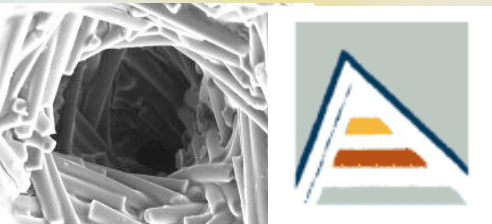




High density carbon materials for hydrogen storage

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



High density carbon materials for hydrogen storage

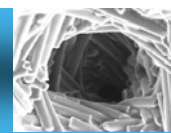
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UNIVERSITY OF ALICANTE (<http://www.ua.es>)



UA museum





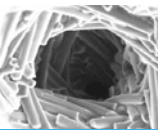
■ Introduction

■ Experimental and equipments

■ H₂ storage results at RT & 77K

■ Reporting H₂ data; weight/volume ?

■ Conclusions





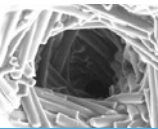
HYDROGEN FOR AUTOMOTIVES

is an interesting objective but...

Still a challenge !

➤ 500-600 km driving needs \longrightarrow 5-7 kg H₂

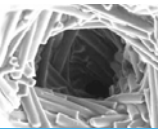
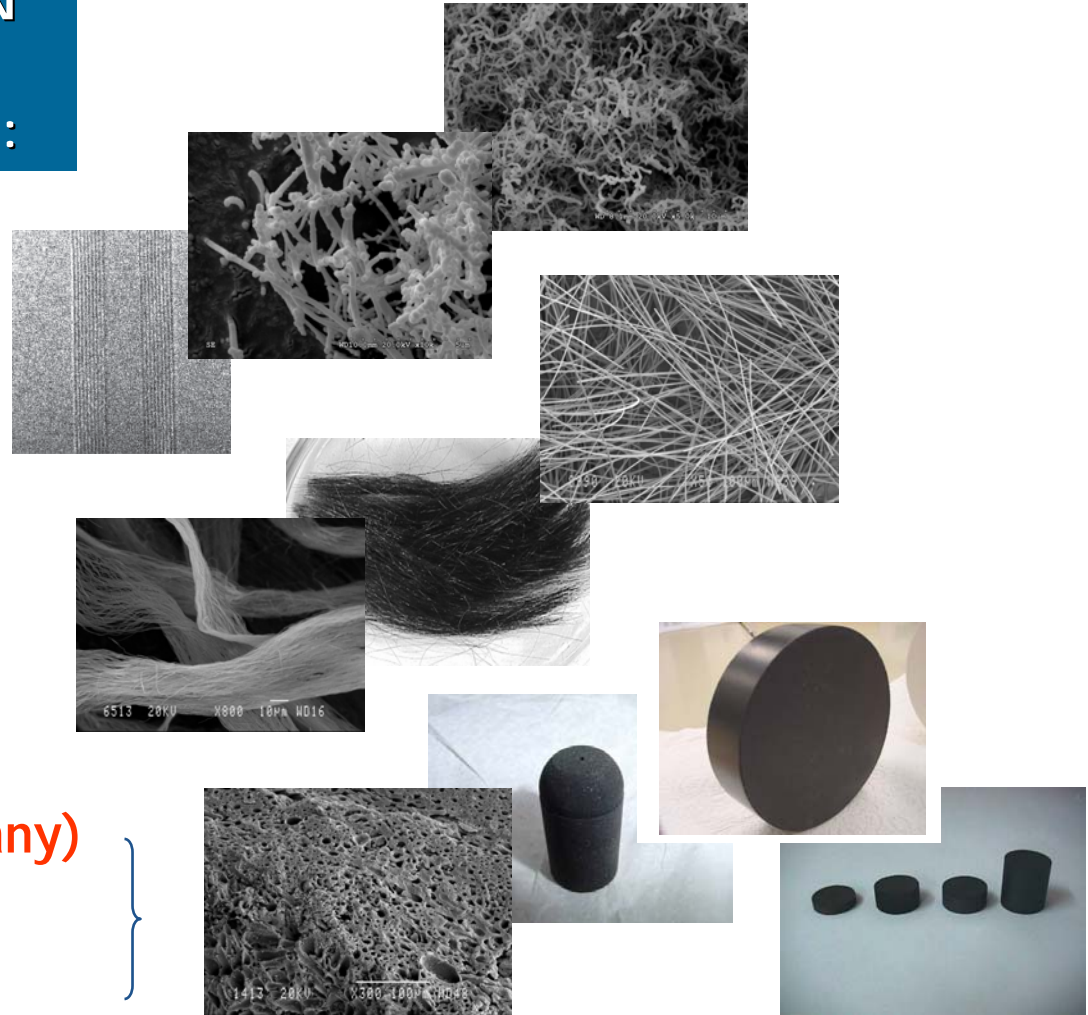
- Compressed Hydrogen (10-70 MPa)
- Liquid Hydrogen (20K)
- Metal Hydrides, .. \longrightarrow Absorption
- Metal Organic Frameworks } Adsorption
- **Carbon Materials**





OUR STUDY ON CARBON COVERS DIFFERENT ACTIVATED MATERIALS:

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



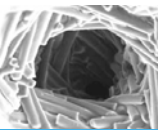


ACs PERFORMANCES CAN BE TAILORED DURING ACTIVATION

- ➔ Surface area
- ➔ Porosity (volume & and PDS)
- ➔ Density
- ➔ Thermal and electrical conductividad
- ➔ Surface chemistry (oxygen groups)
- ➔ Shapes & forms (powder, pellet, monolith...)

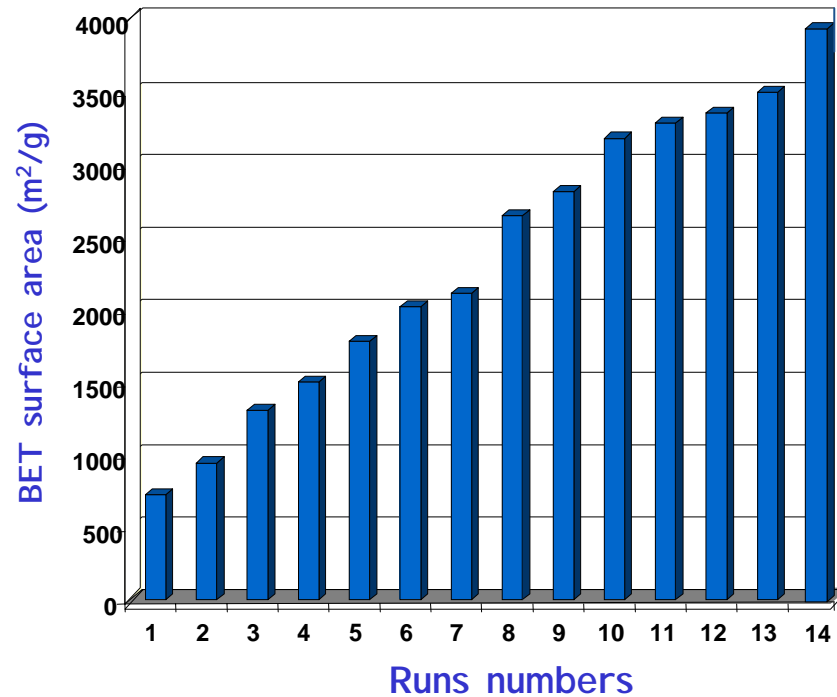
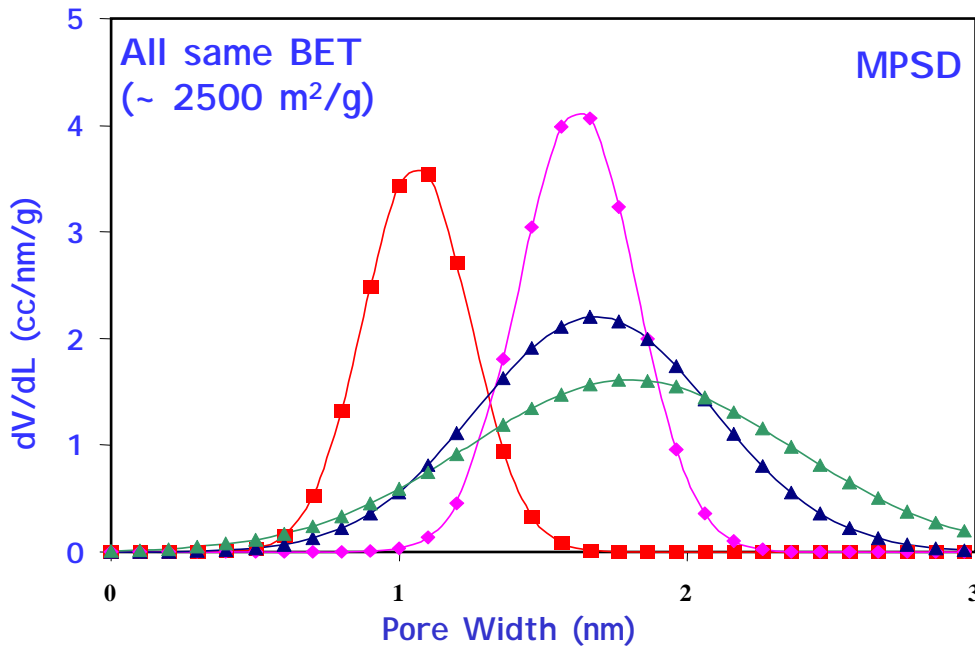


All these
properties are
important for
H₂ storage !

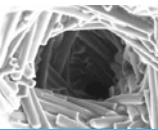




EXAMPLE SHOWING CONTROL OF THE PSDs AND OF BET SURFACE



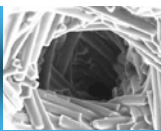
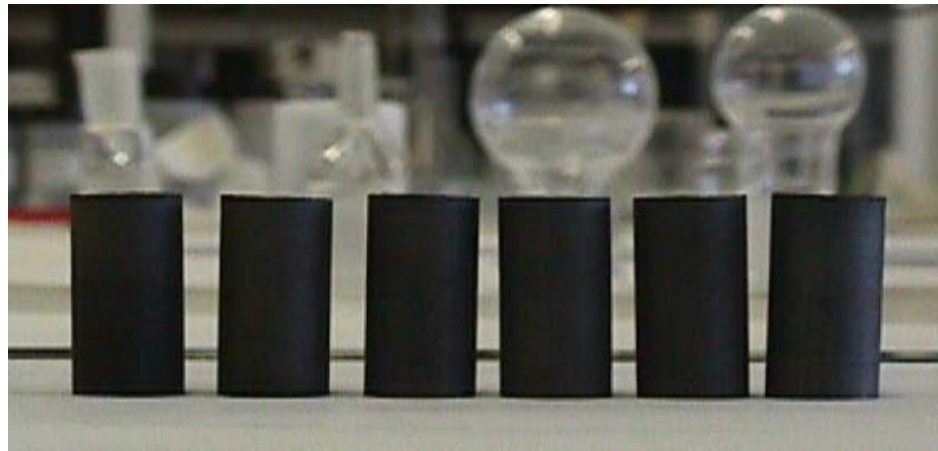
A. Linares-Solano, D. Lozano-Castelló, M. A. Lillo-Ródenas, and D. Cazorla-Amorós
Carbon Activation by Alkaline Hydroxides, in Chemistry and Physics of Carbon, Volume 30 (2008)





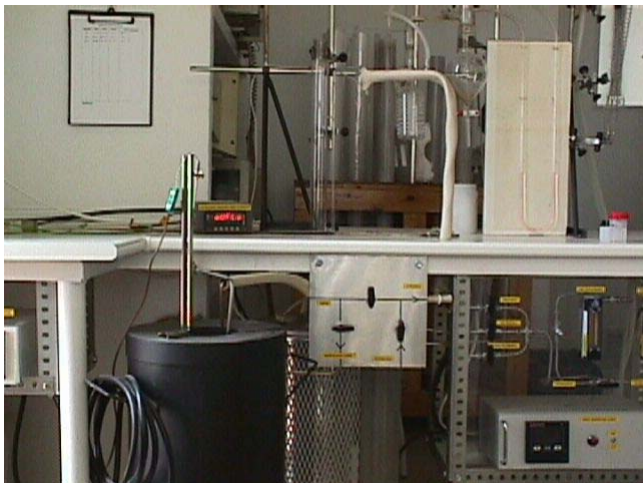
ADDITIONAL ACs ADVANTAGES

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





LABORATORY SCALE ACTIVATION

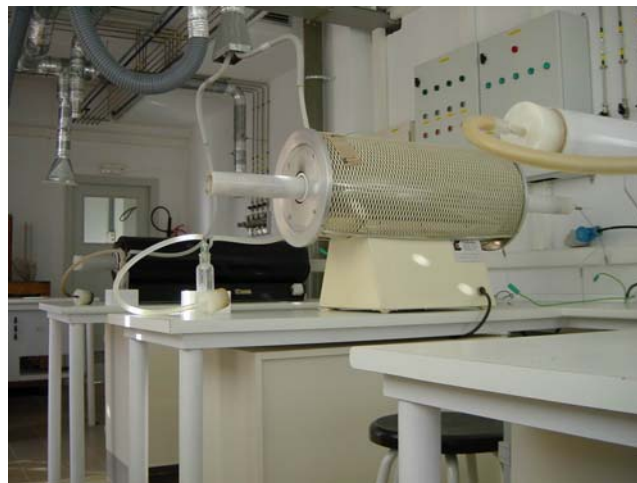


Fluidized bed reactor

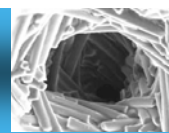
PHYSICAL & CHEMICAL ACTIVATION



Fixed bed



Fixed bed





CHARACTERIZATION: SUB-ATMOSPHERIC ADSORPTION



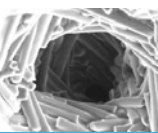
Porous texture
(surface, pore volume)
and **PSD**



2 Autosorbs-6 (Quantachrome)



ASAP 2020 (Micromeritics)





CHARACTERIZATION: HIGH-PRESSURE ADSORPTION

Cyclic unit



Gravimetric units

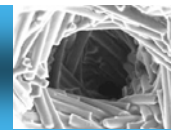
77 - 298 K
<1- 4 MPa



Volumetric unit

77 - 750 K
1-20 MPa

H₂ storage



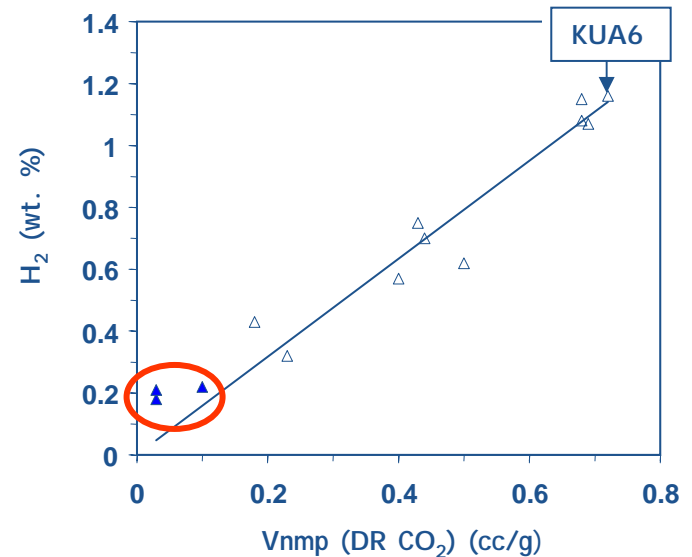
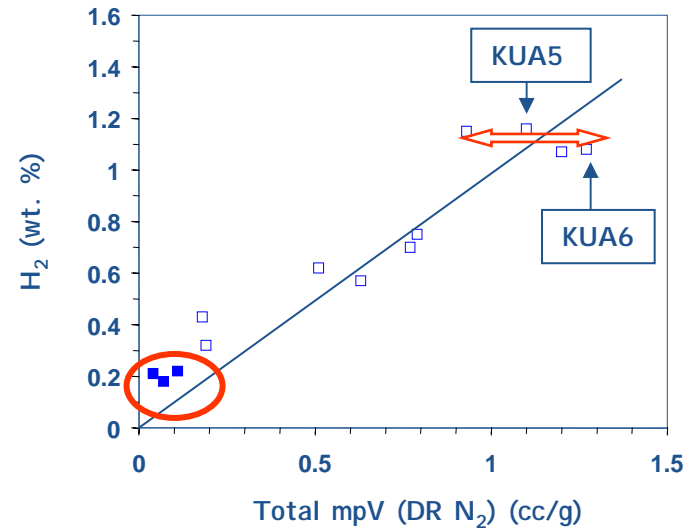
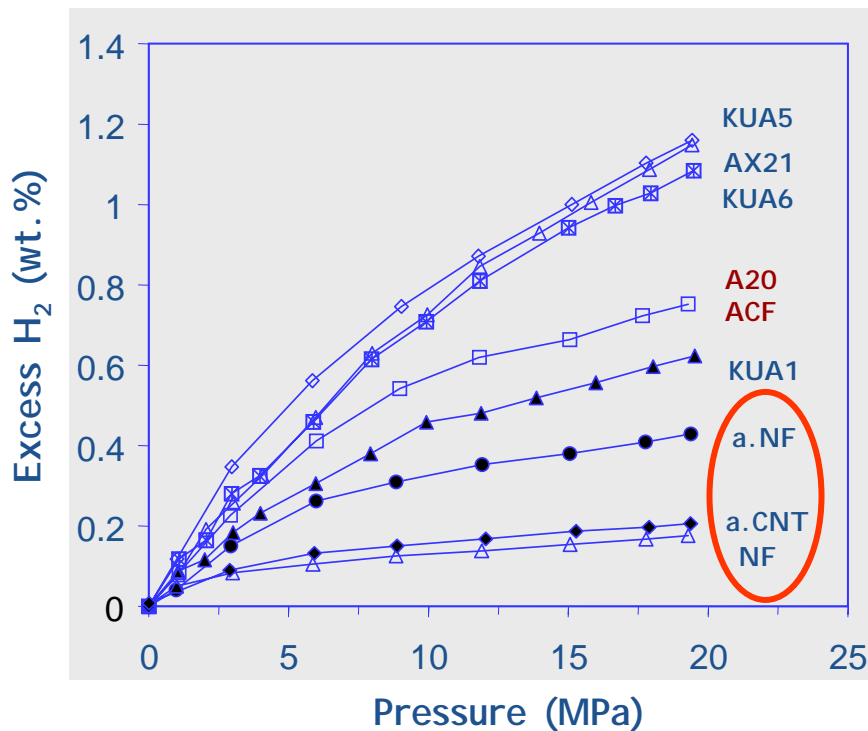
Results

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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

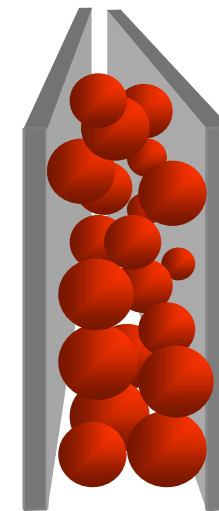
H₂ STORAGE (1-20 MPa)

High micropore volume

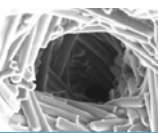
Control of pore size distribution

High packing density

BALANCE



0.6-0.7 nm





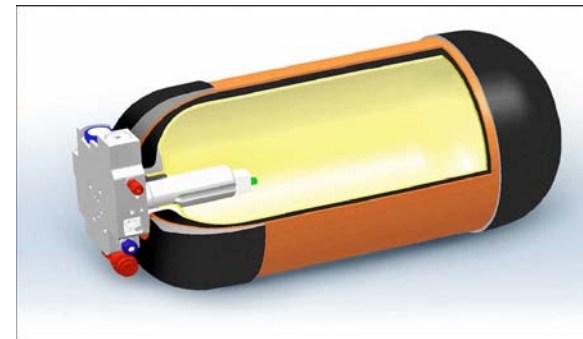
HYDROGEN STORAGE AT ROOM TEMPERATURE (70 MPa): CONCLUSIONS

H₂ STORAGE (30-70 MPa)

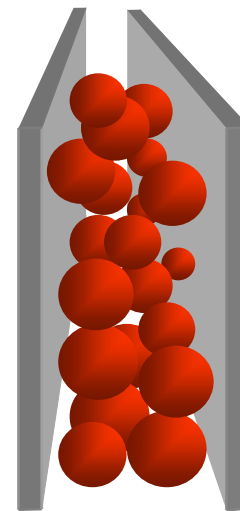
High micropore volume

High packing density

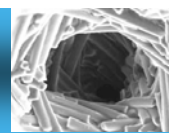
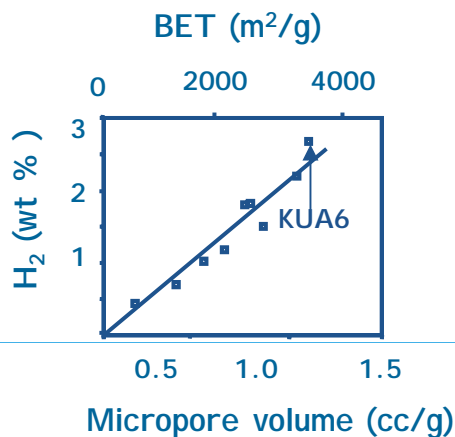
BALANCE



(700 bar)



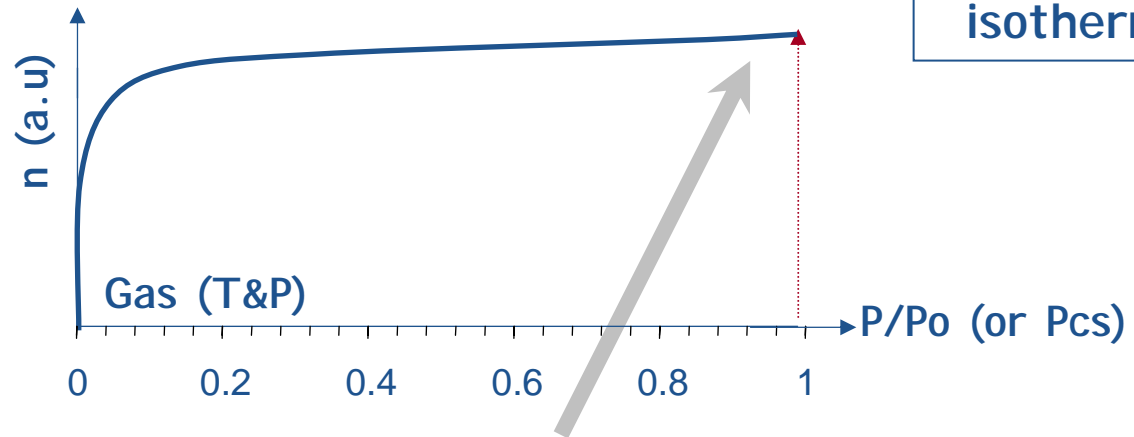
>> 0.7 nm



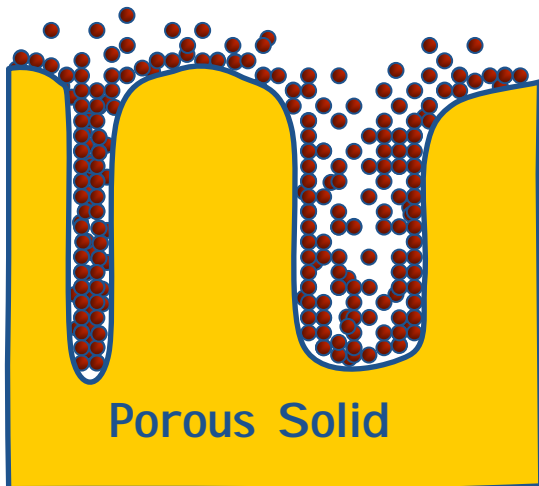


ADSORPTION ON MICROPORES

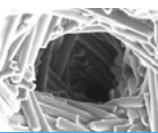
Adsorption isotherm



High P/P_o

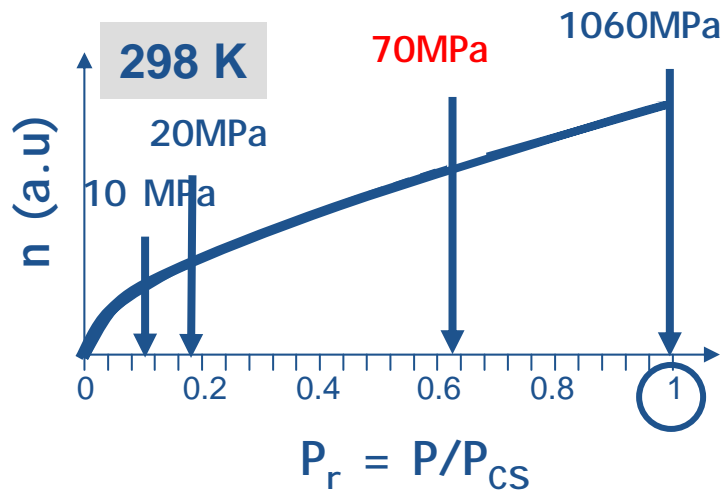


$$n = f(P)_{T, gas, solid}$$





FUNDAMENTALS OF H2 HIGH PRESSURE ADSORPTION

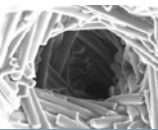
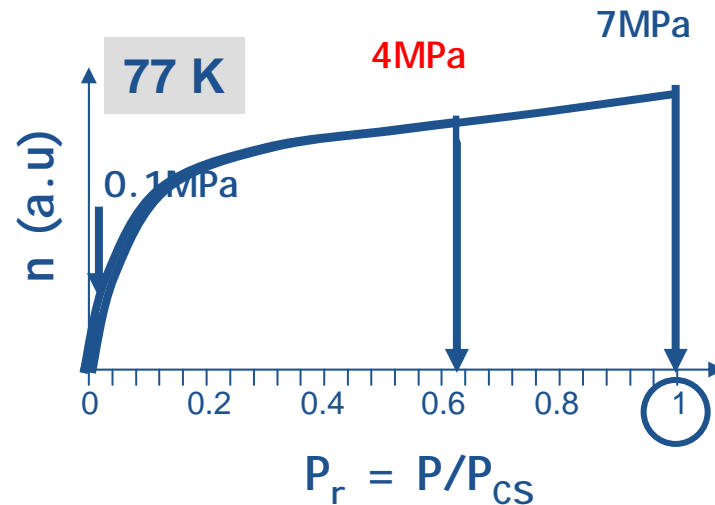


Supercritical conditions both at 298K & 77K

Dubinin approach

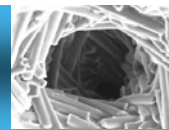
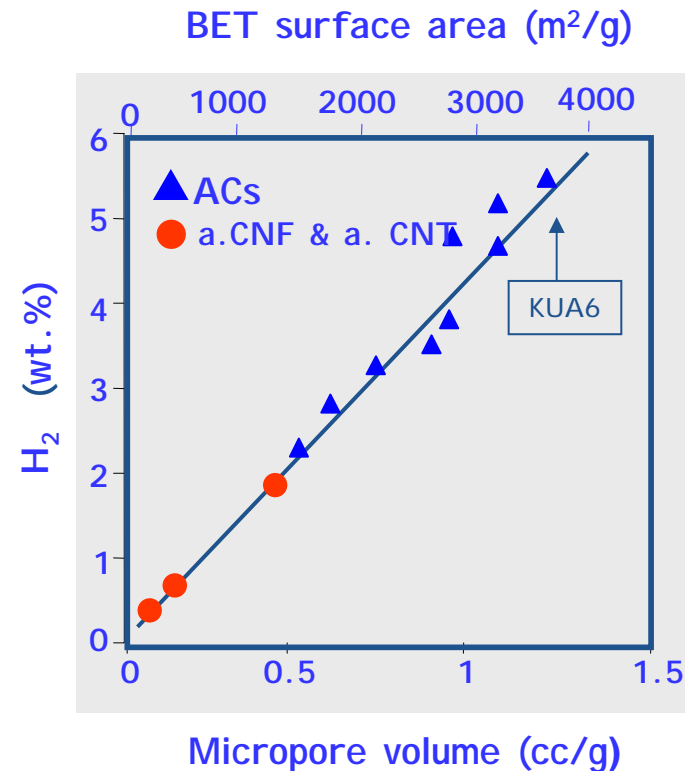
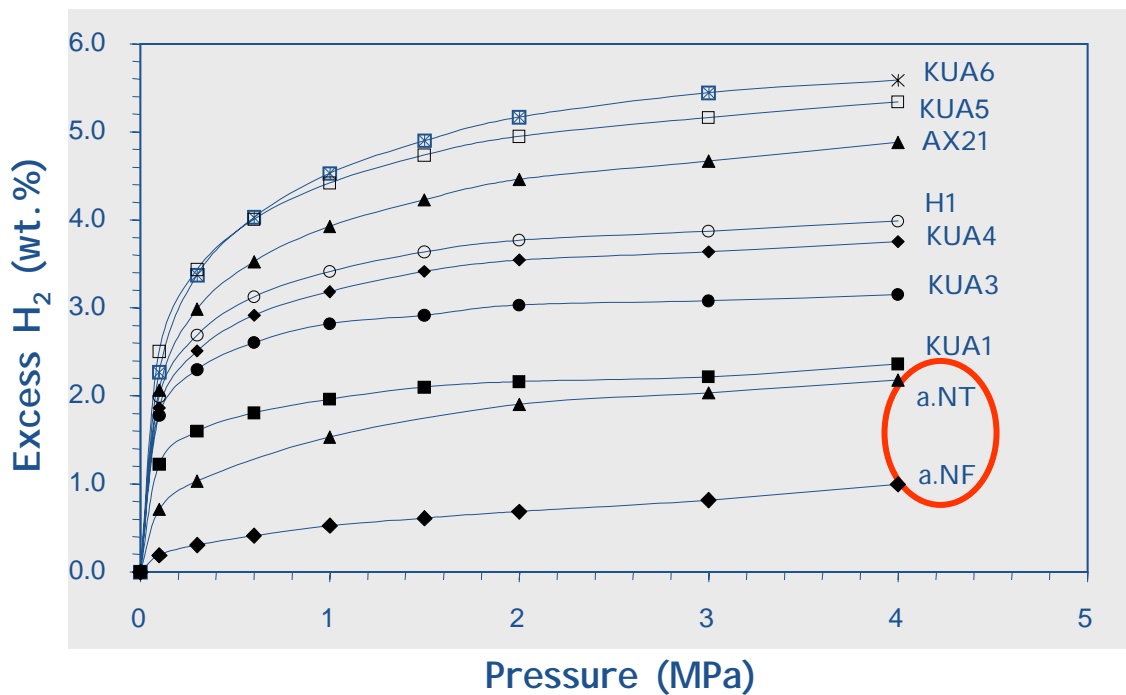
$$P_{CS} = P_c(T/T_c)^2$$

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





HYDROGEN STORAGE AT 77K (4 MPa): CONCLUSIONS

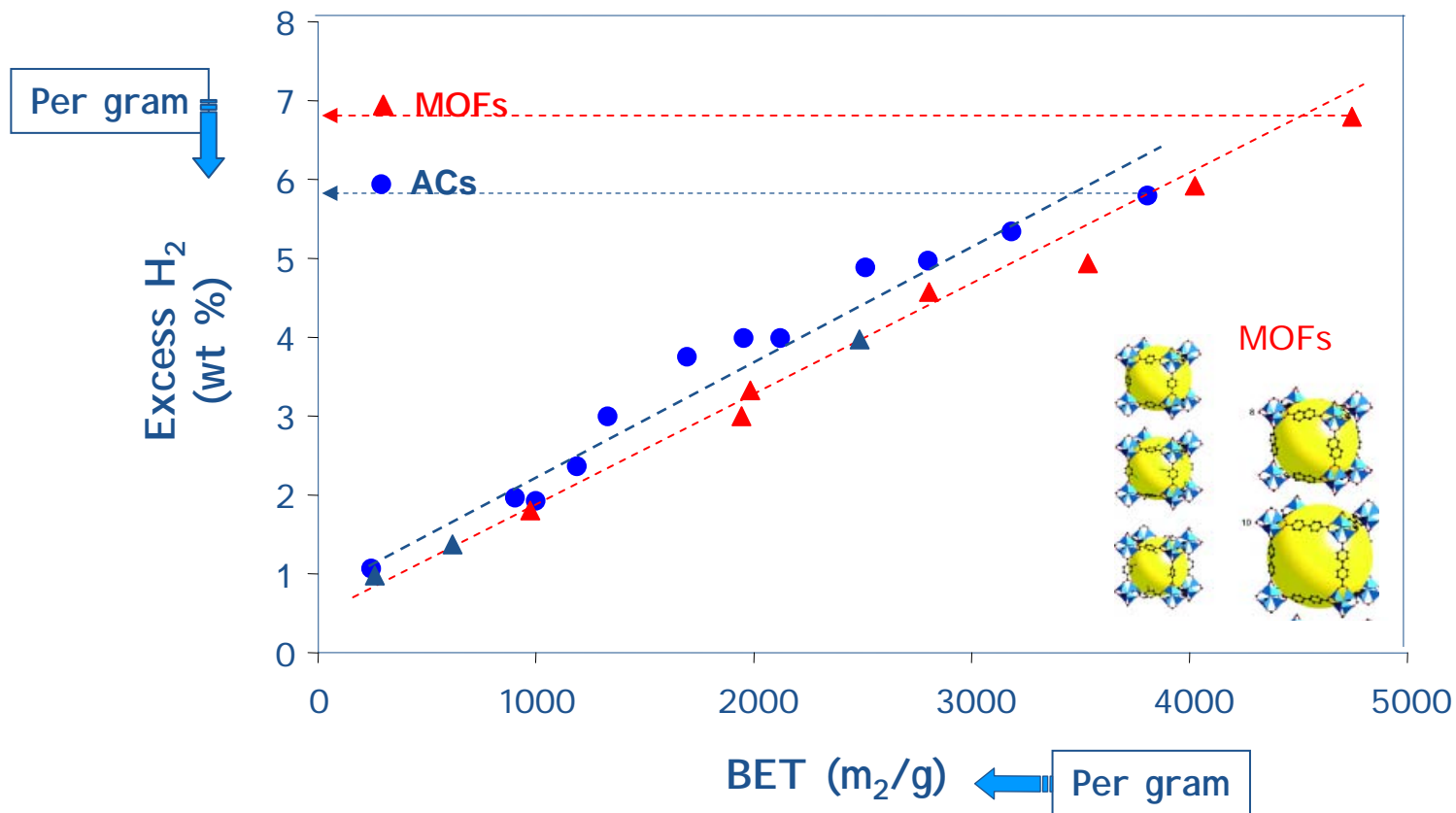


High density carbon materials for hydrogen storage

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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 VEHICLE APPLICATIONS:
SAMPLE WEIGHT OR SAMPLE VOLUME ?



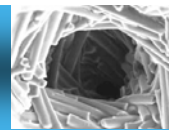
Adsorption in
gravimetric basis



Adsorption in
volumetric basis



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



Results

High density carbon materials for hydrogen storage

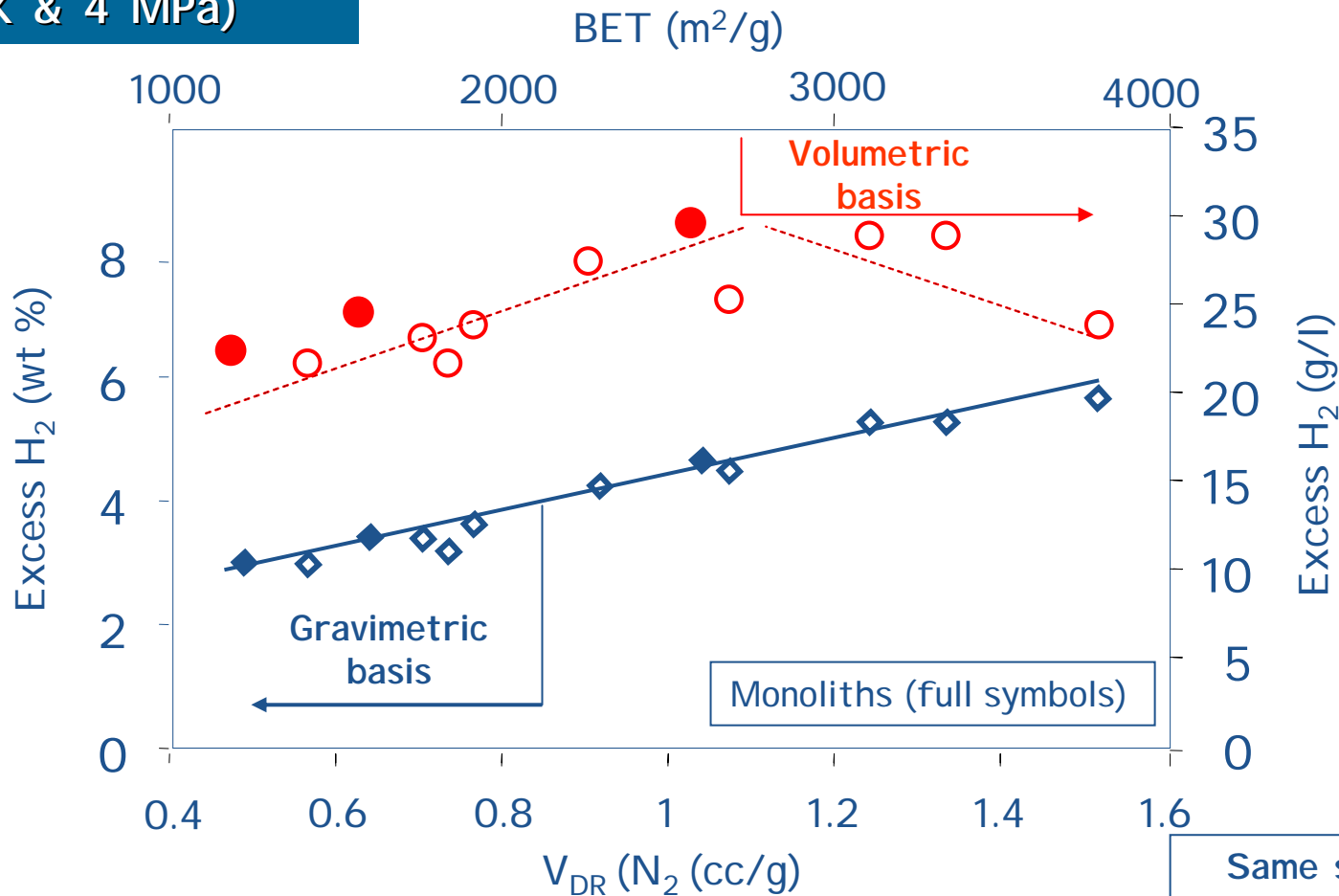
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HYDROGEN STORAGE (77K & 4 MPa)

Importance of:

POROSITY + DENSITY

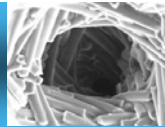
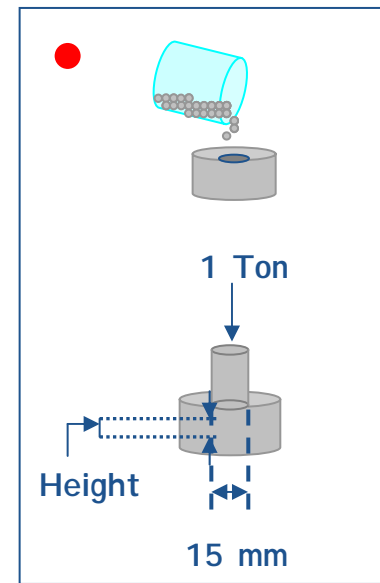
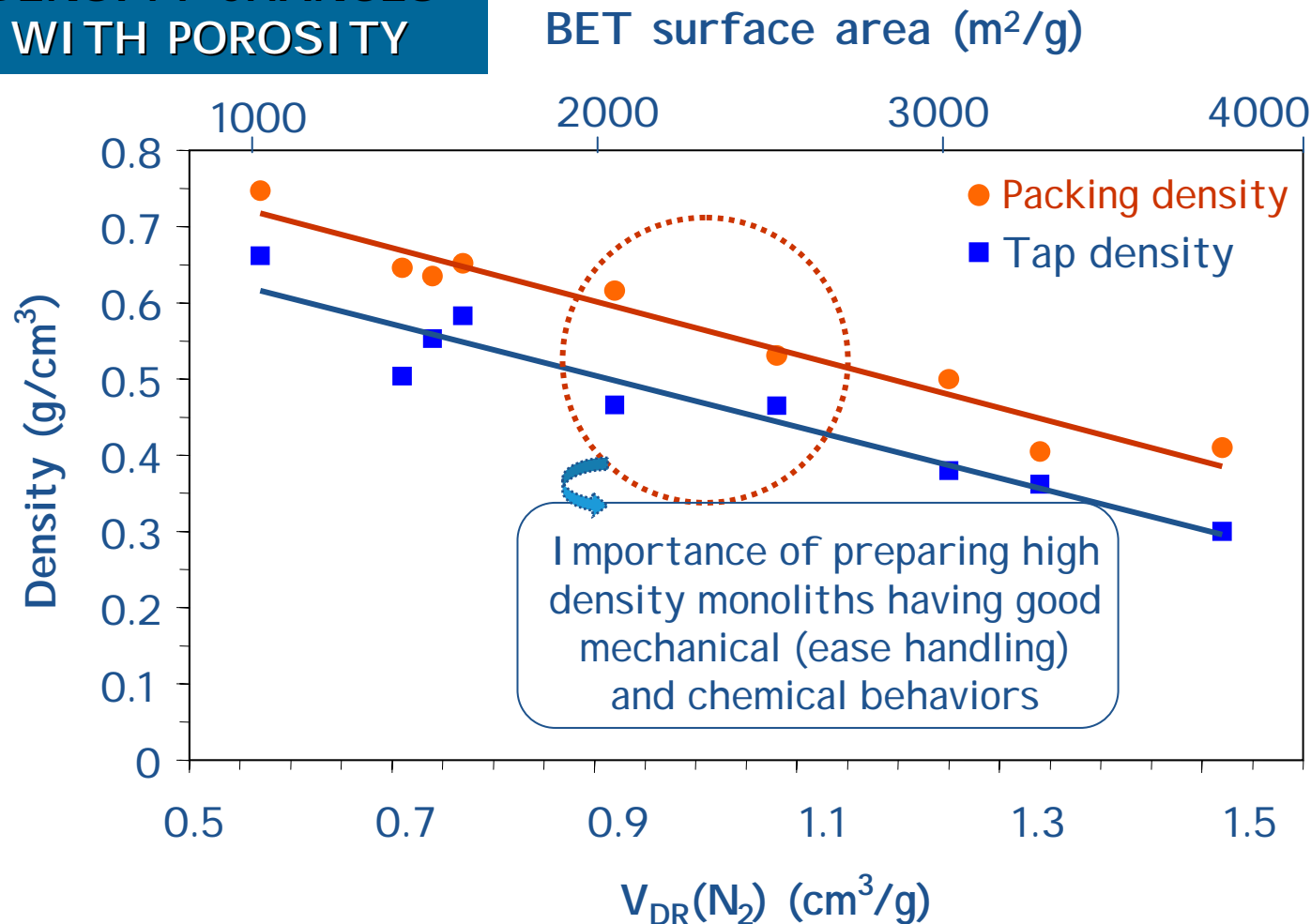


Monoliths (full symbols)

Same situation occurs for MOFs !



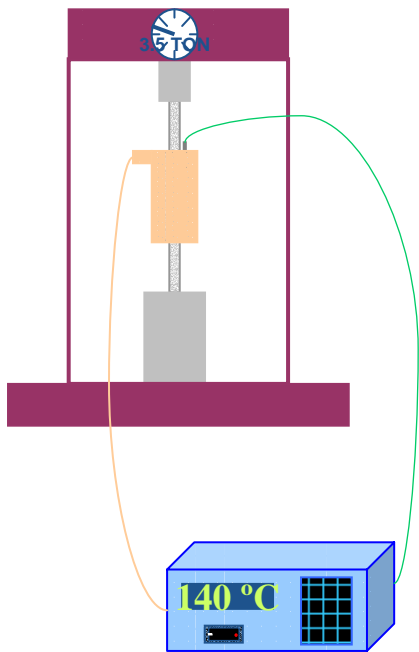
DENSITY CHANGES WITH POROSITY





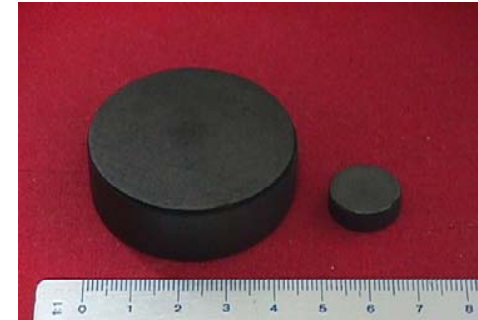
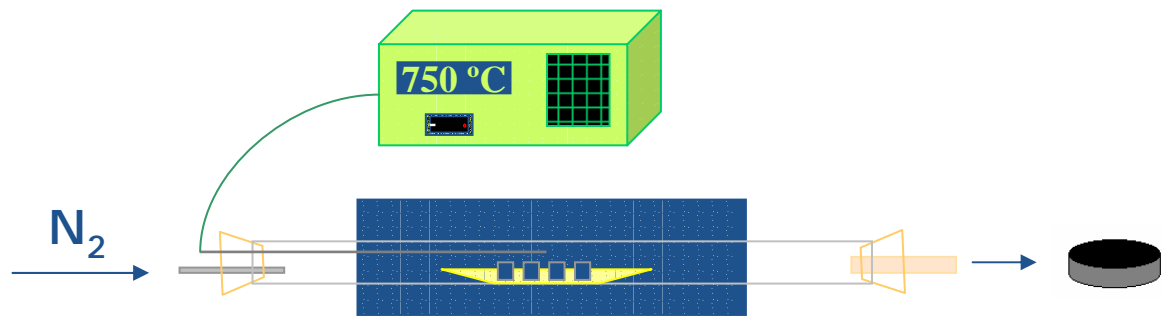
AC MONOLITH PREPARATION

1) Pressing



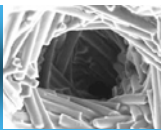
ACTIVATED CARBON + BINDER

2) Carbonization



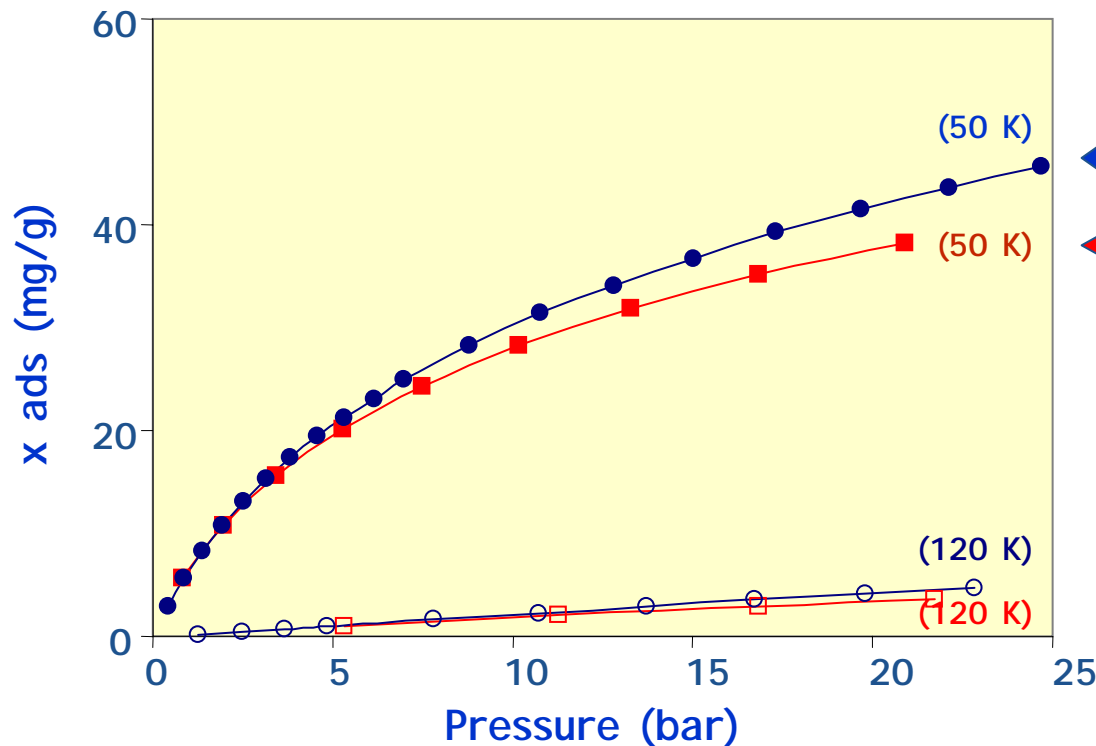
ACTIVATED CARBON MONOLITHS (ACM)

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



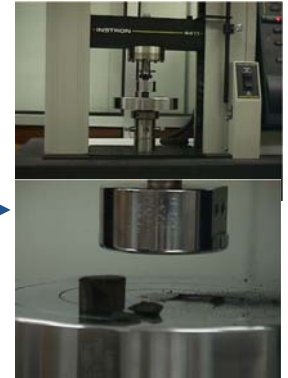


HIGH PRESSURE ADSORPTION AT DIFFERENT TEMPERATURES & PRESSURES ON CARBON MONOLITH



Compression strenght

> 22 MPa →

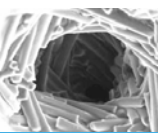


← AC1 (powder)

← AC1M

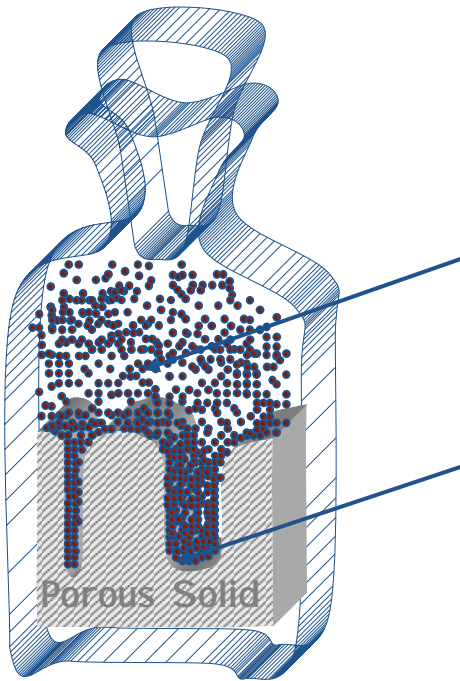


Sample	Packing density (cc/g)
AC1	0.4
AC1M	0.7

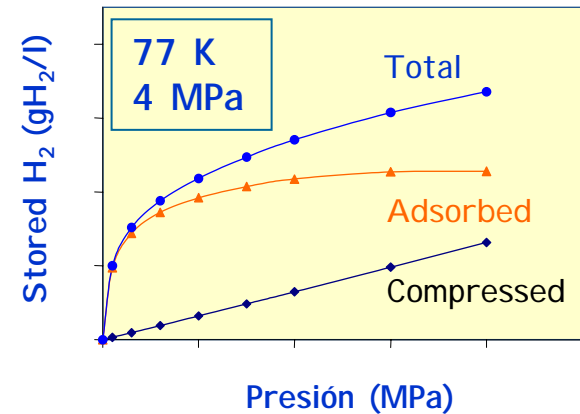
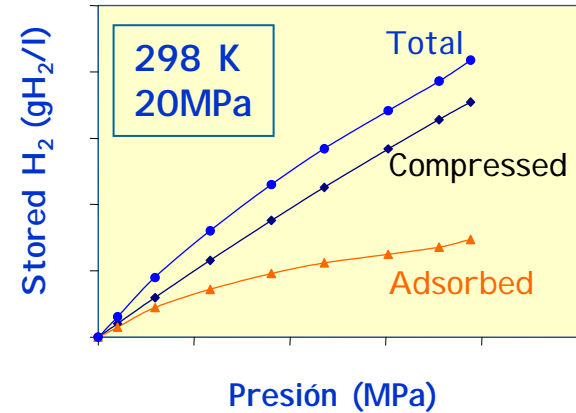




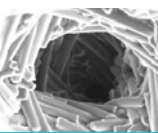
TOTAL H₂ STORAGE CAPACITY CONCEPT



$$\begin{aligned} &\text{Compressed gas} \\ &+ \\ &\text{Adsorbed gas} \\ &= \\ &\text{Total stored H}_2 \end{aligned}$$



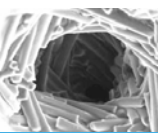
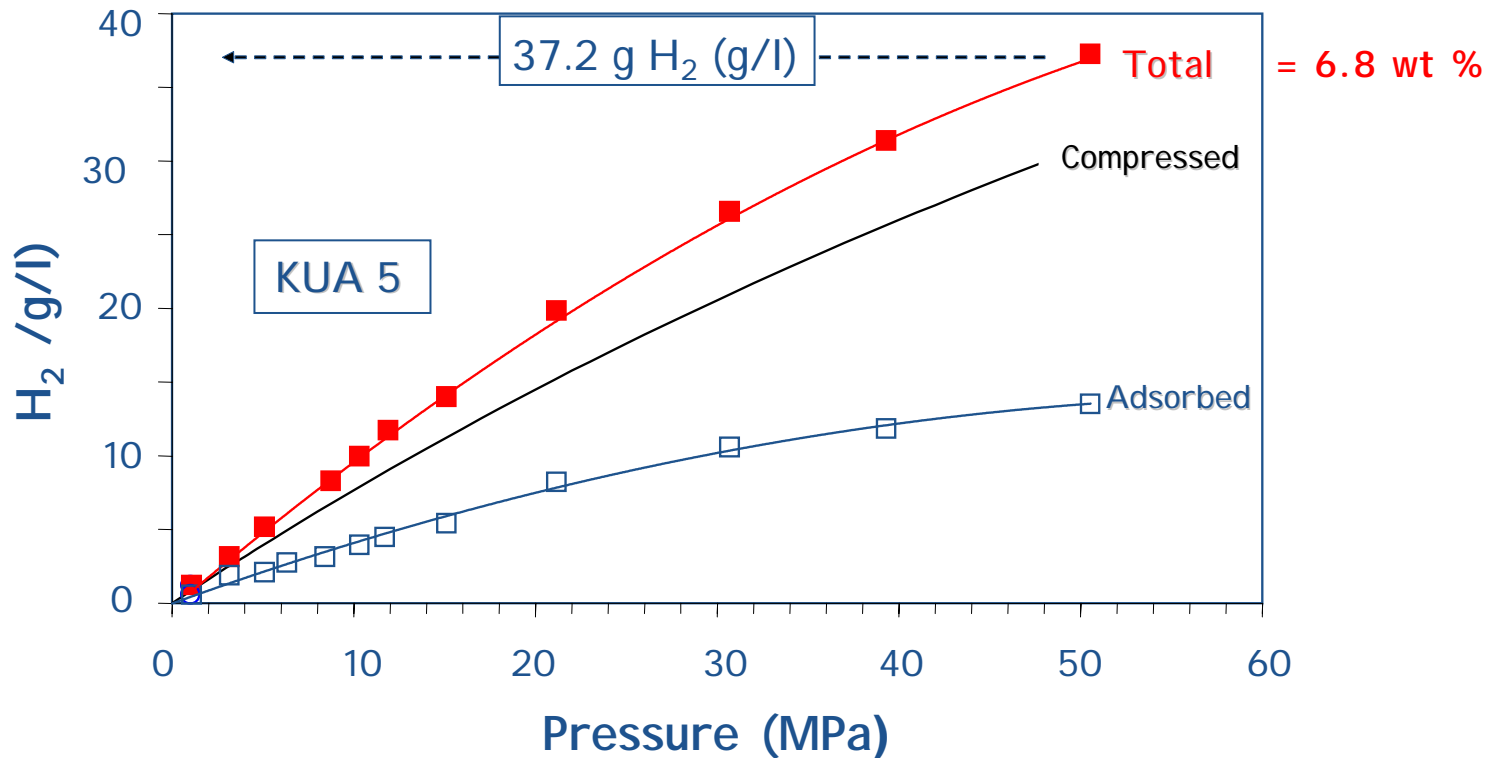
M. Jordá-Beneyto, M. Kunowsky, D. Lozano-Castelló, F. Suárez-García, D. Cazorla-Amorós and A. Linares-Solano. Hydrogen storage in carbon materials in "Carbon Materials: Theory and Practice" (2008). Editor, Artur P. Terzyk





TOTAL H₂ STORAGE AT 298 K & 70MPa

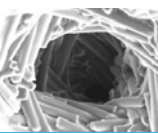
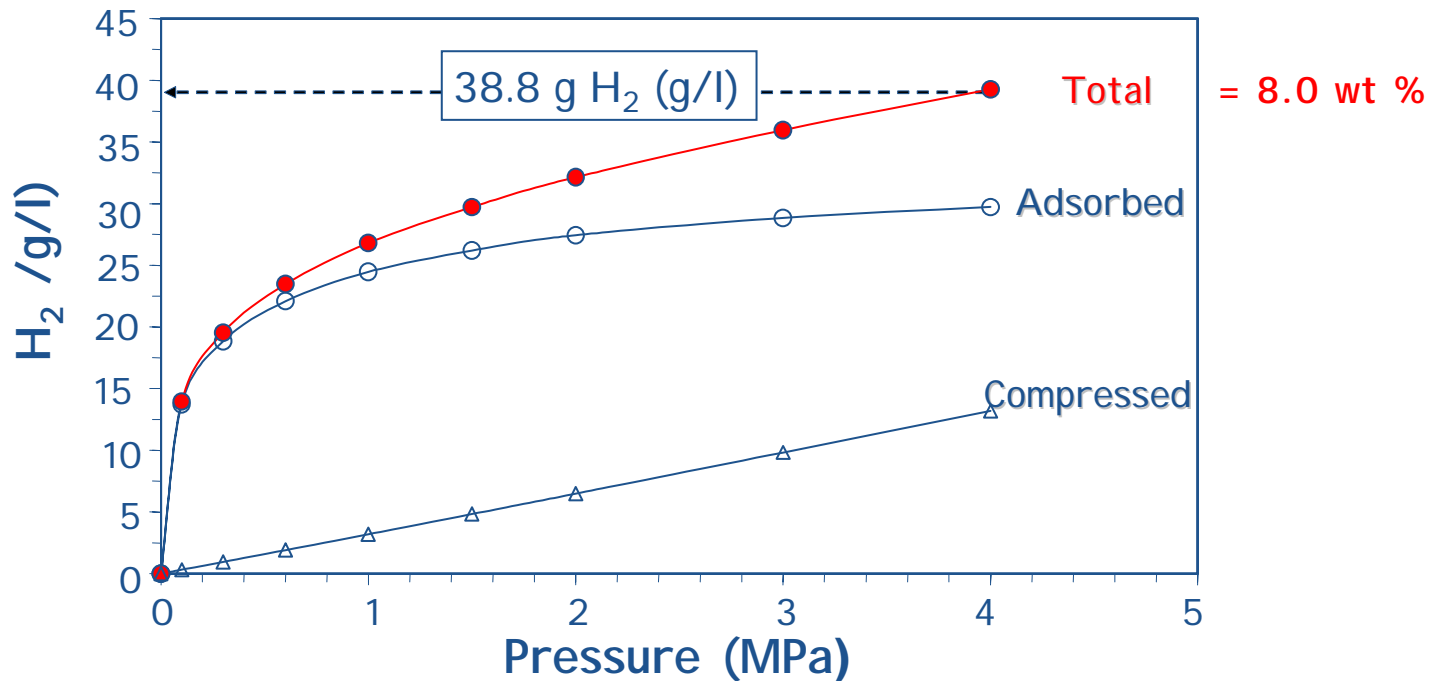
Best samples: KUA6 & KUA 5





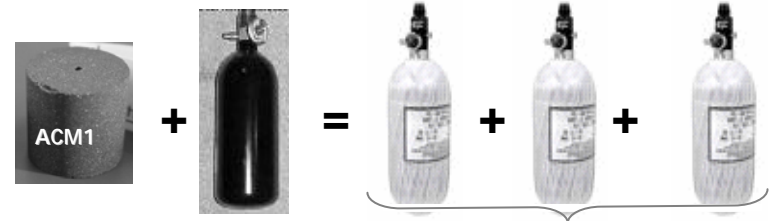
TOTAL H₂ STORAGE AT 77 K & 4MPa

Best sample: KUA 6

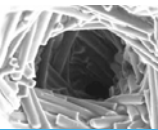
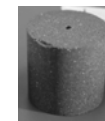
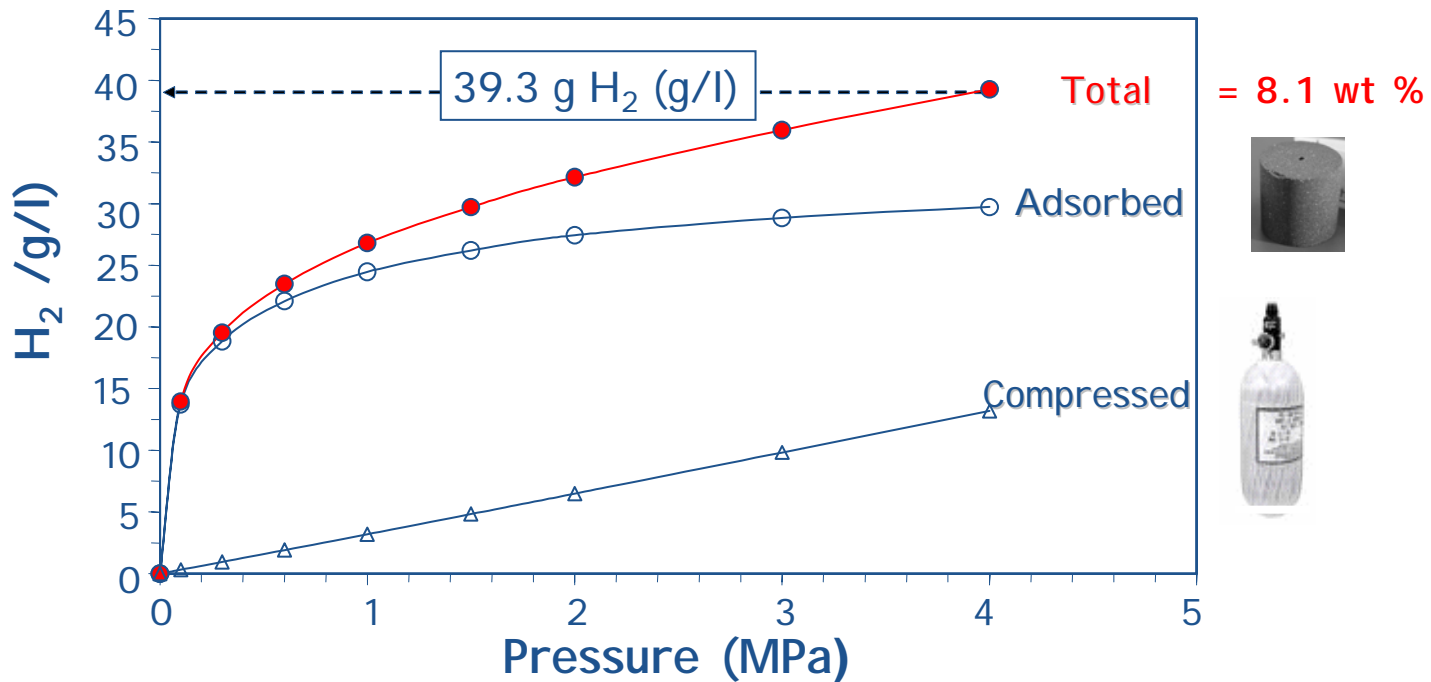




TOTAL H₂ STORAGE AT 77 K & 4MPa

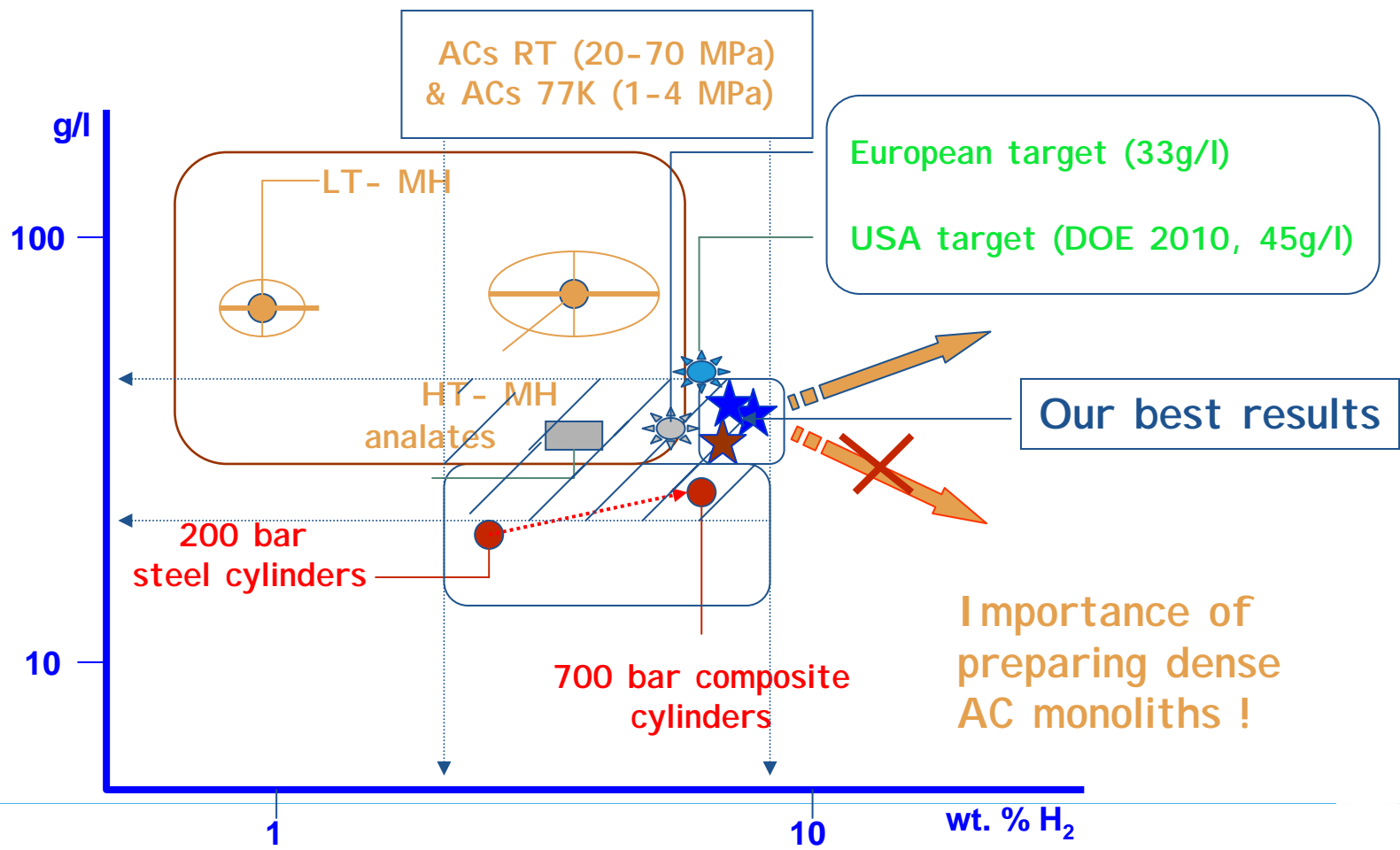


Best monolith sample ACM1





SUMMARY OF HYDROGEN STORED IN CURRENTLY AUTOMOTIVE DEVICES

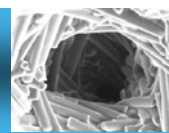


Importance of preparing dense AC monoliths !





- Advanced SAC can be prepared in many forms (powder, monolith, ...) having good chemical, thermal & mechanical behaviors and high H₂ storage capacity
- The density of the adsorbents has to be reported and H₂ storage be expressed in a volumetric basis (attention to MOFs)
- Carbon Monolith seems very suitable for H₂ carrier allowing to reach high value of total H₂ storage value (40g H₂/l)
- RT H₂ storage (20MPa) needs:
 1. High MPV
 2. Narrow micro PSD
 3. High density
- For 77 K (4MPa) needs:
 1. High MPV
 2. High density





Thanks for your attention !

High density carbon materials for hydrogen storage

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D. Lozano-Castelló, F. Suárez-García,
D. Cazorla-Amorós

Carbon Materials and Environment Research Group
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Department of Inorganic Chemistry
University of Alicante, Spain

