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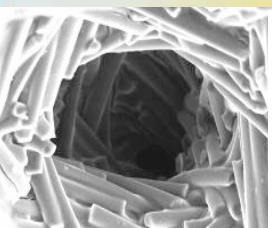
Materials Innovations in an Emerging Hydrogen Economy
February 24-27, 2008
Hilton Oceanfront | Cocoa Beach, Florida USA

High density carbon materials for hydrogen storage

A. Linares-Solano, M. Jordá-Beneyto, D. Lozano-Castelló, F. Suárez-García, D. Cazorla-Amorós



Carbon Materials and Environment Research Group
(http:/www.ua.es/grupo/mcma)
Department of Inorganic Chemistry
University of Alicante, Spain

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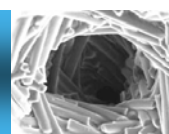
UNIVERSITY OF ALICANTE
(http://www.ua.es)

- Introduction
- Experimental and equipments
- H_2 storage results at RT & 77K
- Reporting H_2 data; weight/volume ?
- Conclusions



HYDROGEN FOR AUTOMOTIVES

is an interesting objective but...

Still a challenge !

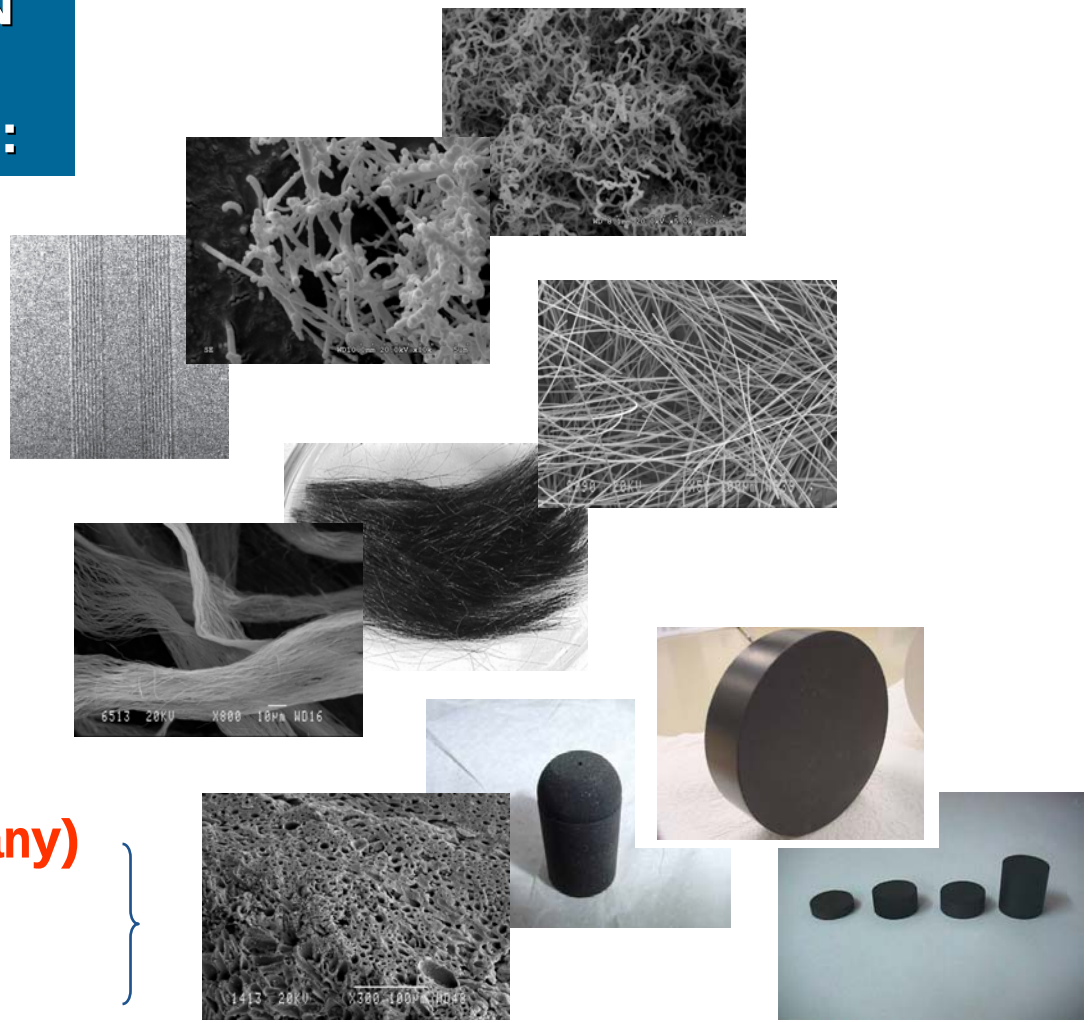
- **500-600 km driving needs → 5-7 kg H_2**

- **Compressed Hydrogen (10-70 MPa)**
- **Liquid Hydrogen (20K)**
- **Metal Hydrides,..** → **Absorption**
- **Metal Organic Frameworks** } **Adsorption**
- **Carbon Materials** }

High density carbon materials for hydrogen storage

OUR STUDY ON CARBON COVERS DIFFERENT ACTIVATED MATERIALS:

- Carbon nanotubes
- Carbon nanofibers
- Carbon microfibers
- Carbon fibers
- Carbon precursors (many)
- Carbon monoliths



ACs PERFORMANCES CAN BE TAILORED DURING ACTIVATION

- Surface area
- Porosity (volume & and PDS)

↑

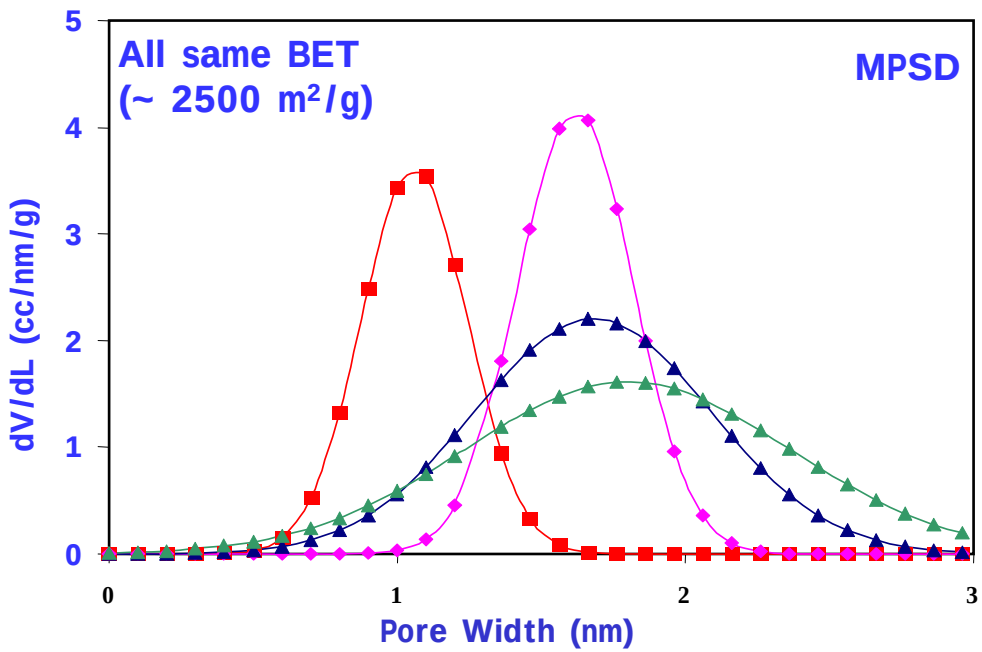
- Density
- Thermal and electrical conductividad

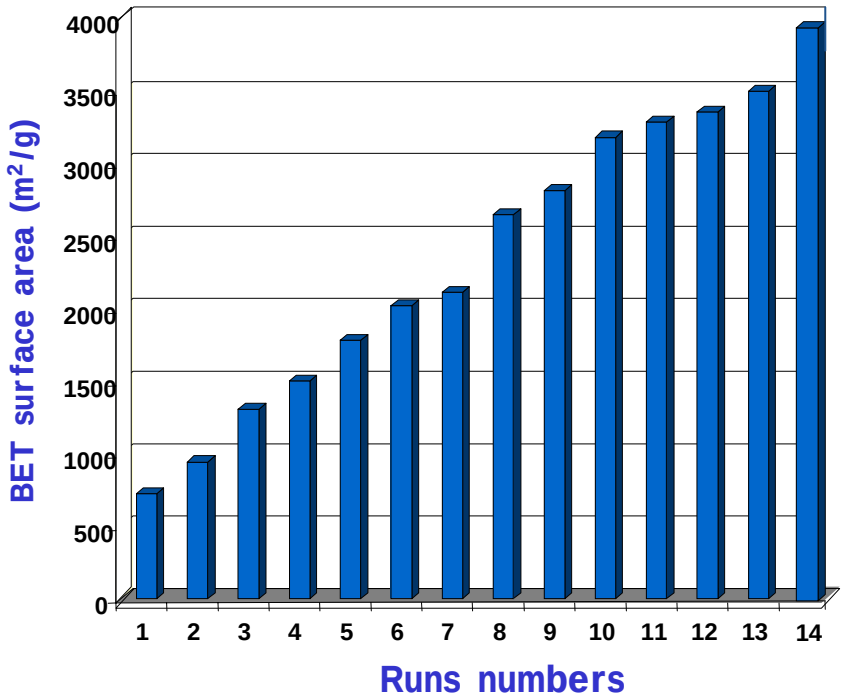
↑

- Surface chemistry (oxygen groups) ↓
- Shapes & forms (powder, pellet, monolith...)

All these properties are important for H_2 storage !

EXAMPLE SHOWING CONTROL OF THE PSDs AND OF BET SURFACE

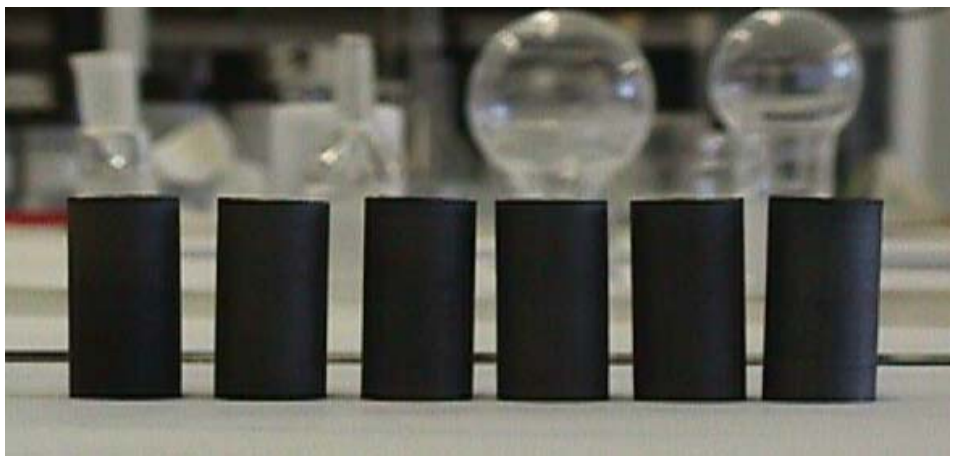




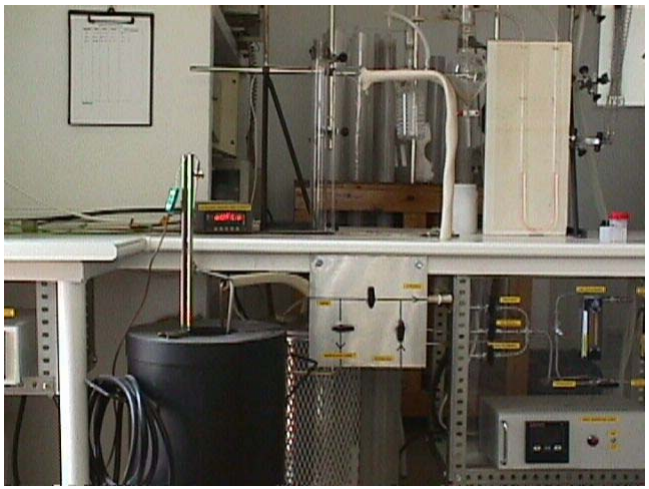
A. Linares-Solano, D. Lozano-Castelló, M. A. Lillo-Ródenas, and D. Cazorla-Amorós
Carbon Activation by Alkaline Hydroxides, in Chemistry and Physics of Carbon, Volume 30 (2008)

ADDITIONAL ACs ADVANTAGES

- Low cost & well known process
- Easiness to machine
- Good chemical stability
- Good thermal & mechanical stability



LABORATORY SCALE ACTIVATION



Fluidized bed reactor

PHYSICAL & CHEMICAL ACTIVATION

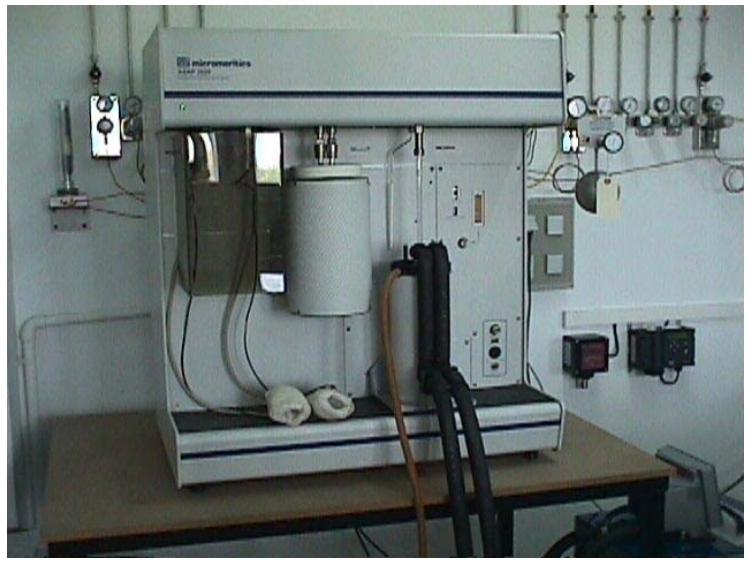
Fixed bed

Fixed bed

CHARACTERIZATION: SUB-ATMOSPHERIC ADSORPTION

→ **Porous texture (surface, pore volume) and PSD**

2 Autosorbs-6 (Quantachrome)



ASAP 2020 (Micromeritics)

CHARACTERIZATION: HIGH-PRESSURE ADSORPTION

H_2 storage

Gravimetric units

77 – 298 K
<1- 4 MPa

Volumetric unit

77 – 750 K
1-20 MPa

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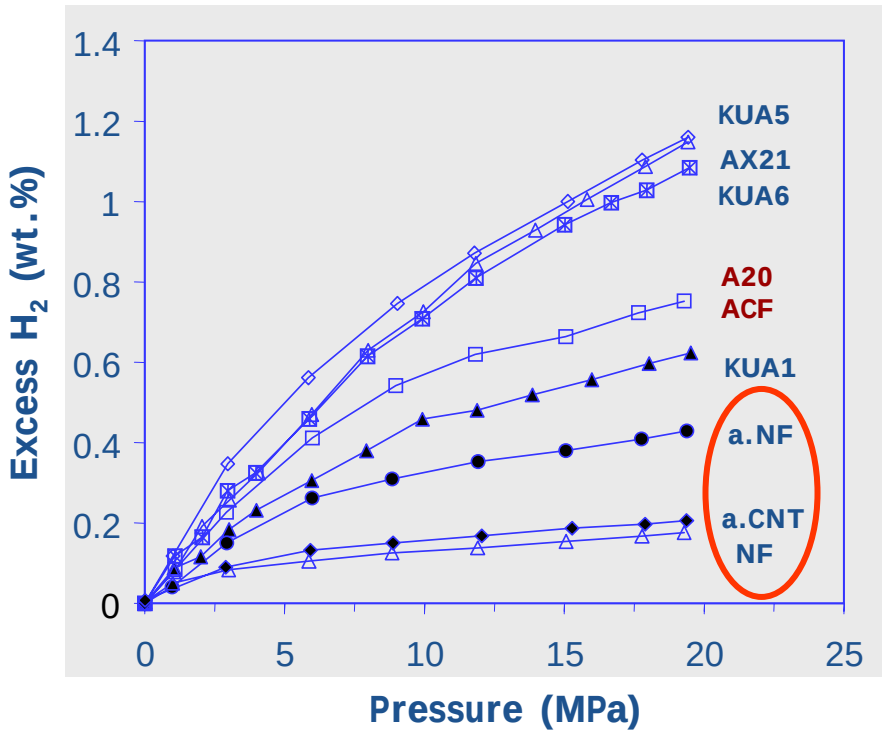
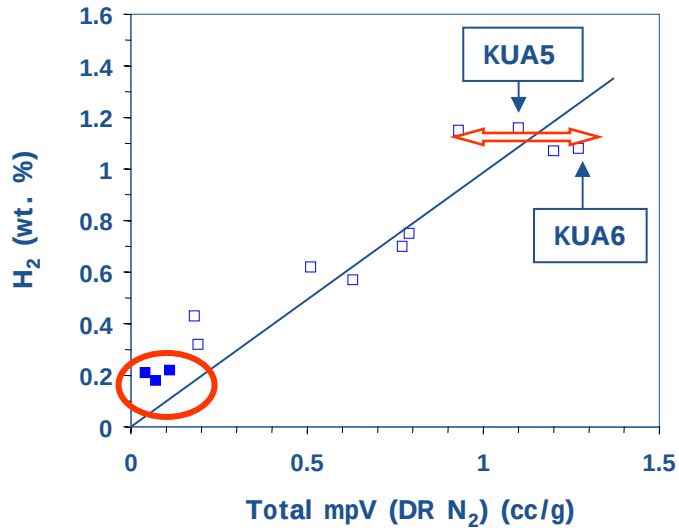
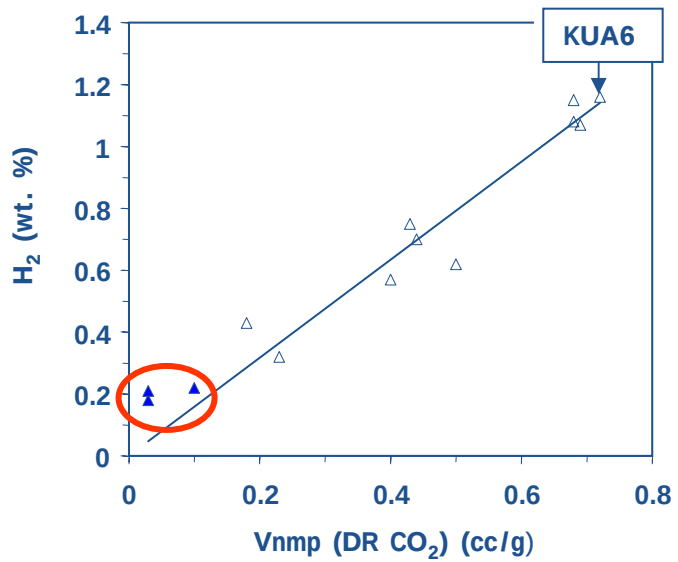
HYDROGEN STORAGE AT ROOM TEMPERATURE (20 MPa)







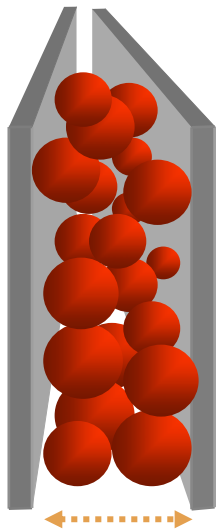
M. Jordá-Beneyto, D. Lozano-Castelló, F. Suárez-García, D. Cazorla-Amorós and A. Linares-Solano. Hydrogen storage on chemically activated carbon nanomaterials at high pressures, Carbon 45, 293–303 (2007)

HYDROGEN STORAGE AT ROOM TEMPERATURE (20 MPa): CONCLUSIONS

H_2 STORAGE (1-20 MPa)

- High micropore volume
- Control of pore size distribution
- High packing density

BALANCE



0.6-0.7 nm

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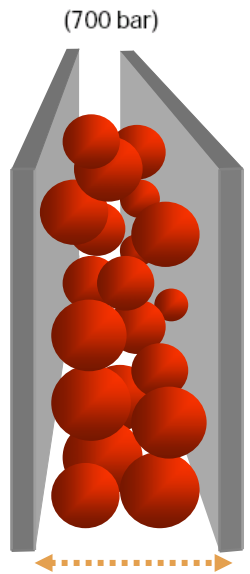
HYDROGEN STORAGE AT ROOM TEMPERATURE (70 MPa): CONCLUSIONS

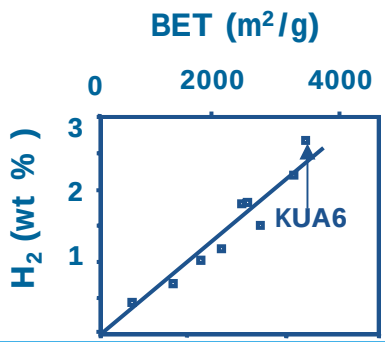
H_2 STORAGE (30-70 MPa)

- High micropore volume
- High packing density

BALANCE

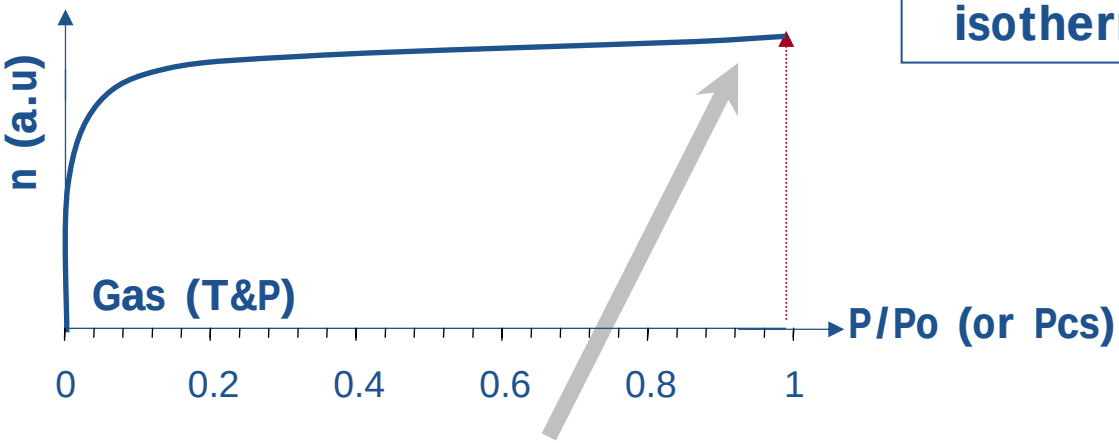


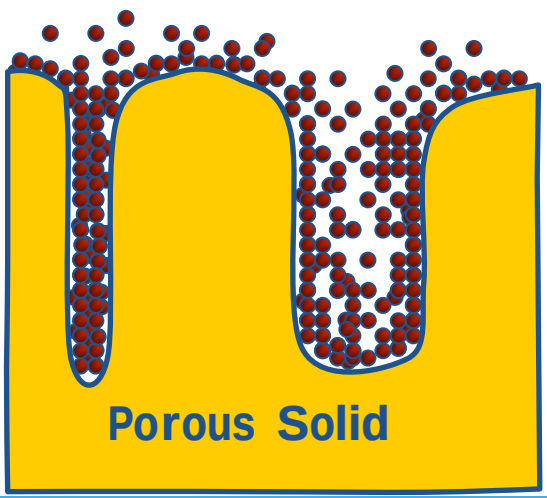
>> 0.7 nm



ADSORPTION ON MICROPORES

Adsorption isotherm



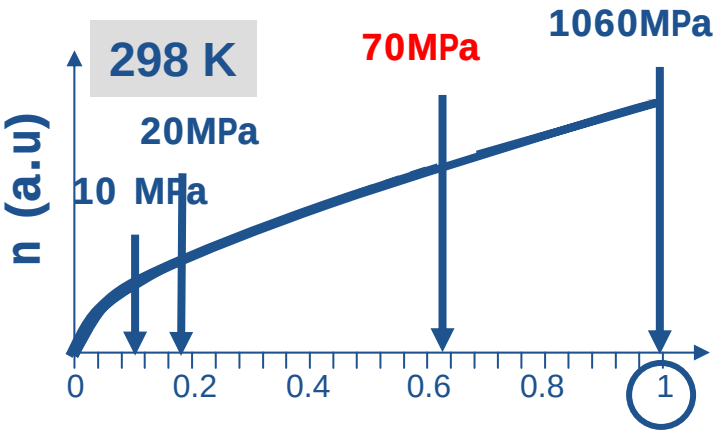


High P/Po

$$n = f(P)_{T,\ gas,\ solid}$$

FUNDAMENTS OF H2 HIGH PRESSURE ADSORPTION

Critical Temperature (T_C)	33.19 K
Critical Pressure (P_C)	13.150 bar
Critical Density (D_C)	0.0301 g/ml
Normal Boiling Point	20.39 K

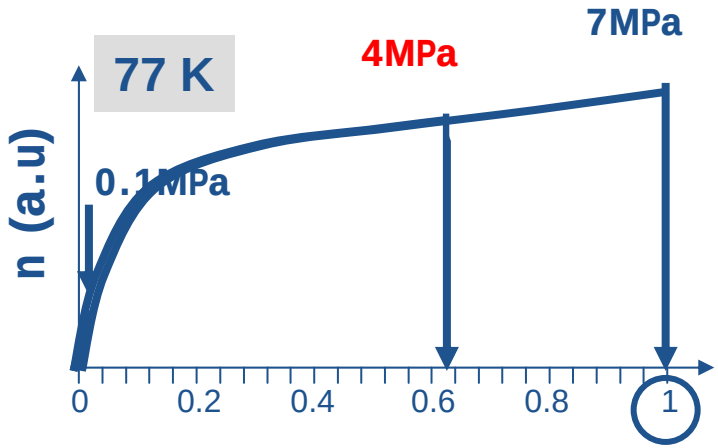


$P_r = P/P_{CS}$

Supercritical conditions both at 298K & 77K

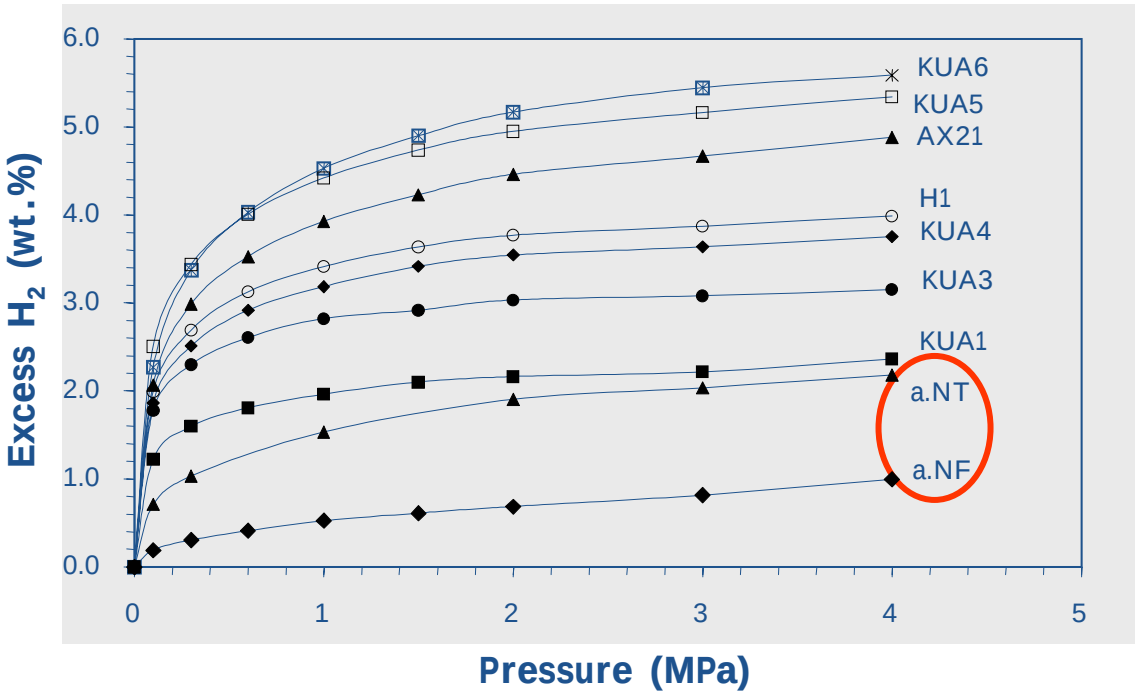
Dubinin approach

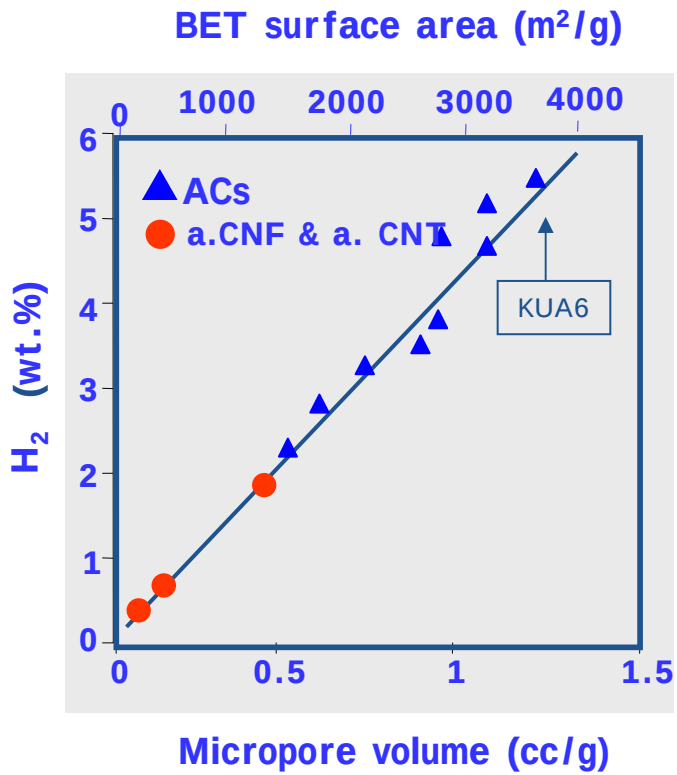
$$P_{CS} = P_C(T/T_C)^2$$



$P_r = P/P_{CS}$

HYDROGEN STORAGE AT 77K (4 MPa): CONCLUSIONS





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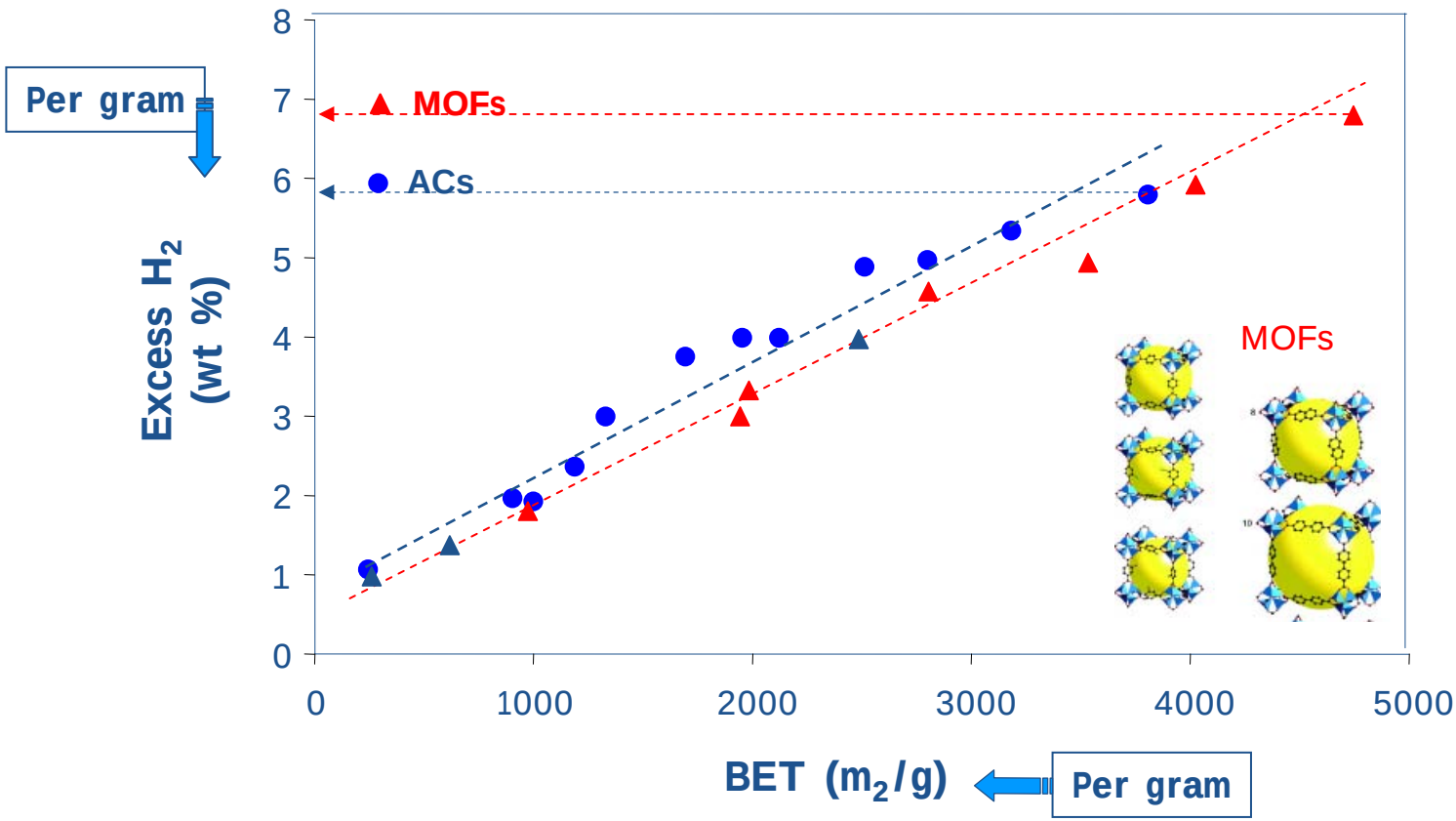
HYDROGEN STORAGE (ACs and MOFs, 77 K)



Adapted from Wong – Foy A.G. et al. J.Am. Chem Soc. 2006, 128, 3494-3495, including additional data (▲)

FOR HYDROGEN VEHICULE APPLICATIONS: SAMPLE WEIGHT OR SAMPLE VOLUME ?

Adsorption in gravimetric basis ? **Adsorption in volumetric basis**

- H_2 uptakes much better when reported per unit of volume
- Density has to be measured !

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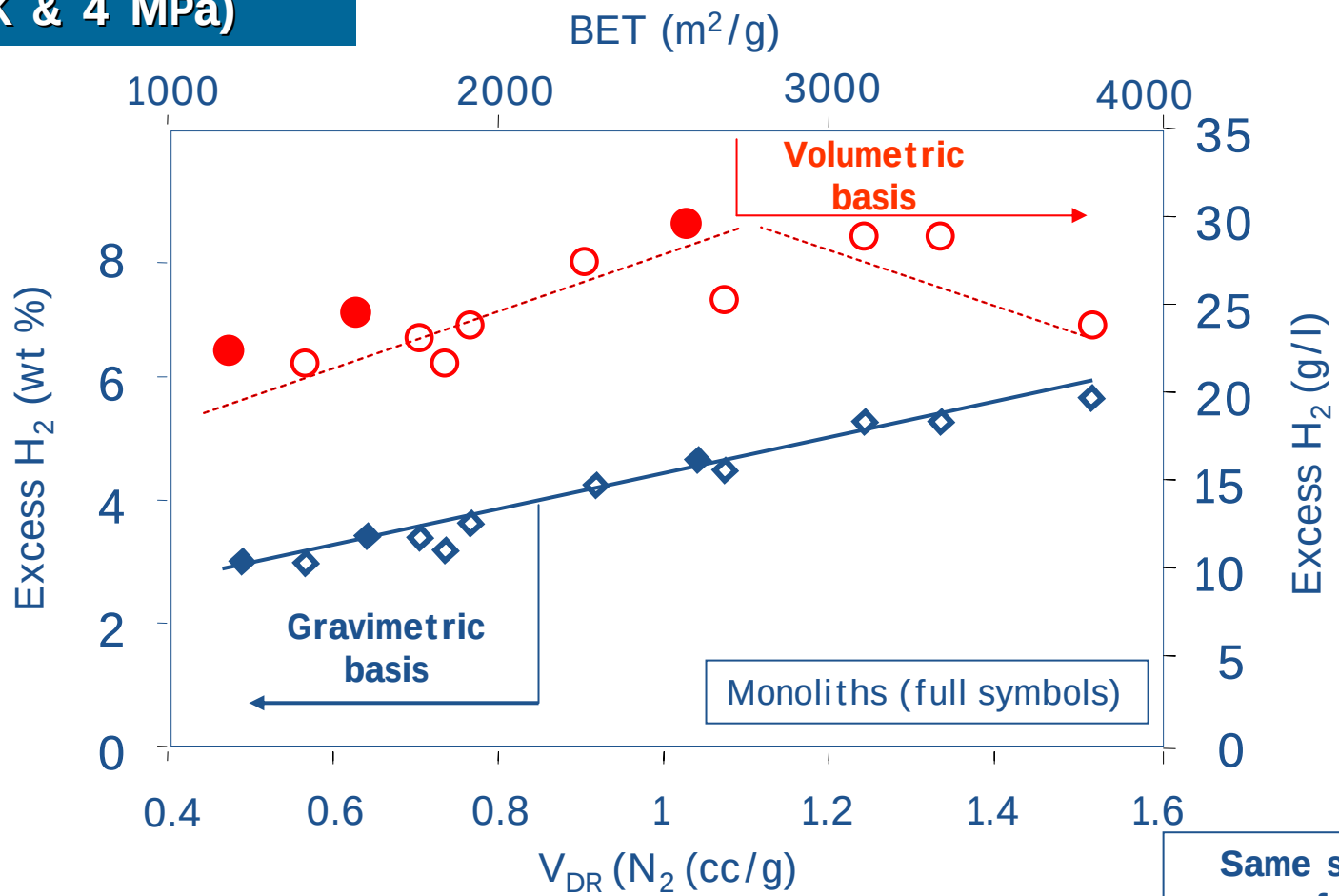
HYDROGEN STORAGE (77K & 4 MPa)

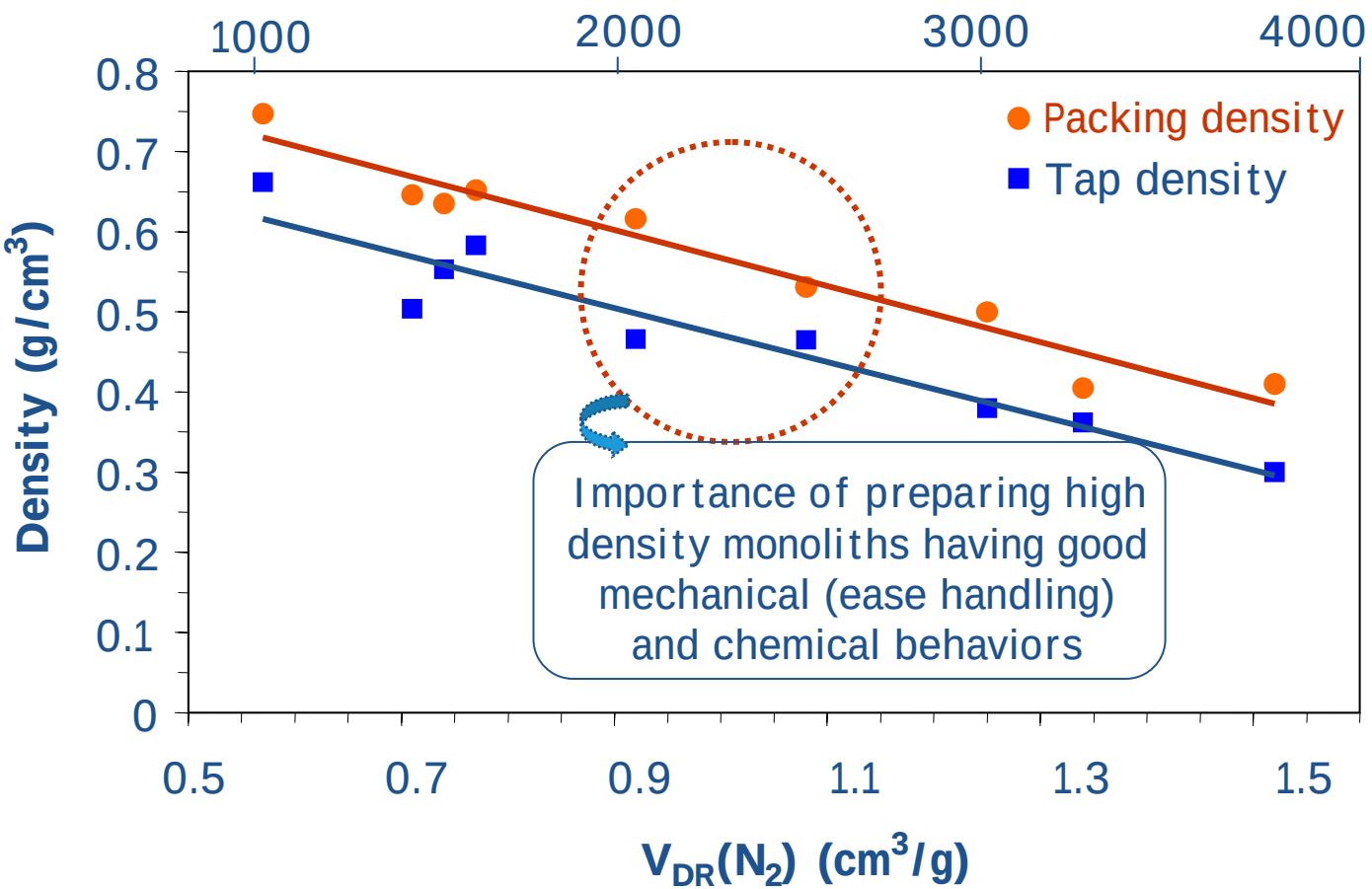
Importance of: → **POROSITY +** **DENSITY**

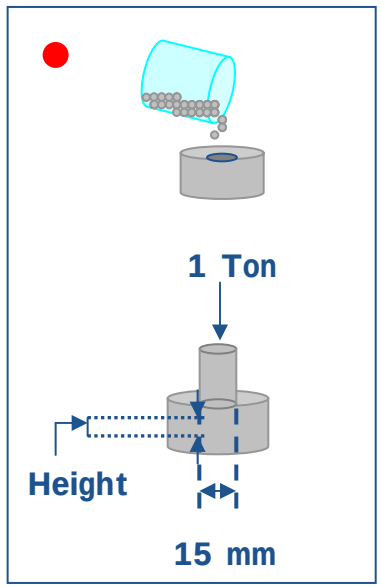


Same situation occurs for MOFs !

M. Jordá-Beneyto, D. Lozano-Castelló, F. Suárez-García, D. Cazorla-Amorós and A. Linares-Solano. Advanced Activated Carbon monolith for Hydrogen storage, Microporous and Mesopoporous Materials (in press, 2008)

DENSITY CHANGES WITH POROSITY





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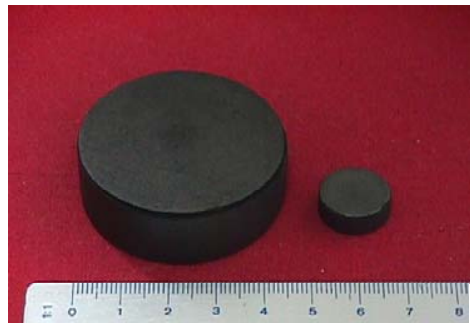
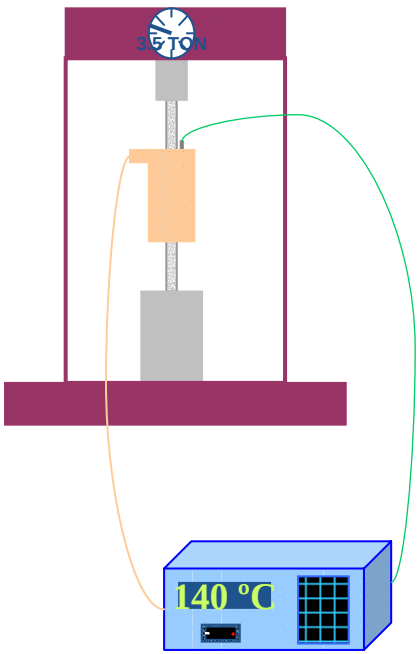
AC MONOLITH PREPARATION

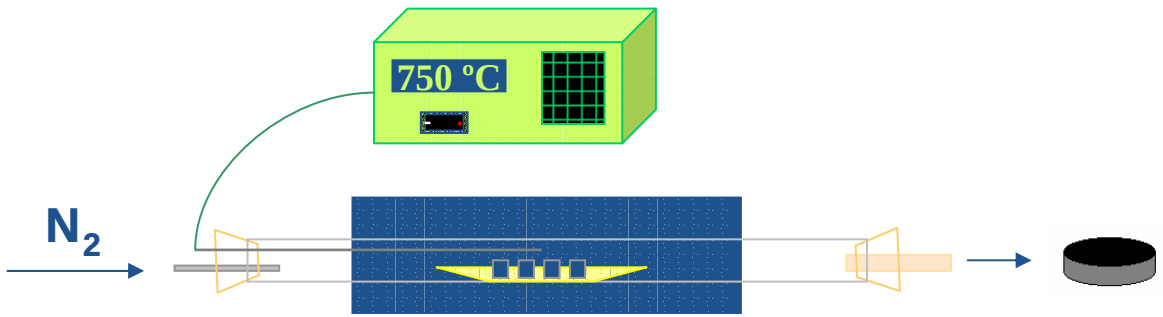
ACTIVATED CARBON + BINDER



1) Pressing



2) Carbonization



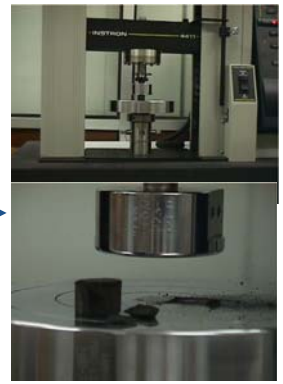
ACTIVATED CARBON MONOLITHS (ACM)

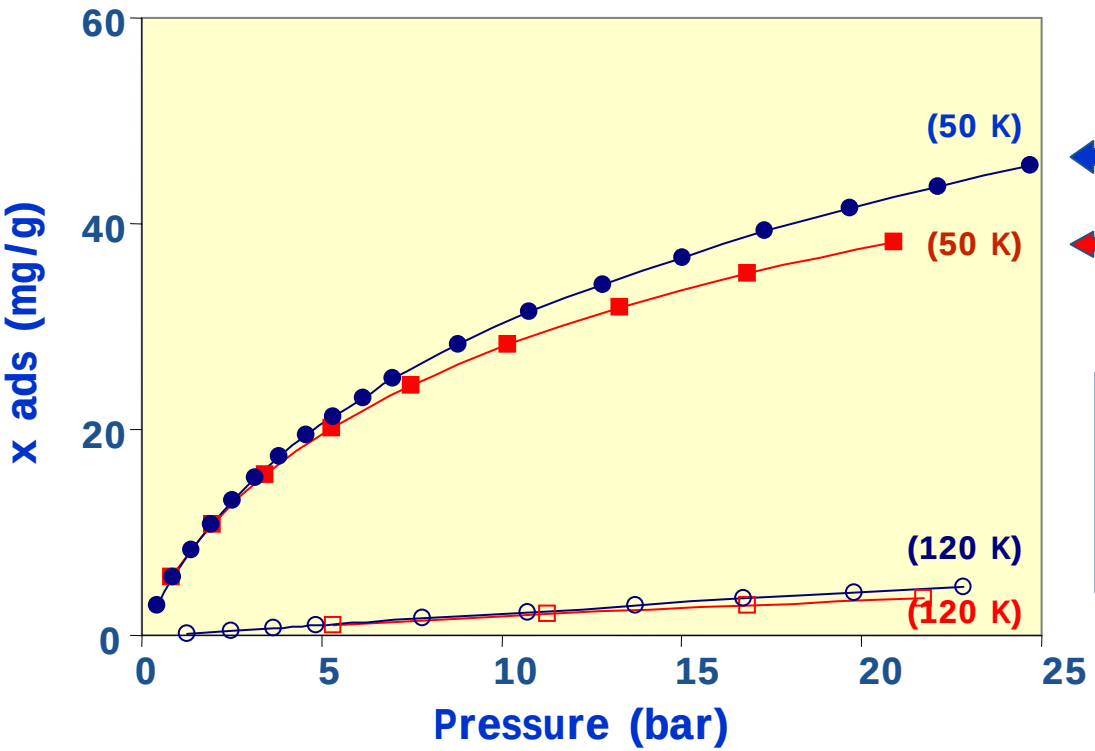
S_{BET} (m^2/g) ~	1000	2000	3000
Density (g/cm^3) ~	1.0	0.7	0.5

High density carbon materials for hydrogen storage

HIGH PRESSURE ADSORPTION AT DIFFERENT TEMPERATURES & PRESSURES ON CARBON MONOLITH

Compression strenght
> 22 MPa



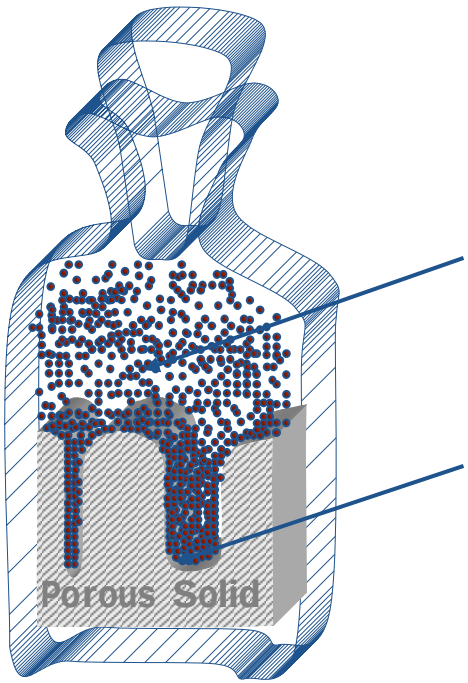


AC1 (powder)

AC1M

Sample	Packing density (cc/g)
AC1	0.4
AC1M	0.7

TOTAL H_2 STORAGE CAPACITY CONCEPT



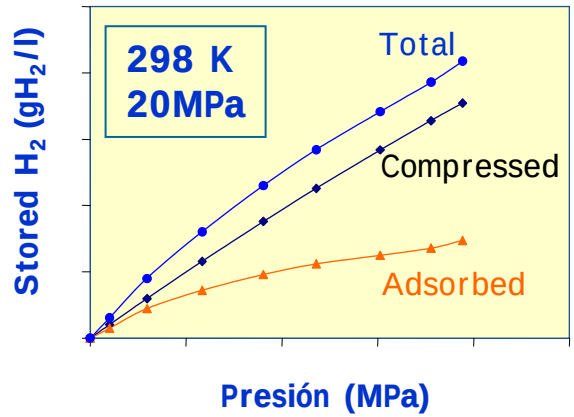
Compressed gas

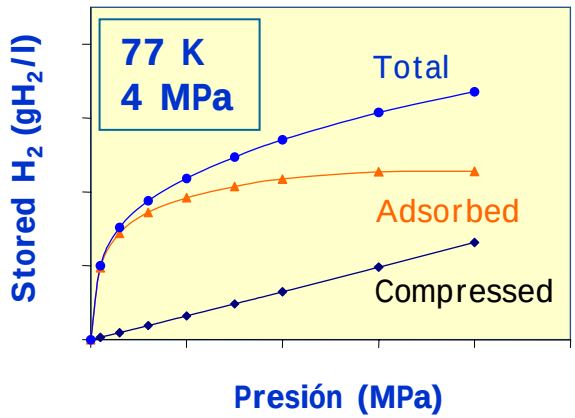
+

Adsorbed gas

=

Total stored H_2

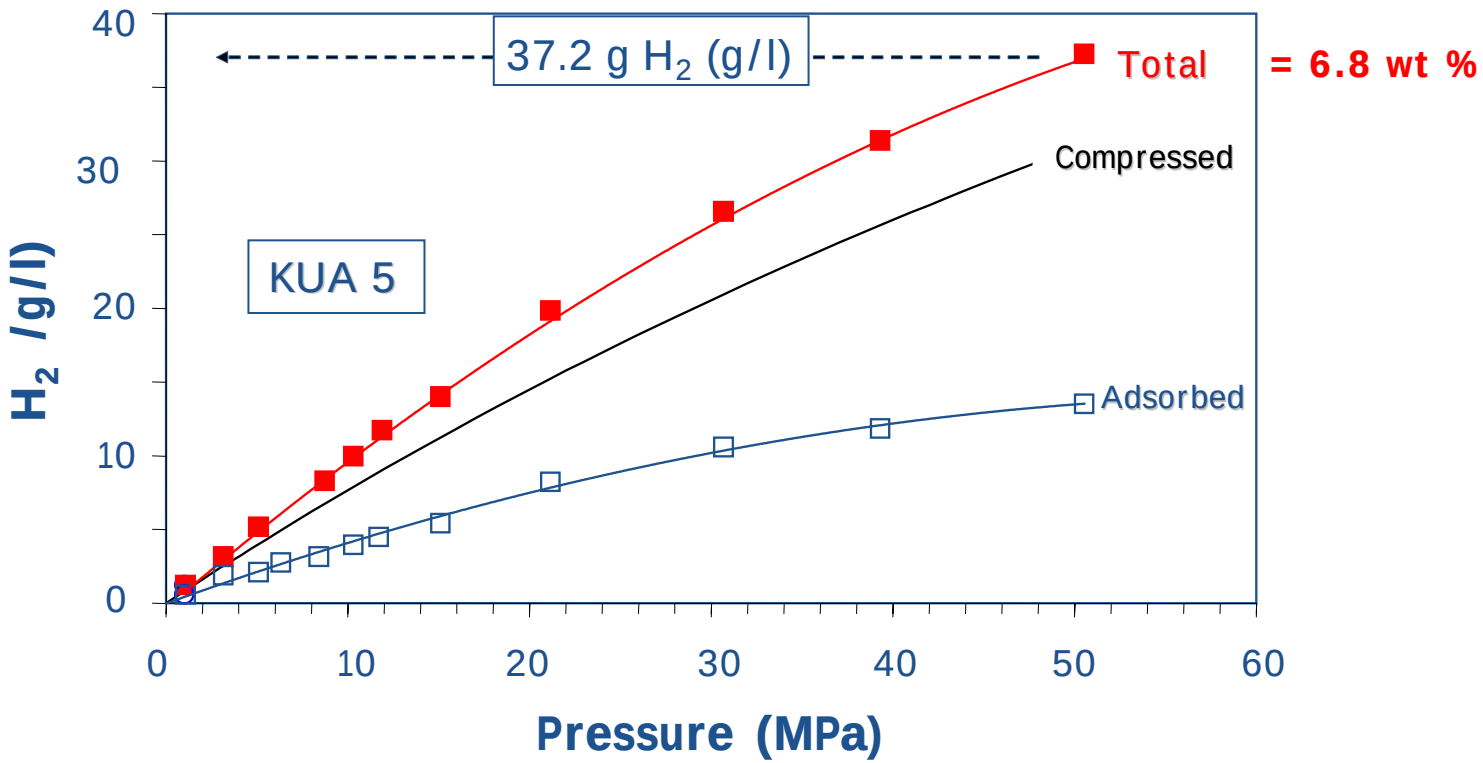




M. Jordá-Beneyto, M. Kunowsky, D. Lozano-Castelló, F. Suárez-García, D. Cazorla-Amorós and A. Linares-Solano. Hydrogen storage in carbon materials in "Carbon Materials: Theory and Practice" (2008). Editor, Artur P. Terzyk

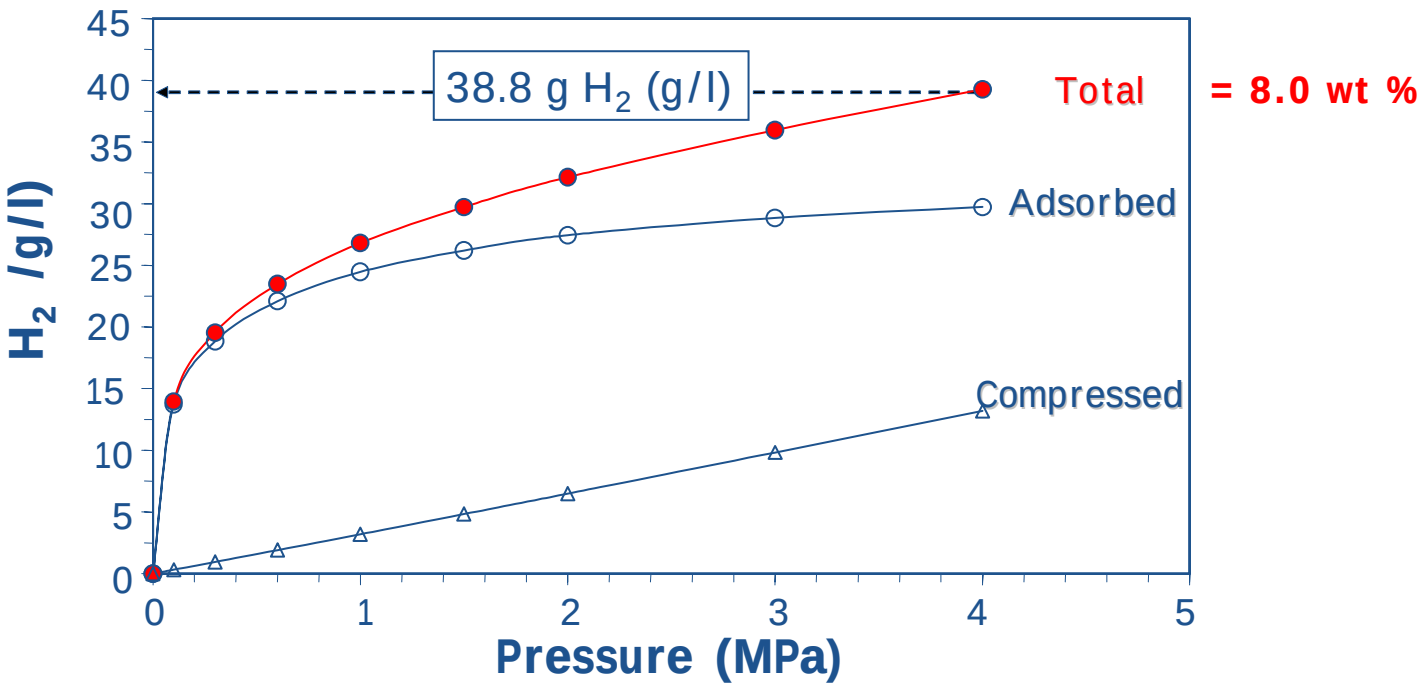
TOTAL H_2 STORAGE AT 298 K & 70MPa

Best samples: KUA6 & KUA 5



TOTAL H_2 STORAGE AT 77 K & 4MPa

Best sample: KUA 6



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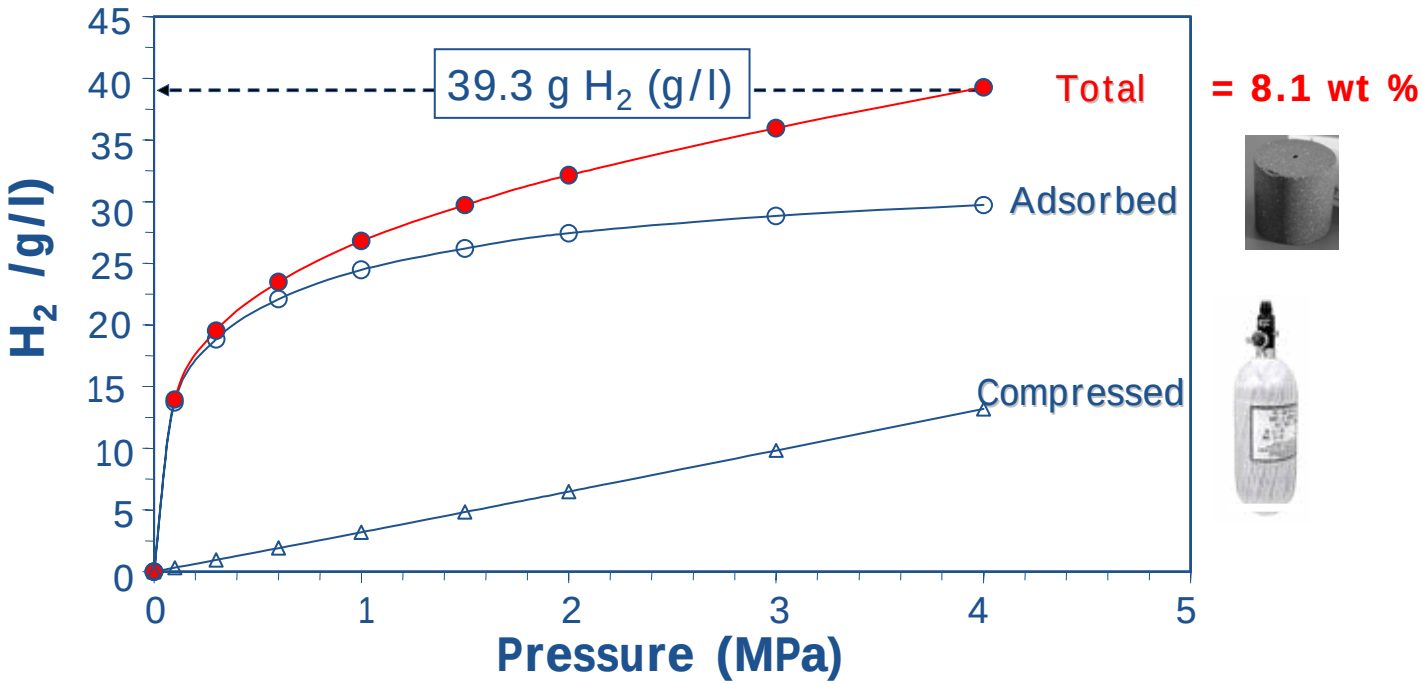
TOTAL H_2 STORAGE AT 77 K & 4MPa

Best monolith sample ACM1



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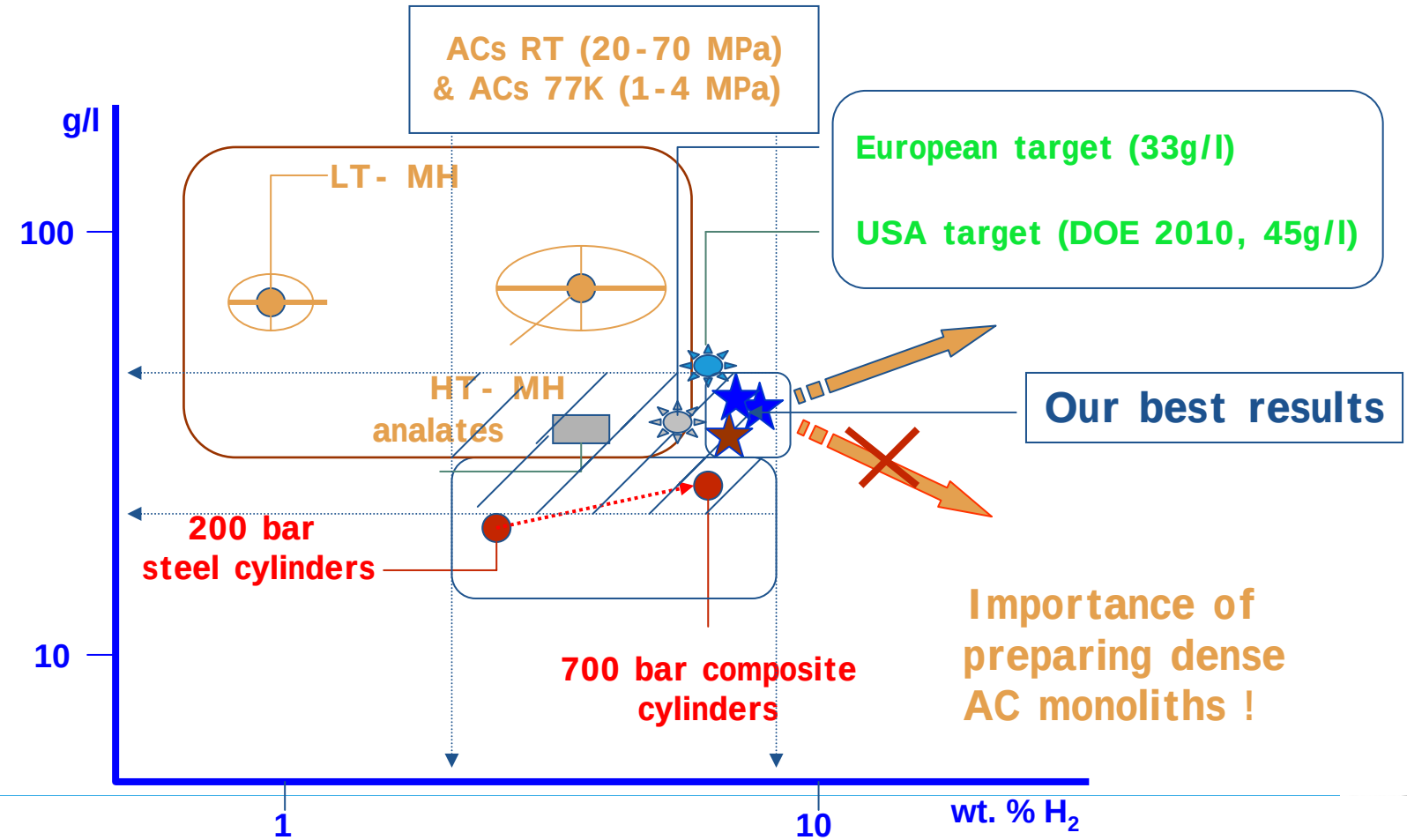
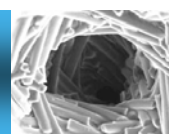
SUMMARY OF HYDROGEN STORED IN CURRENTLY AUTOMOTIVE DEVICES



- **Advanced SAC can be prepared in many forms (powder, monolith,...) having good chemical,thermal & mechanical behaviors and high H_2 storage capacity**
- **The density of the adsorbents has to be reported and H_2 storage be expressed in a volumetric basis (attention to MOFs)**
- **Carbon Monolith seems very suitable for H_2 carrier allowing to reach high value of total H_2 storage value (40g H_2/l)**
- **RT H_2 storage (20MPa) needs:**
  1. **High MPV**
  2. **Narrow micro PSD**
  3. **High density**
- **For 77 K (4MPa) needs:**
  1. **High MPV**
  2. **High density**



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Thanks for your attention !

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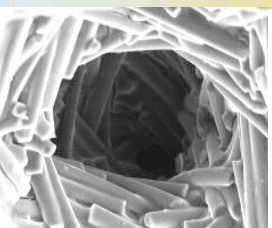

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