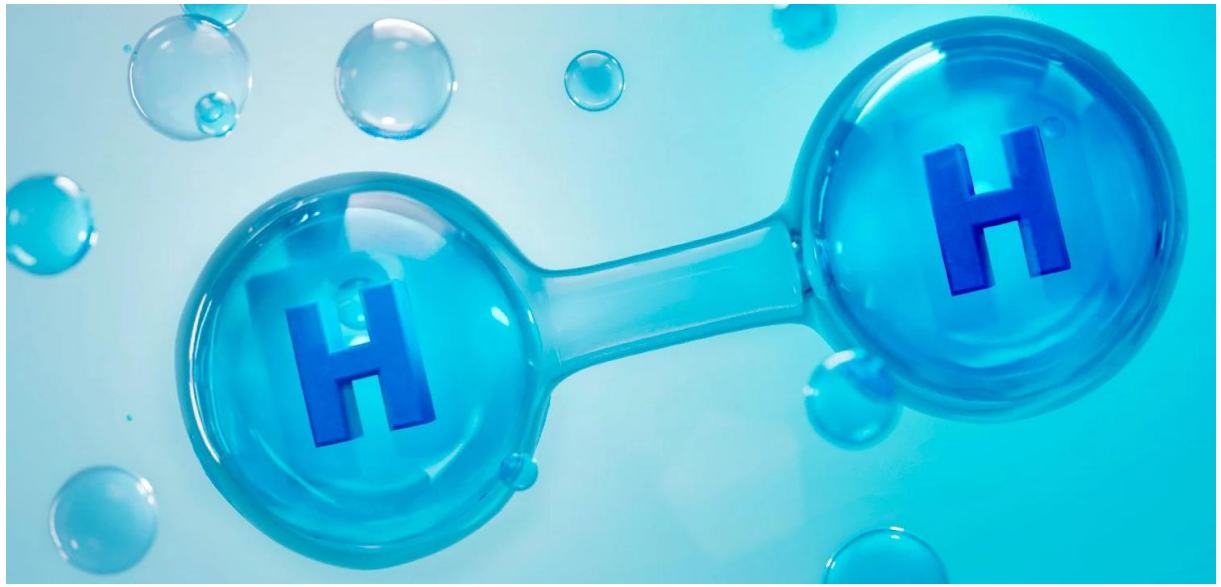
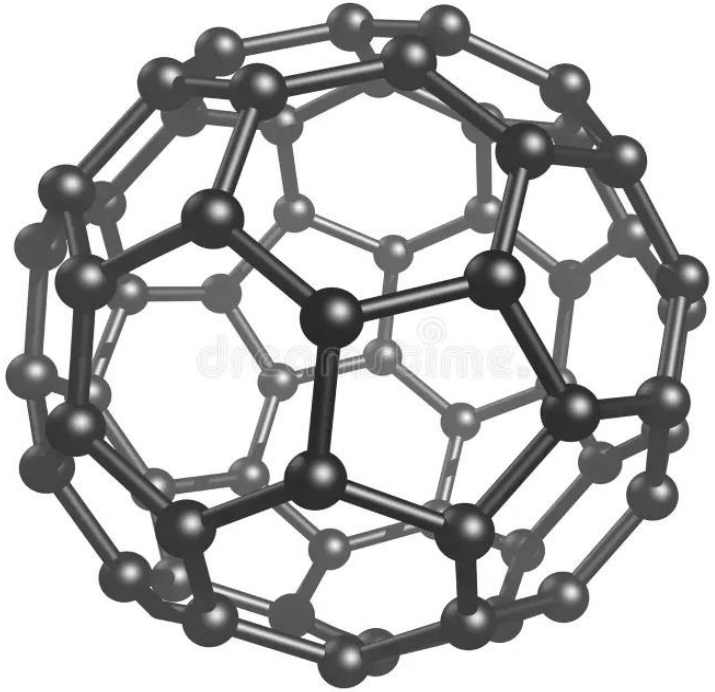
UNIVERSITÀ DI PARMA

Hydrogen storage

From gas cylinders to fullerides





Outline

- "General problem" of H storage
- Storage methods
- Role of carbon materials
- Lithium intercalated fullerides

General problem of H storage

- Hydrogen: lightest element of PT
- Three possible isotopes: H, D and T
- Molecular form: H_2
- Van der Waals equation:

$$p(V) = \frac{n \cdot R \cdot T}{V - n \cdot b} - a \cdot \frac{n^2}{V^2}$$

Volume occupied per molecule

Repulsion constant

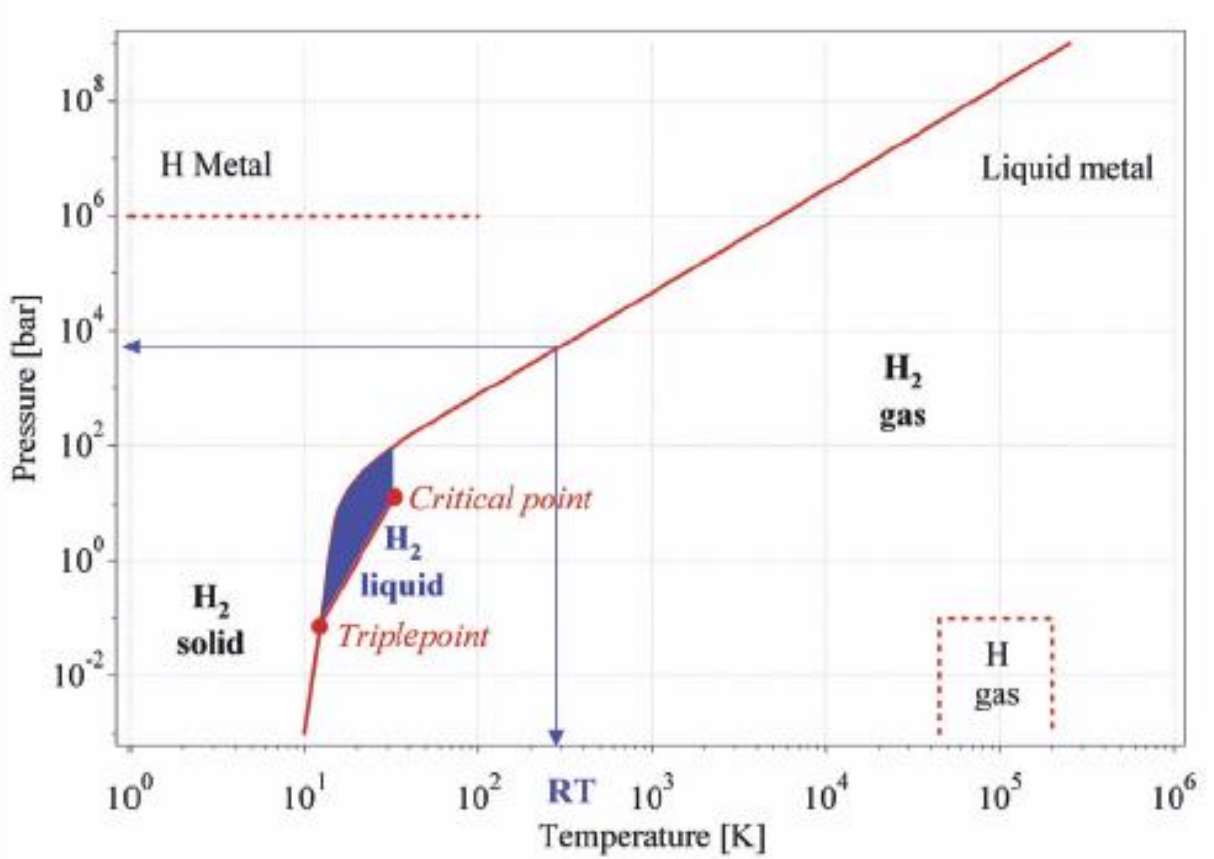


Fig. 1 Primitive phase diagram for hydrogen[46]. Liquid hydrogen only exists between the solidus line and the line from the triple point at 21.2 K and the critical point at 32 K.

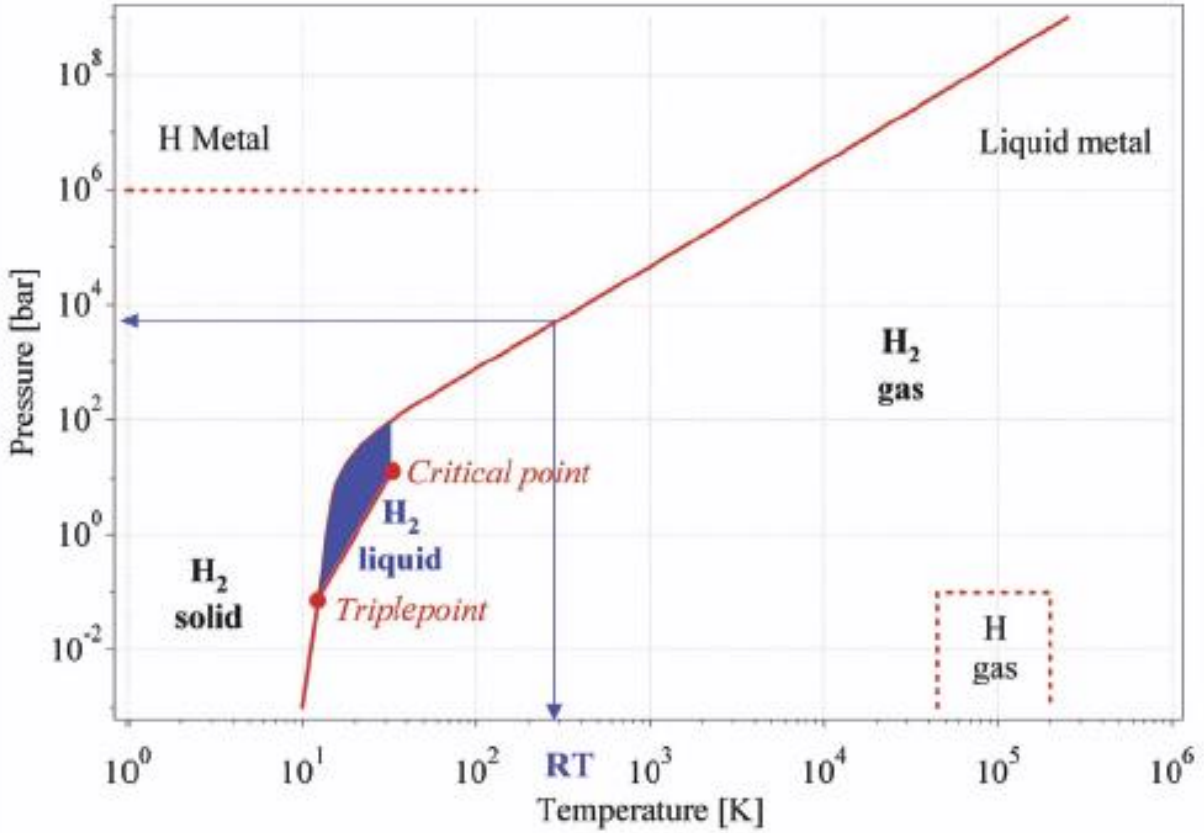
A. Züttel, *Materials for hydrogen storage*. In *materialstoday*, Elsevier Ltd. (2003)

General problem of H storage

- H at RT and atmospheric pressure: 1kg $\equiv 11m^3$

- Storage:
  - work to compress
  - T below T_c
  - interaction with another material

- Reversibility of H uptake and release



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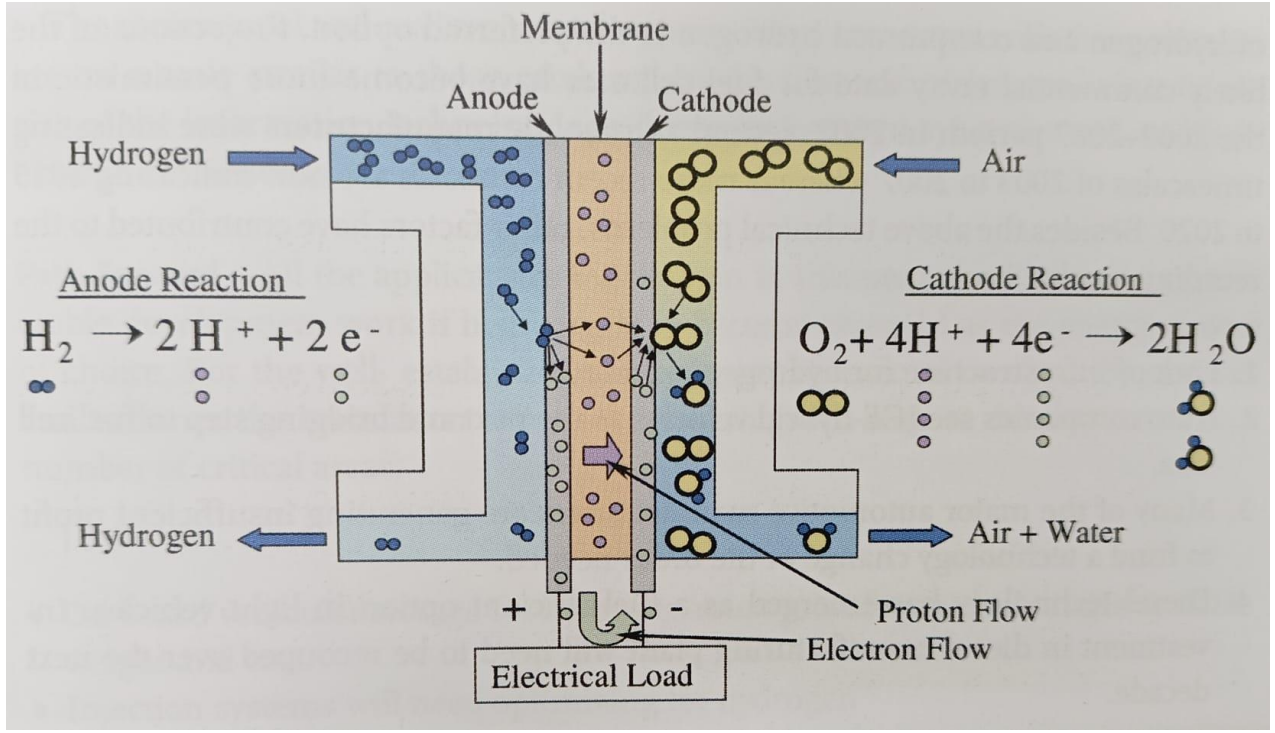
Why do we want to store H?

- To produce energy:

1. Heat production by direct combustion with air

2. Reaction with O in rocket type combustors

3. Electrochemical conversion in fuel cell



J.D. Speight, *The Hydrogen Cycle*. In *Hydrogen as a future energy carrier*, Wiley-VCH. (2008)

High pressure gas cylinders

- $p \sim O(10^2 - 10^3 MPa)$
- $\frac{d_w}{d_0} = \frac{\Delta p}{2 \cdot \sigma_v + \Delta p}$

  Δp → Overpressure

  σ_v → Tensile strength
- Gravimetric density decreases with increasing pressure
- High work to compress

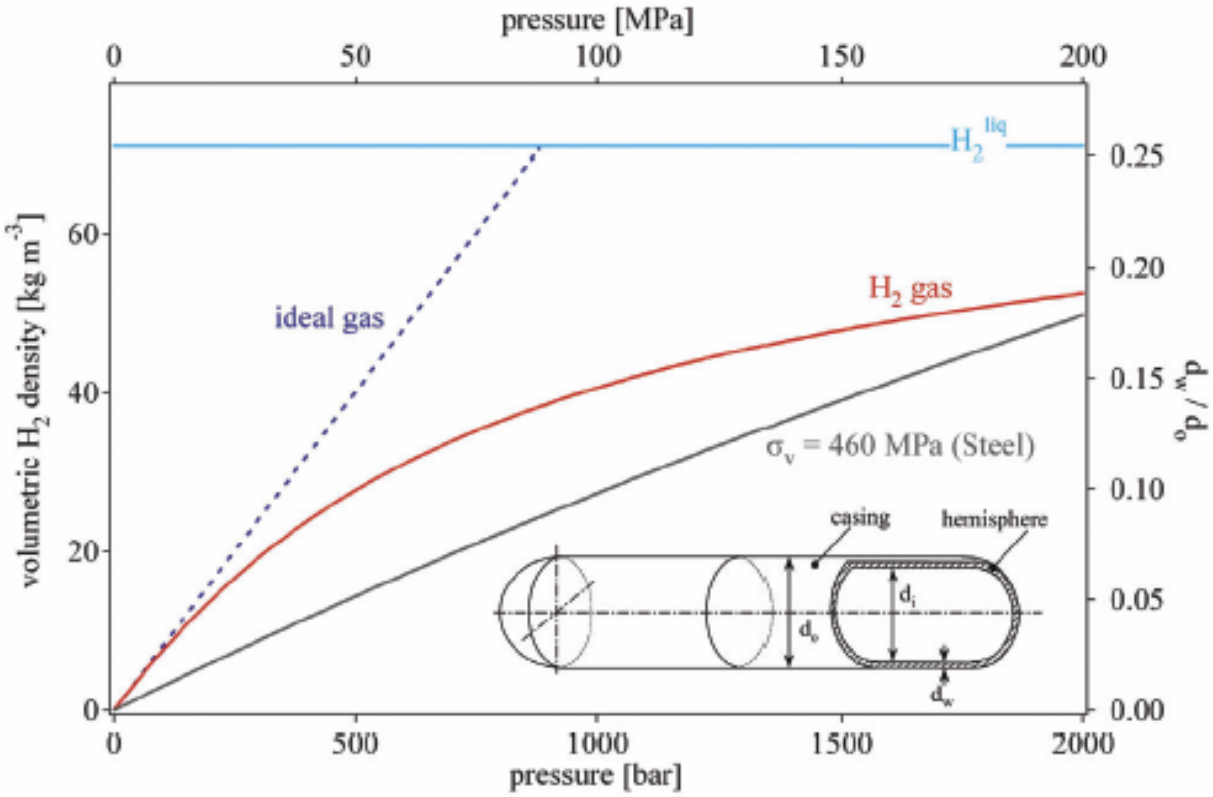
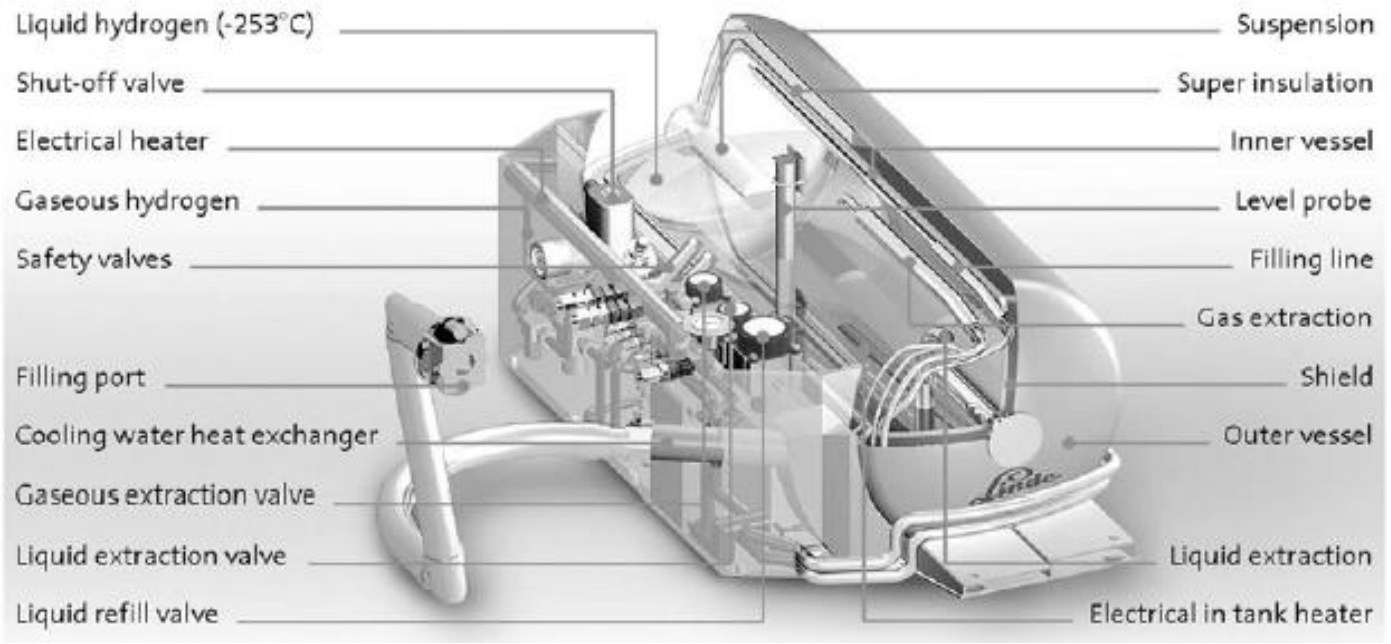


Fig. 2 Volumetric density of compressed hydrogen gas as a function of gas pressure, including the ideal gas and liquid hydrogen. The ratio of the wall thickness to the outer diameter of the pressure cylinder is shown on the right hand side for steel with a tensile strength of 460 MPa. A schematic drawing of the pressure cylinder is shown as an inset.

A. Züttel, *Materials for hydrogen storage*. In *materialstoday*, Elsevier Ltd. (2003)

Liquid hydrogen

- Stored in cryogenic tanks at 21.2 K at 1atm pressure
- Large amount of energy for liquefaction
- Continuous boil-off rate (depends on the vessel)



M. Felderhoff et al. , *Hydrogen storage: the remaining scientific and technological challenges*. In *Adv. Mater.*, (2006)

Physisorption

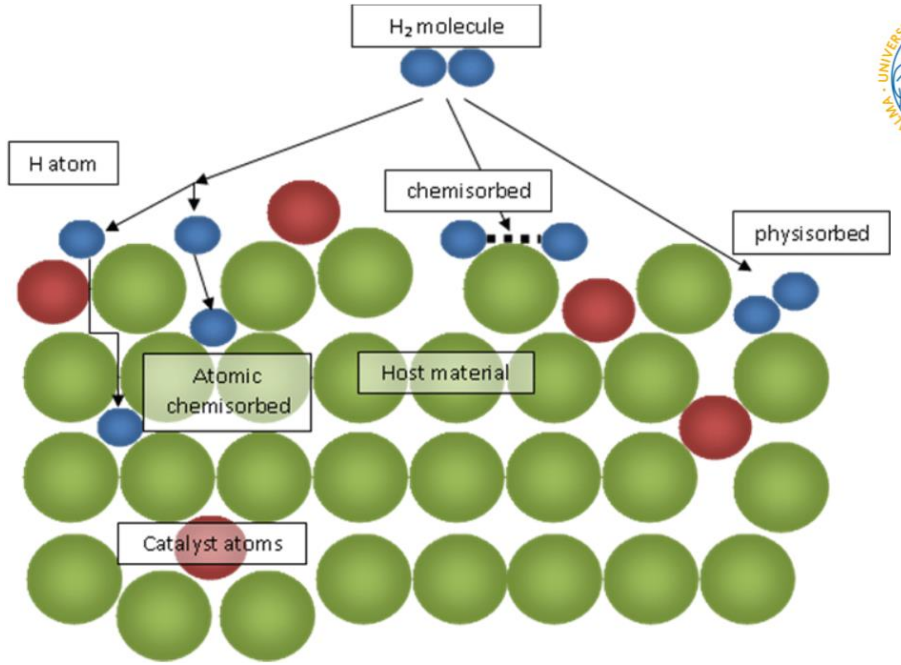
- Adsorption of H on a surface, Van der Waals forces
- Lennard-Jones potential:

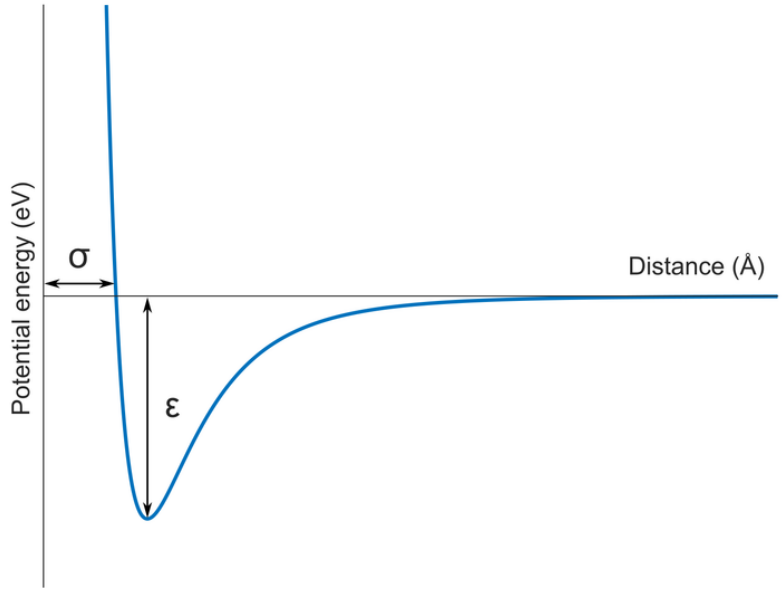
$$U(s) = 4\varepsilon\left[\left(\frac{\sigma}{s}\right)^{12} - \left(\frac{\sigma}{s}\right)^{6}\right]$$

Potential parameters

Distance

- At low T but no energy barrier
- Formation of a monolayer

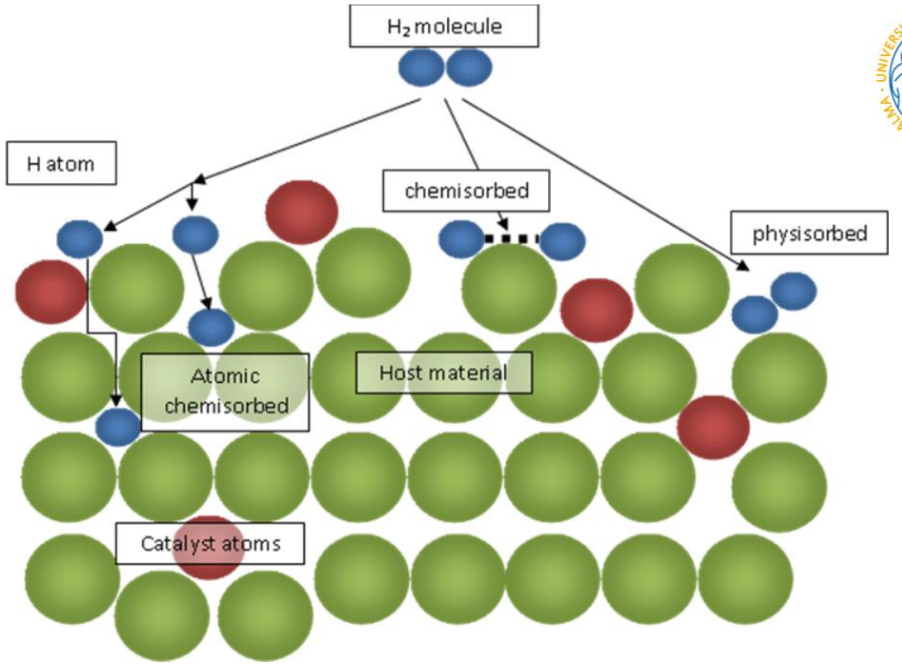


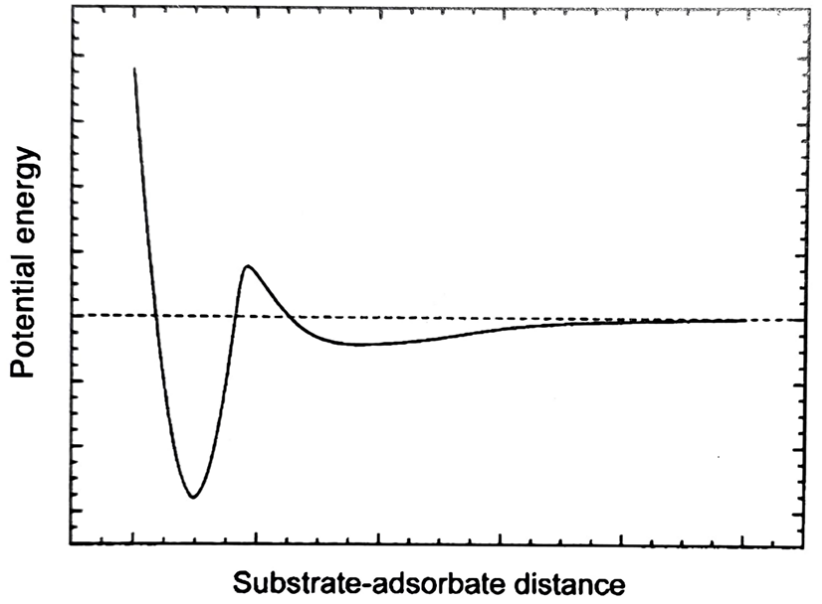


A. Züttel, *Materials for hydrogen storage*. In *materialstoday*, Elsevier Ltd. (2003). Images from *researchgate.net*

Chemisorption

- Covalent bonds
- Activation energy required (high T)
- Slow kinetics to equilibrium surface coverage
- Desorption only at high T

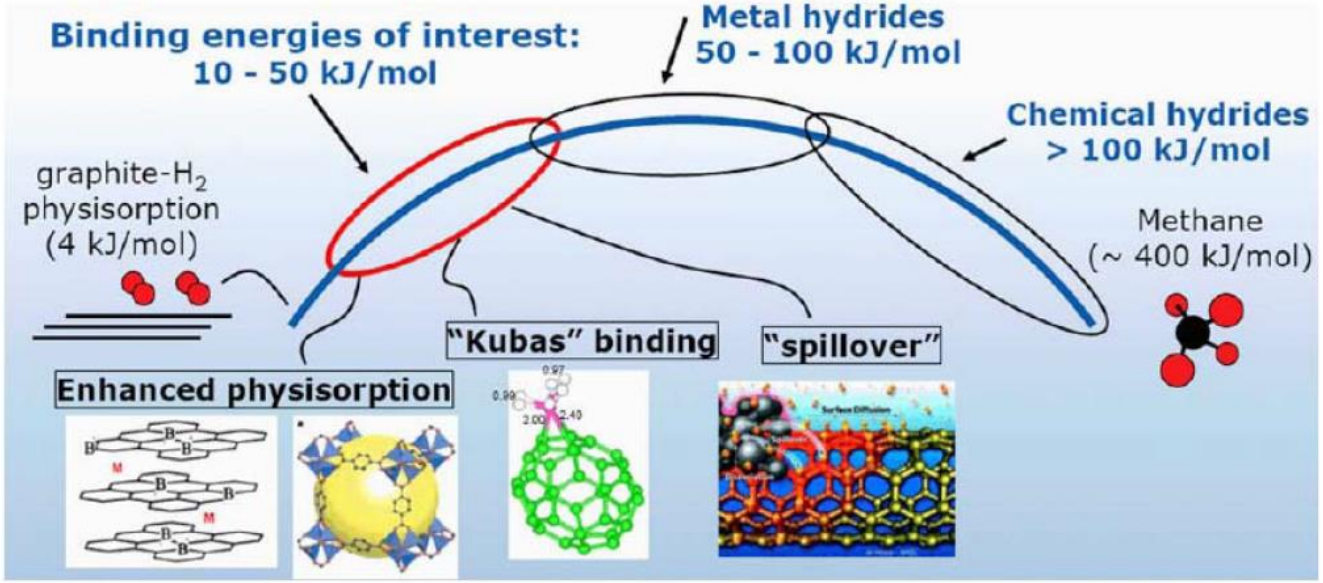




A. Züttel, *Materials for hydrogen storage*. In *materialstoday*, Elsevier Ltd. (2003). Images from *researchgate.net*

Binding energies

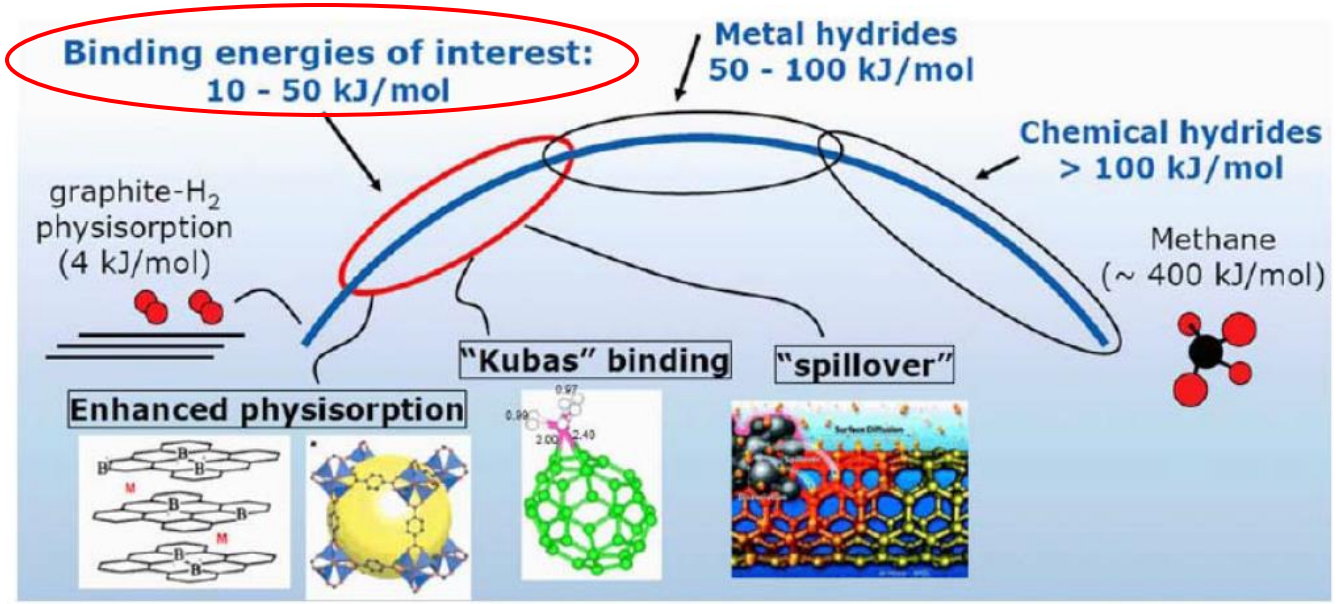
- Different mechanisms, different BE
- Physisorption: at low T, low BE
- Chemisorption by metal hydrides and ammonia complexes: at high T, high BE



R. Ströbel, J. Garche, P. T. Moseley, et al. J. Power Sources **159**, 781 (2006)

Useful range

- Enhanced physisorption: spacers increase graphene layers distance
- Kubas binding: complexes of TM, donation of charge between orbitals
- Spillover: catalytic additives



R. Ströbel, J. Garche, P. T. Moseley, et al. J. Power Sources **159**, 781 (2006)

Physisorption on carbon materials

- Carbon materials:
  - low densities
  - high porosities
  - high specific surface area

- Hydrogen uptake limited by:
  - his density
  - pore structure of the adsorbent
  - pore volume of the narrowest pores

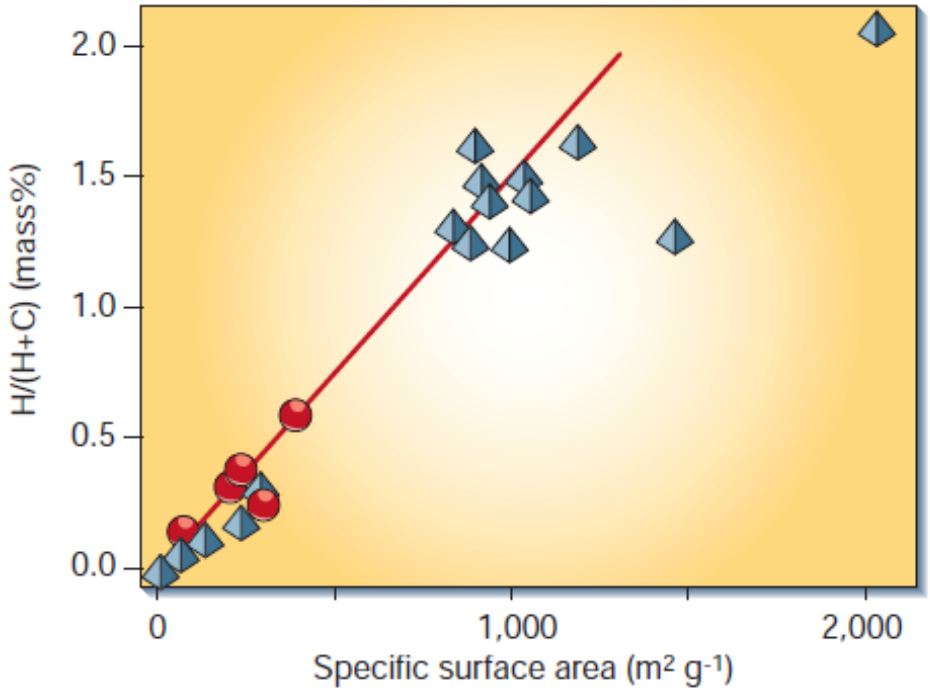
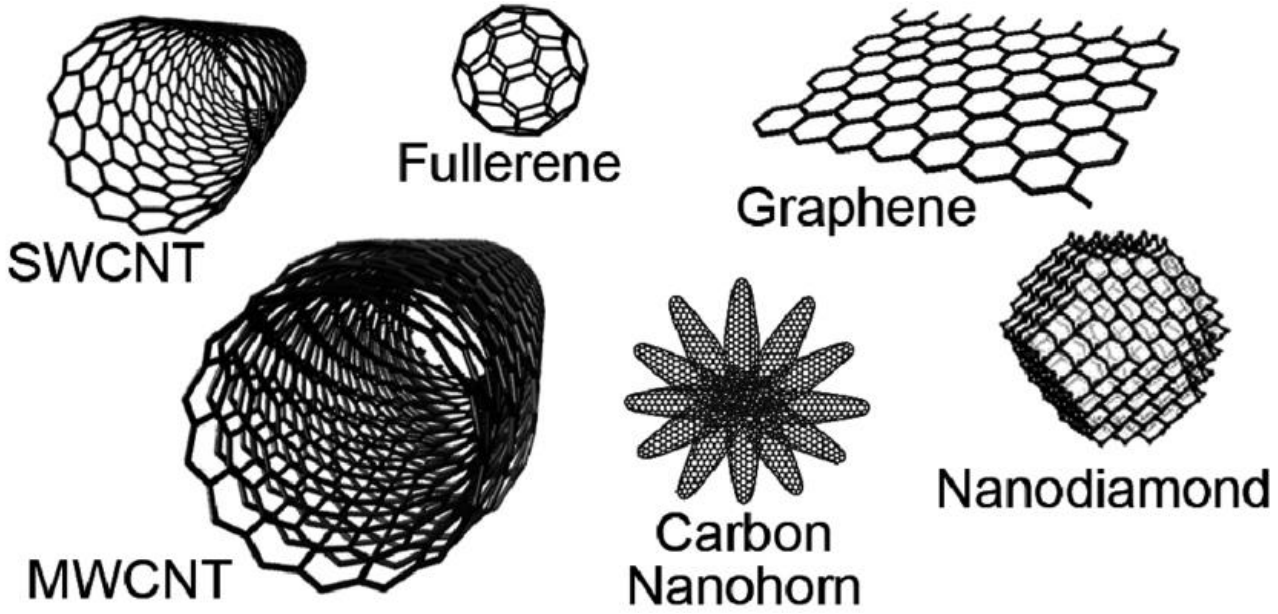


Figure 2 Reversibly stored amount of hydrogen on various carbon materials versus the specific surface area of the samples. Circles represent nanotube samples (best-fit line indicated), triangles represent other nanostructured carbon samples[17].

Nijkamp et al. , Hydrogen storage using physisorption—materials demands. *Appl. Phys. A* **72,** 619–623 (2001)

Nanostructured carbon

- Cheap, not toxic or polluting
- H_2 adsorption at low T: high amounts and fully reversible, but…
- Physisorption energy too small
- Chemisorption: too high binding energy



M. Ricco' et al. , *Research plan UNIPARMA*. Image from *researchgate.net*

Nanostructured carbon

- Increase physisorption energy by:

1. Curving, $sp^2 - sp^3$ hybridization

2. Charging, polarization of H_2 by surface electric field

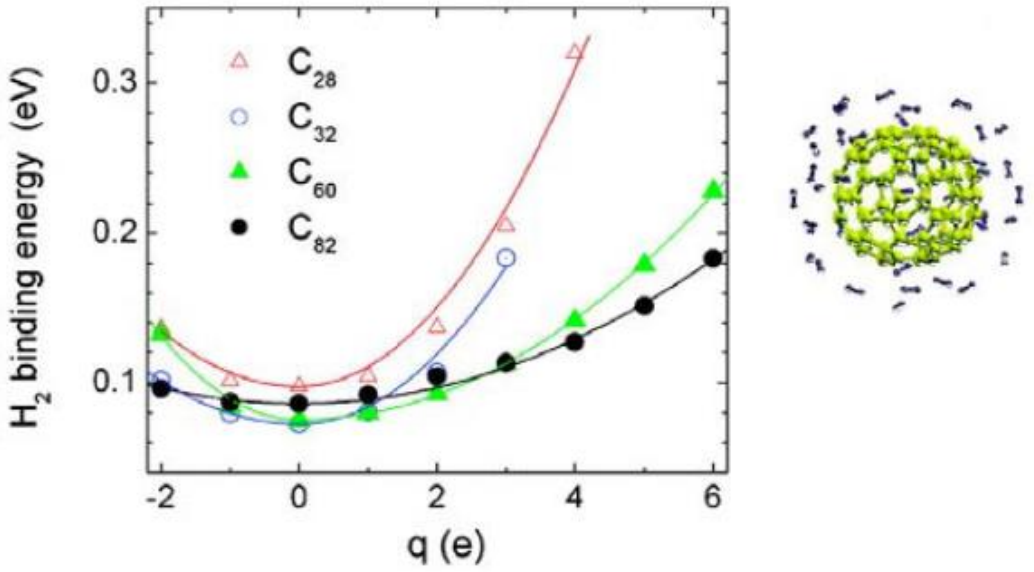


Fig. 2 Binding energy of molecular hydrogen on charged or neutral fullerenes (adapted from [1]).

Nanostructured carbon

- Increase physisorption energy by:

3. Metal ions decoration, electrostatic or orbital interactions

4. Metal complexes interaction (metal-ethylene or metal fullerenes)

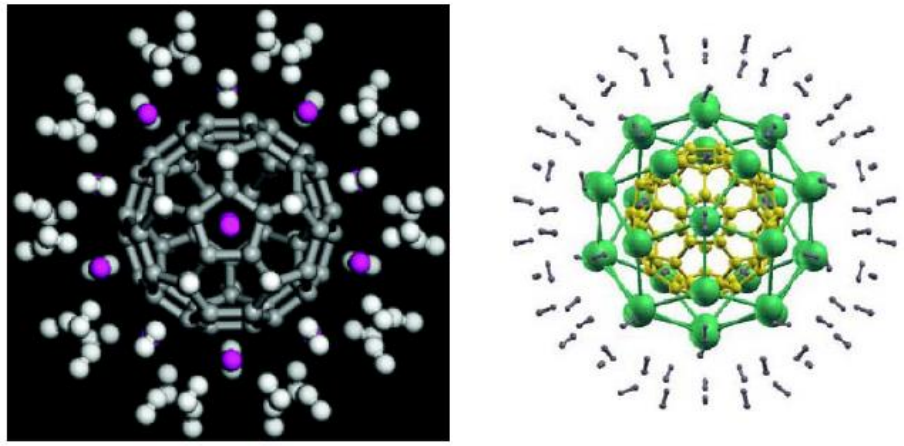


Fig. 5 Computed structures of $Li_{12}C_{60}$ and $Ca_{32}C_{60}$ and their estimated absorbed H_2 (adapted from [5], [7, 8]).

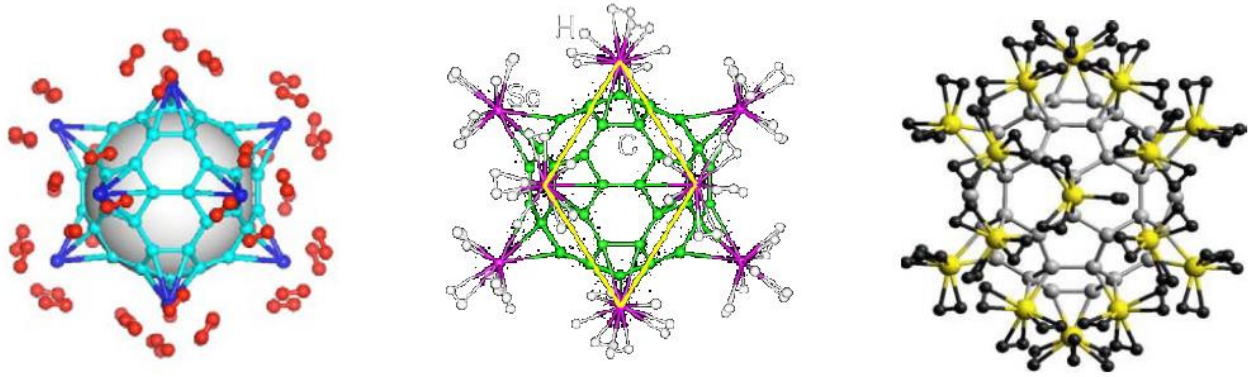
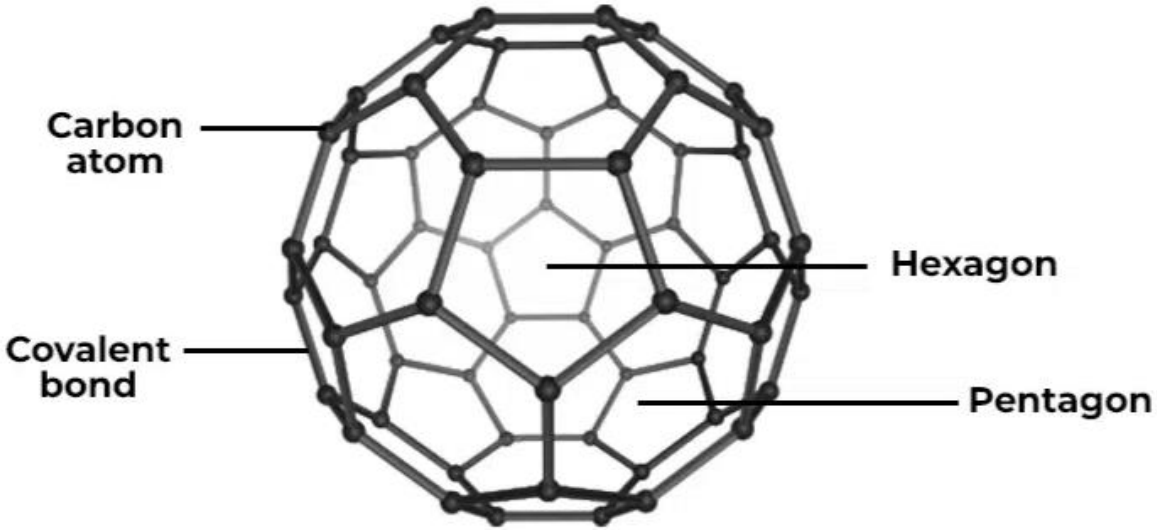


Fig. 4. Computed structures of $Ti_{12}C_{60}$, $Sc_{12}C_{60}$ and $Ni_{30}C_{60}$ (fron the left). The H_2 molecules they can adsorb are also represented. (adapted from [2] [6]).

H storage in fullerenes

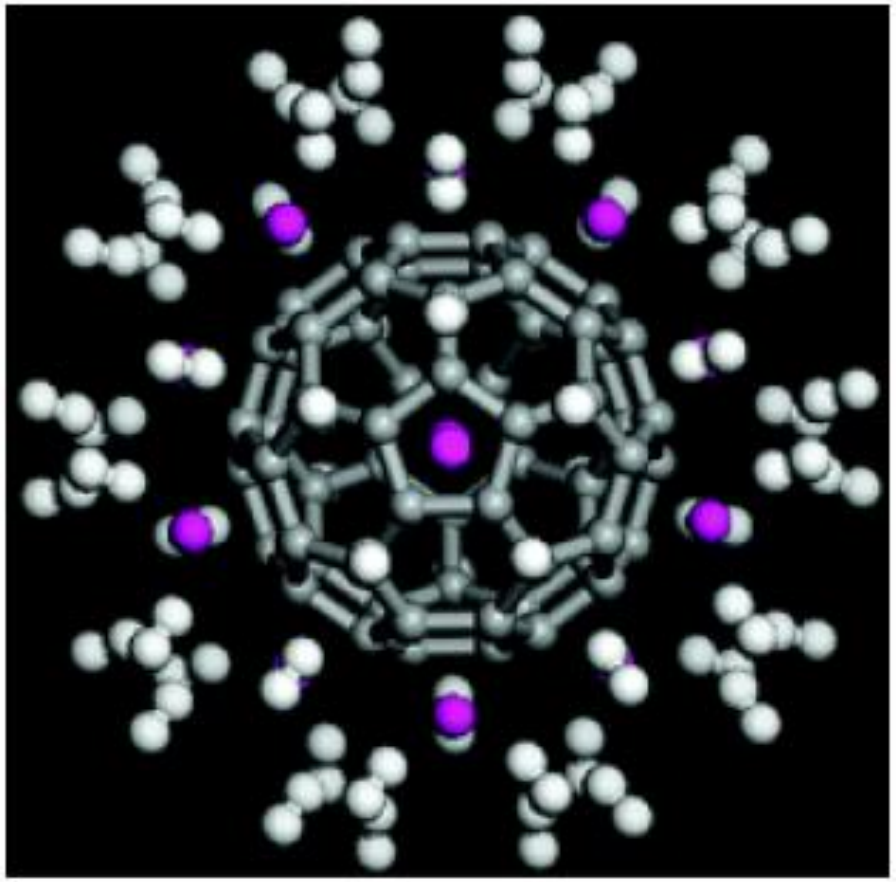
- C_{60} potential H storage material
- $C_{60}H_{36}$: $4.8\ mass\%\ H_2$
- $C_{60}H_{60}$: $7.7\ mass\%\ H_2$ at 600 °C and 30 bar
- Prolungated hydrogenation leads to fragmentation



P. Mauron et al. , *Hydrogen Sorption in $Li_{12}C_{60}$*. In J. Phys. Chem. C 2013, 117, 22598−22602. Image from *reasearchgate.net*

Lithium intercalated fullerides

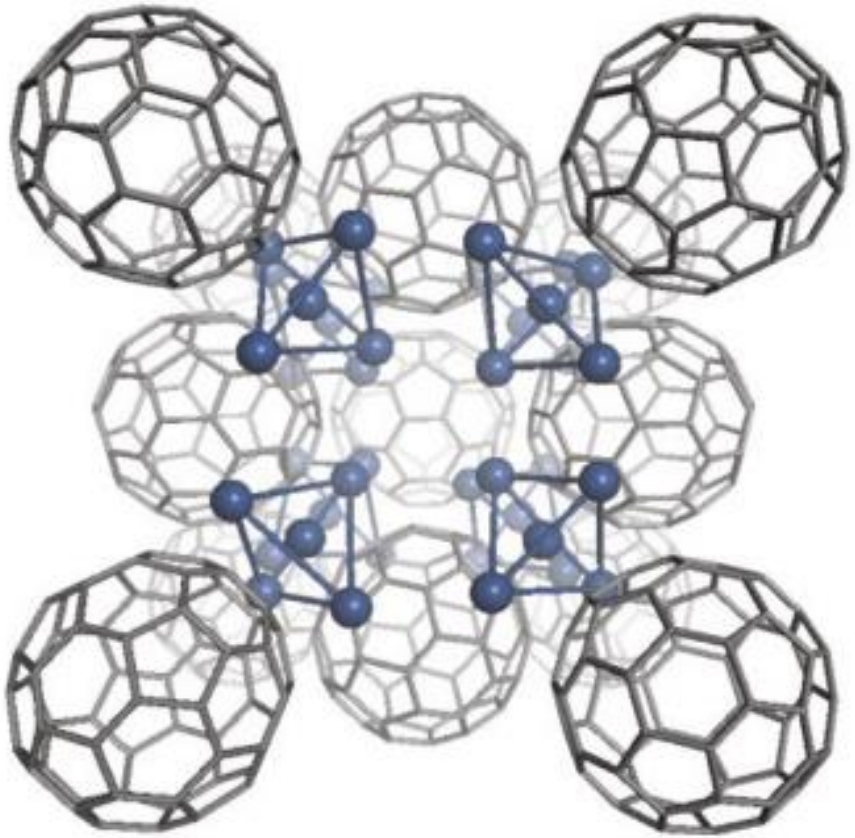
- Alkali ions in pentagons
- Li_9C_{60}: up to 2.6 $mass\%$ H_2 at 250 °C and 30 bar H_2
- $Li_{12}C_{60}$: 3.5 $mass\%$ H_2 at 250 °C and 105 bar H_2



P. Mauron et al. , *Hydrogen Sorption in $Li_{12}C_{60}$*. In J. Phys. Chem. C 2013, 117, 22598−22602. Image from *Research plan UNIPARMA*

$Li_{12}C_{60}$

- Alkali cluster in octahedral void of fcc structure
- Li donates electrons to C_{60}
- Decreasing dissociation energy barrier of H_2



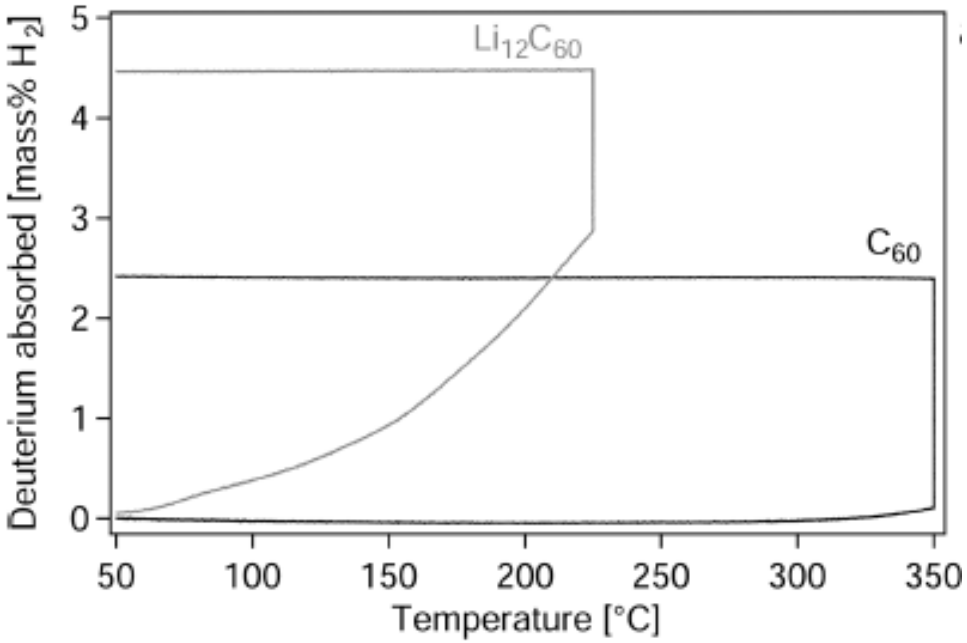
M. Gaboardi et al. , *Hydrogen storage mechanism and lithium dynamics in $Li_{12}C_{60}$ investigated by μSR*. In CARBON 90 (2015) 130 –137, Elsevier Ltd. (2015)

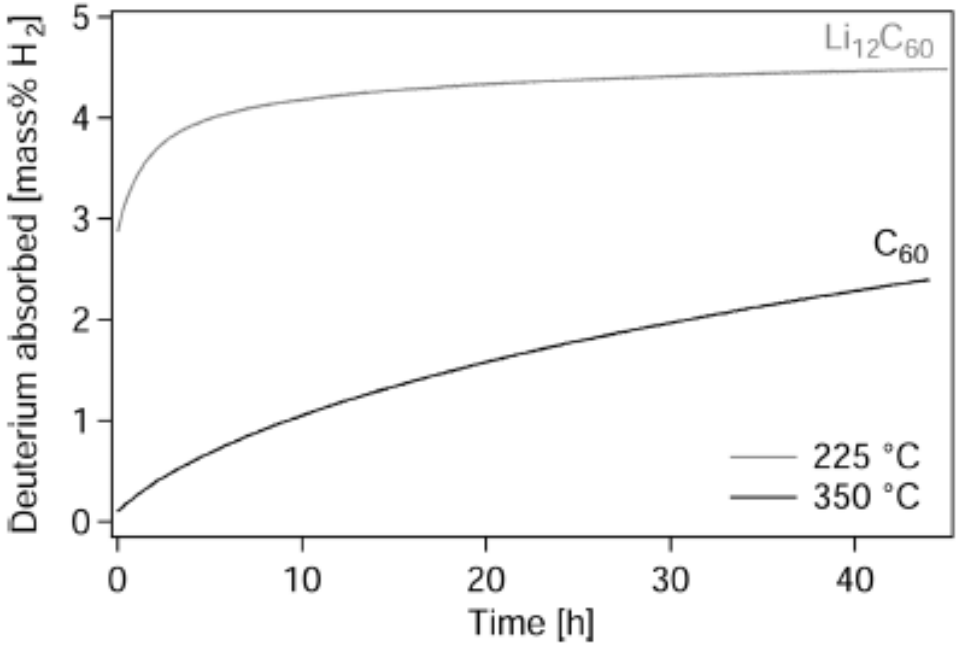
$Li_{12}C_{60}$

- Deuterium absorption
- Two step cycle in T:

1. $p_1 = 190bar\ D_2$
2. $p_2 = 100bar\ D_2$

- Desorption studied at $p_3 = 100bar\ D_2$

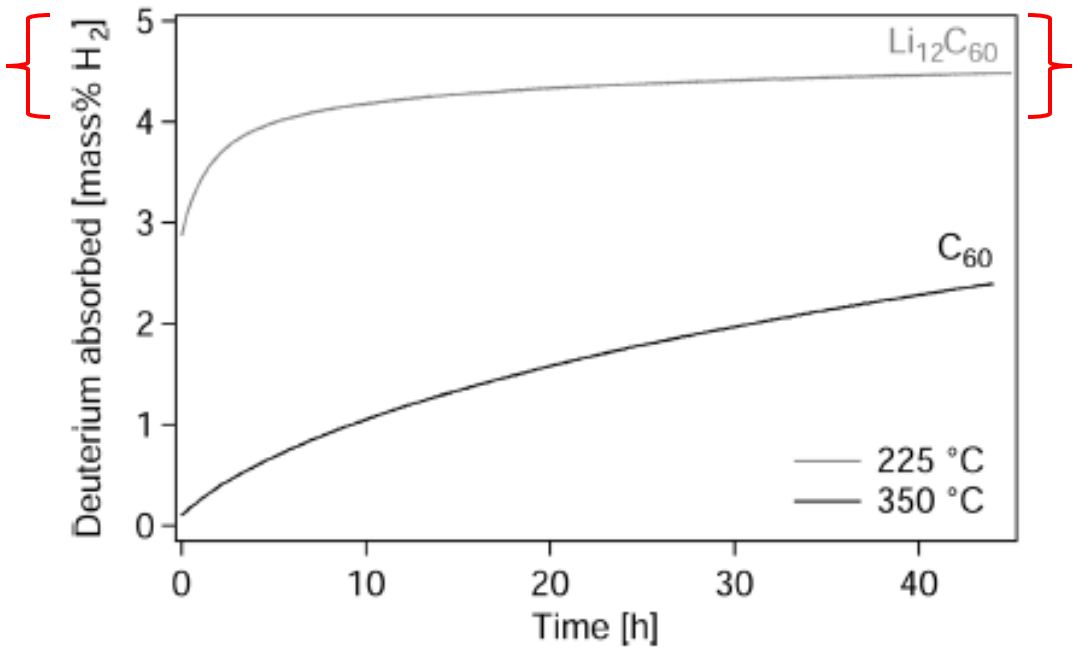


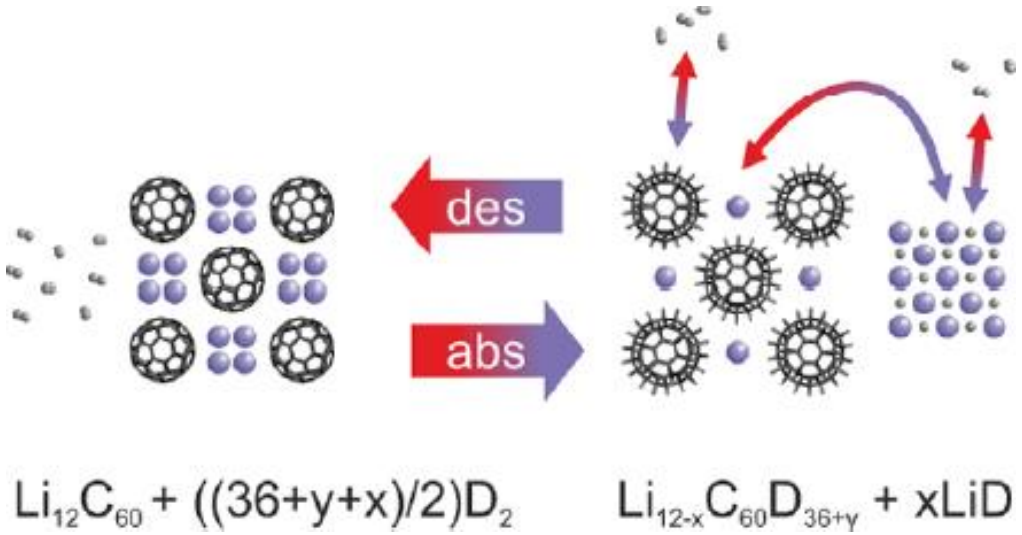


P. Mauron et al. , *Hydrogen Sorption in $Li_{12}C_{60}$*. In J. Phys. Chem. C 2013, 117, 22598−22602

$Li_{12}C_{60}$

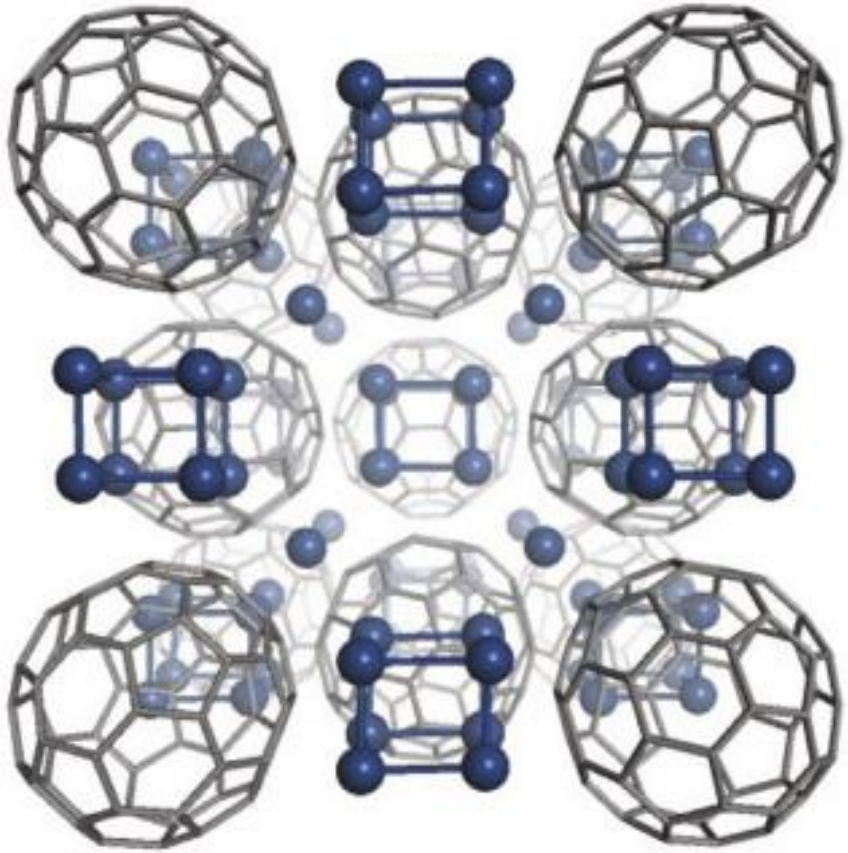
- Covalent bond C-D
- Formation of $C_{60}D_{36}$ and LiD
- $9.5\ mass\%\ D_2 \sim 5\ mass\%\ H_2$
- Li improves sorption properties and storage capacity
- Desorption above 300 °C





$Li_{12}C_{60}$

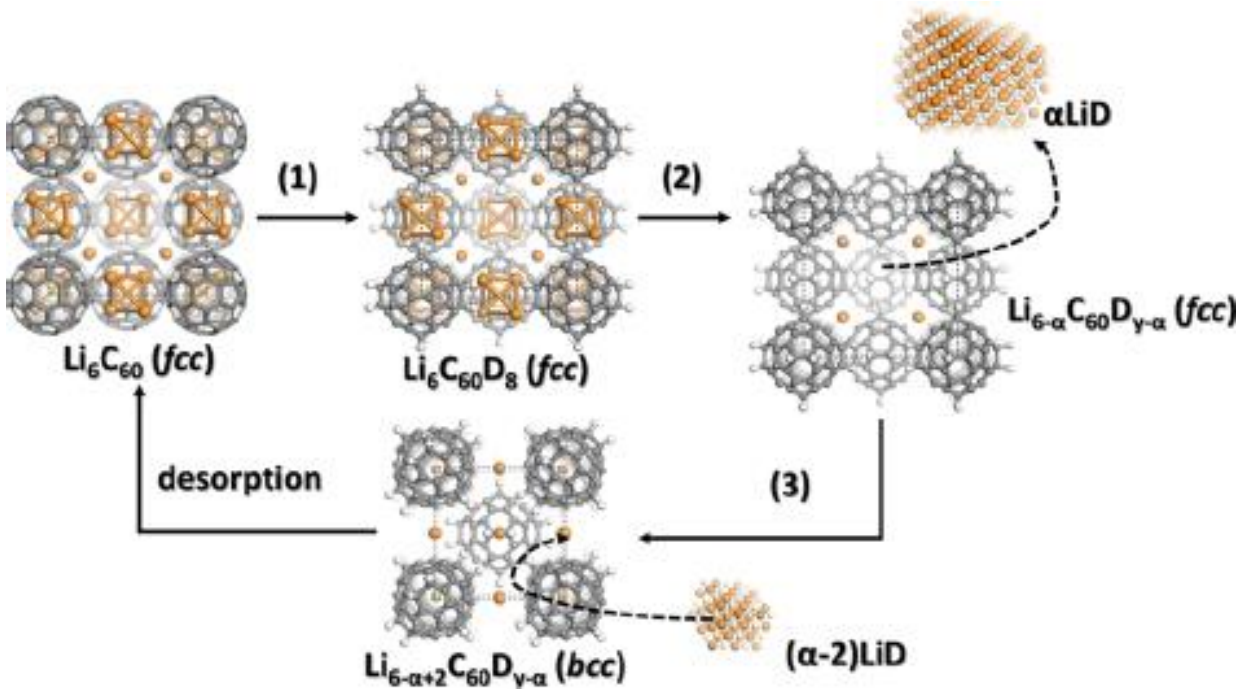
- At high T, Li ion diffusion
- H_2 dissociation operated by Li cluster
- Presence of C_{60} reduces T to form LiH
- Li suitably decreased, C_{60} hydrogenation



M. Gaboardi et al. , *Hydrogen storage mechanism and lithium dynamics in $Li_{12}C_{60}$ investigated by μSR*. In CARBON 90 (2015) 130 –137, Elsevier Ltd. (2015)

Li_6C_{60}

- Distorted fcc structure at RT
- Deuteration starting between 130-140°C at $60bar\ D_2$
- Segregation of LiD at 200°C
- Reintercalation of Li^+ at 315°C
- Up to $5\ mass\%\ H_2$, reversible at suitable T



M. Gaboardi et al. , *In Situ Neutron Powder Diffraction of Li_6C_{60} for Hydrogen Storage*. In J. Phys. Chem. C 2015, 119, 19715−19721

Li_6C_{60}

- Insertion of TM (Pt and Pd)
- Hydrogenation up to 350°C at $100bar\ H_2$
- $5.9\ mass\%\ H_2$
- Aggregates of Pt and Pd: surface catalytic activity

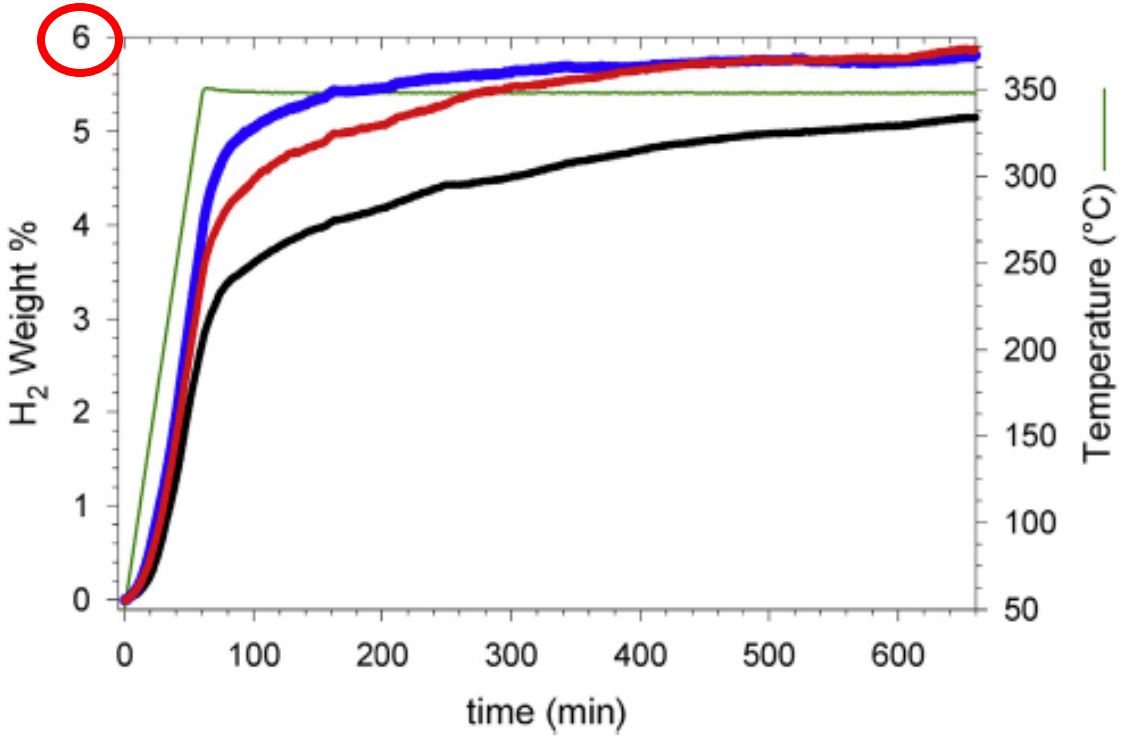


Fig. 1 – Kinetic absorption curves for the Li_6C_{60} sample (black, bottom line), for the Pt decorated sample (red, middle line) and for the Pd containing one (blue, top line).

M. Aramini et al., *Addition of transition metals to lithium intercalated fullerides enhances hydrogen storage properties*. In international journal of hydrogen energy 39 (2014) 2124-2131 Elsevier Ltd. (2013)

To sum up…

- $Li_{12}C_{60}$:

1. uptake of $5\ mass\%\ H_2$
2. Better conditions than pure C_{60} (and «traditional» methods)

- Li_6C_{60}:

1. uptake of $5\ mass\%\ H_2$
2. TM intercalation leads to $\sim 6\ mass\%\ H_2$
3. Better conditions than pure C_{60} (and «traditional» methods)

- Increasing Li stoichiometry for engineering of more efficient hydrogen storage materials

- Intercalation of different TM and different synthesis methods