MefHySto

Metrology for Advanced Hydrogen Storage Solutions

Final Meeting

WP4 : Metrology for Reversible Hydrogen Storage Technologies

MAHYTEC A Hensoldt Company.

BAM Bundesanstalt für Materialforschung und -prüfung

Ha FOUNDATION FOR THE DEVELOPMENT OF NEW HYDROGEN TECHNOLOGIES IN ARAGON

MAX PLANCK INSTITUTE FOR INTELLIGENT SYSTEMS

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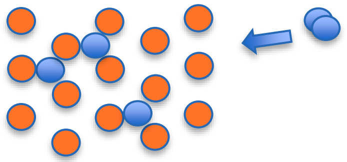
EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Metrology of hydrides:

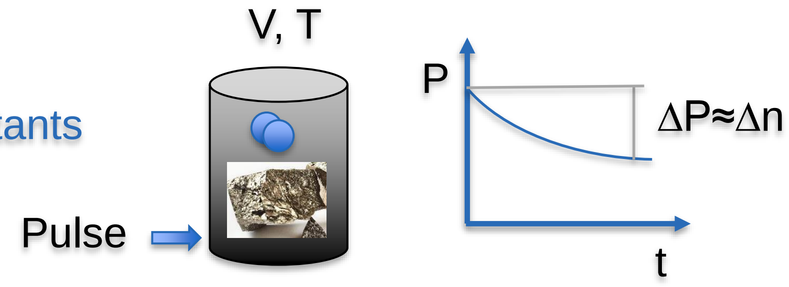
- Objective: determine thermodynamics and kinetics



Static methods:

- Gravimetric method: mass hydrogen/mass hydride
- Volumetric method (Sieverts): hydrogen pressure evolution because of absorption

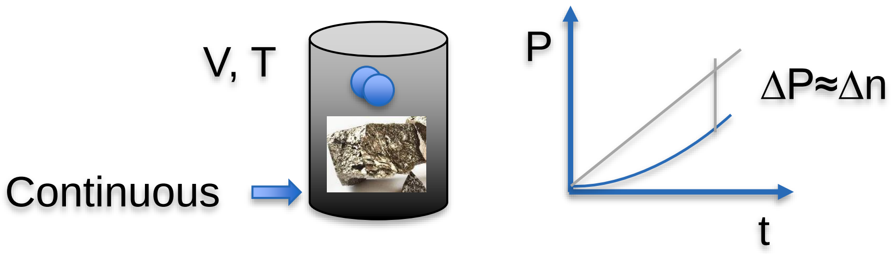
Pollutants



Dynamic method:

- Mass flow vs. time

Thermal conductivity



Pollutants:

- Hydrides are sensible to pollutants
- Reference standard: ISO 14687 (ISO 16111)
- Selected pollutants: N_2, CO, CO_2, O_2, H_2O

Pollutants	Proportion of pollutant in H2		
	1x	5x	10x
N2	100µmol/mol 0,01% **100ppm**	500µmol/mol 0,05% 500ppm	1000µmol/mol 0,1% 1000ppm
CO	0,2µmol/mol 0,00002% **0,2ppm**	1µmol/mol 0,0001% 1ppm	
CO2	2µmol/mol 0,0002% **2ppm**	10µmol/mol 0,001% 10ppm	
O2	5µmol/mol 0,0005% **5ppm**	25µmol/mol 0,0025% 25ppm	
H2O	5µmol/mol 0,0005% **5ppm**	25µmol/mol 0,0025% 25ppm	

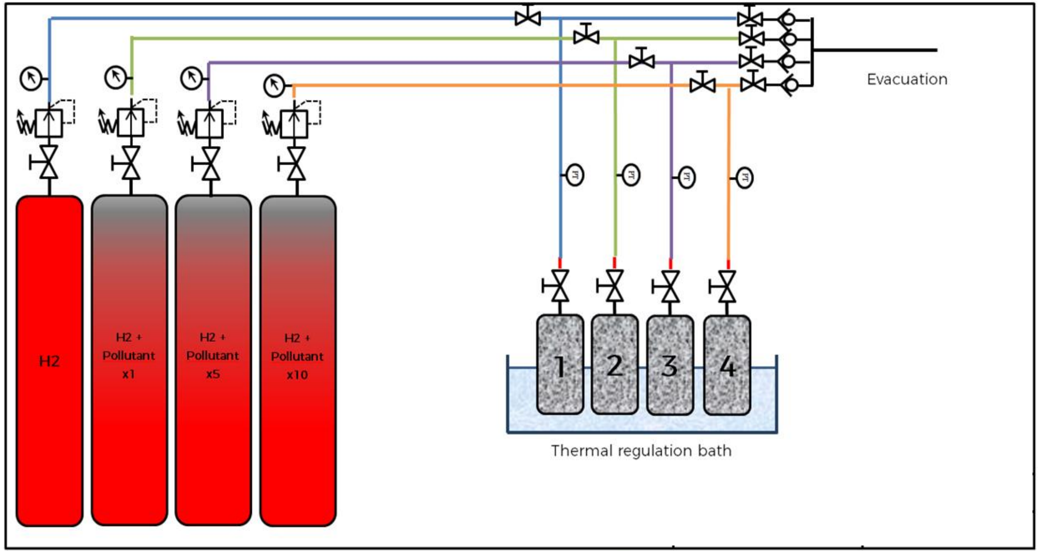
Pollutants - methodology:

Set-up:

- All measurement was made on the same ingot
- Maximum 50 cycles (1 month)
- Temperature regulated at 22°C

Sampling:

- Gravimetric measurement each cycle
- PCT control curves (Sieverts) every 5 cycles



Pollutants - methodology:

Test tank for 100 g of hydride

Test bench

Bottles of mixture with hydrogen and pollutants

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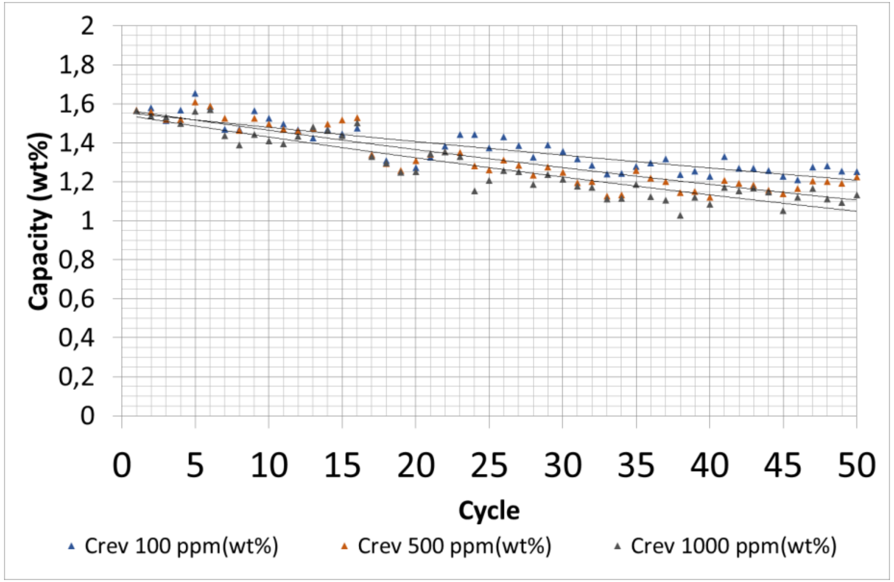
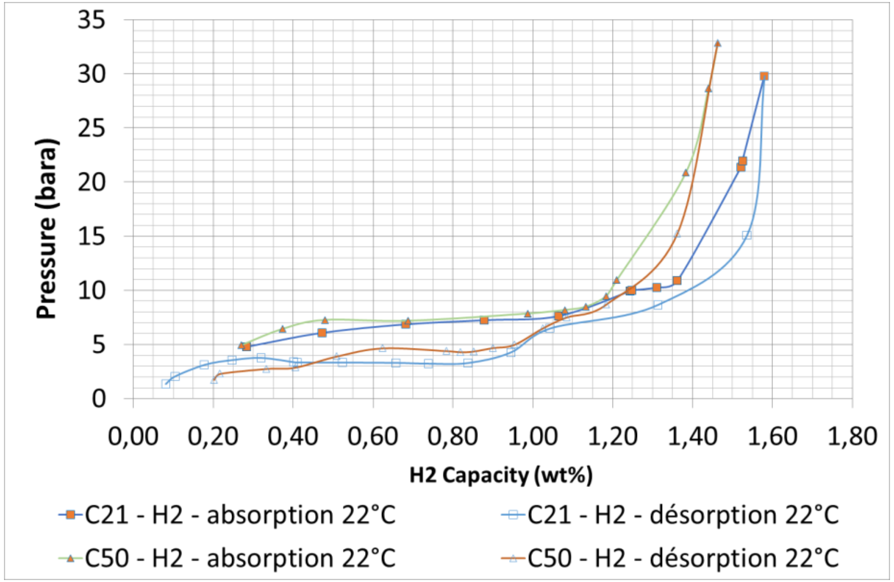
Metrology for Advanced Hydrogen Storage Solutions

Pollutants – results nitrogen case:



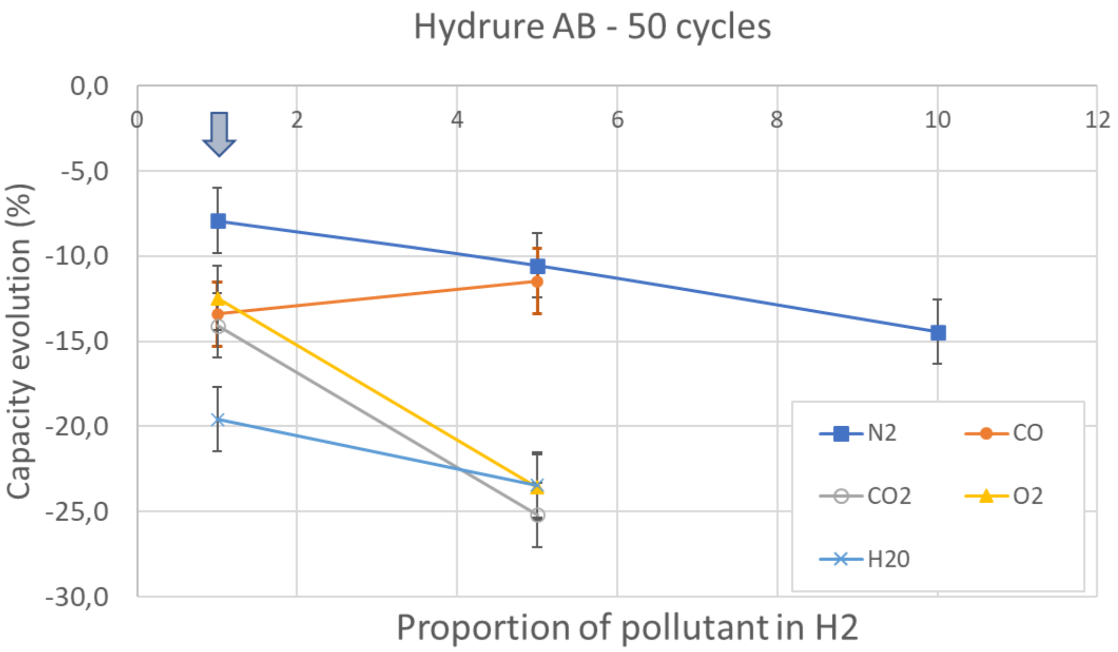
Reversible capacity under H_2 + N_2 on 50 cycles



PCT curves at 22°C – cycles 20 and 50 – N2

Pollutants – summary of results:

Pollutants and proportions		Cycle 1 to 5	Cycle 46 to 50
Crev average (wt%)	H_2 4.5	1,548	1,355
	N_2: 100 ppm	1,576	1,255
	N_2: 500 ppm	1,556	1,198
	N_2: 1000 ppm	1,539	1,125
	CO: 0,2 ppm	1,492	1,106
	CO: 1 ppm	1,431	1,097
	CO_2: 2 ppm	1,507	1,107
	CO_2: 10 ppm	1,486	0,926
	O_2: 5 ppm	1,371	1,029
	O_2: 25 ppm	1,341	0,858
	H_2O: 5 ppm	1,441	0,980
	H_2O: 25 ppm	1,406	0,901



WP4: Metrology for Reversible Hydrogen Storage Technologies: Metal hydride storage and cryo-storage in metal-organic frameworks

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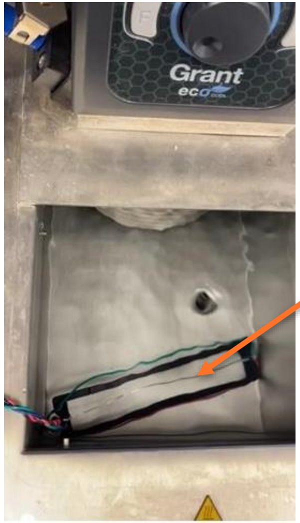
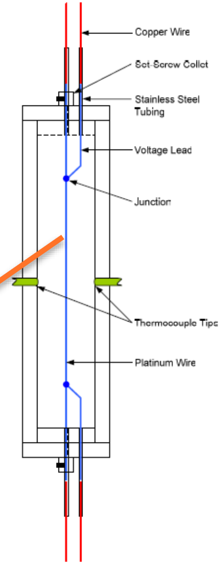
Thermal conductivity:

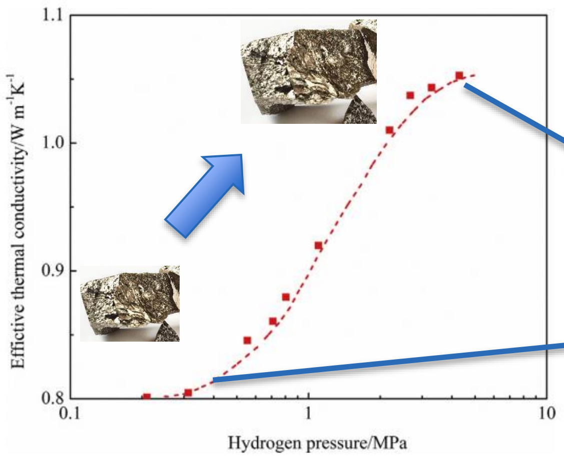
- Importance: container reaction time ≈ effective thermal conductivity
- Methods to measure effective thermal conductivity of powders





Thermal conductivity:

- Particularity of the hydride case
  - Conductivity of single particle vs conductivity of bulk (Suissa 1984)
  - Swelling →effective thermal conductivity affected



Typical values: 0.1 – 1 W/(m.K)

Absorbed: larger particles
→ lower porosity → higher κ_{eff}

Desorbed: smaller particles
→higher porosity → lower κ_{eff}

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HYDROGEN STORAGE IN METAL-ORGANIC FRAMEWORKS (MOFs)

Michael Hirscher

MPI Intelligent Systems, Stuttgart, Germany
WPI-AIMR, Tohoku University, Sendai, Japan

CURRENT TECHNOLOGY: HIGH PRESSURE STORAGE

Toyota 2018 Mirai

70 MPa

5 kg H_2

122.4 L

41 gH_2/L

87.5 kg

5.7 wt%

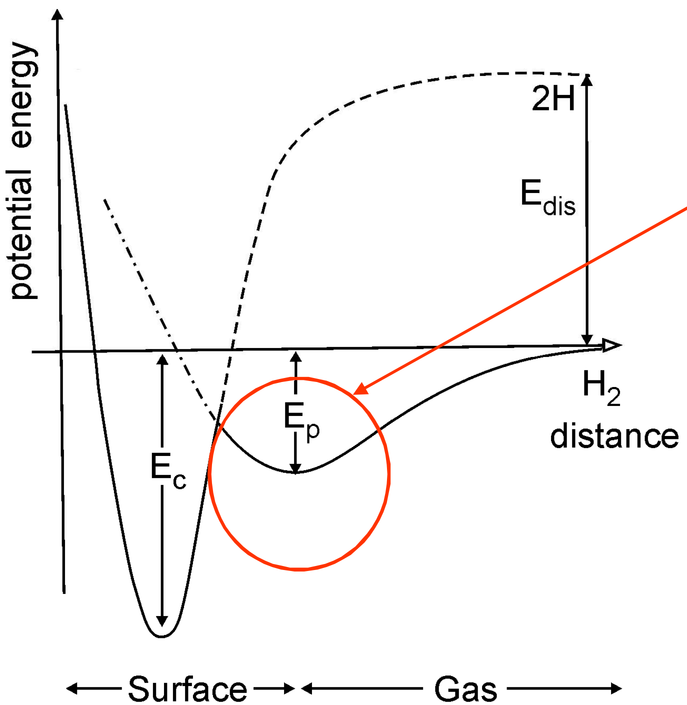
500 km range

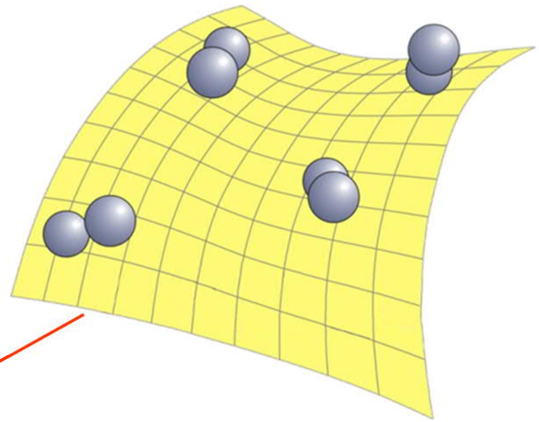
< 5 min refuelling

Storage: 70 MPa, 5.7 wt% and 41 g/L

https://www.toyota.com/content/ebrochure/2018/mirai_FuelCellTech.pdf

HYDROGEN STORAGE BY PHYSISORPTION





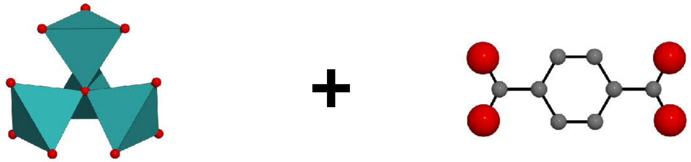
Surface area!

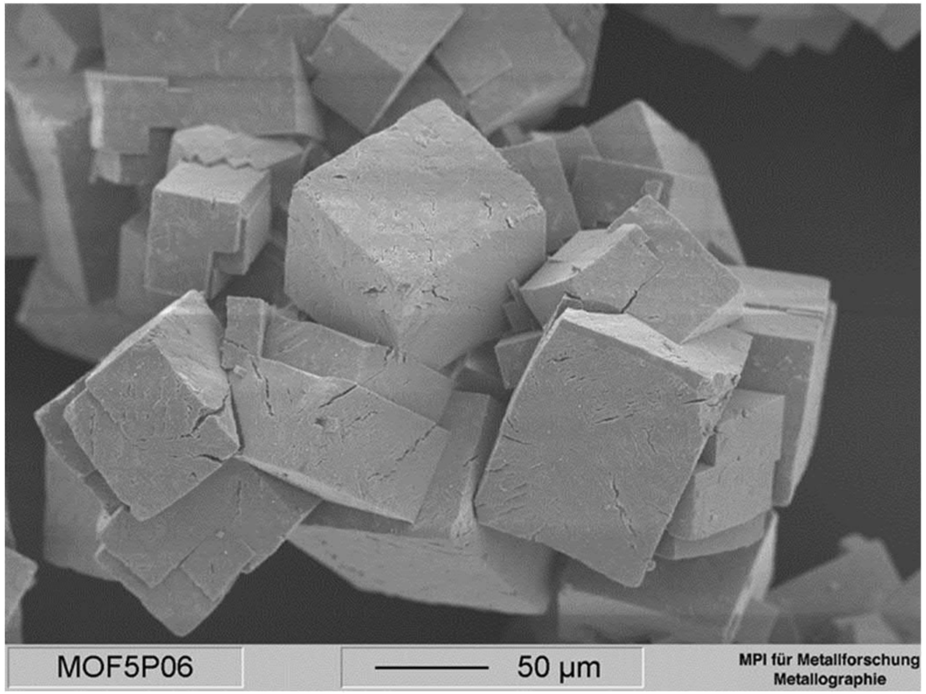
Physisorption
- molecules
- van der Waals forces
- 1 – 10 kJ/mol

Advantages:
- reversible
- fast kinetics
- but, low temp.

METAL-ORGANIC FRAMEWORKS (MOFs)

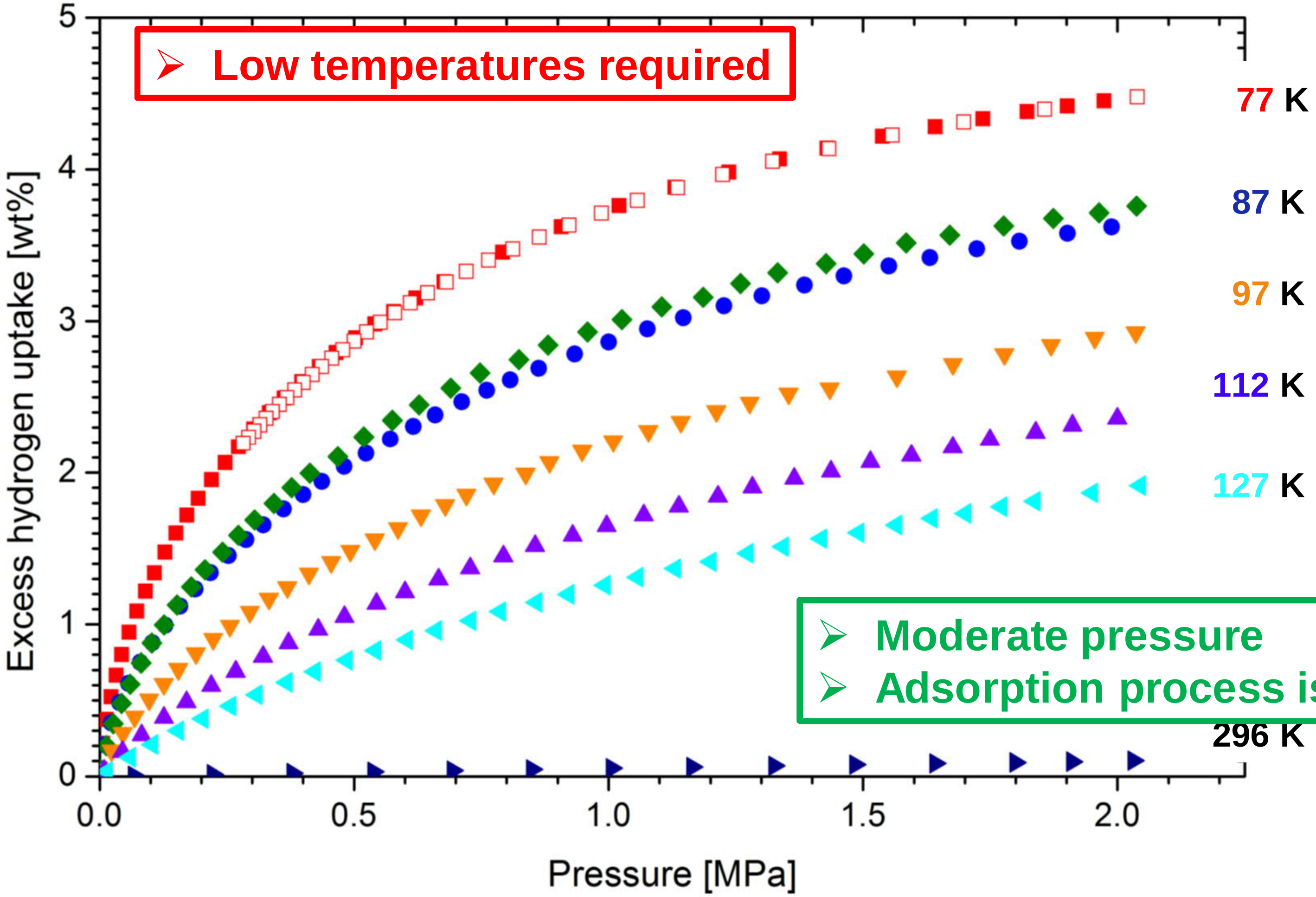
MOF-5





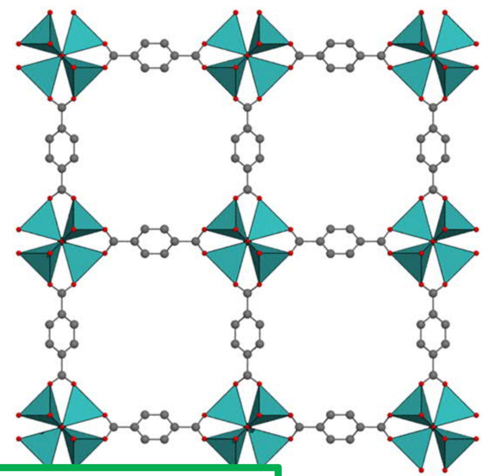
M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe & O.M. Yaghi, Science **295** (2002) 46

HYDROGEN ADSORPTION ISOTHERMS IN MOF-5



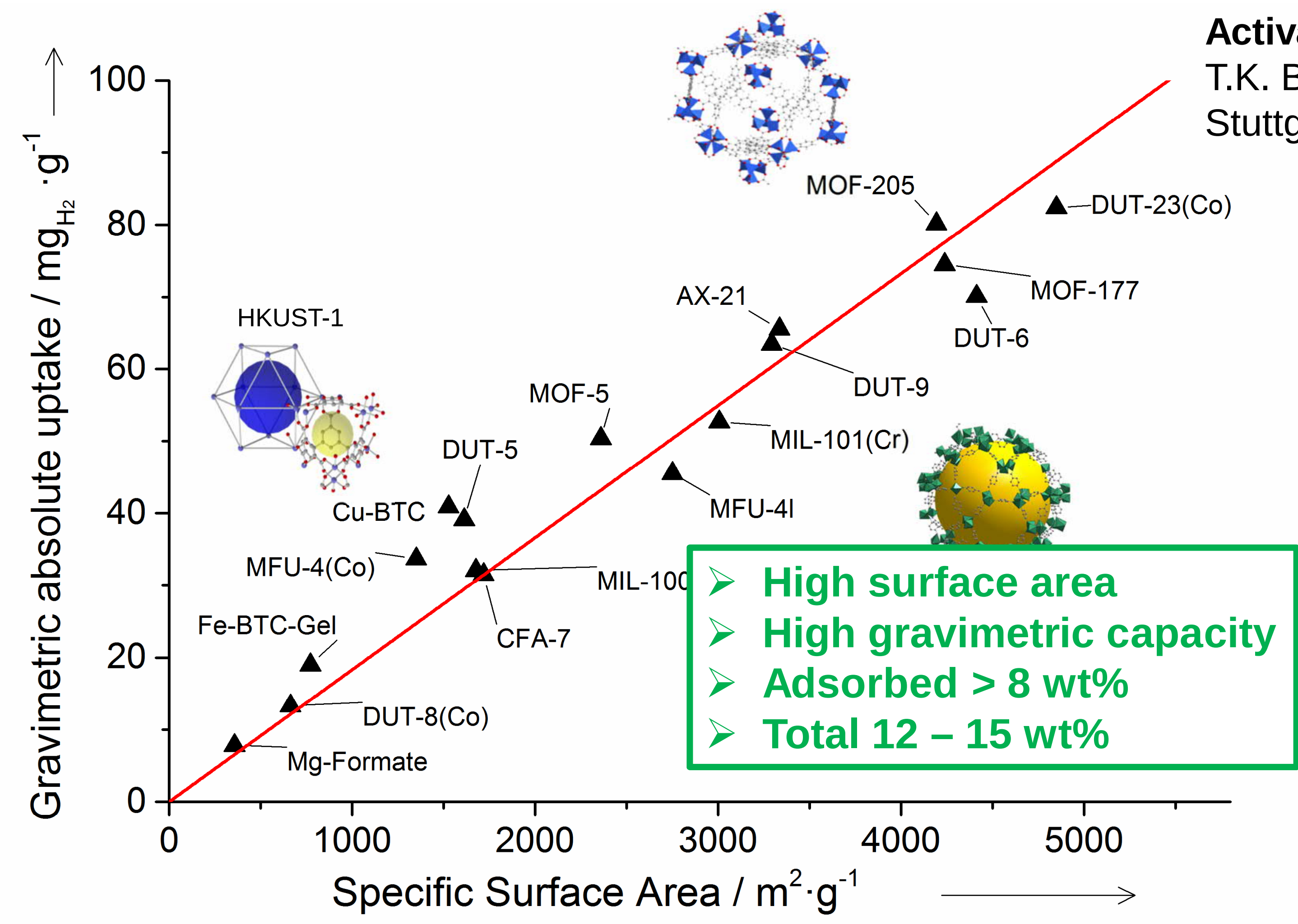
- ➢ Low temperatures required

Metal-organic framework
MOF-5



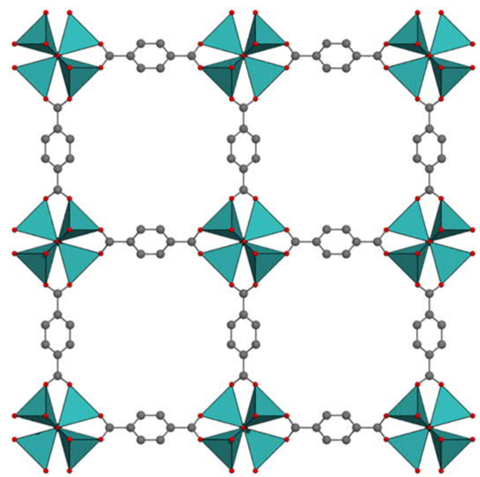
- ➢ Moderate pressure
- ➢ Adsorption process is fully reversible

GRAVIMETRIC CAPACITY AT 77 K AND CHAHINE'S RULE



- High surface area
- High gravimetric capacity
- Adsorbed > 8 wt%
- Total 12 – 15 wt%

Activated carbons R. Chahine, T.K. Bose, Proc. 11th WHEC Stuttgart, Dechema, Germany 1996

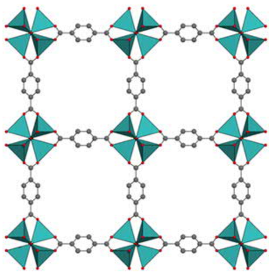


Metal-organic framework MOF-5

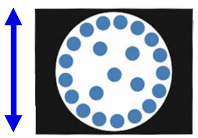
R. Balderas-Xicohténcatl, M. Schlichtenmayer, M. Hirscher, *Energy Technol.* **6** (2018) 578

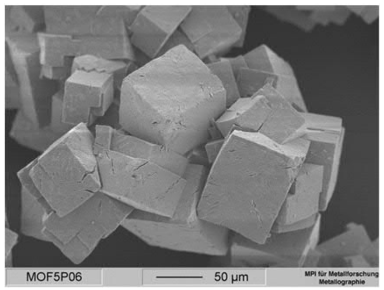
FROM GRAVIMETRIC TO VOLUMETRIC CAPACITY DENSITY IS NEEDED

Single crystal density
(X-ray diffraction XRD)

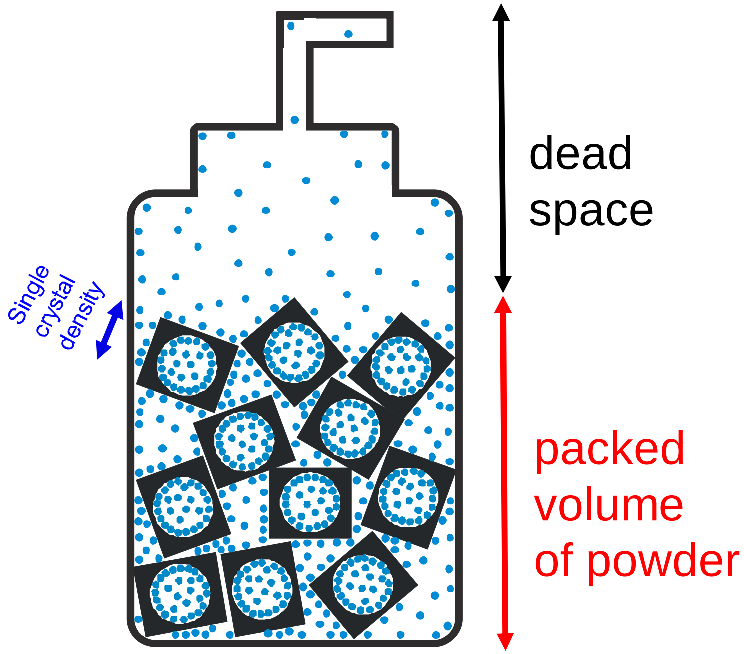


Single crystal density



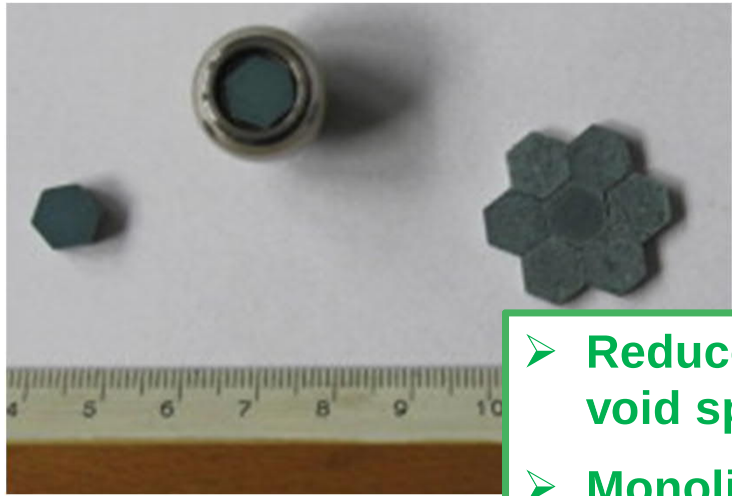


Packing density



Maurice Schlichtenmayer, Dr.rer.nat. thesis Universität Stuttgart, 2012

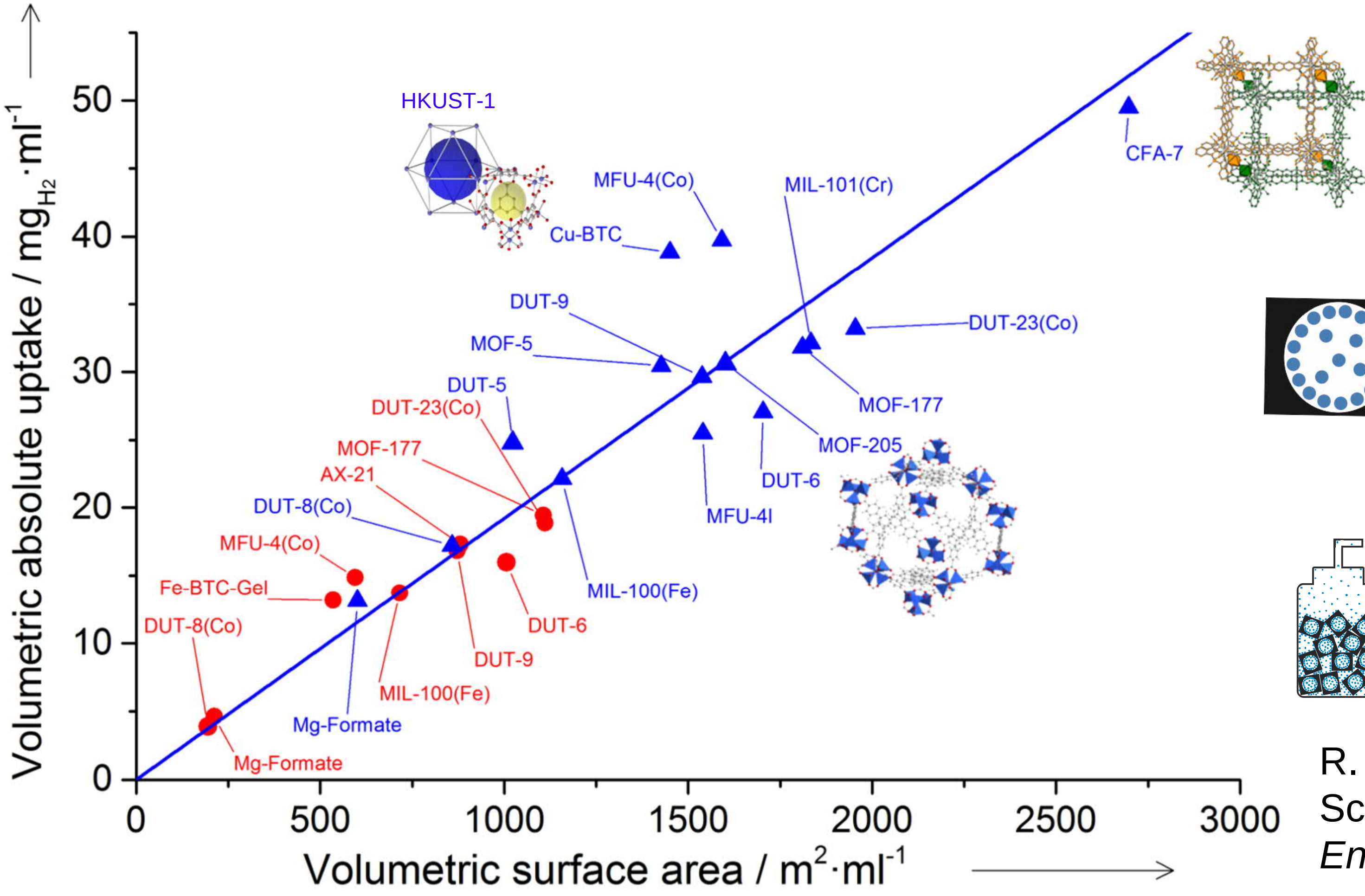
	Single crystal density	Packing density
MOF-177	0.427 g/ml	0.26 g/ml



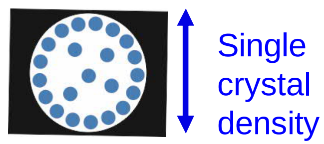
- **Reduce void space**
- **Monoliths**

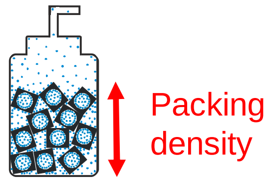
Hydrogen cryo-adsorption by hexagonal prism monoliths of MIL-101 G. Blanita, I. Coldea, I. Misan, D. Lupu, *Int. J. Hydr. Energy* **30** (2014) 17040

VOL. H_2 UPTAKE AT 77 K / VOL. SURFACE AREA



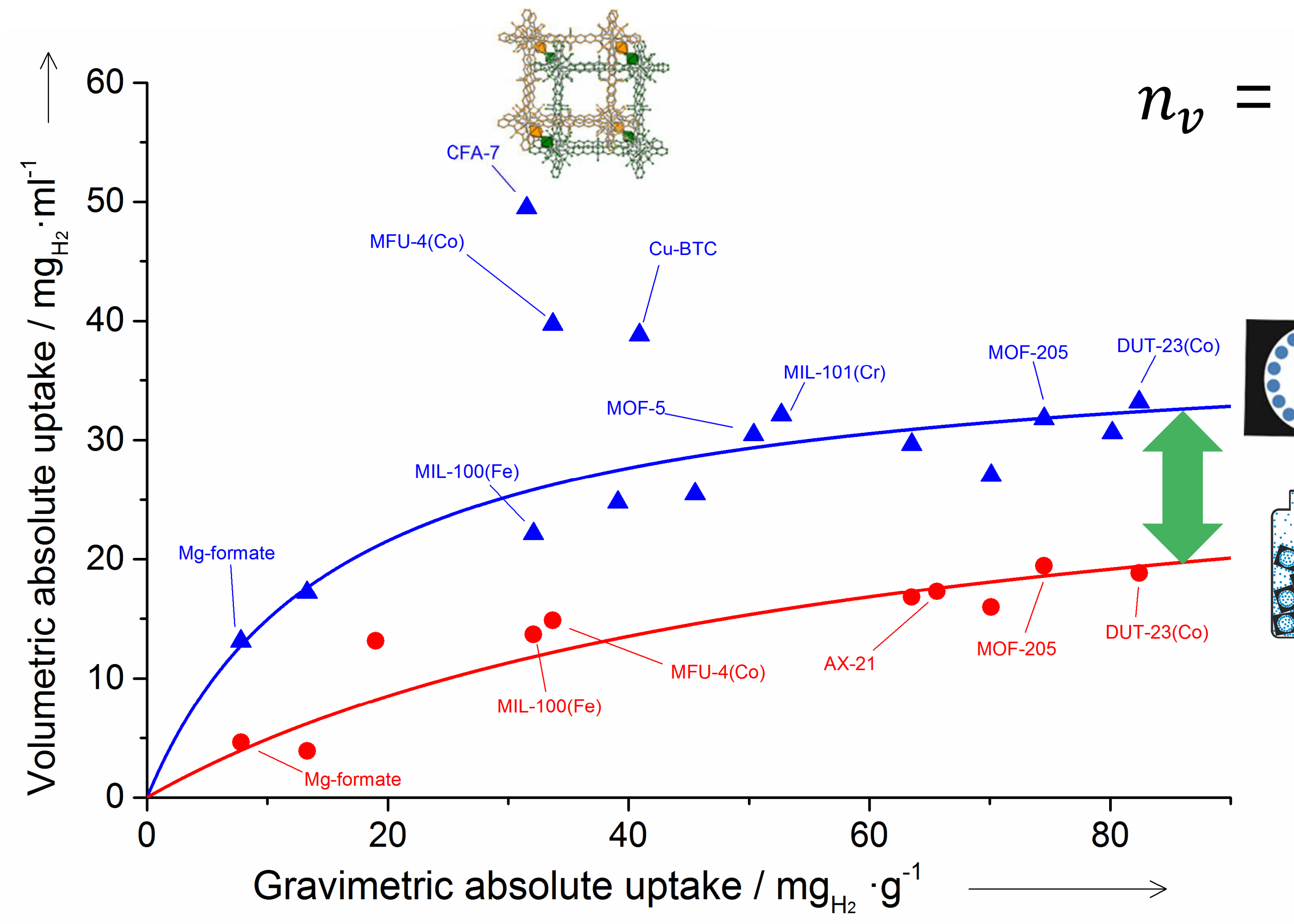
R. Balderas-Xicohténcatl, P. Schmieder, D. Denysenko, D. Volkmer, M. Hirscher, *Energy Technol.* **6** (2018) 510



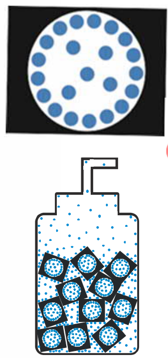


R. Balderas-Xicohténcatl, M. Schlichtenmayer, M. Hirscher, *Energy Technol.* **6** (2018) 578

VOLUMETRIC vs GRAVIMETRIC H_2 UPTAKE AT 77 K



$$n_v = \frac{n_g}{\frac{\alpha}{\kappa} \cdot n_g + V_0}$$

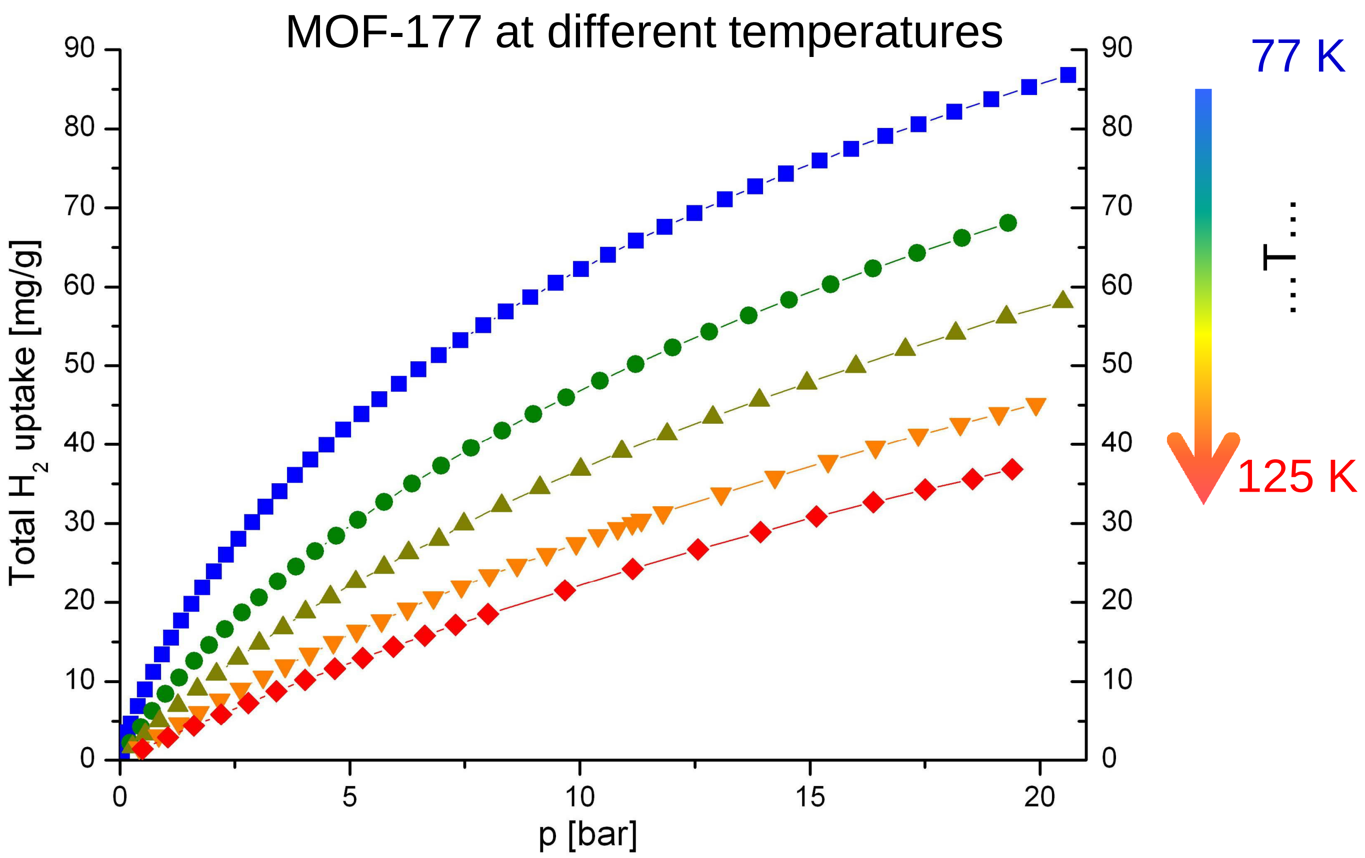


appox. factor 2

- **Compaction**
- **Pelletizing**
- **Monoliths**

R. Balderas-Xicohténcatl, M. Schlichtenmayer, M. Hirscher, *Energy Technol.* **6** (2018) 578

HYDROGEN USABLE (WORKING/DELIVERABLE) CAPACITY

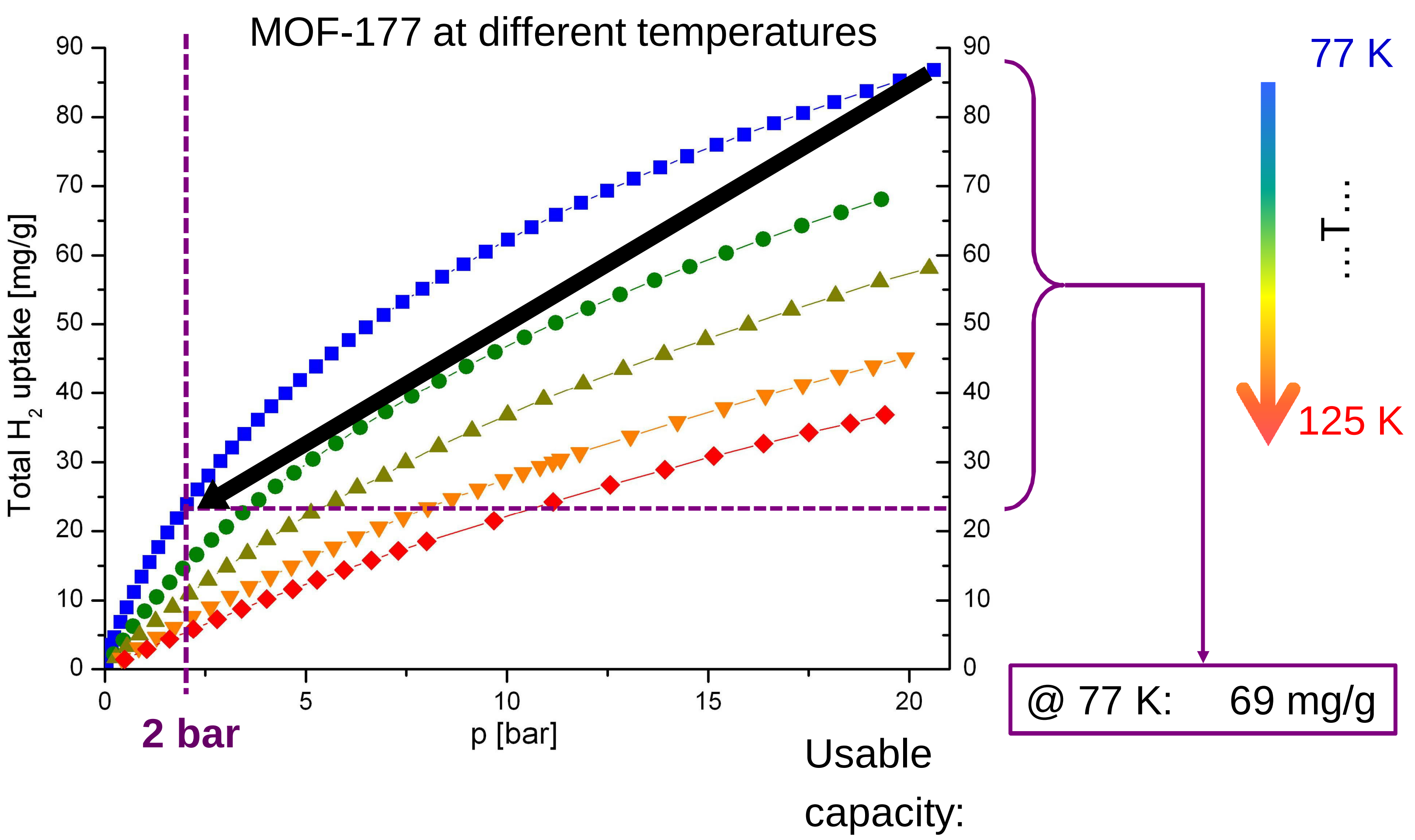


Maurice Schlichtenmayer, 2011 MRS Spring Meeting, San Francisco

M. Schlichtenmayer et al., *Int. J. of Hydrogen Energy* **36** (2011) 586

M. Schlichtenmayer and M. Hirscher, *Appl. Phys. A* **122** (2016) 379

USABLE CAPACITY BY PRESSURE SWING AT CONSTANT *T*

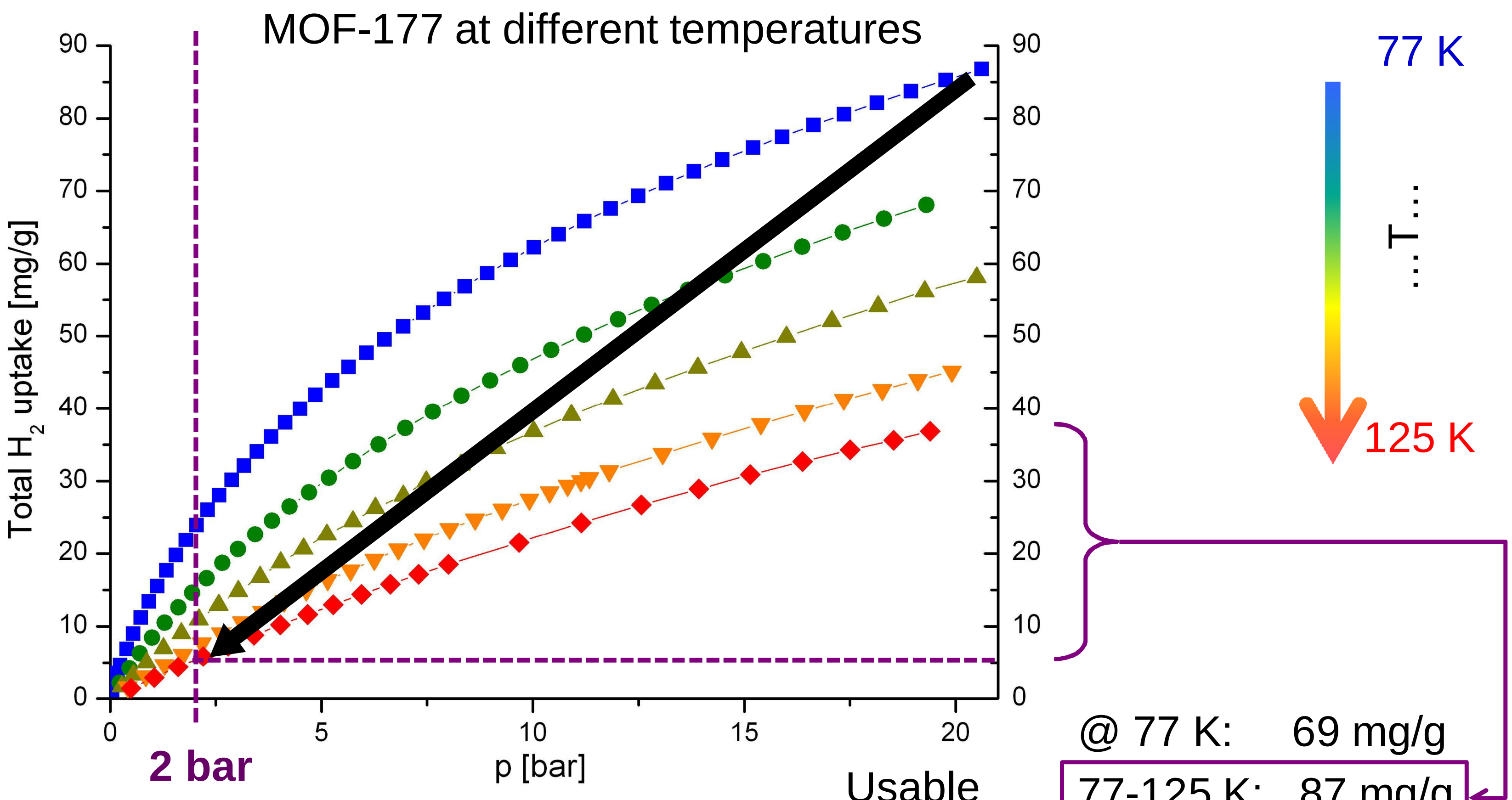


Maurice Schlichtenmayer, 2011 MRS Spring Meeting, San Francisco

M. Schlichtenmayer et al., *Int. J. of Hydrogen Energy* **36** (2011) 586

M. Schlichtenmayer and M. Hirscher, *Appl. Phys. A* **122** (2016) 379

COMBINED TEMPERATURE AND PRESSURE SWING



Maurice Schlichtenmayer, 2011 MRS Spring Meeting, San Francisco

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M. Schlichtenmayer and M. Hirscher, *Appl. Phys. A* **122** (2016) 379

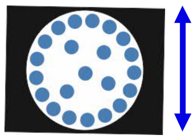
Usable capacity:

@ 77 K: 69 mg/g

77-125 K: 87 mg/g

COMBINED TEMPERATURE AND PRESSURE SWING

Balancing volumetric and gravimetric uptake in highly porous materials for clean energy Z. Chen et al. O.K. Farha, *Science* **368** (2020) 297
"… best deliverable hydrogen capacities (14.0 wt %, **46.2 g/L**) under a combined temperature and pressure swing (**77 K/100 bar → 160 K/5 bar**)."



Fine-Tuning a Robust Metal−Organic Framework toward Enhanced Clean Energy Gas Storage
Z. Chen et al. O.K. Farha, *JACS* **143** (2021) 18838
"MFU-4l-Li displays one of the best volumetric deliverable hydrogen capacities of **50.2 g/L** under combined temperature and pressure swing conditions (**77 K/100 bar → 160 K/5 bar**) while maintaining a moderately high gravimetric capacity of 9.4 wt %."

MOST-H_2

Novel metal organic framework adsorbents for efficient storage of hydrogen

1st June 2022 – 31st May 2026

HORIZON-CL4-2021-RESILIENCE-01-17:
Advanced materials for hydrogen storage
Grant Agreement No: 101058547

Optimal MOF performance & properties targets		$_{mono}$Sorb performance targets
Usable H_2 capacity	>10 (wt%), >50(g/L)	Usable H_2 capacity: >9 (wt%), >45(g/L)
BET Area	>5000 m^2/g, >2500 m^2/cm^3	$_{mono}$Sorb production targets (TRL 5)
Crystal density	d_c >0.4 g/cm^3	>10 kg, < 20 €/kg
Porosity	ε >75%	MOST-tank target (TRL 5)
Pore size	1.5 nm < w < 2.5 nm	500 g H_2, ~10 L, ~8-10 kg of $_{mono}$Sorb,
Total Pore Volume	TPV>2 cm^3/g	operating between 100 bar@80K and 5 bar@160K

SUMMARY AND OUTLOOK

Hydrogen storage by physisorption on MOFs

- Fast kinetics and excellent reversibility
- Upscaled production demonstrated
- Reduced pressure < 10 MPa
  → cost reduction but low temperature required
- Large specific surface area 4500 - 5000 m2/g
  Upper limit for surface basically reached
- High gravimetric storage capacity at 77 K and < 5 MPa
  excess ~ 8 wt%, total 12 – 15 wt%
- Volumetric absolute capacity at 77 K
  powder 20 g/L → monoliths 40 g/L
  H_2 molecules → limit density of liquid H_2
- Temperature and pressure swing → 50 g/L
  (77 K/10 MPa → 160 K/5 MPa)

Thank you for your attention!

Future concepts

- Increase volumetric capacity
  → monoliths
  → interpenetrated structures

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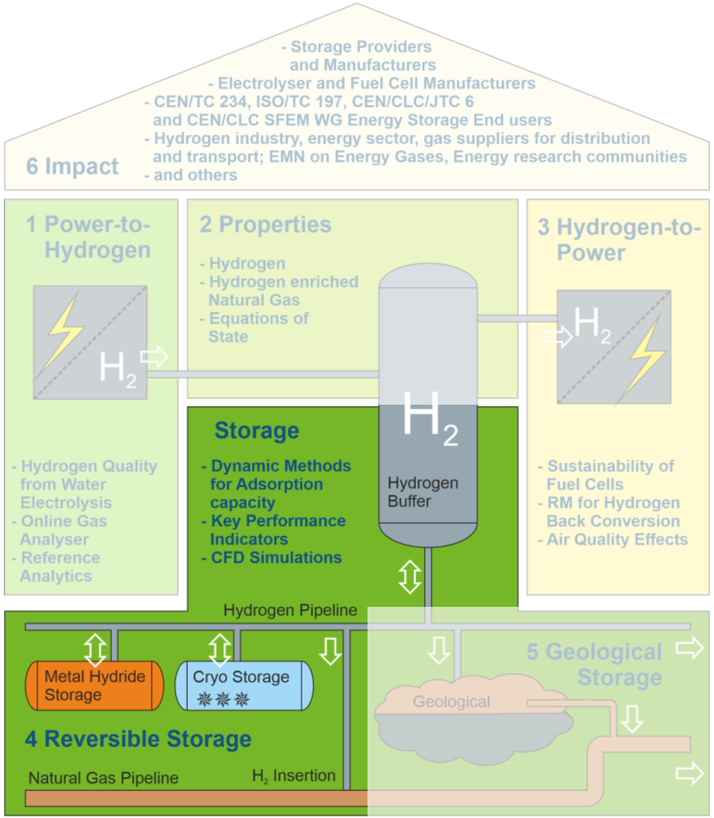
WP 4: Metrology for Reversible Hydrogen Storage Technologies (Metal Hydride Storage, Cryo Storage)

Establishment of validated protocols for experimental at hydrogen ad/absorption; **determination of relevant thermodynamic properties**

Task 4.1: Design and development of a device to measure effective **thermal conductivity**

Task 4.2: Develop dynamic methods for hydrogen ad/absorption capacity and **influence of pollutants**

Task 4.3: Develop **reference materials** and reference methods for hydrogen ad/absorption capacity



MefHySto
Metrology for Advanced Hydrogen Storage Solutions

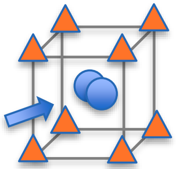
Introduction:

- Hydrogen storage
  - Gas (high pressure or high volume)
  - Liquid (-252 °C, boild-off)
  - Combined with solid materials

H_2 adsorption

Physical interaction

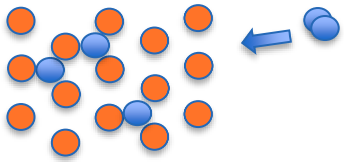
Porous materials



H absorption

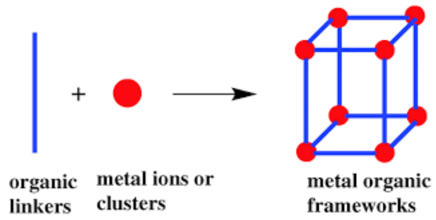
Chemical interaction

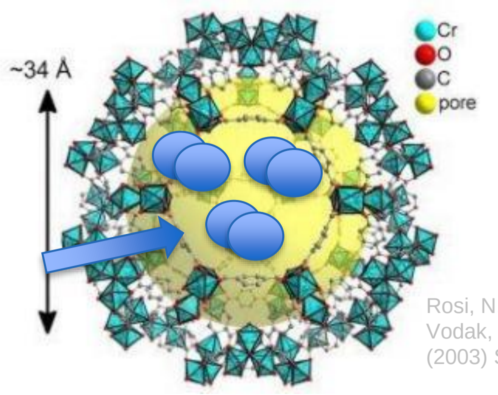
Bulk materials



Introduction:

- Hydrogen storage by adsorption (« H_2 cages »)



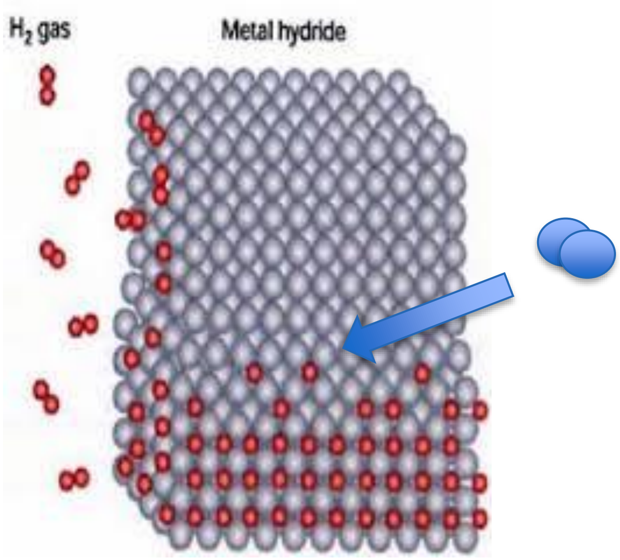


Rosi, N.L., Eckert, J., Eddaoudi, M., Vodak, D.T., O'Keefe, M., Yaghi, O.M. (2003) Science, 300, 1127

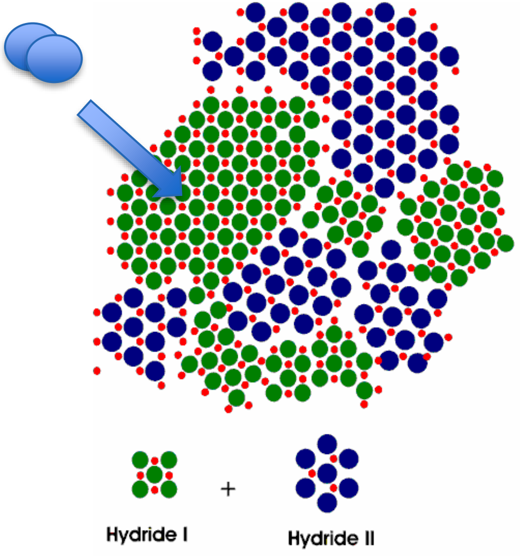
Metal-organic frameworks (MOF)

Introduction:

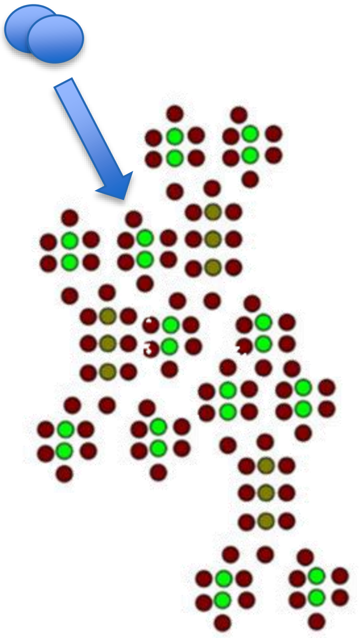
- Hydrogen storage by absorption (« H sponge»)



Metallic bounding



Covalent bounding



Ionic bounding

WP4: Metrology for Reversible Hydrogen Storage Technologies: Metal hydride storage and cryo-storage in metal-organic frameworks

Metal hydride main features:

- Reversible absorption-desorption
- Phase change: volume expansion
- Large operational pressure and temperature conditions
- Low gravimetric density
- Sensible to gases (→ pollutans study)
- Production:
  - Chemical sinthesis
  - Ball milling
  - Melting

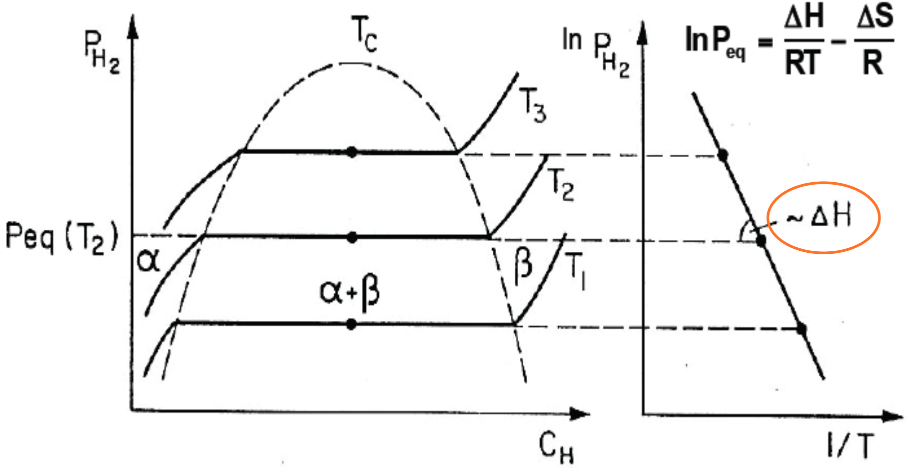
Cast

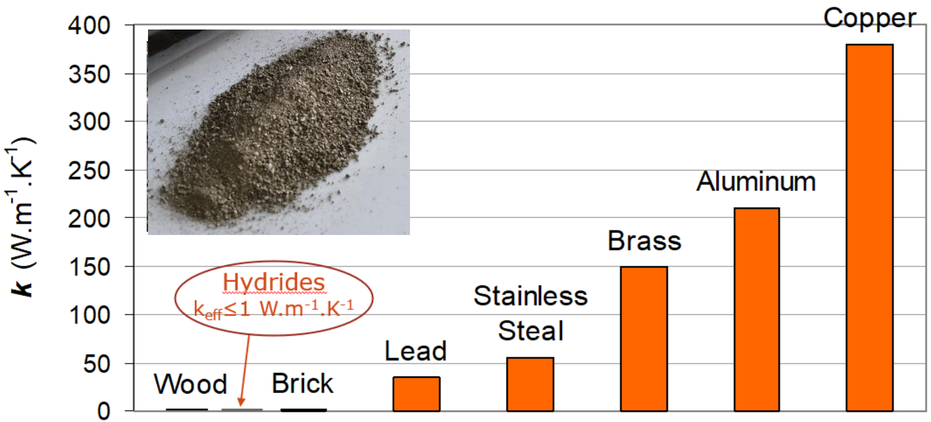
Crush

Metal hydride characterisation:

- Kinetics
- Thermodynamics
- Thermal properties (→ conductivity study)

Sieverts device





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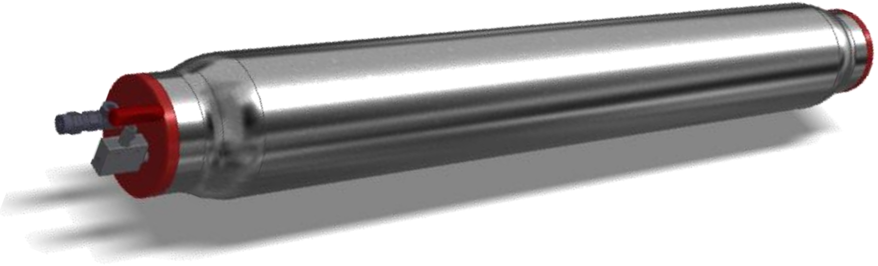
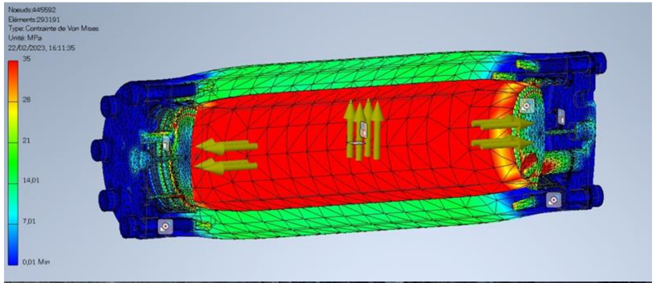
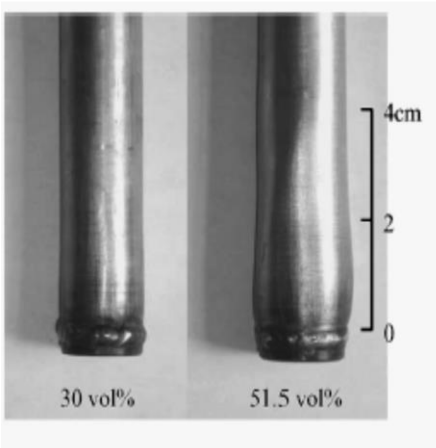
Hydride containers:

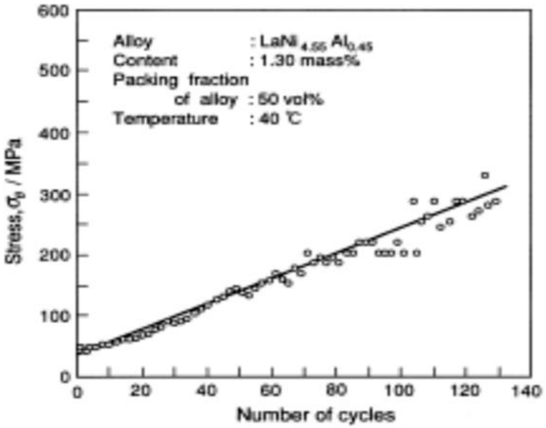
- ISO 16111 (suggested H_2 minimal quality)
- Need of filtering
- Thermal and mechanical issues



Qin F. Int J Hydrogen Energy 2008;33(2):709-17





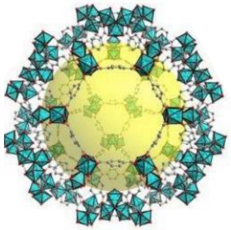


WP4: Metrology for Reversible Hydrogen Storage Technologies: Metal hydride storage and cryo-storage in metal-organic frameworks

Summary:

- Hydrogen can be ab(d)sorbed by solids
- Hydrides are sensible to gases
- There is a large range of possible pressure and pressure conditions
- Thermal and mechanical aspects should be considered for container design

Pollutants



Thermal conductivity

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Final Meeting

WP4 : Metrology for Reversible Hydrogen Storage Technologies

MAHYTEC A Hensoldt Company.

BAM Bundesanstalt für Materialforschung und -prüfung

Ha FOUNDATION FOR THE DEVELOPMENT OF NEW HYDROGEN TECHNOLOGIES IN ARAGON

MAX PLANCK INSTITUTE FOR INTELLIGENT SYSTEMS

Maximiliano Melnichuk
maximiliano.melnichuk@mahytec.com

EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

MefHySto

Metrology for Advanced Hydrogen Storage Solutions

Development of reference materials and methods for hydrogen ad/absorption capacity

Michael Hirscher

BAM Bundesanstalt für Materialforschung und -prüfung

MAX PLANCK INSTITUTE FOR INTELLIGENT SYSTEMS

EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

REPRODUCIBILITY AS A CORNERSTONE OF SCIENCE

Karl Popper, The Logic of Scientific Discovery, Hutchinson, London, 1959

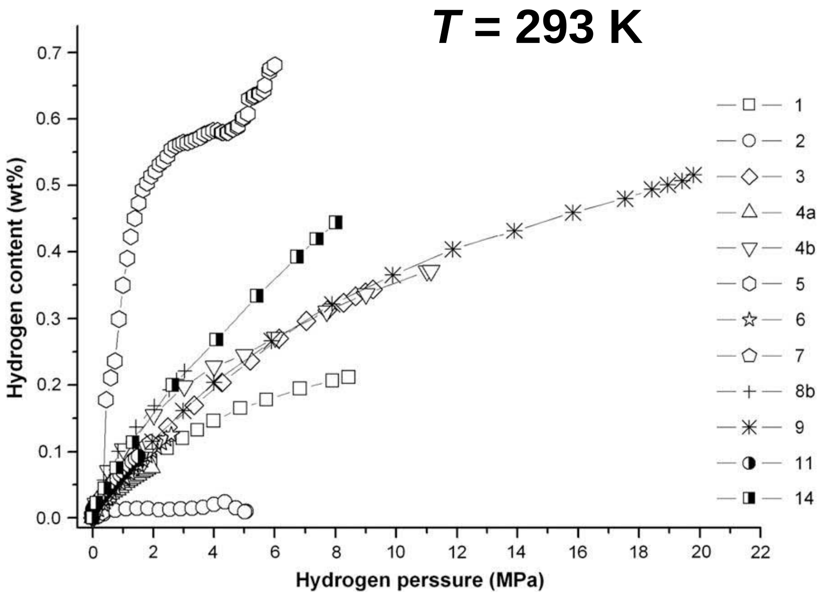
Darren P. Broom and Michael Hirscher, *Energy Environ. Sci.* **9** (2016) 3368

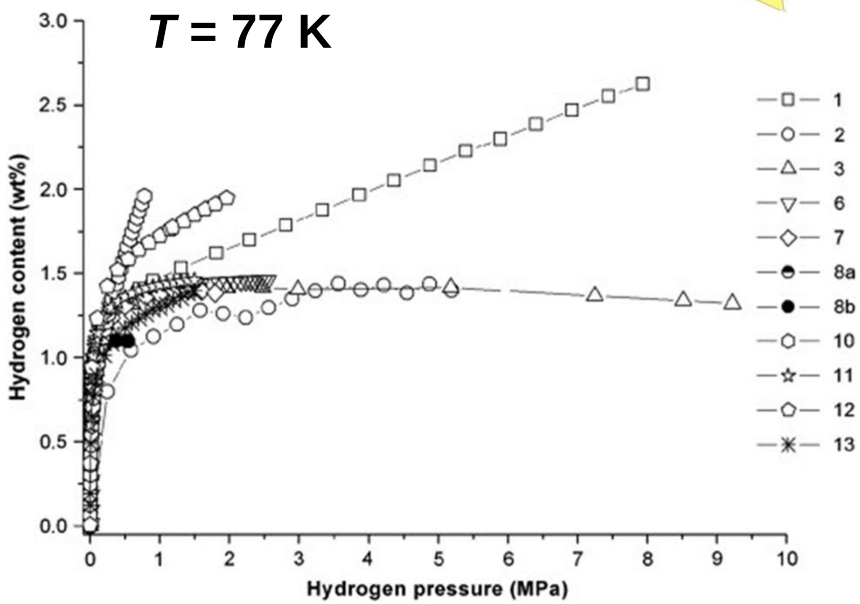
Motivated by continuing problems in the literature but also due to lack of a clear overview (newcomers must work hard to untangle the story)

- Carbon nanostructures (nanotubes and nanofibres)
- BN nanotubes and conducting polymers
- MOFs (e.g. MOF-5) and hydrogen storage by spillover
- Some studies containing irreproducible data are still being cited regularly

Round Robin Analysis of Hydrogen Storage Capacity

A Round Robin characterisation of the hydrogen sorption properties of a carbon based material, C. Zlotea, P. Moretto, T. Steriotis, *Int. J. Hydrogen Energy* **34** (2009) 3044





International Laboratory Comparison

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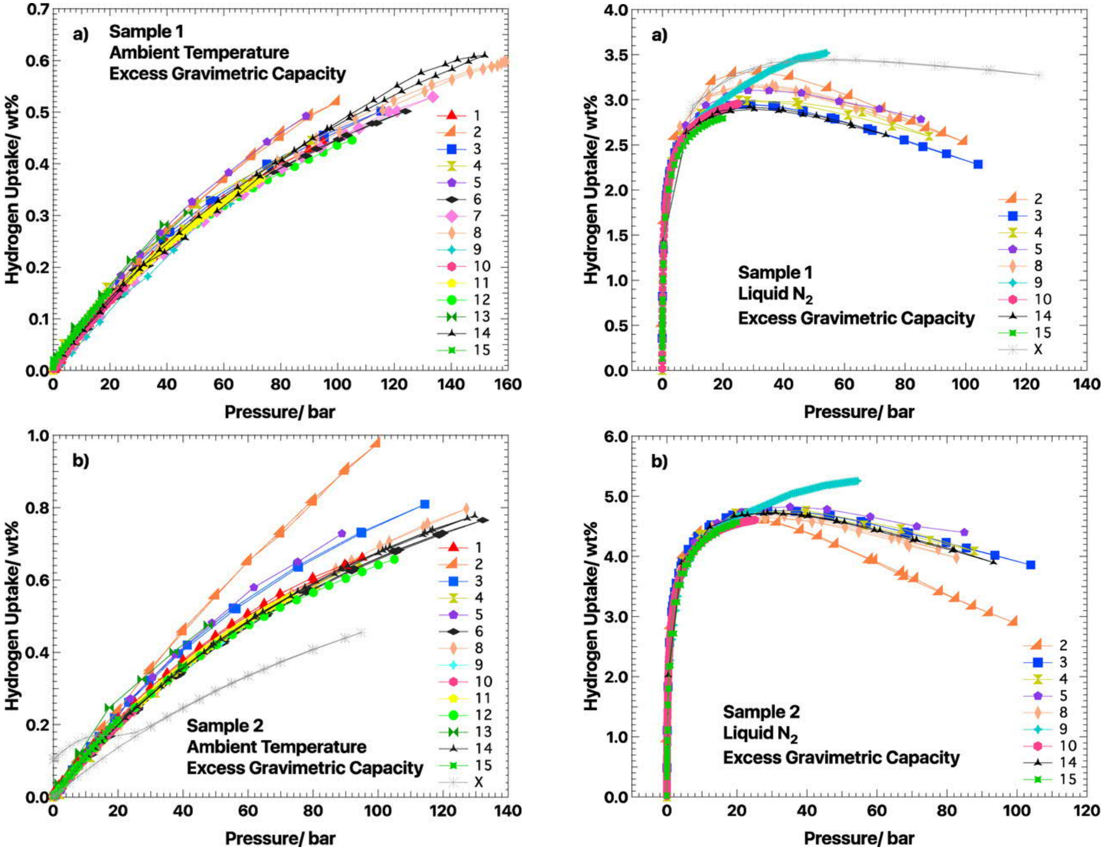
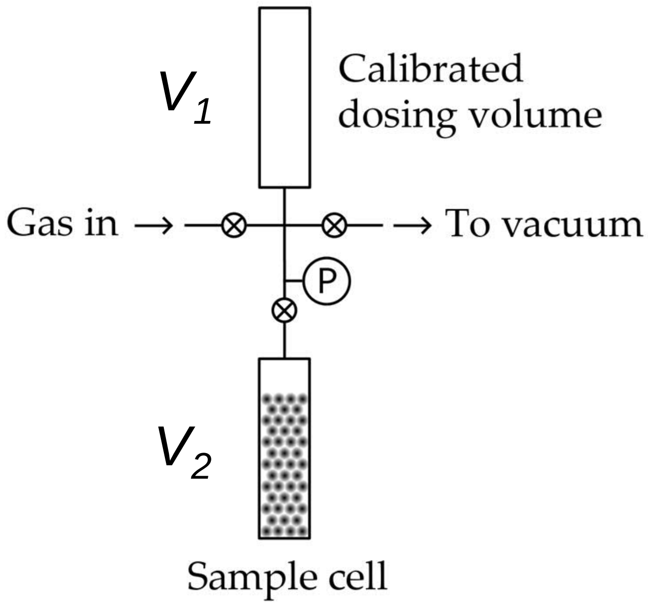
An International Laboratory Comparison Study of Volumetric and Gravimetric Hydrogen Adsorption Measurements
Katherine E. Hurst et al.
ChemPhysChem **20** (2019) 1997

NREL
Transforming ENERGY



Manometric (Sieverts) Technique



Volume V_1 is filled to a pressure P_i while the sample cell is held at vacuum

The connecting valve is then opened to dose gas to the sample, and the final pressure, P_f , measured

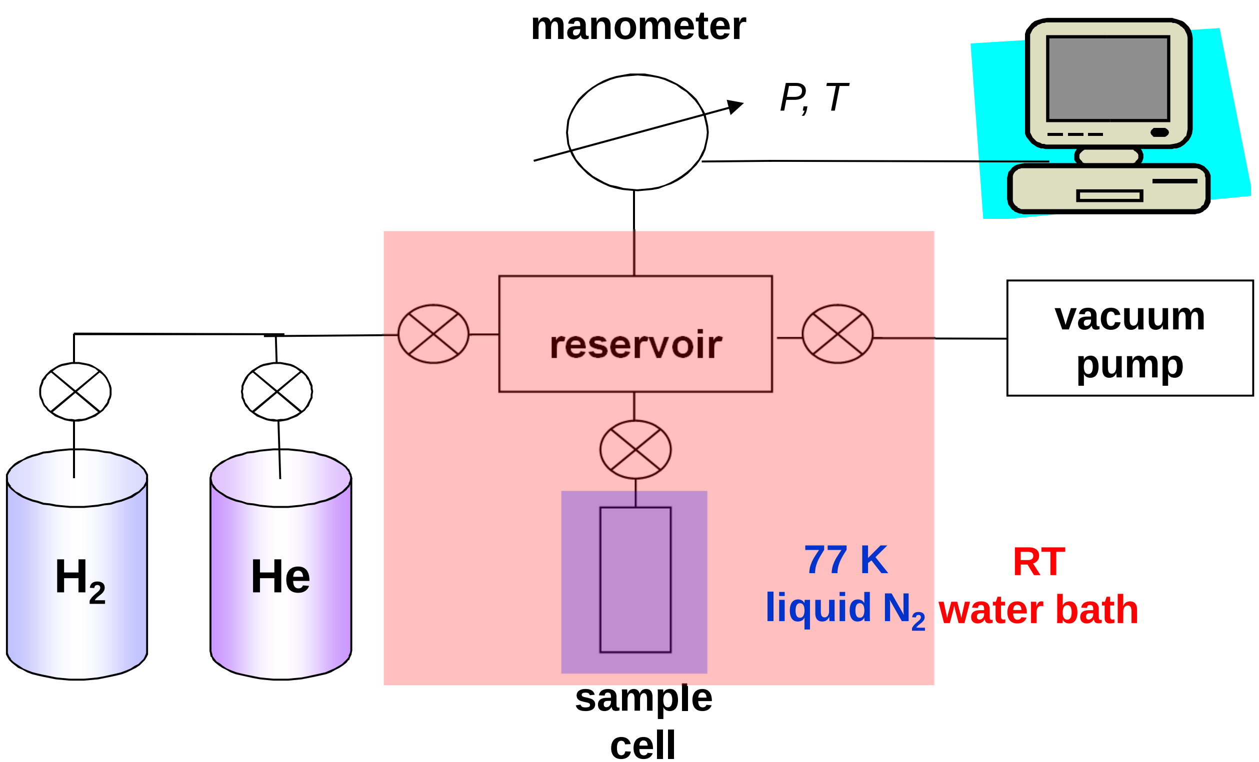
The number of moles sorbed is then given by,

$$\Delta n = \frac{P_i V_1}{Z_{Pi,T} RT} - \frac{P_f (V_1 + V_2)}{Z_{Pf,T} RT}$$

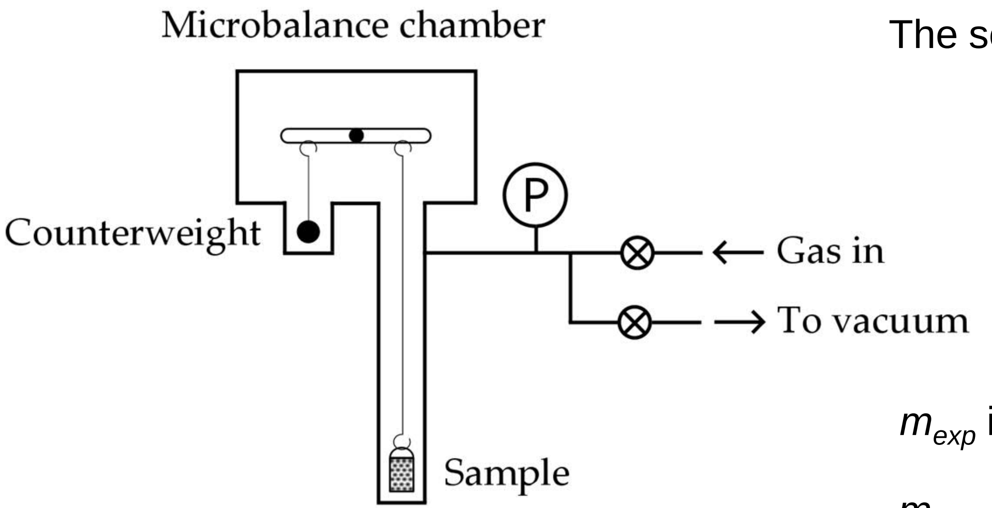
where $Z_{i,T}$, and $Z_{f,T}$,are the gas compressibility factors at P_i and P_f, respectively, and V_2 is the dead volume of the sample cell

To determine an entire isotherm, this dosing and measurement process is then repeated for each data point

Manometric (Sieverts) Technique



Gravimetric Technique



buoyancy correction

The sorbed quantity is given by,

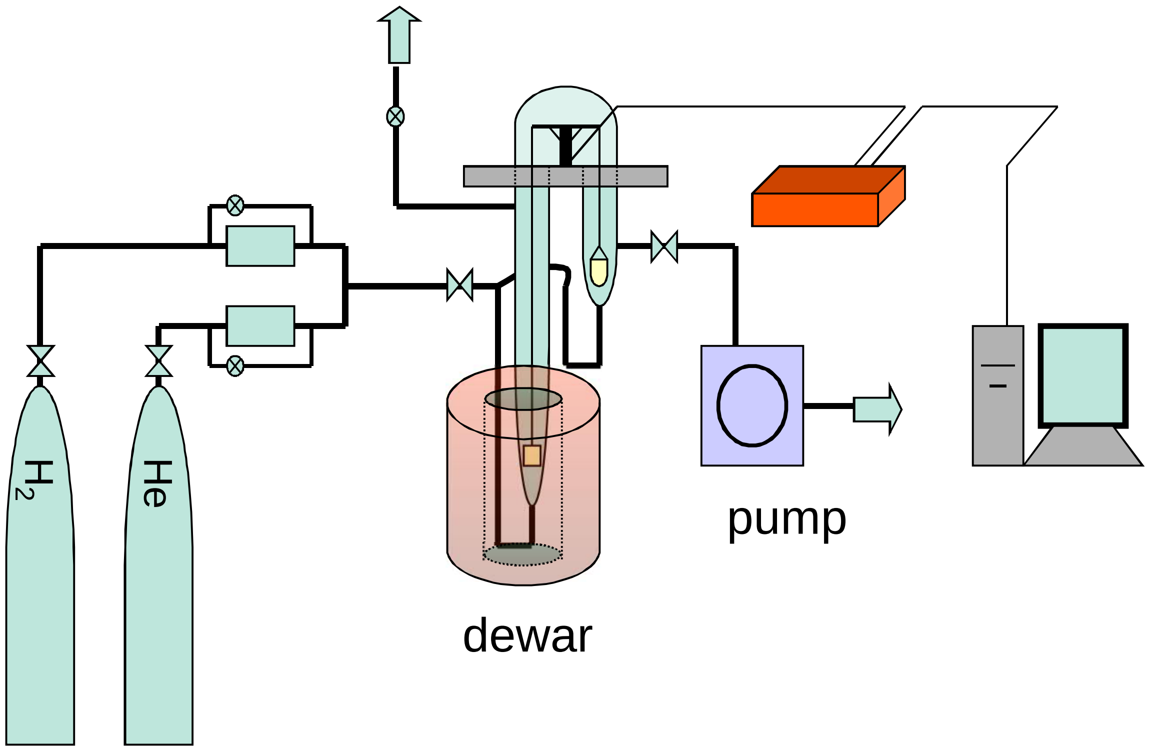
$$m_H = m_{\exp} - m_{solid} + \rho_g \left(\frac{m_{solid}}{\rho_{solid}} \right)$$

m_{exp} is the experimentally-measured mass

m_{solid} is the mass of the solid under vacuum

ρ_g and ρ_{solid} are the densities of the gas and the solid

Gravimetric Technique



Improving Reproducibility in Hydrogen Storage Material Research

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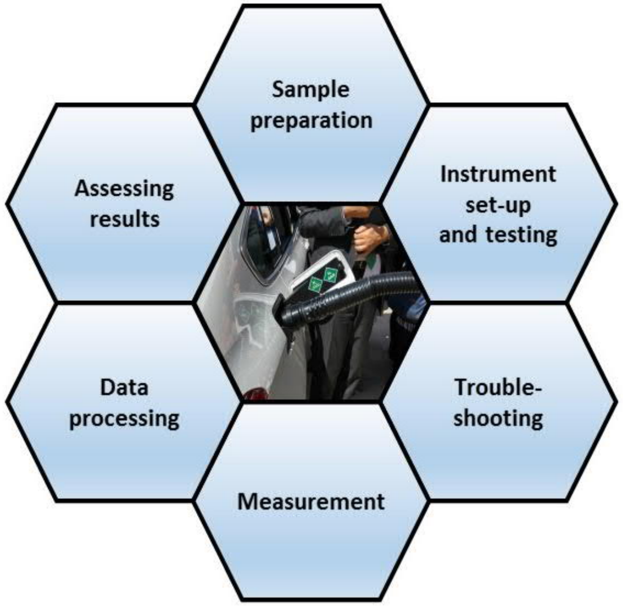
Darren P. Broom and M. Hirscher,
ChemPhysChem **22** (2021) 2141



Sample preparation

Synthesis and purification
↓
Characterization
↓
Is the sample pure enough?
↓
Is enough sample available?

Instrument set-up and testing

Calibrate instrument
↓
Perform blank scans
↓
Validate using reference materials
↓
Is the instrument sensitive enough for available sample size?

Troubleshooting

Is the H_2 gas supply pure enough?
↓
Are there leaks in the instrument?
↓
Are all devices properly calibrated?
↓
Is temperature stable enough?

Measurement

Is the sample too small?
↓
Is it fully activated?
↓
Are there too many isotherm points?
↓
Are the equilibration times long enough?

Data processing

Is the dry sample mass correct?
↓
Is the sample density correct?
↓
Is the equation of state accurate enough?
↓
Is the hydrogen storage capacity defined properly?

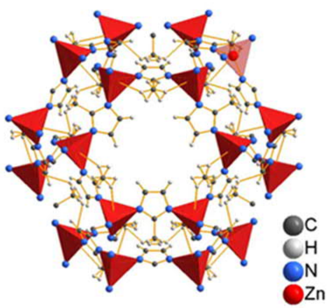
Assessing results

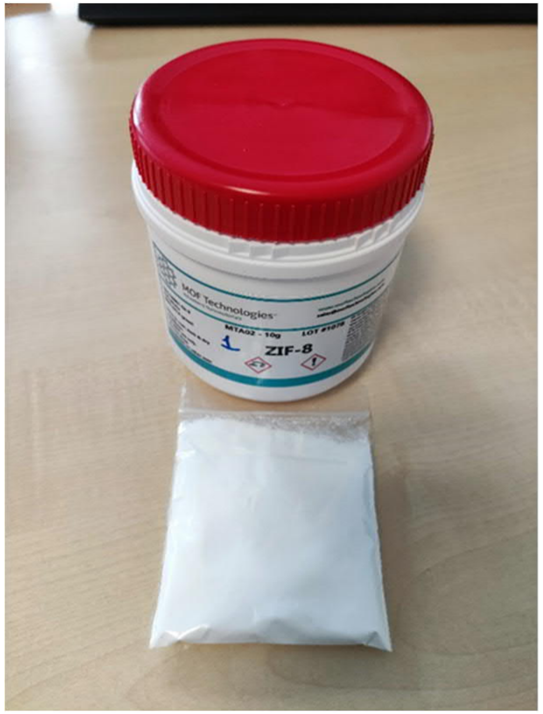
Is the isotherm shape physically reasonable?
↓
Are the isotherms repeatable?
↓
Is there any unexpected hysteresis?
↓
Do the sorption/desorption isotherms cross?

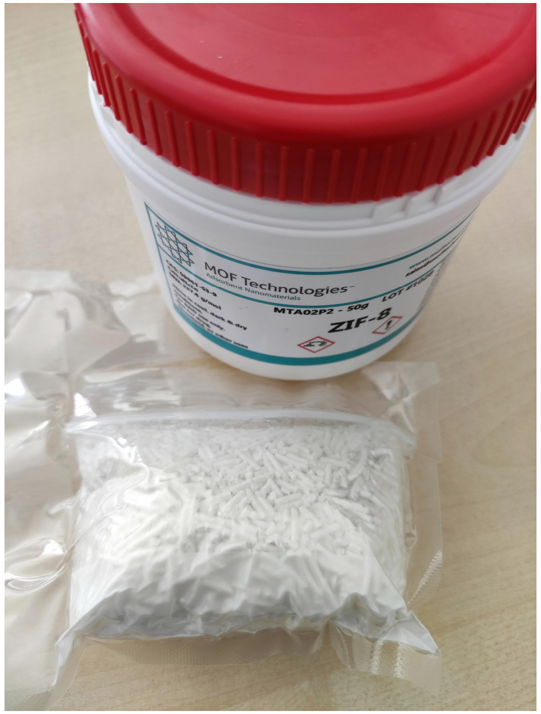
Reference Material

ZIF-8 powder and pellets

Zeolitic Imidazolate Framework-8 (ZIF-8) is a porous metal-organic framework with high thermal and mechanical stability







Structure Comparison: Powder / Pellets

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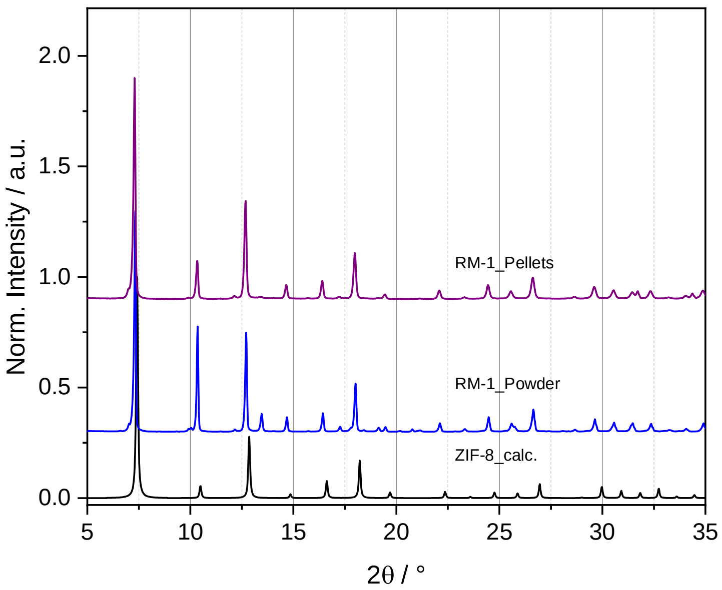
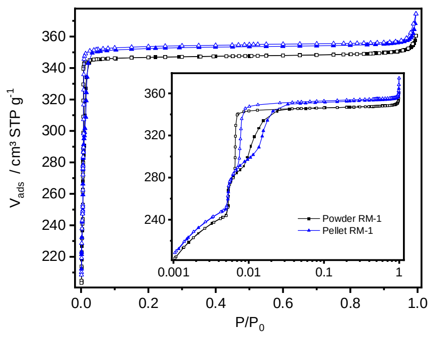
X-Ray diffraction to compare crystallinity



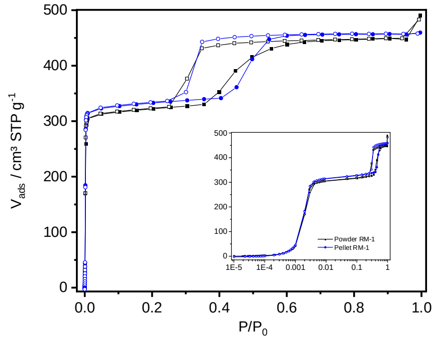
The crystal phase does not change after packing powders into pellets

Adsorption-desorption experiments to compare porosity

N_2 at –196 °C (BAM)



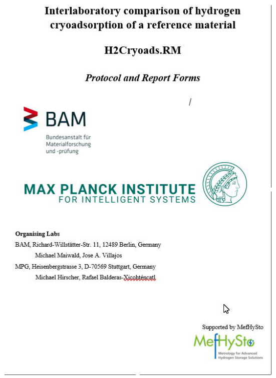
Ar at –186 °C (MPG)



Sample	A_{BET} (m²/g)	Pore volume (cm³/g)
RM-1 Powder	1115	0.54
RM-1 Pellets	1142	0.55

Slight increase (2 %) of porous properties after pelletizing

Interlaboratory Comparison Study


Interlaboratory comparison of hydrogen cryoadsorption of a reference material

H2Cryoads.RM

Protocol and Report Forms

BAM

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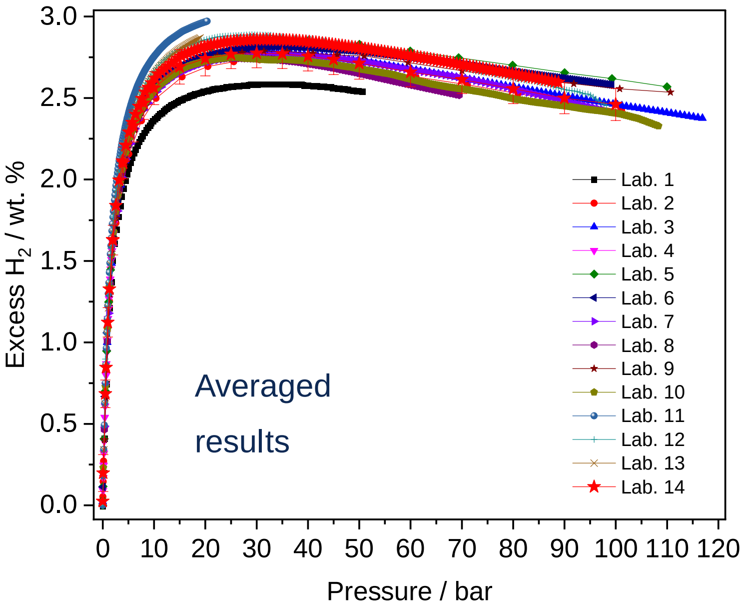
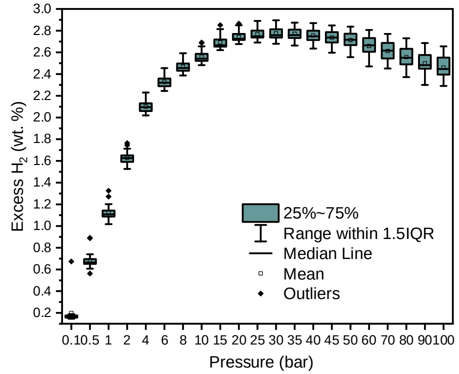
Organising Labs

Supported by MefHySto

Posters 2 and 3



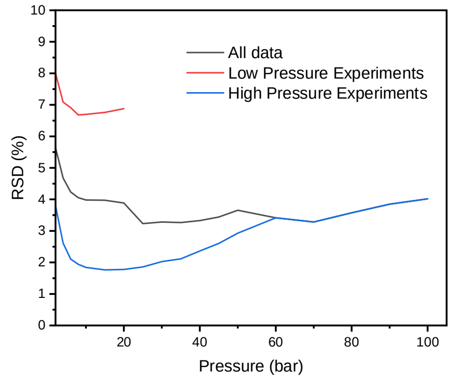
RM-1 was analysed by 14 laboratories from 10 participants with proven experience in the measurement of H_2 uptake at –196 °C



Low dispersion of data among measurements (max. 4 % between 2 – 80 bar)

Higher RSD (relative standard deviation) at very low and high pressures:

- Low-pressure reading accuracy
- Lower hydrogen uptake



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Thanks for your attention

Michael Hirscher hirscher@is.mpg.de

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research and innovation programme and the EMPIR Participating States