STORHY
Train-IN 2006

# Session 4.1: Solid Storage Technology

Dr. M. Fichtner (FZK)

25th – 29th September 2006
Ingolstadt

# *Hydrogen Storage in Solids*

## *Principles and Methods*

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***EUROCOURSE TRAIN-IN***
***Sept 28, 2006***

# Outline

## Introduction

- ▷ General Energy Situation

## Principles of Hydrogen Storage

- ▷ Physisorption Materials
- ▷ Physical laws
- ▷ Recent developments

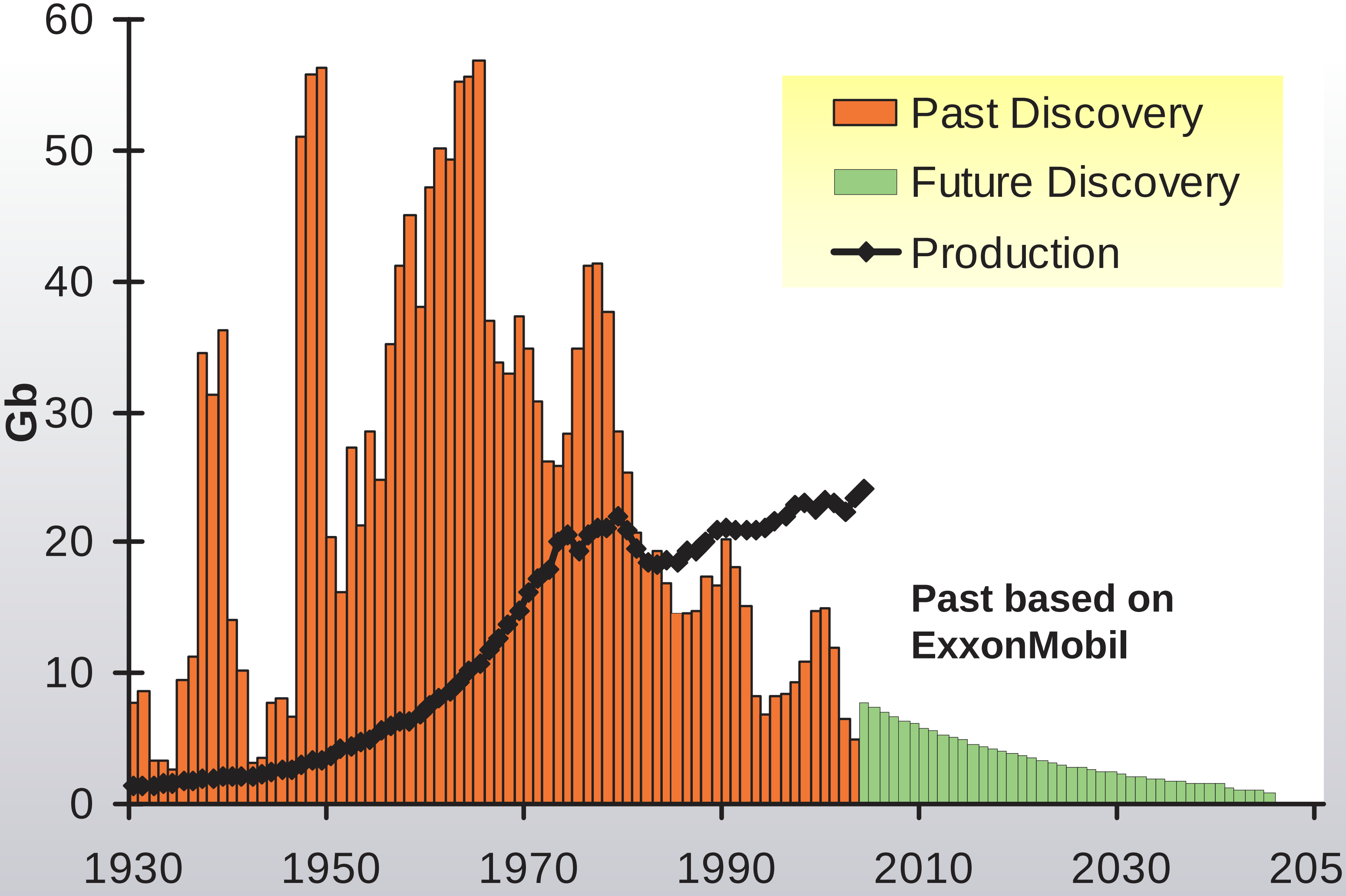
- ▷ Chemisorption Materials
- ▷ Thermodynamics
- ▷ Kinetics
- ▷ Other experimental methods
- ▷ Material Systems

## Safety

## Conclusion

# Situation : Oil ressources

*There is a widening gap !*



***source: C. Campbell, Oil Depletion Analysis Centre, London, 2003***

# Situation: Oil Production

***“Hubbert´s Peak”; Prof. M.K. Hubbert, Geophysicist at MIT, in “Science” 1956***

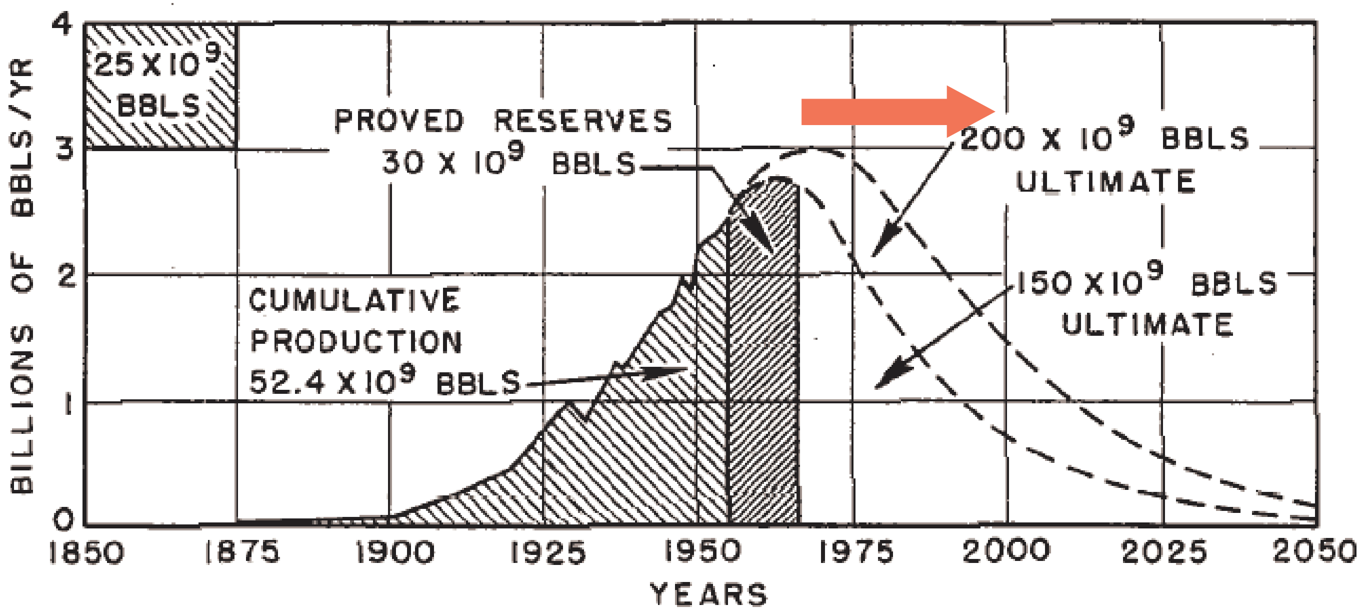
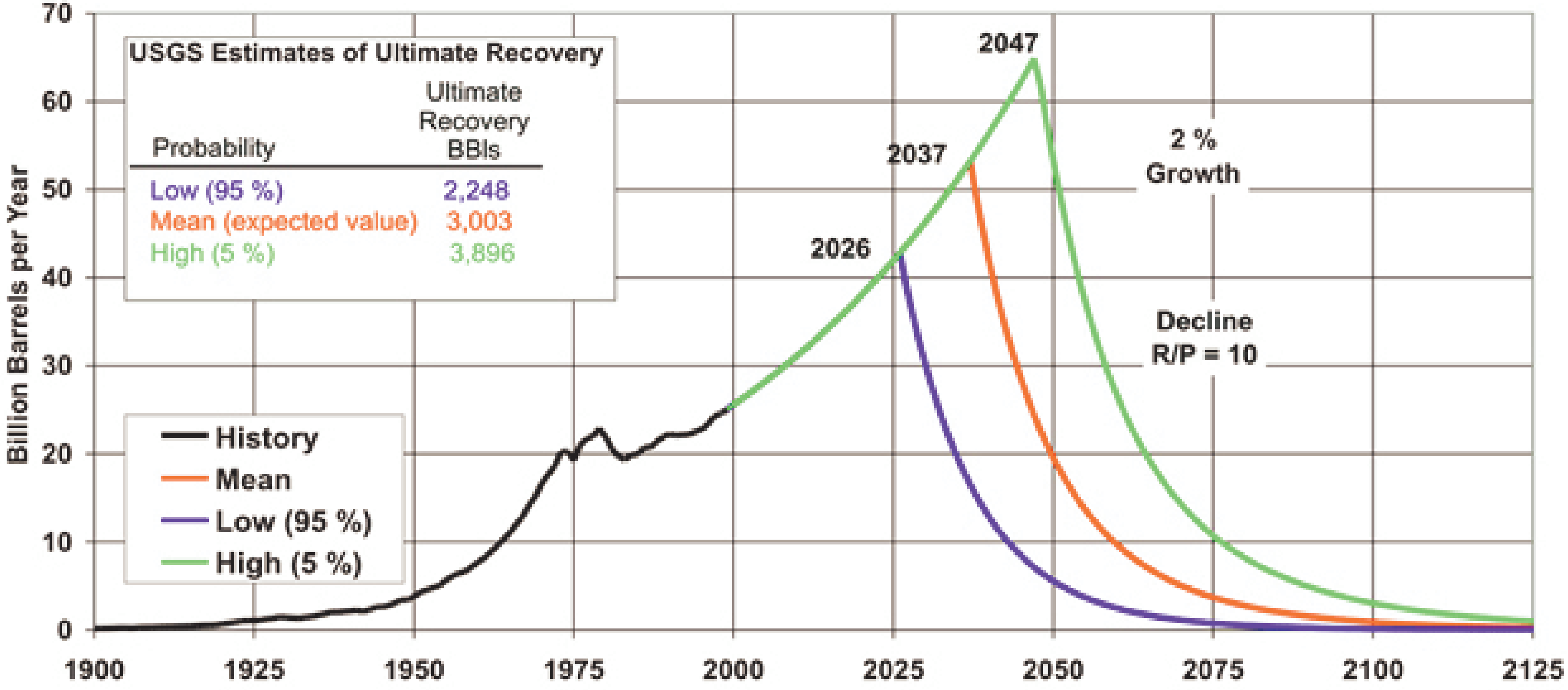


Figure 21 – Ultimate United States crude-oil production based on assumed initial reserves of 150 and 200 billion barrels.

# *Prediction : Estimated production curve - The optimists*

***Basis: United States Geological Survey (USGS)***

Figure 2. Annual Production Scenarios with 2 Percent Growth Rates and Different Resource Levels (Decline R/P=10)



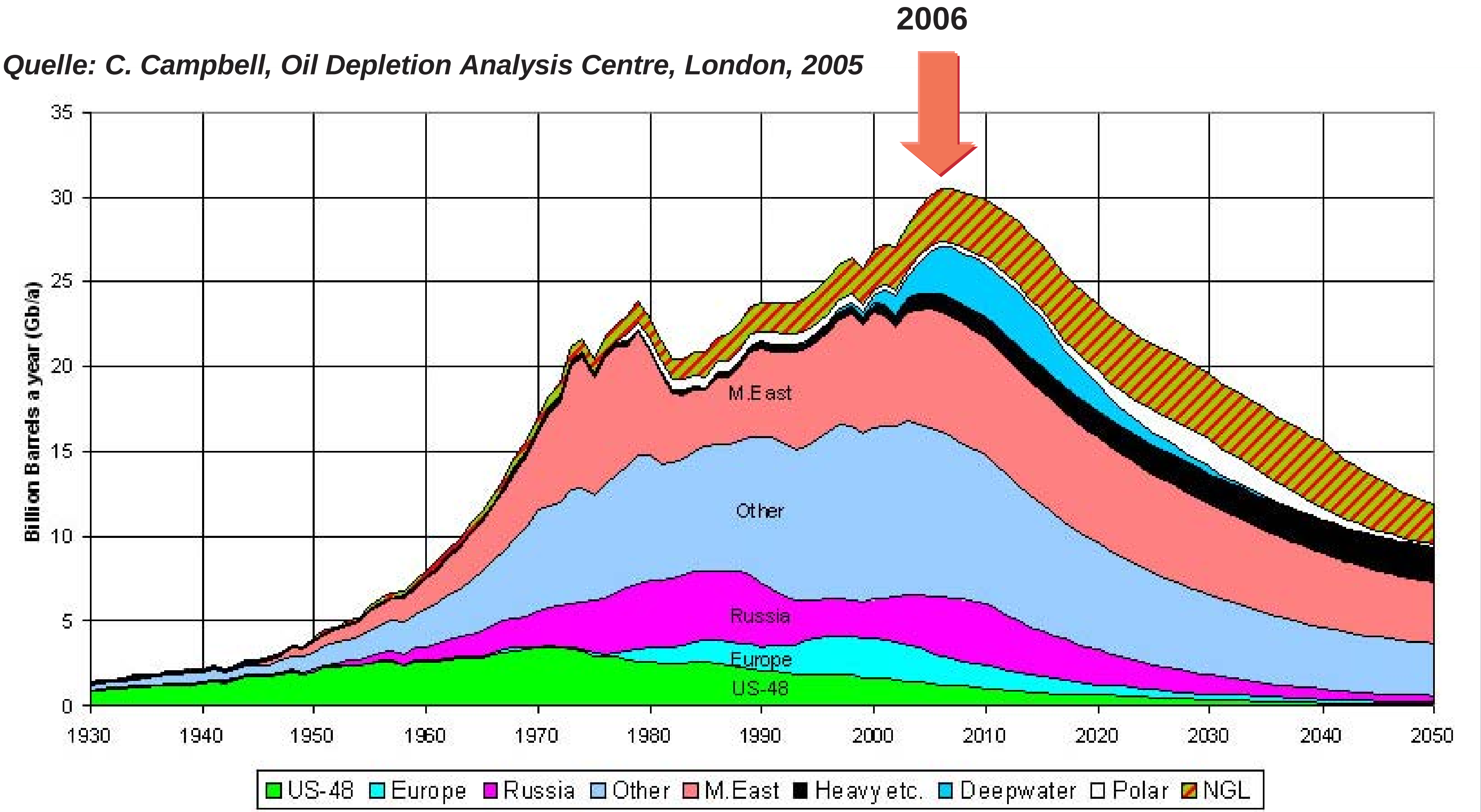
Source: Energy Information Administration
Note: U.S. volumes were added to the USGS foreign volumes to obtain world totals.

**Daily consumption: curr. 48 Mio Barrels per day**

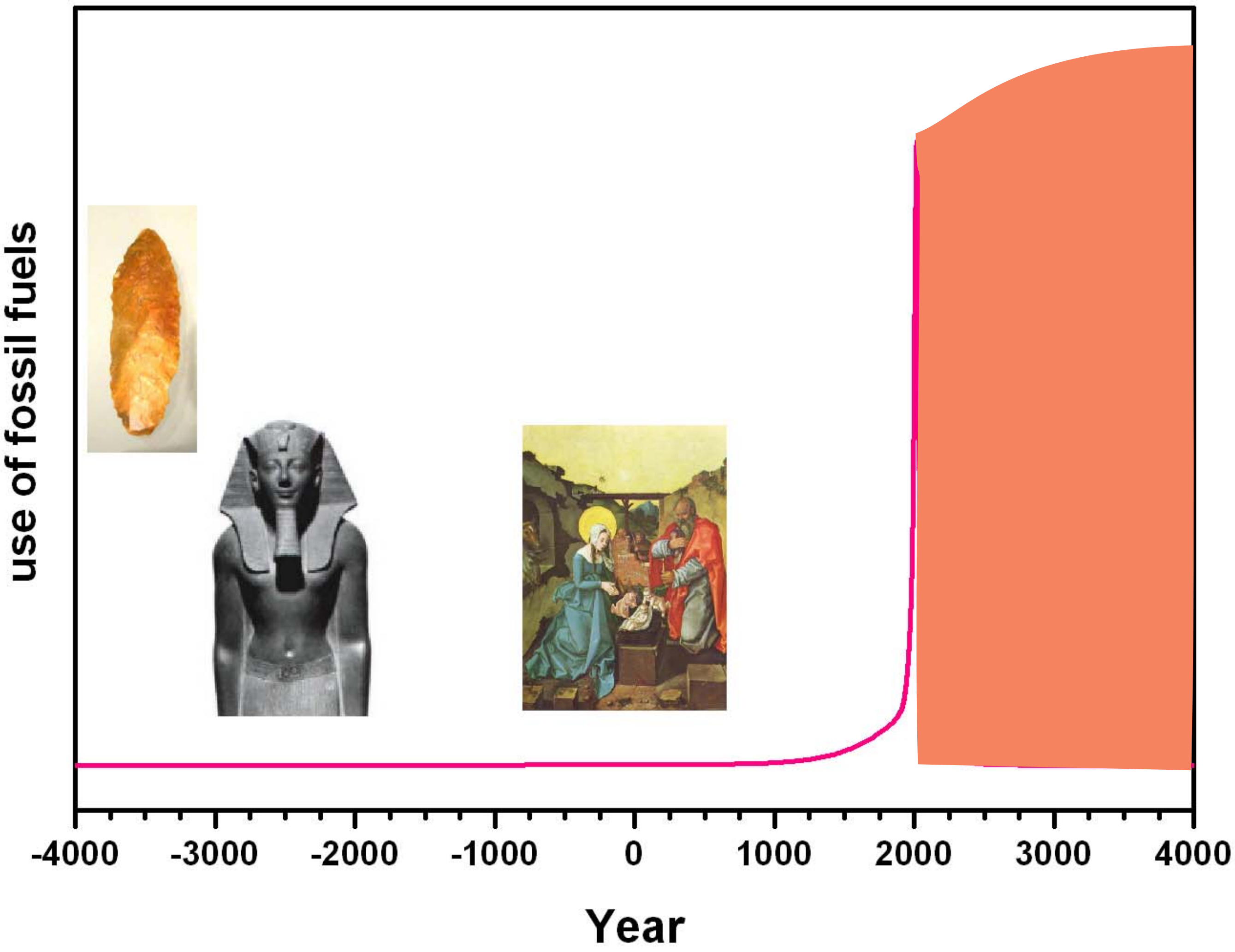
**THURSDAY, OCTOBER 27, 2005**
***"Saudi oil forecasts are doubted"***
***45 Bill. Instead of 99 Bill. Barrels***
**By Jeff Gerth (The New York Times)**

# *Prediction : Estimated production curve – The pessimists*

***Quelle: C. Campbell, Oil Depletion Analysis Centre, London, 2005***



# *Fossil Fuels On a Historical Timescale*



# The car problem…

## Permanent Problem:

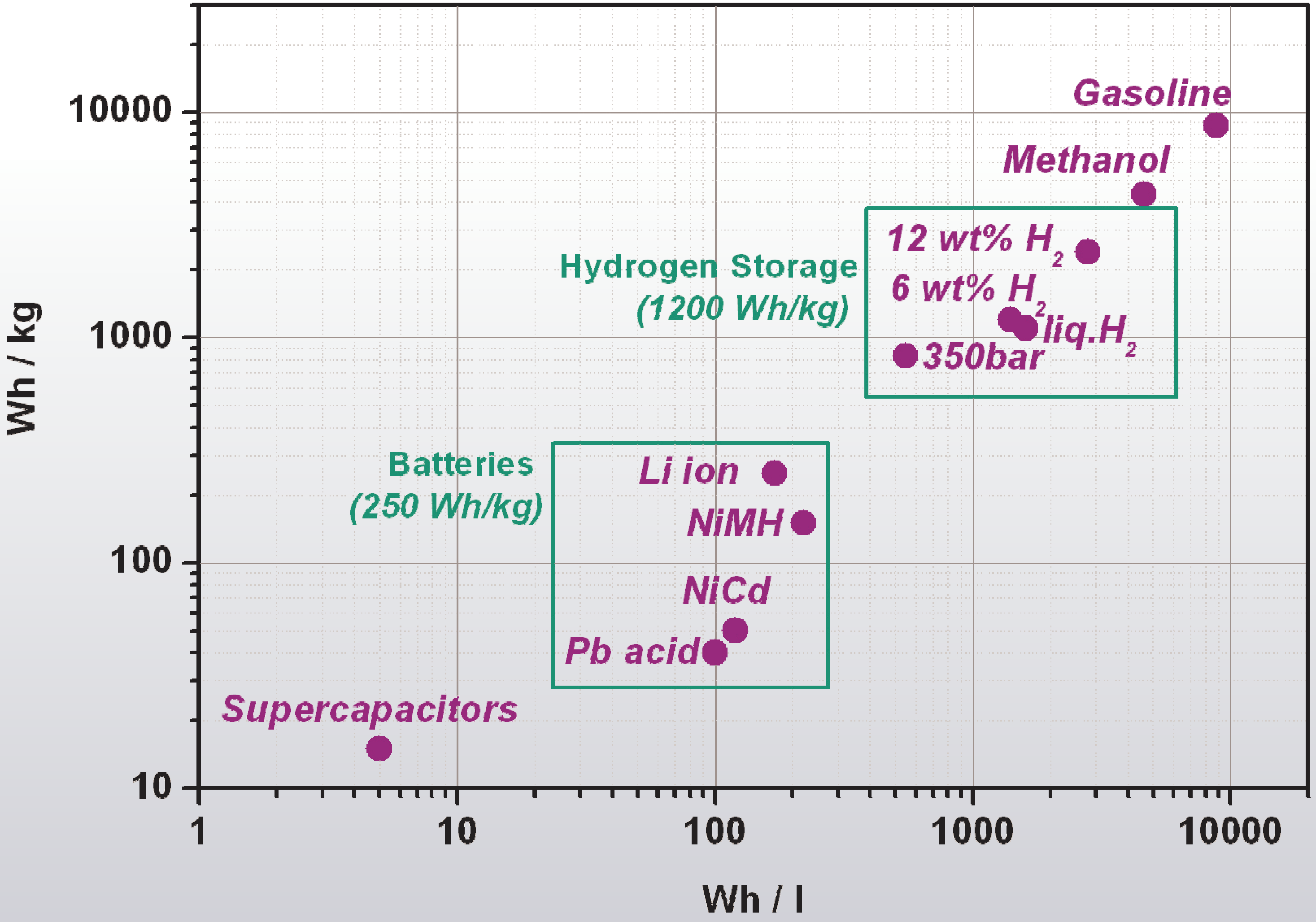
## Energy storage in vehicles

***The first cars were electric vehicles (1885) !***

**Speed record:**

**Jenatzy´s world record vehicle „La Jamais Contente“ (1899) reached 106 km/h**

# Why Hydrogen?



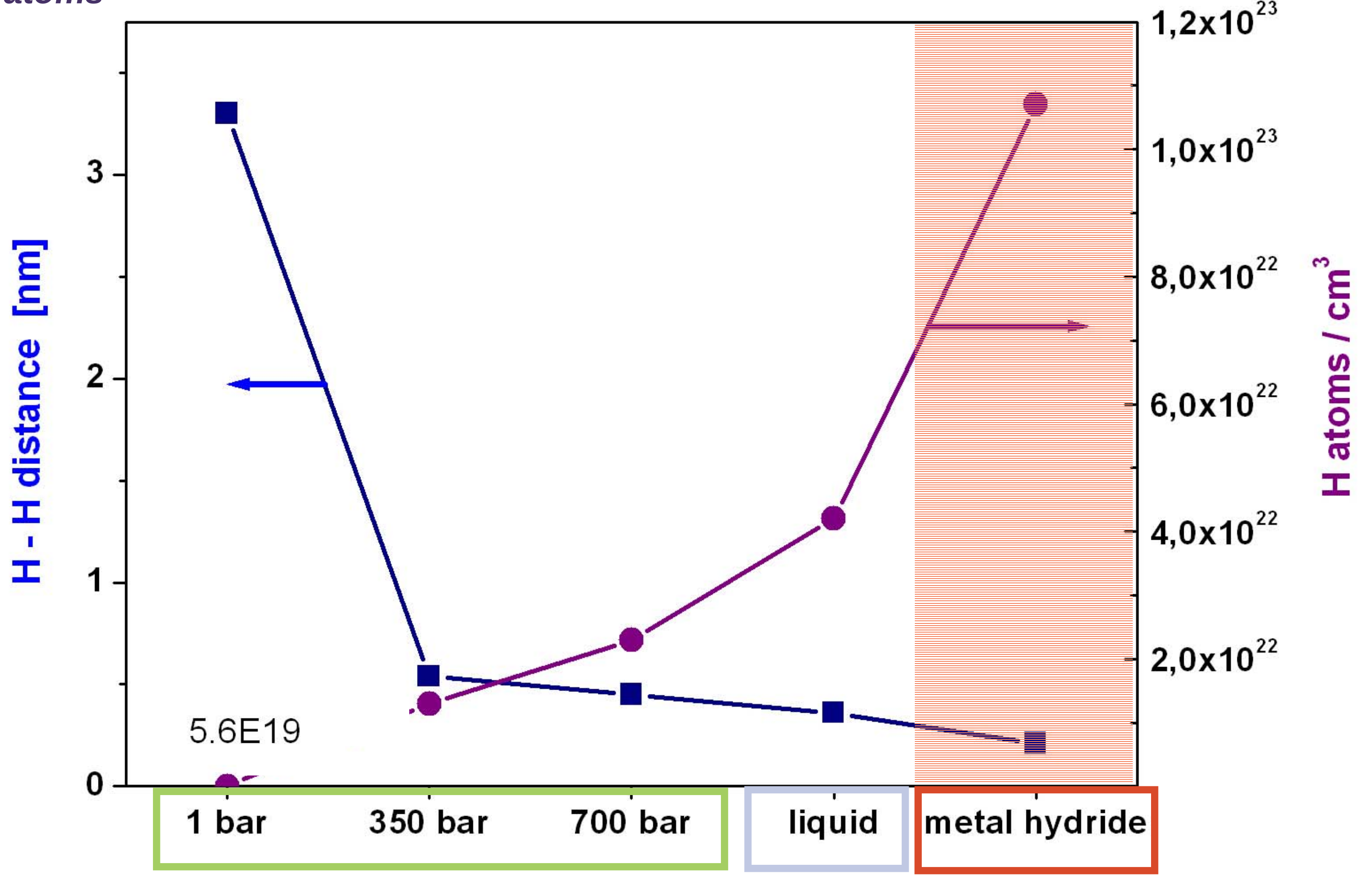
*Liquid fuels can store more energy per volume and mass compared to $H_2$ storage-systems (incl. Tank, Valves etc.).*

*Energy Storage in $H_2$ is by a factor 10 better than the best batteries.*

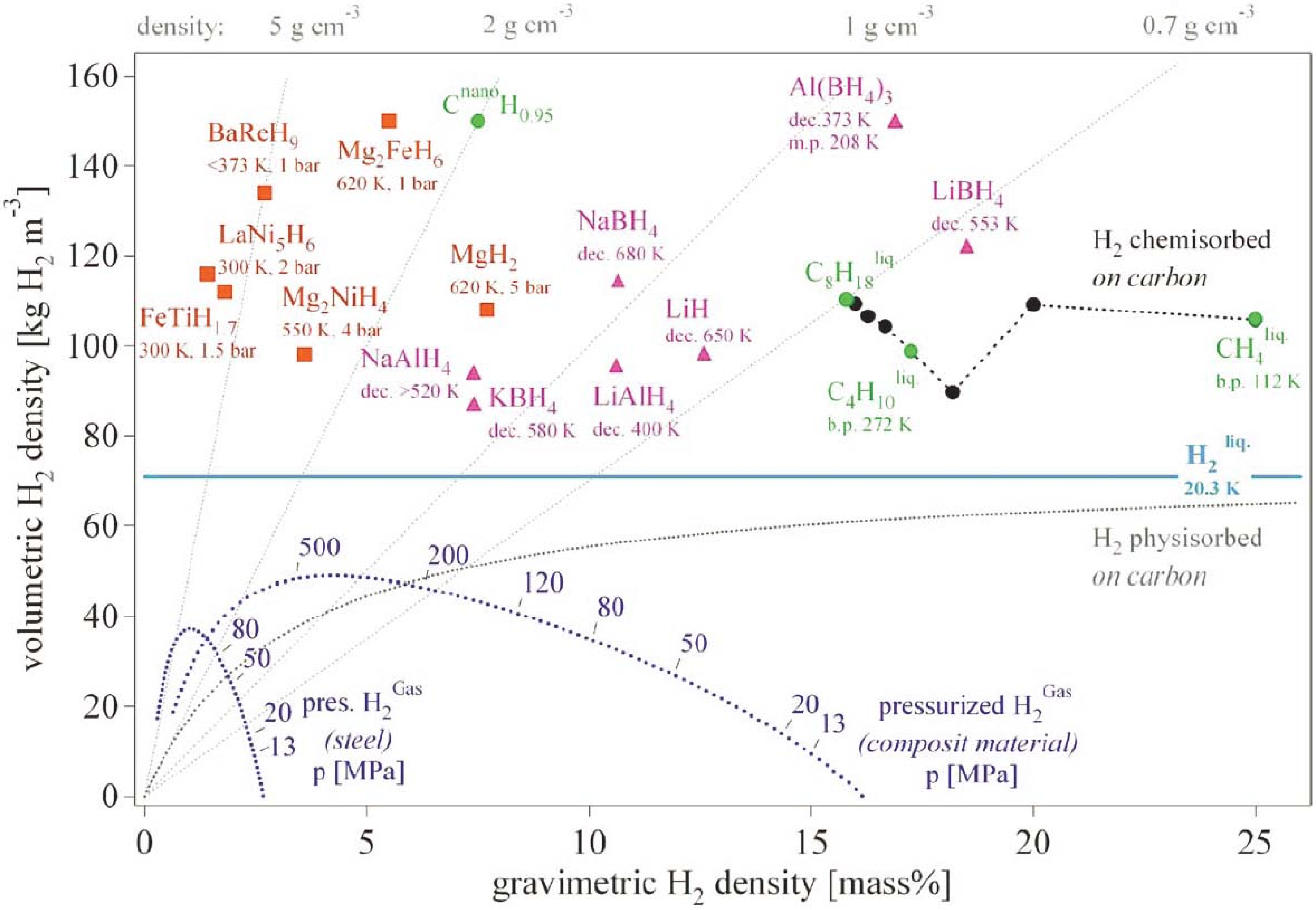
# *Physical limits for H storage*

*Mean distance between $H_2$ molecules and H atoms*

*volumetric storage density*



# Research Directions



**(from: Züttel et al. 2004)**

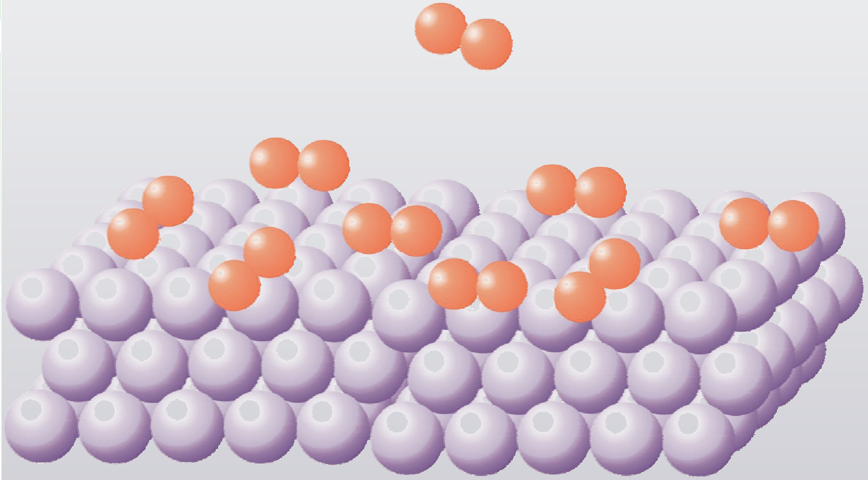
# *How is the hydrogen bound ?*

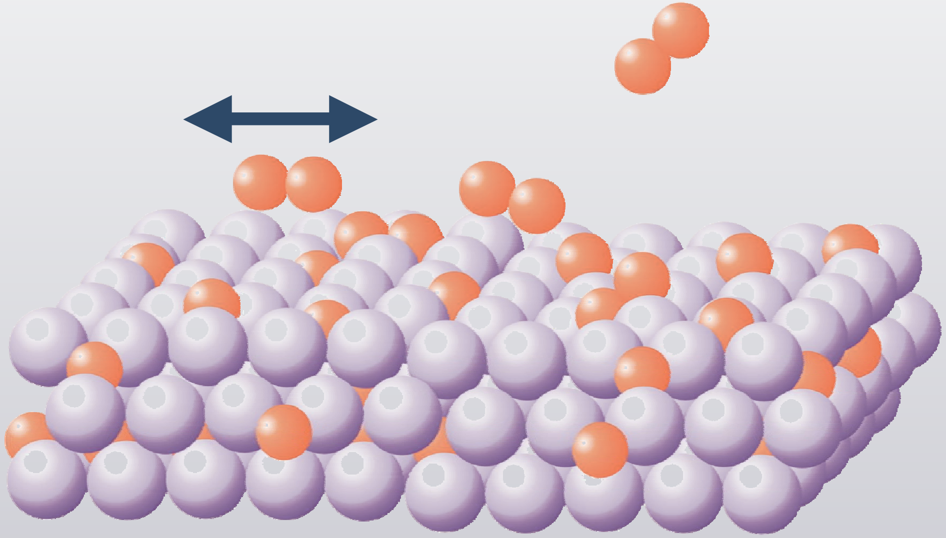
***Physisorption***

*Weak binding of $H_2$ –molecules at the surface (long range Van der Waals interactions)*

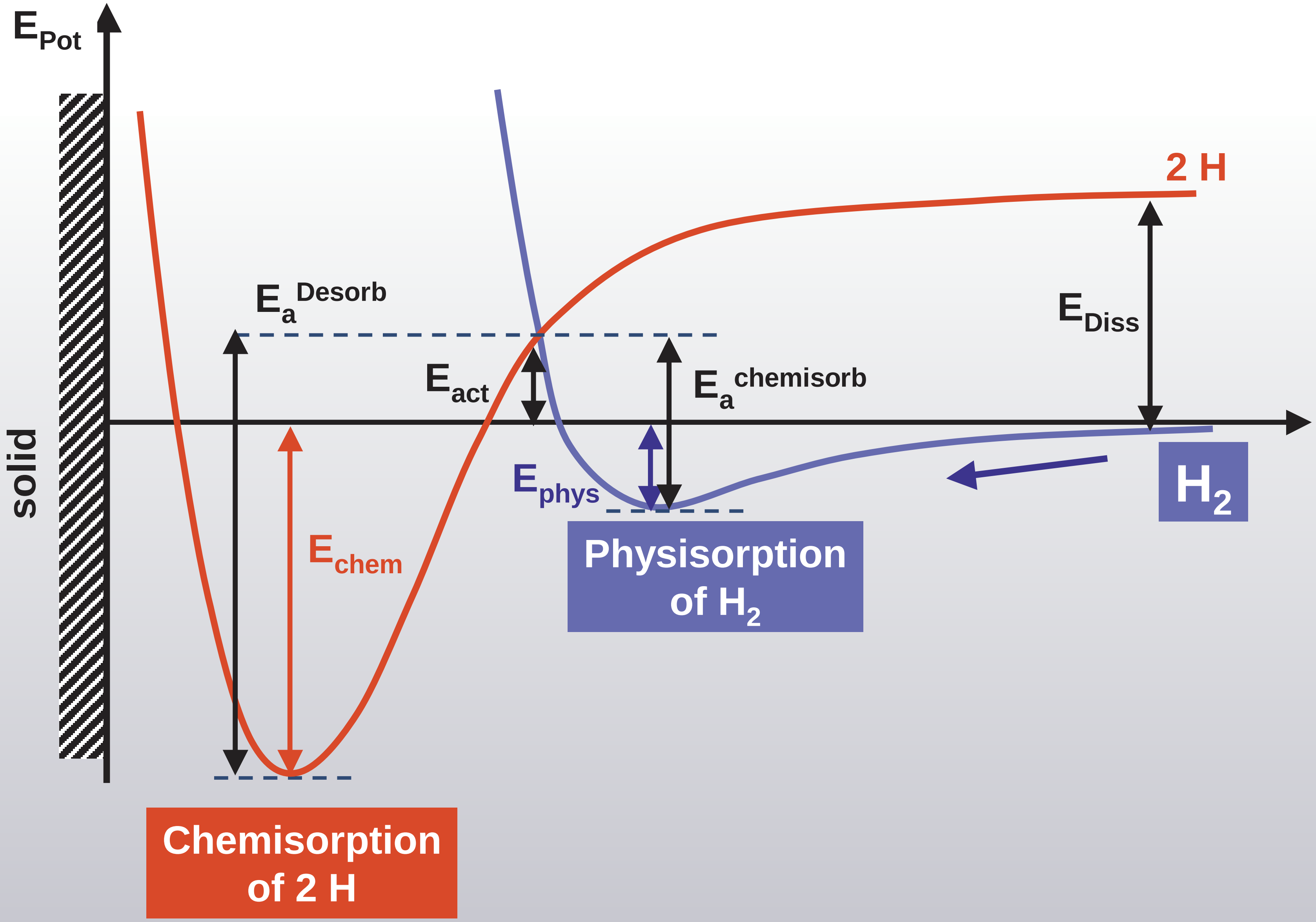
***Chemisorption***

*Splitting of $H_2$ molecule*
*Chemical bonding of H atoms in host lattice*





# Energy Diagram for Physisorption/Chemisorption



M. Fichtner, Sept. 06

# Physisorption of Hydrogen

**Adsorbed amount of $H_2$**

$$m_{adsorbed} = \frac{M_{adsorbate} \, S_{specific}}{S_{monolayer}}$$

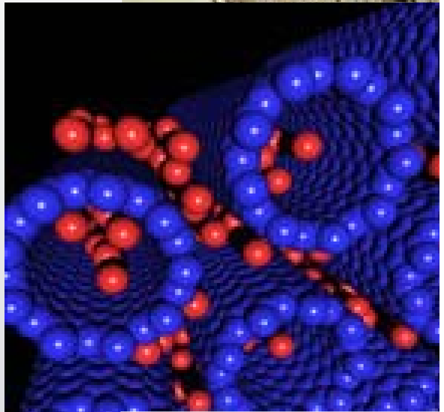
**Surface area of a monolayer of 1 mol $H_2$**

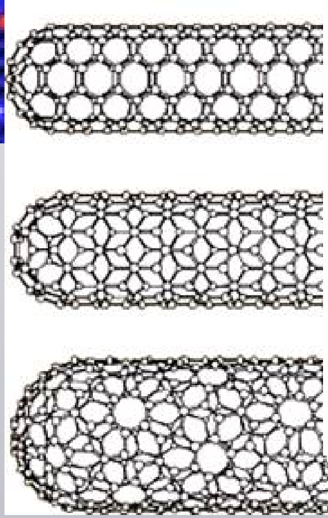
$$S_{monolayer}(H_2) = \frac{\sqrt{3}}{2}\left(\sqrt{2N_A}\,\frac{M_{adsorbate}}{\rho_{liquid}}\right)^{2/3} = 85.9 \cdot 10^3 \, \frac{m^2}{mol(H_2)}$$

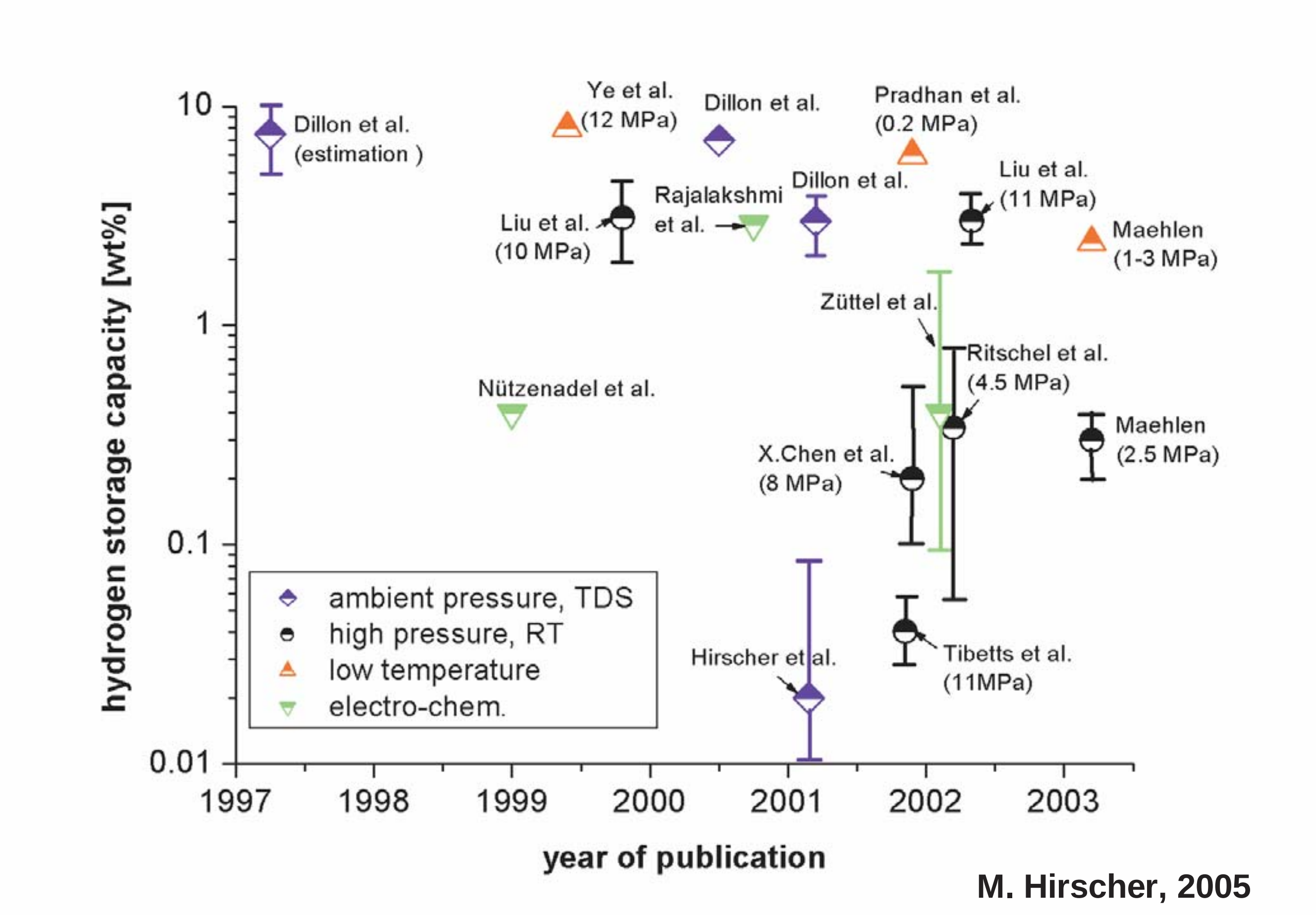
**Density of liquid $H_2$** $\rho_{liquid} = 70.8 \, \frac{kg}{m^3}$

# *Physisorption Materials: Carbon-nanotubes?*

***First reports about high H-contents were most probably experimental errors !***



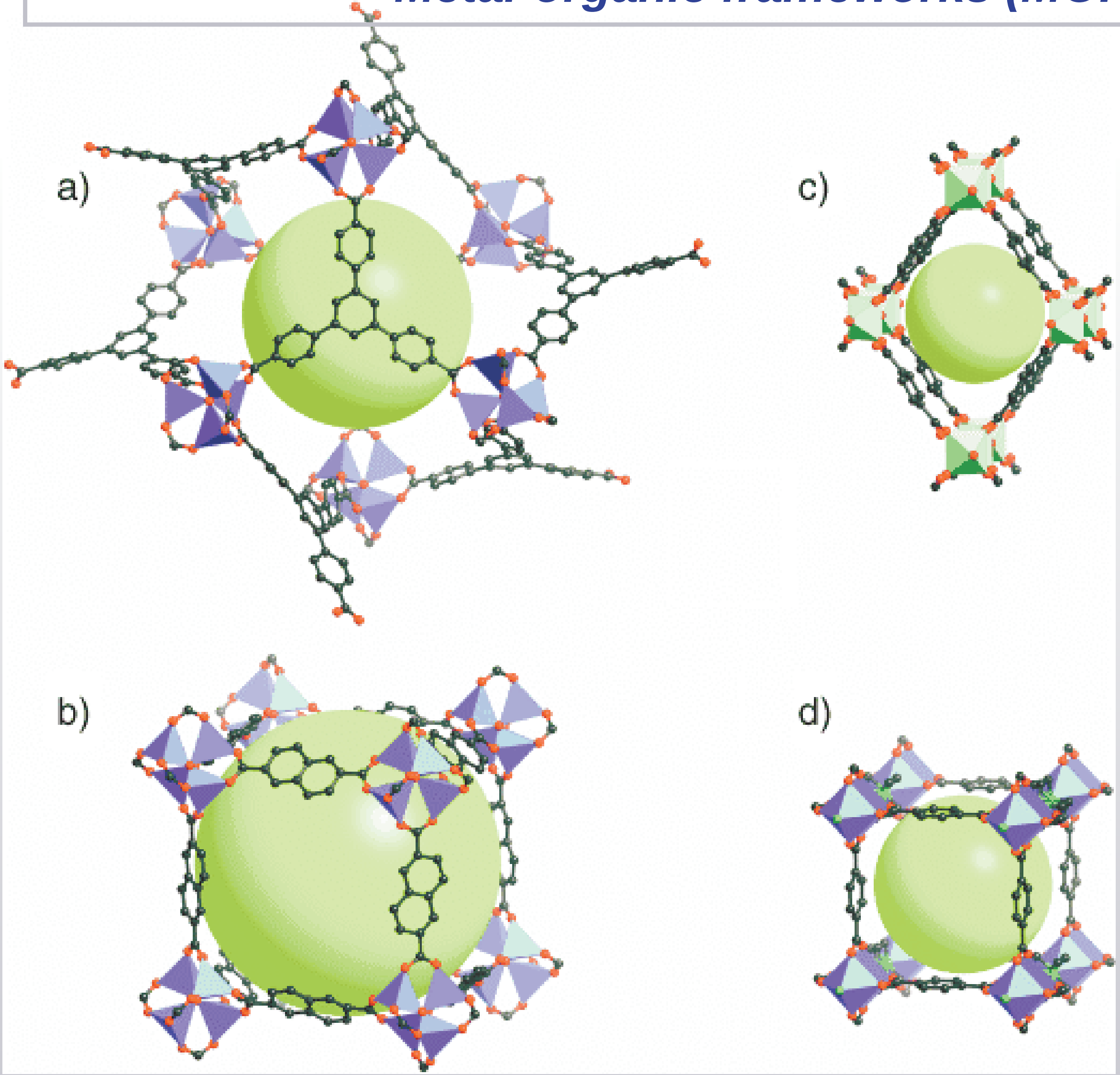




**M. Hirscher, 2005**

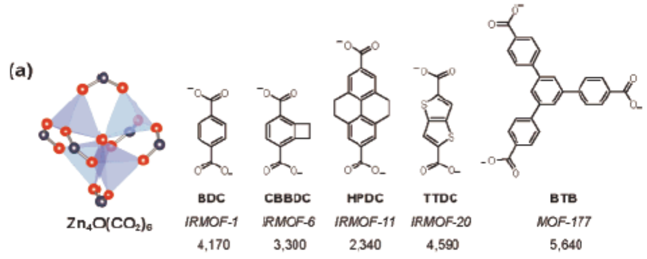
# *Examples Physisorption Materials:*

# *Metal-organic frameworks (MOFs)!*



**Yaghi et al., Angew. Chem. Int . Ed. (2005)**

# *MOFs : H storage capacity*



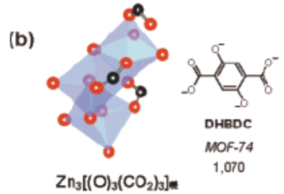
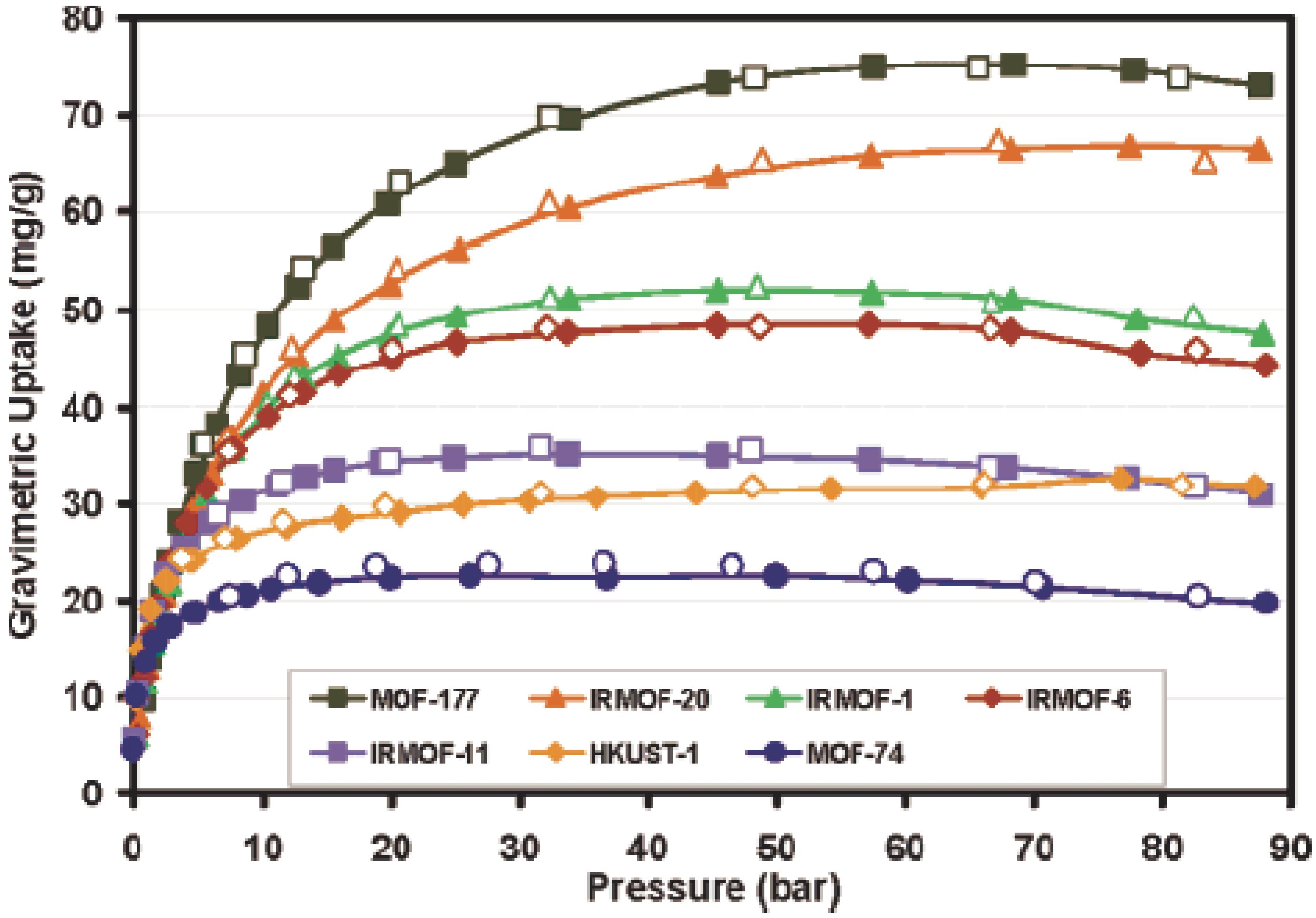


*Figure 1.* (a) $Zn_4O(CO_2)_6$-based
parentheses: *IRMOF-1* (BDC),
*IRMOF-20* (TTDC), and
$\{Zn_3[(O)_3(CO_2)_3]\}_\infty$ $3_1$ helices
$Cu_2(CO_2)_4$ paddlewheels and BT
below each link for the correspo

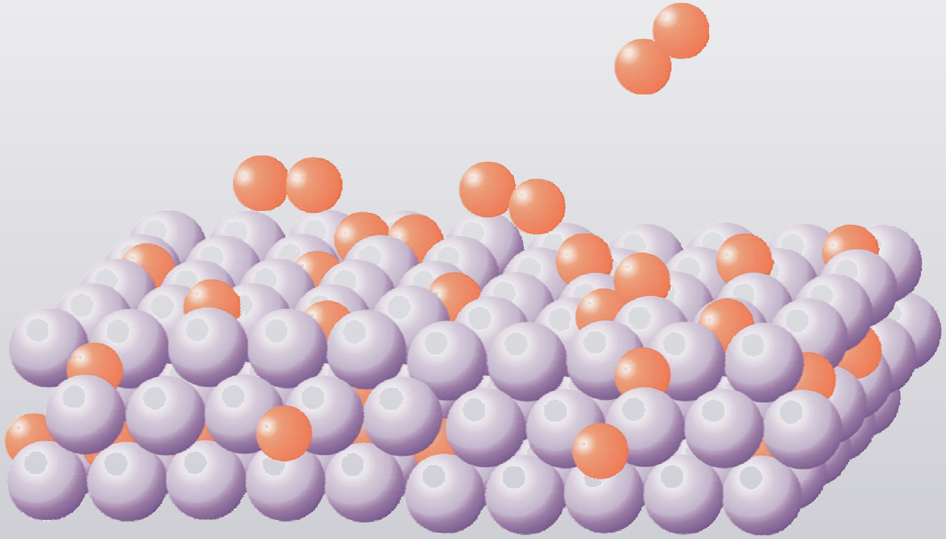
**7.5 wt% @ 77 K, 40 bar**



**Yaghi et al., JACS, 2006**

# *Chemisorption with interstitial hydrides: The concept*

1. ***Adsorption***
2. ***Splitting of $H_2$ molecule.***
3. ***Chemical bonding of H atoms at interstitial sites of the host lattice.***

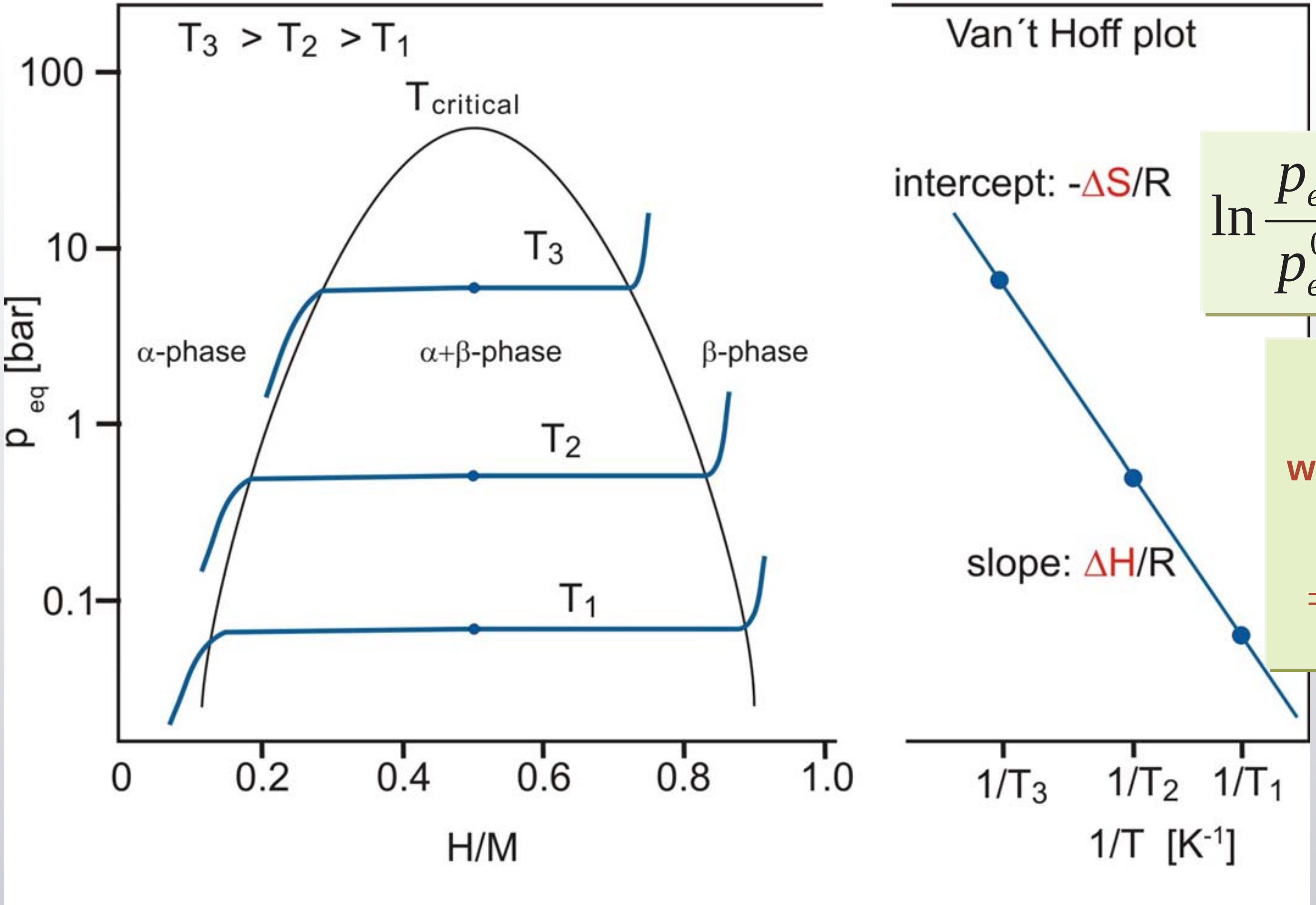


M. Fichtner, Sept. 06

# *Chemisorption: Thermodynamics*

$$M + H_2 \rightleftharpoons MH_2 \quad / \Delta H, \Delta S$$

$$\boxed{\Delta G = \Delta H - T \cdot \Delta S}$$



$$\ln\frac{p_{eq}}{p_{eq}^{0}} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

***„Ideal Hydride“***

**with $\Delta G = 0$ at 300 K**

**⇒ $\Delta H = T\Delta S$**

**⇒ $\Delta H \approx 40$ kJ/mol $H_2$**

**Determination of equilibrium conditions**

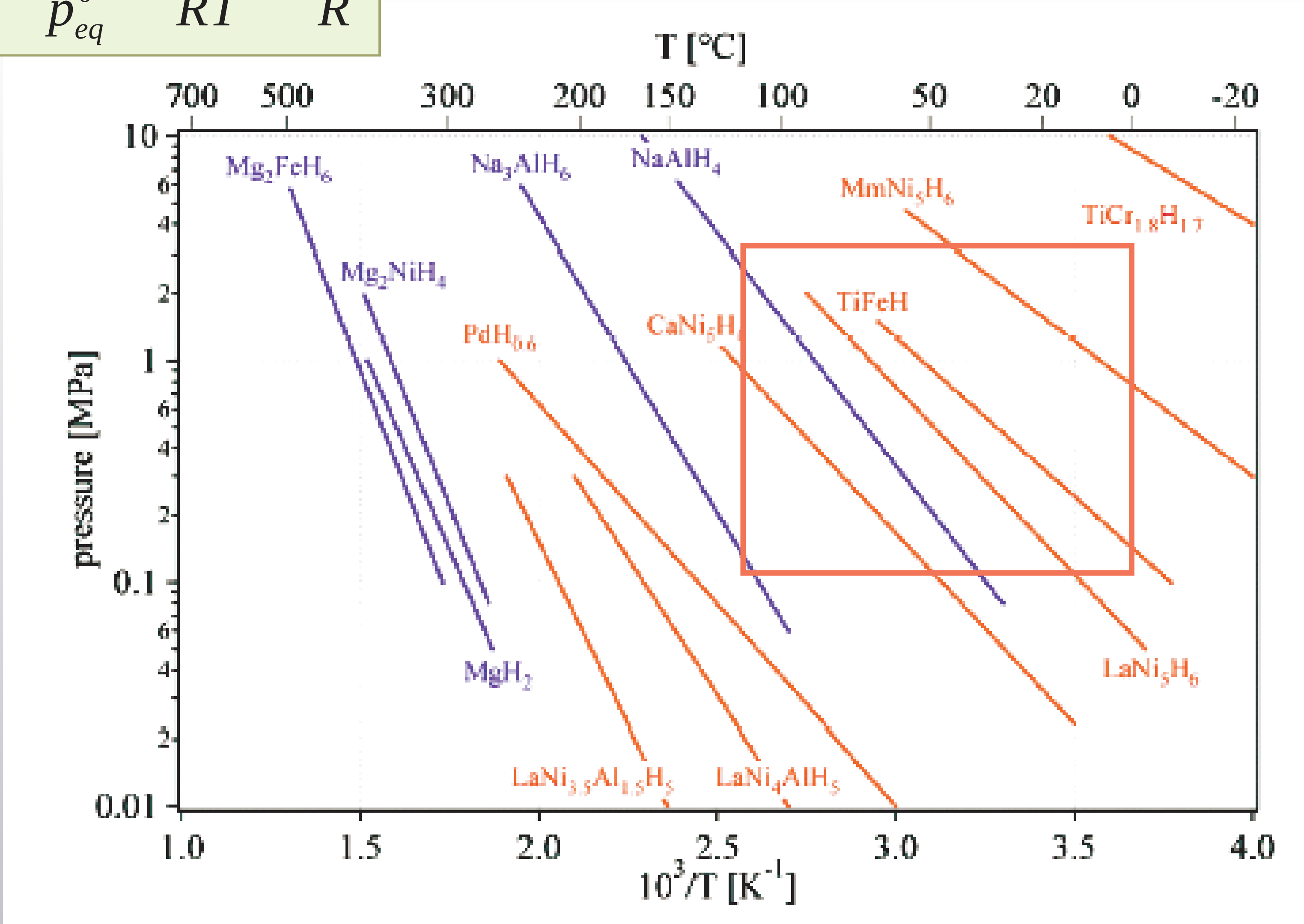
**⇒ Pressure-Composition Isotherms (PCI)**

# *Thermodynamics:*

## *Equilibrium pressures of hydrides / Van´t Hoff Diagram*

$$\ln \frac{p_{eq}}{p_{eq}^{0}} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

***Van´t Hoff Equation***



# Is this the real world for an egineer ?

**Sometimes…**

**Thermodynamics ⇒ optimal case for p, T**

***In practise, there can be <u>kinetic barriers</u> which interfere with the transformation and slow it down***

# Kinetics

# Activation Energies, rate constants

## Transformation of metal hydrides

**Reaction Rate:**

$$\frac{df}{dt} = y(f) \cdot k(T)$$

$f$ = reacted fraction

$T$ = Temperature

**Temperature dependence of reaction constant:**

**→ Arrhenius law**

$$k(T) = k_0 \cdot \exp\left(-\frac{E_A}{RT}\right)$$

$E_A$ = activation energy

$k_0$ = preexponential factor (const)

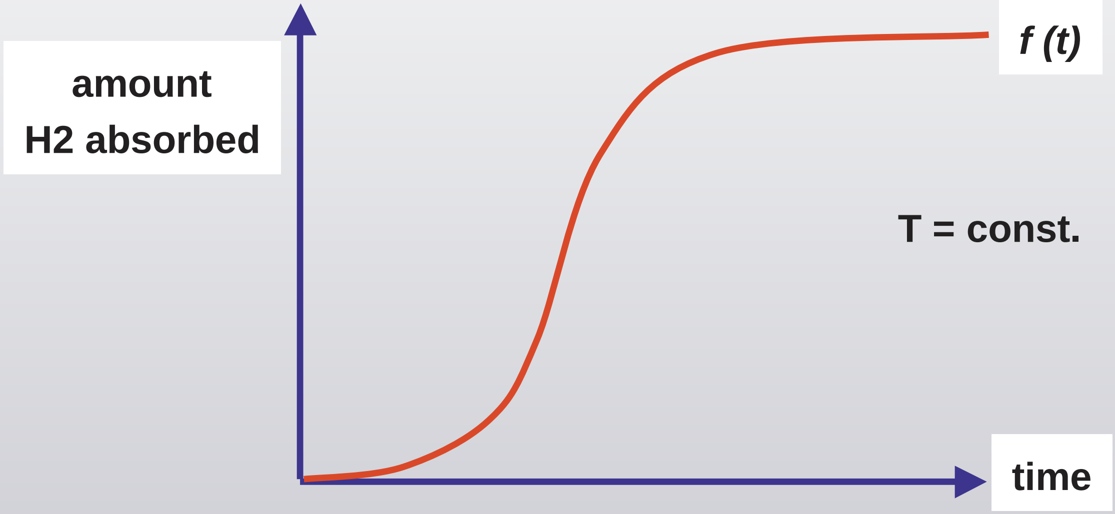
# Experimental Methods

## 1.: Isothermal Experiment

$$\frac{df}{dt} = y(f) \cdot k(T)$$

→ *k(T) is constant and y(f) can be determined easily.*

→ *$E_A$ by measuring k at different T´s.*



*In the case of sigmoidal shaped behaviour:*

# *Nucleation and Growth:*

# *Johnson-Mehl-Avrami (JMA) equation*

$$f = 1 - \exp\{-(kt)^{\eta}\}$$

- The equation generally describes the reacted fraction *f* when the rate limiting process for the formation of the new phase is its nucleation and growth.

- Small exponents $\eta$ between 0.5 and 1.5 denote a diffusion-limited growth process of the new phase. When a constant number of nuclei are assumed, the exponent $\eta$ is equal to 0.5, 1, and 1.5 for one-, two-, and three-dimensional diffusion-limited growth, respectively.

- Growth is then driven by the concentration gradients of the atomic species involved at the grain boundaries. The growth rate itself is limited by the specimen with the slowest diffusion.

## *2.: Constant reacted fraction / non isothermal methods:*

*For $E_A$ >> $RT$*, which is fulfilled for most solid-state reactions, a simple relation between the heating rate $\beta = dT/dt$ *and $T_0$ (for a constant reacted fraction) can be applied:*

$$\ln\left(\frac{\beta}{T_0^2}\right) = -\frac{E_A}{RT_0} + C$$

***Kissinger-Akahira-Sunose method***

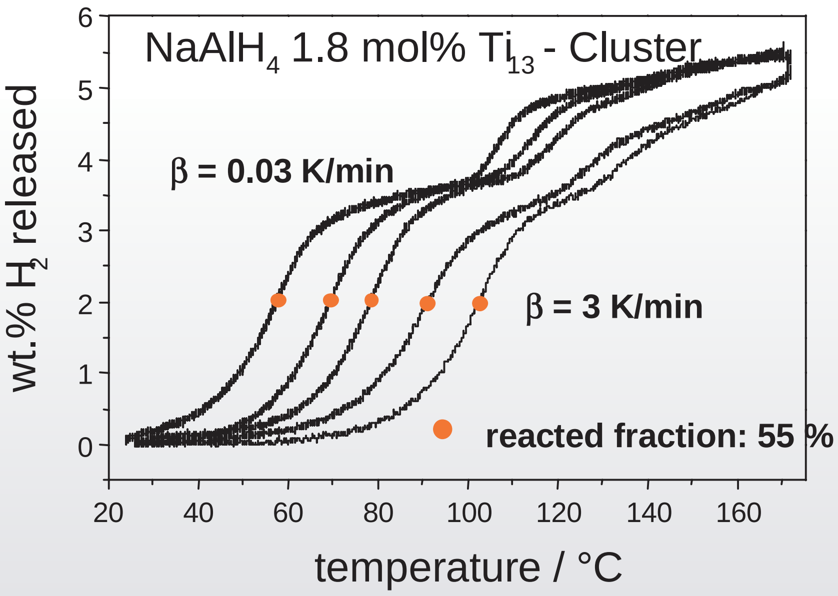
*As an alternative, a certain stage of reaction may be defined at the maximum rate df/dt of the reacted fraction at $T_{max}$ per time.*

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = -\frac{E_A}{RT_{max}} + C$$

***Kissinger method***

**Various instrumental techniques, such as HP-DSC and TGA-MS can be used for temperature ramp experiments.**

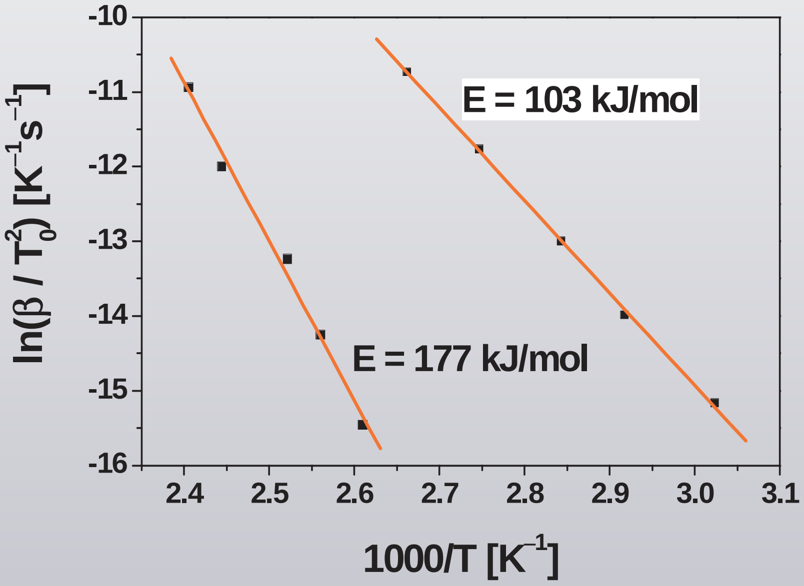
# *Example: Determination of Activation Energies*



$$\frac{df}{dt} = y(f) \cdot k(T)$$

$f = f_0$, $k = k_0 \exp(-E/RT)$

$$\Rightarrow \quad \ln\left(\frac{\beta}{T_0^2}\right) = -\frac{E}{RT_0} + C$$



**$Ti_{13}$ – Cluster:**

**E = 103 kJ/mol (1. step)**

**E = 177 kJ/mol (2. step)**

**$TiCl_3$:**

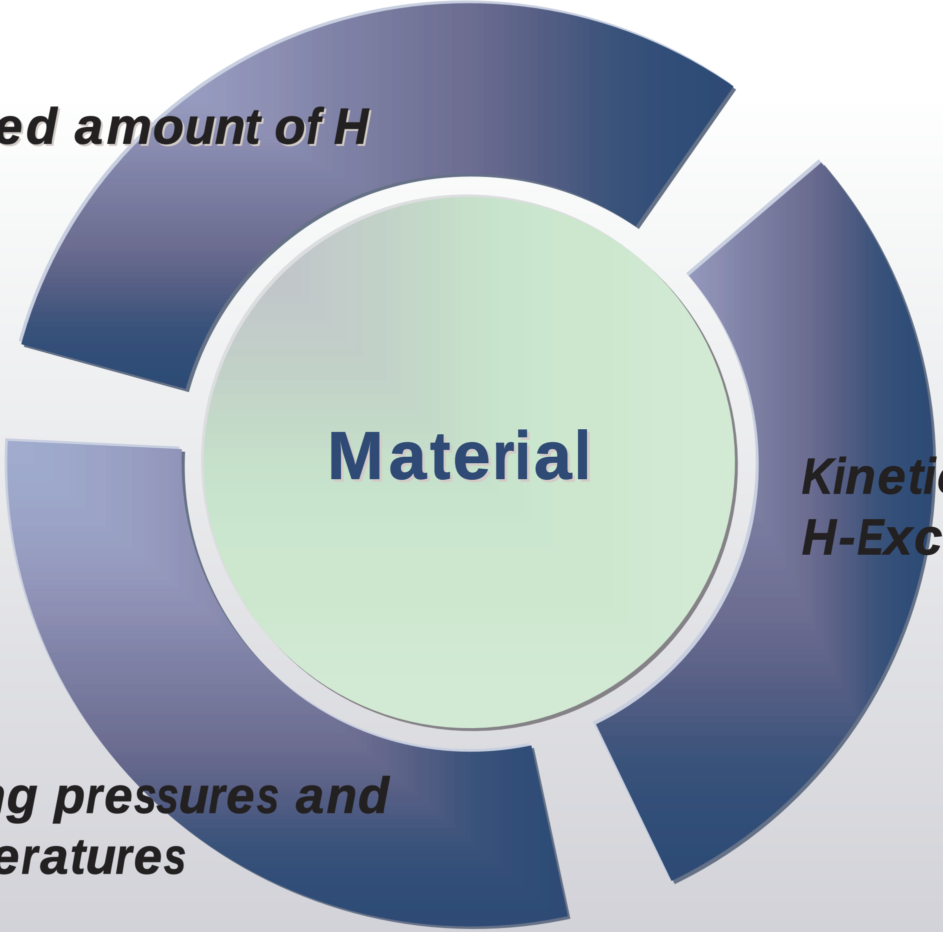
**E = 117 kJ/mol (1. step)**

**O. Kircher, M. Fichtner, JALCOM 404-406, 2005**

# *Properties of hydrogen storage materials and their determination.*

| *Parameter* | *Investigation method* |
|---|---|
| Hydrogen content | Volumetry (Sieverts apparatus)<br>Thermogravimetry (TGA)<br>Electrochemical methods |
| Decomposition temperature | Volumetry<br>Thermal Desorption Spectroscopy (TDS)<br>TGA<br>Differential Scanning Calorimetry (DSC) |
| Equilibrium pressure / temperature | Volumetry |
| Thermodynamic parameters | Volumetry (Van´t Hoff method)<br>HP-DSC |
| Hydrogen exchange kinetics | Volumetry with kinetic reactor<br>DSC or TGA using different heating ramps |
| Specific surface area | BET method |
| *Structure* | |
| Crystal structure / long range order | Single crystal and powder X ray and neutron diffraction |
| Molecular environment | Infrared and Raman spectroscopy |
| Local order | X ray absorption spectrometry (XANES, EXAFS)<br>Inelastic neutron scattering |

# Targeted Physical Properties of a H Storage Material



**Material**

***Stored amount of H***

***Kinetics of H-Exchange***

***Working pressures and -temperatures***

***Nanotechnological approach & combination of different scientific disciplines***

# *Chemisorption: Nanocomposites on hydride basis*

***Nanocomposite***
***= Nanoscale mixture***
***of:***

***H-Carrier***

**Complex light metal hydrides:**

| | |
|---|---|
| **Alanates** | **$M(AlH_4)$** |
| **Boranates** | **$M(BH_4)$** |
| **Amides** | **$M(NH_2)$** |

**&**

***Dopants***

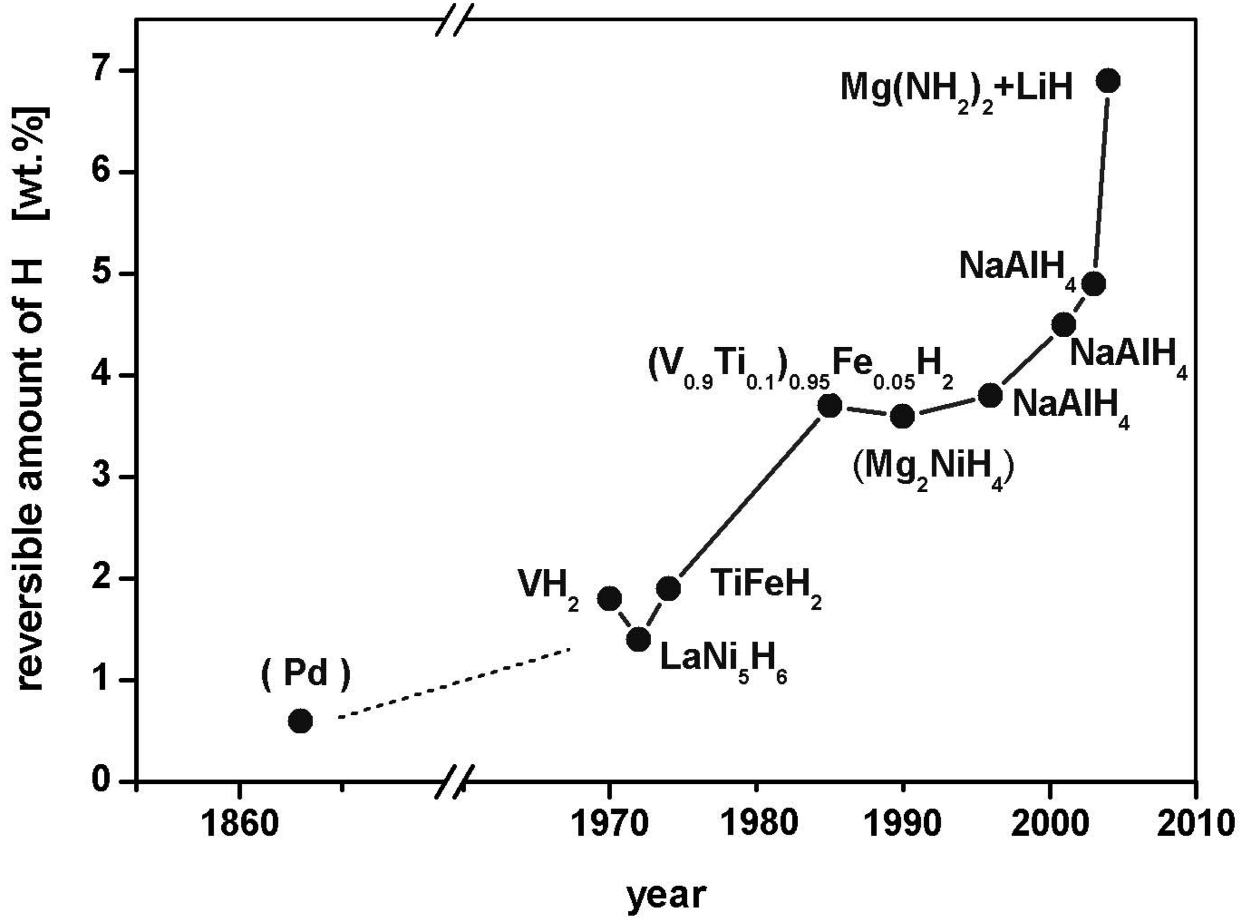
**e.g. Ti Basis**

**Nanoscale**

***The Nanocomposite is the actual storage material.***

***Compared to pure H-Carrier: considerably improved H exchange properties.***

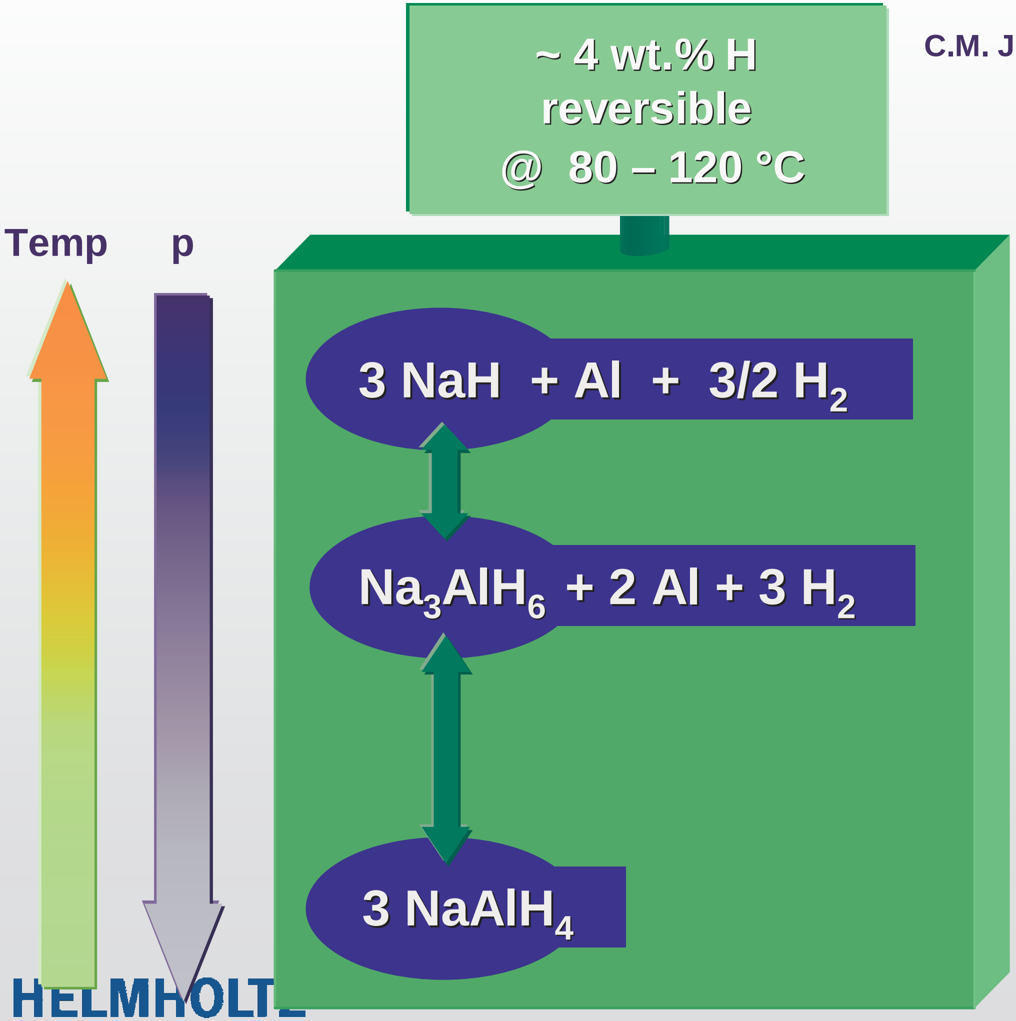
# Development of Low-/ Medium Temperature Storage Materials For Hydrogen



M. Fichtner, Adv. Eng. Mater. 6 (2005) 432

# *Sodium alanate, $NaAlH_4$, as hydrogen carrier*

***Bogdanović 1997 (MPI-KF):*** ***“Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials“ (JALCOM 97)***



**C.M. Jensen et al. , J. Appl. Phys. A 72 (2001) 213 – 219**

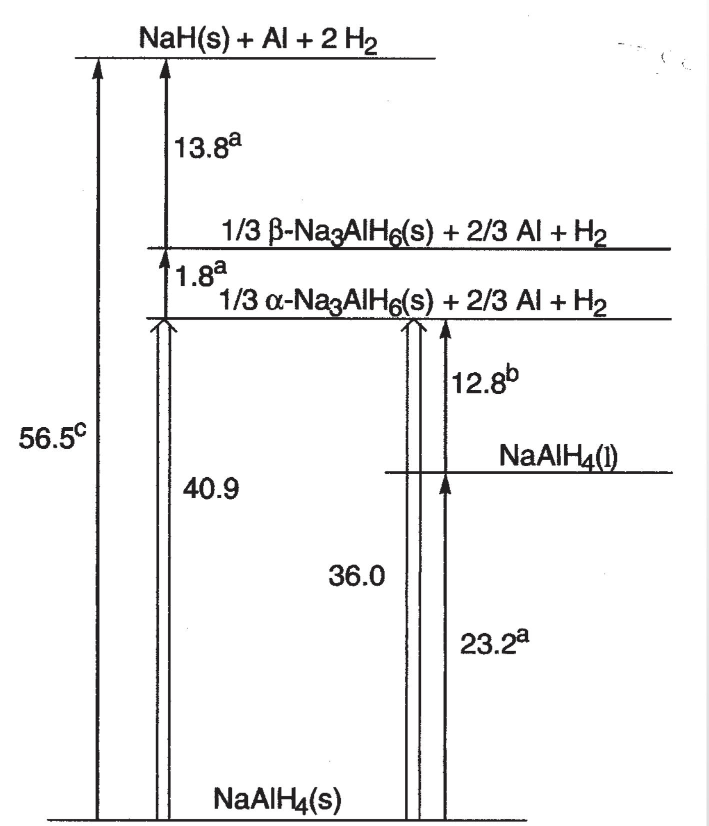
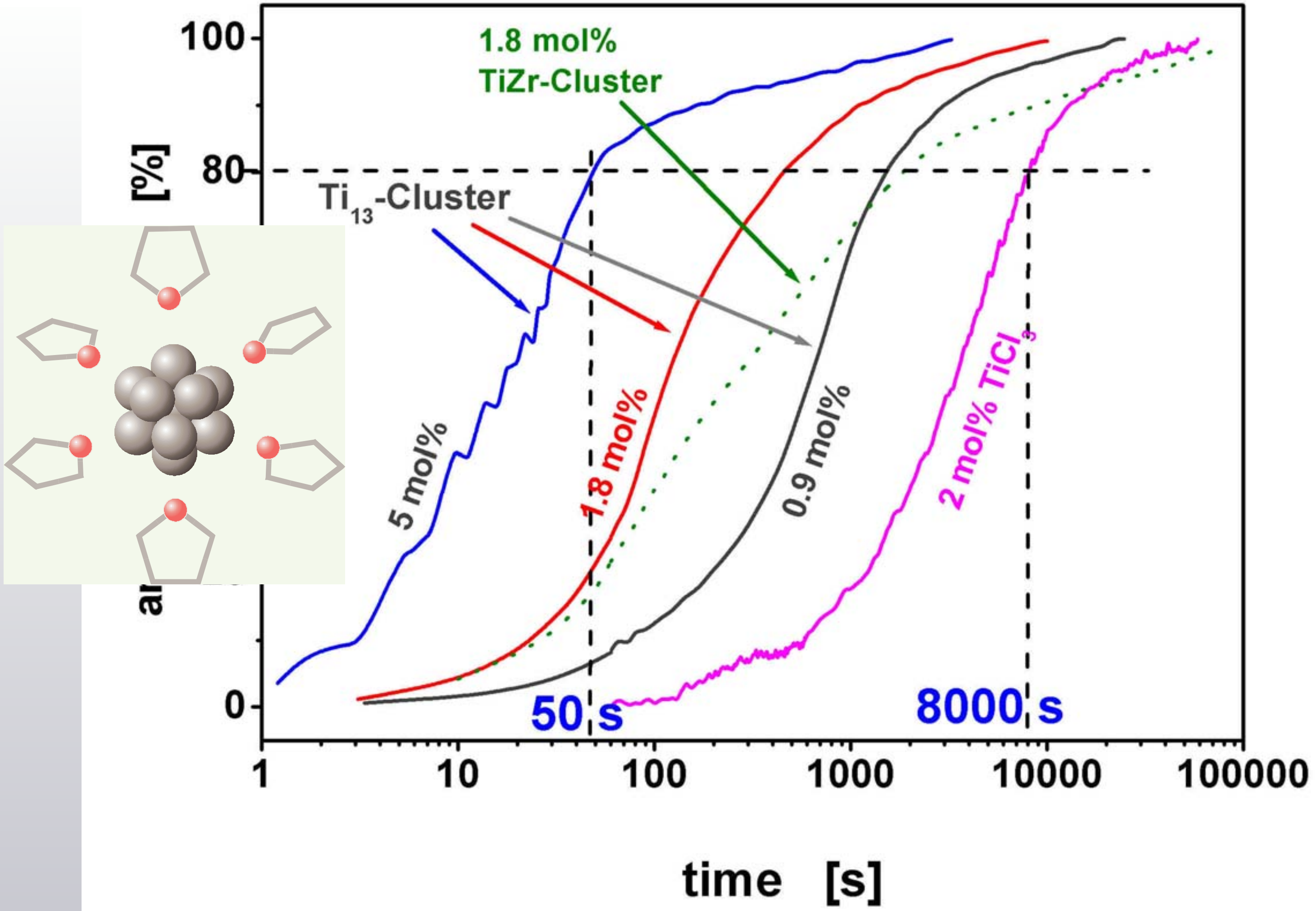


**Fig. 1.** Enthalpy values (kJ/mol) determined for the processes occurring during the uncatalyzed dehydriding of 1 mole of $NaAlH_4$: a [26], b [21], c [18]

# $H_2$ Absorption Kinetics

$NaAlH_4$ + x mol% Ti / 100 °C, 100 bar



M. Fichtner, *Adv. Eng. Mater.* 6 (2005) 443

# *Next Generation of Storage Materials*

**Chemical solid state reactions where hydrogen is exchanged**

- **More hydrogen !**
- **„Adjust“ thermodynamics !**

| | | |
|---|---|---|
| $LiBH_4 + MgH_2 \rightleftharpoons LiH + MgB_2$ | **11.4 wt.% H** | **(Vajo 2003)** |
| $Mg_2Si + 2\ H_2 \rightleftharpoons 2\ MgH_2 + Si$ | **5.1 wt.% H** | **(Vajo 2003)** |
| $2\ LiNH_2 + MgH_2 \rightleftharpoons Li_2Mg(NH)_2 + 2\ H_2$ | **5.9 wt% H** | **(Luo 2003)** |

**Matters of research:**

- **Reversibility**
- **Kinetic barriers**
- **Unwanted by-products**

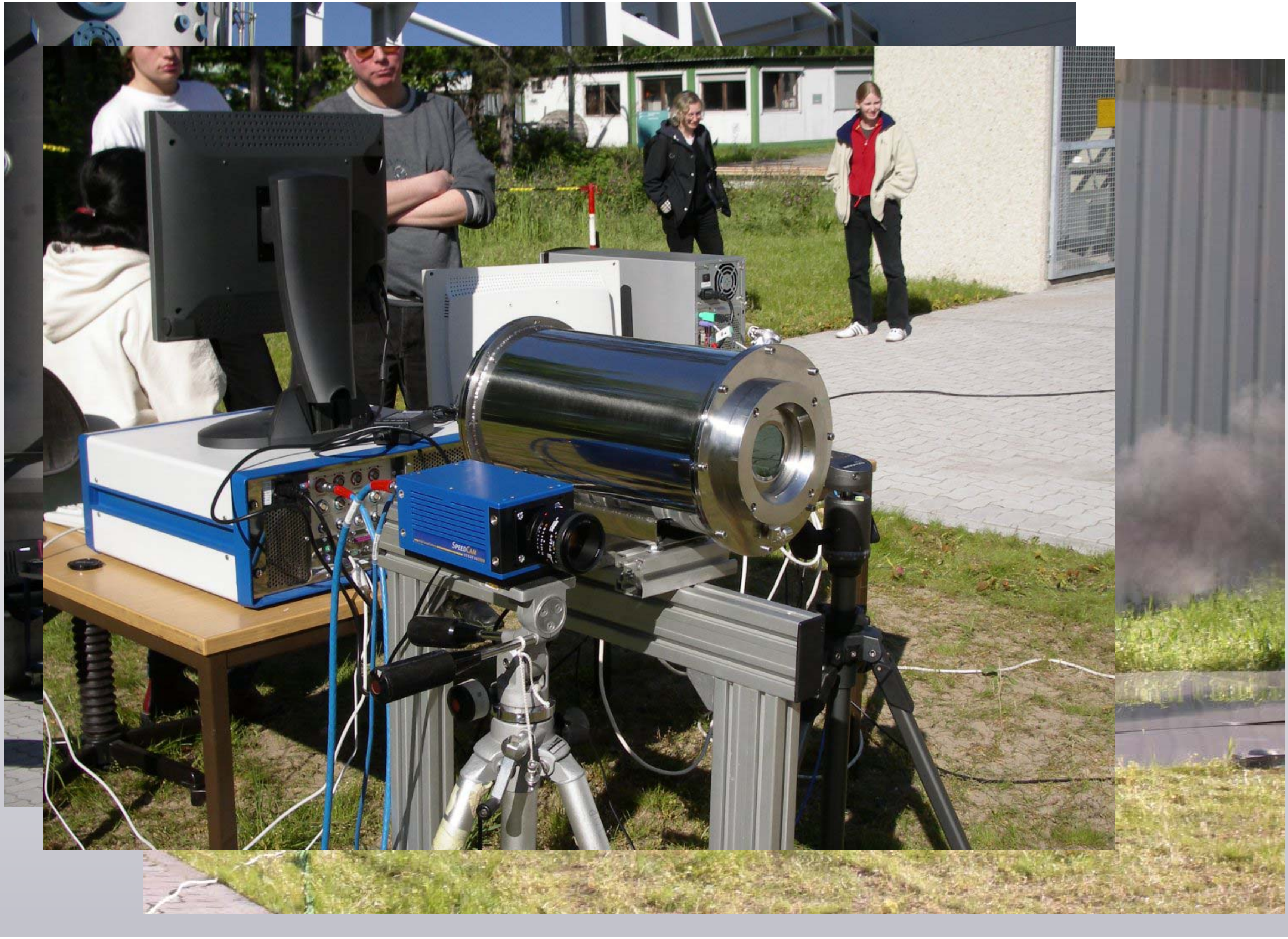
# Hydrogen Safety Center

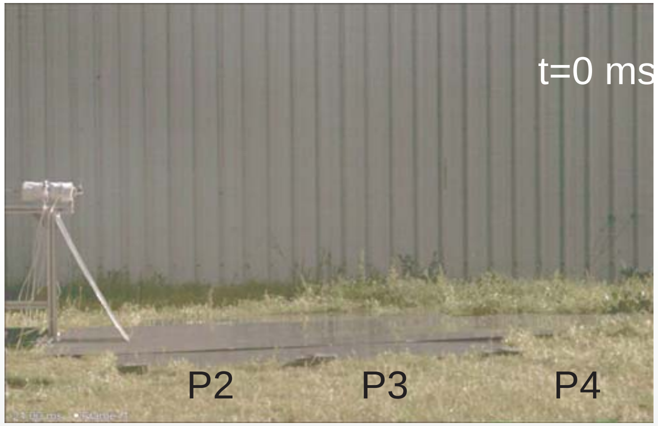
*110 m$^3$ + 60 m$^3$ pressure vessels; test facility (for cars) inside; …..*

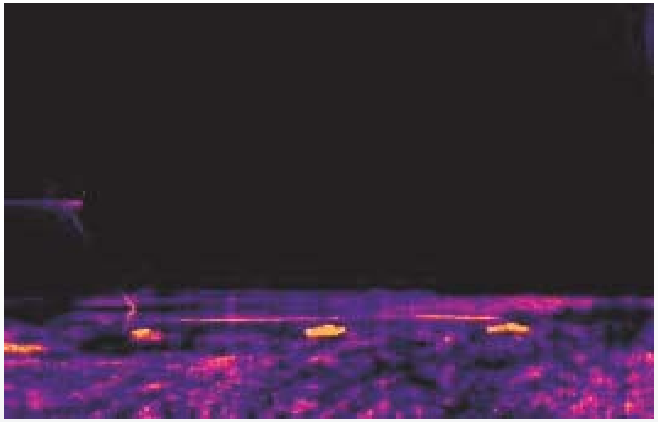
## *First Safety Experiment:*

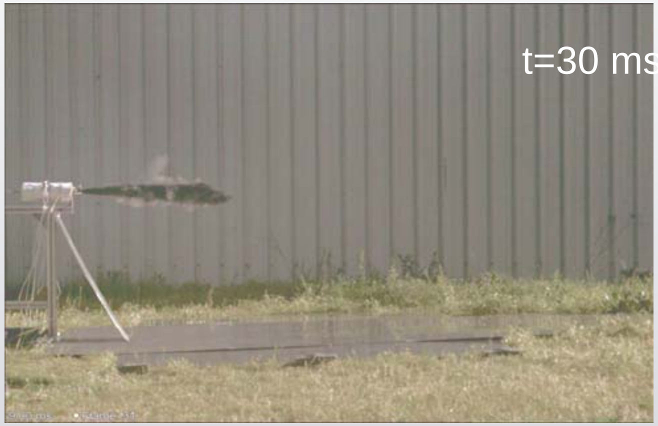
***Tube 2cm diameter, ca. 100 ml nanopowder (7.3 wt.% H)***

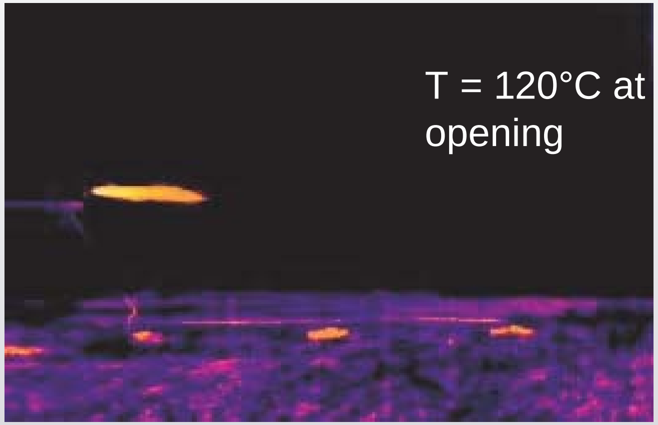
***Rupture disk (p > 8.5 bar H2 ), reached at T = 130 °C***



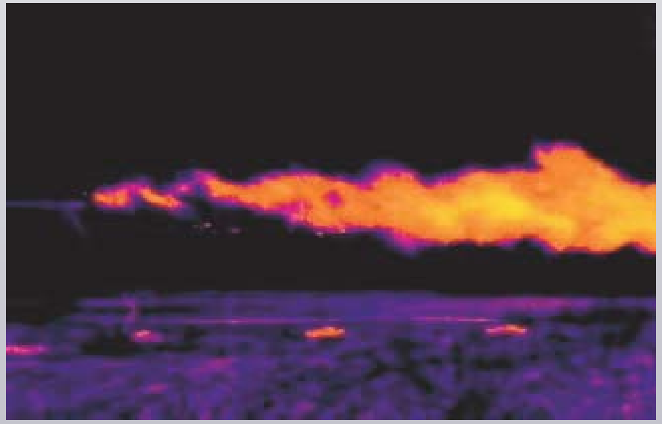






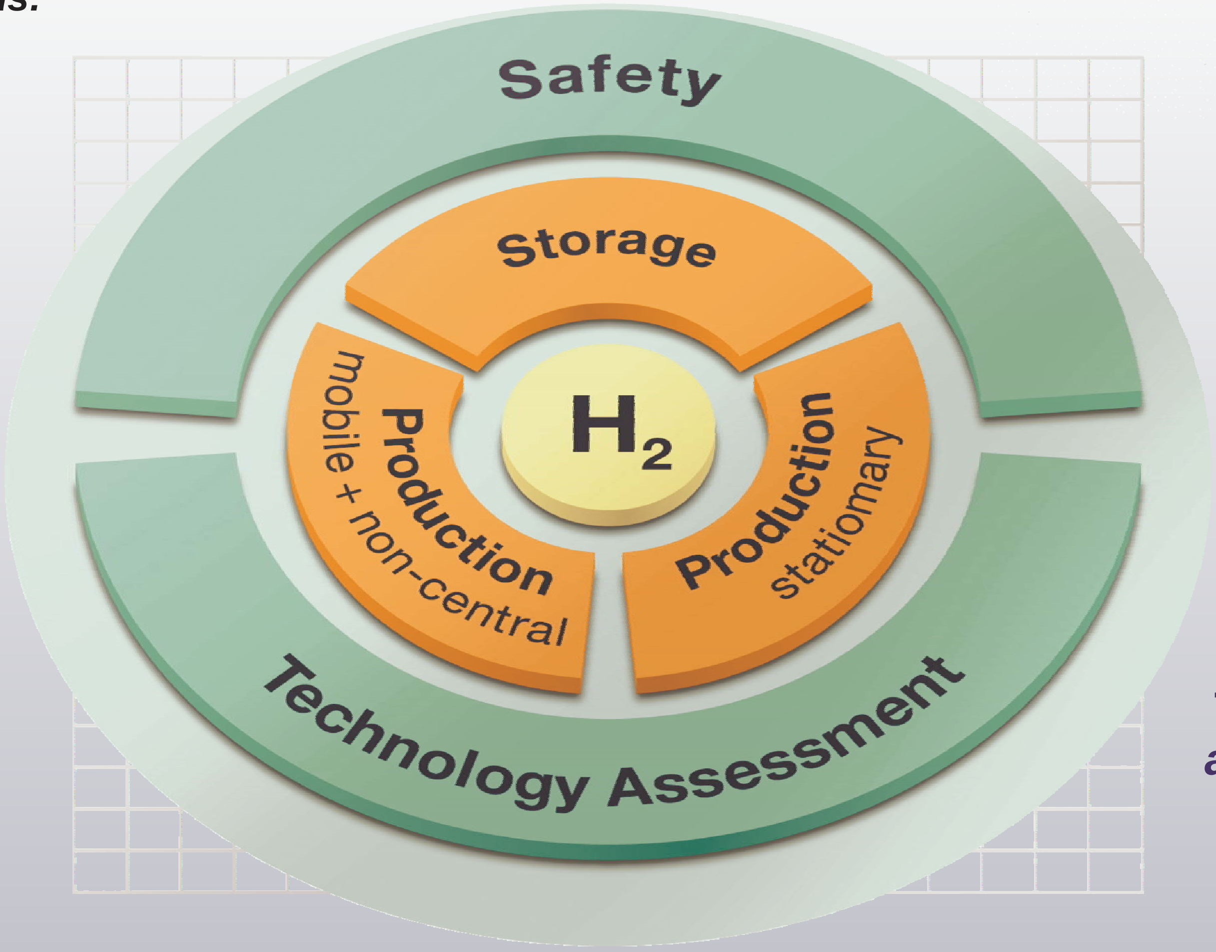


T = 120°C at disk opening



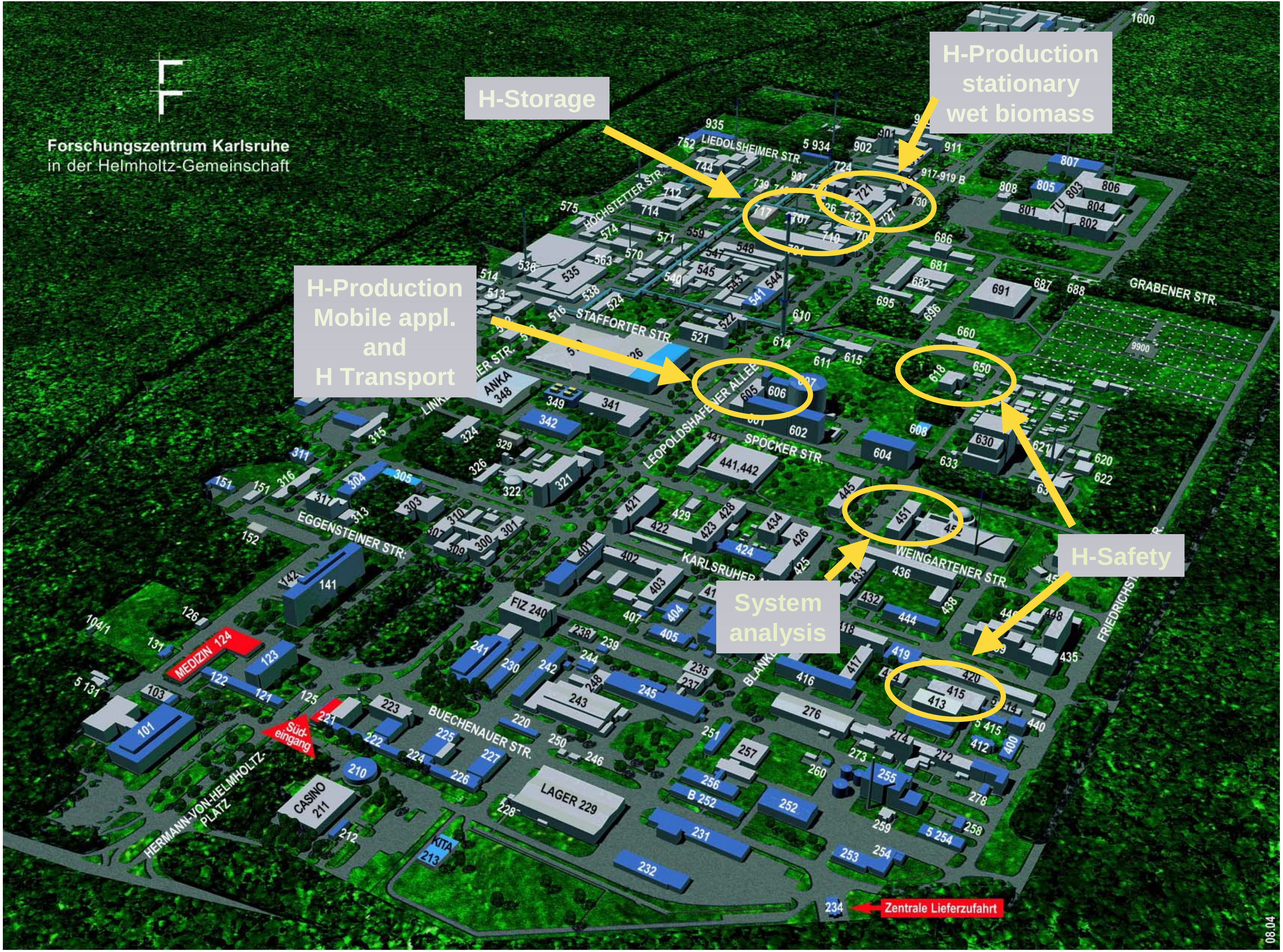
***Largest Public Research Activity on Hydrogen in Germany***
***50 Scientists in 5 Institutes***

***Fields:***



***since June 2006:***

***+ Transportation and Infrastructure***



H-Storage

H-Production
stationary
wet biomass

H-Production
Mobile appl.
and
H Transport

System
analysis

H-Safety

# People in H Storage at FZK

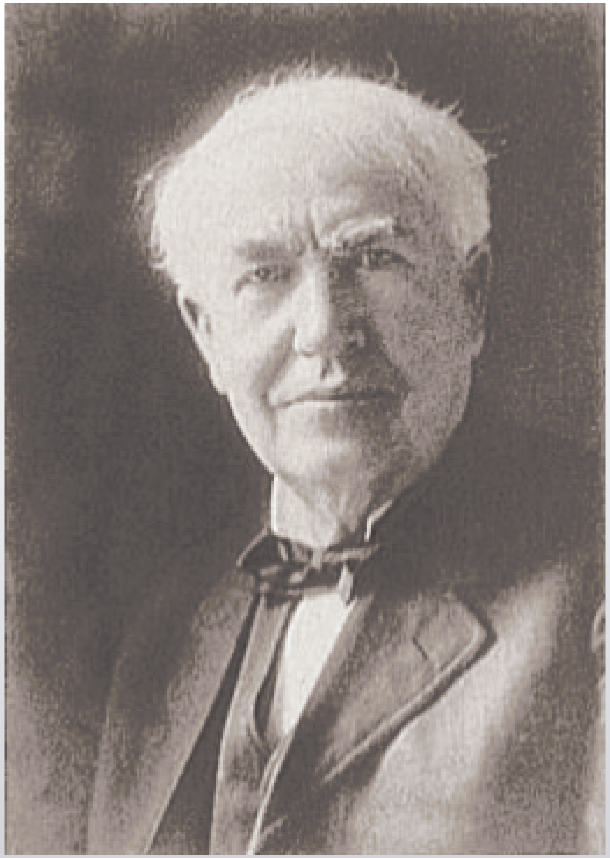
Krzysztof Chłopek
Christoph Frommen
Nobuko Hanada
Johannes Kostka
Aline Léon
Wiebke Lohstroh
Abu N. Rahman
Stephan Wetterauer
Oleg Zabara
Maximilian Fichtner

*Nanostructured Materials*

Olaf Fuhr
*Cluster Chemistry*

Olaf Hübner
*Theoretical Chemistry*

# Thomas A. Edison



www.ThomasEdison.com

*"I'd put my money on the sun and solar energy. What a source of power! I hope we don't have to wait 'til oil and coal run out before we tackle that."*

**(1847-1931)**

# Biofuels + Hybrid concepts !
# The All-New DonCar

# Space Applications…

# Thank you for your

STORHY
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# Session 4.1: Solid Storage Technology

Dr. M. Fichtner (FZK)

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