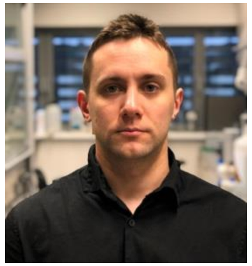
High-density confinement of H_2 in ultramicroporous carbon materials



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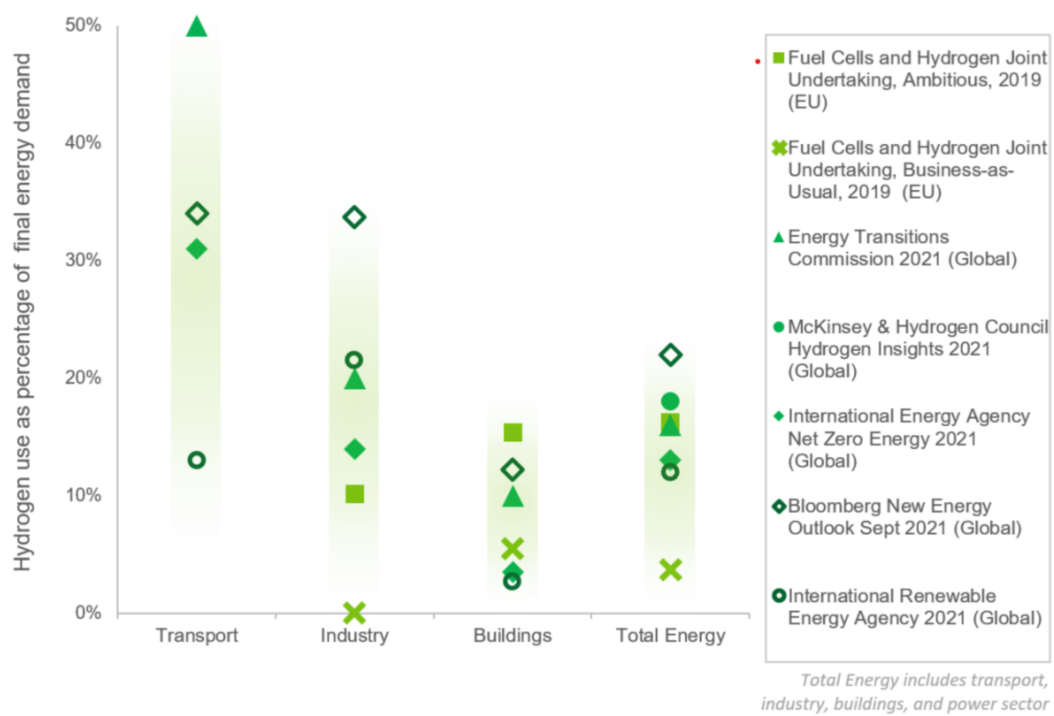
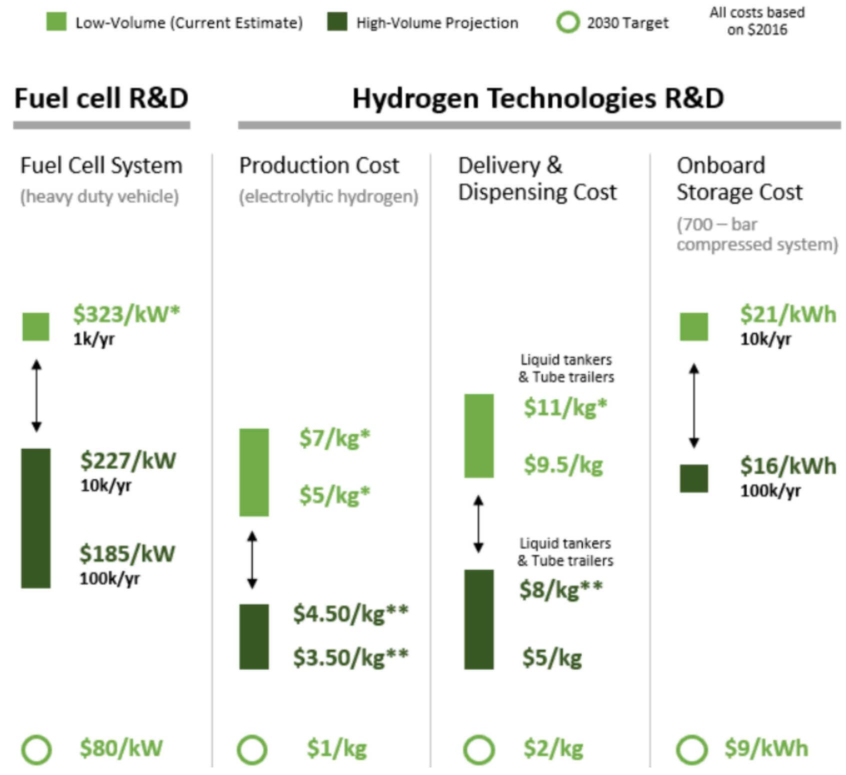
H_2 and its future role in economy

- H_2-based or -supported systems vital for greenhouse gas emission free economy
- A global need of at least 100 Mt of H_2 production by 2030 envisioned to meet climate goals
- 10 Mt + 10 Mt (H_2 production + import) in EU aimed by 2030 through REPowerEU Plan By 2050, renewable H_2 to cover around 10% of EU's energy needs.





U.S. National Clean Hydrogen Strategy and Roadmap, 2023

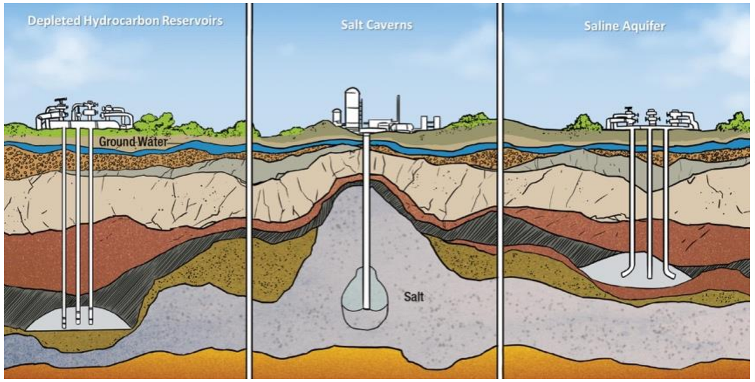
H_2 storage – staying stationary or going mobile

- Compressed (41 g_{H2}/L at 273.15 K and 700 bar)
  Used for mobile applications
  Compression and tank material requirements
- Liquefied (70 g_{H2}/L at 20 K)
  Mobile and stationary applications
  Liquefaction losses, boiloff
- Underground storage (up to 15 g_{H2}/L at 350 bar)
  Stationary applications
  Geographically restricted

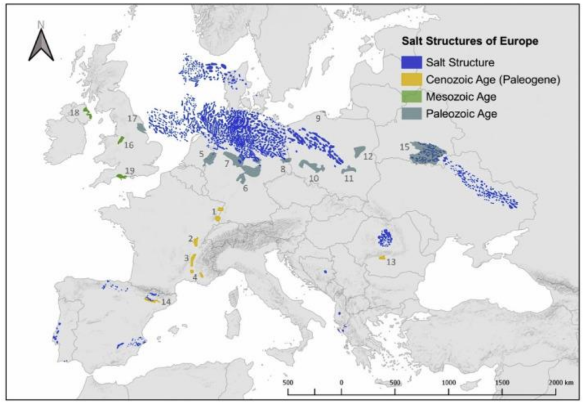
Type IV H_2 tank for 700 bar (left) and 60 bar (right) storage

M. Fiekiewicz et al., Hydrogen Onboard Storage Technologies for Vehicles, 2023

MAHYTEC, QUADRHY technical datasheet



B. N. Tackie-Otoo et al., Fuel 356(15), **2024**, 129609



D. G. Caglayan et al., Int. J. Hydrogen Energy 45(11), **2020**, 6793

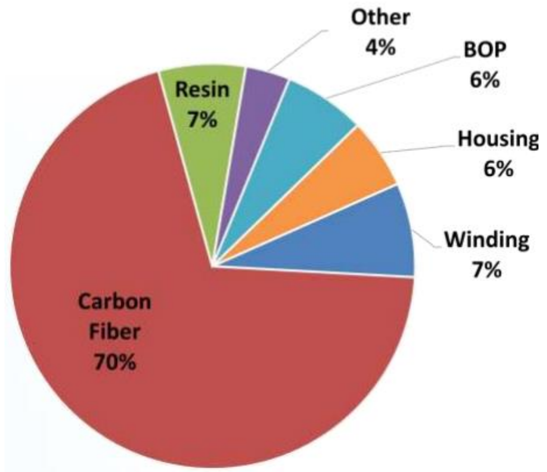
Liquid H_2 tanker Suiso Frontier

Liquefied H_2 tank at Kennedy NASA space center
https://www.energy.gov/sites/default/files/2021-10/doe-perspectives-lh2.pdf

H_2 storage – cost of using contemporary solutions

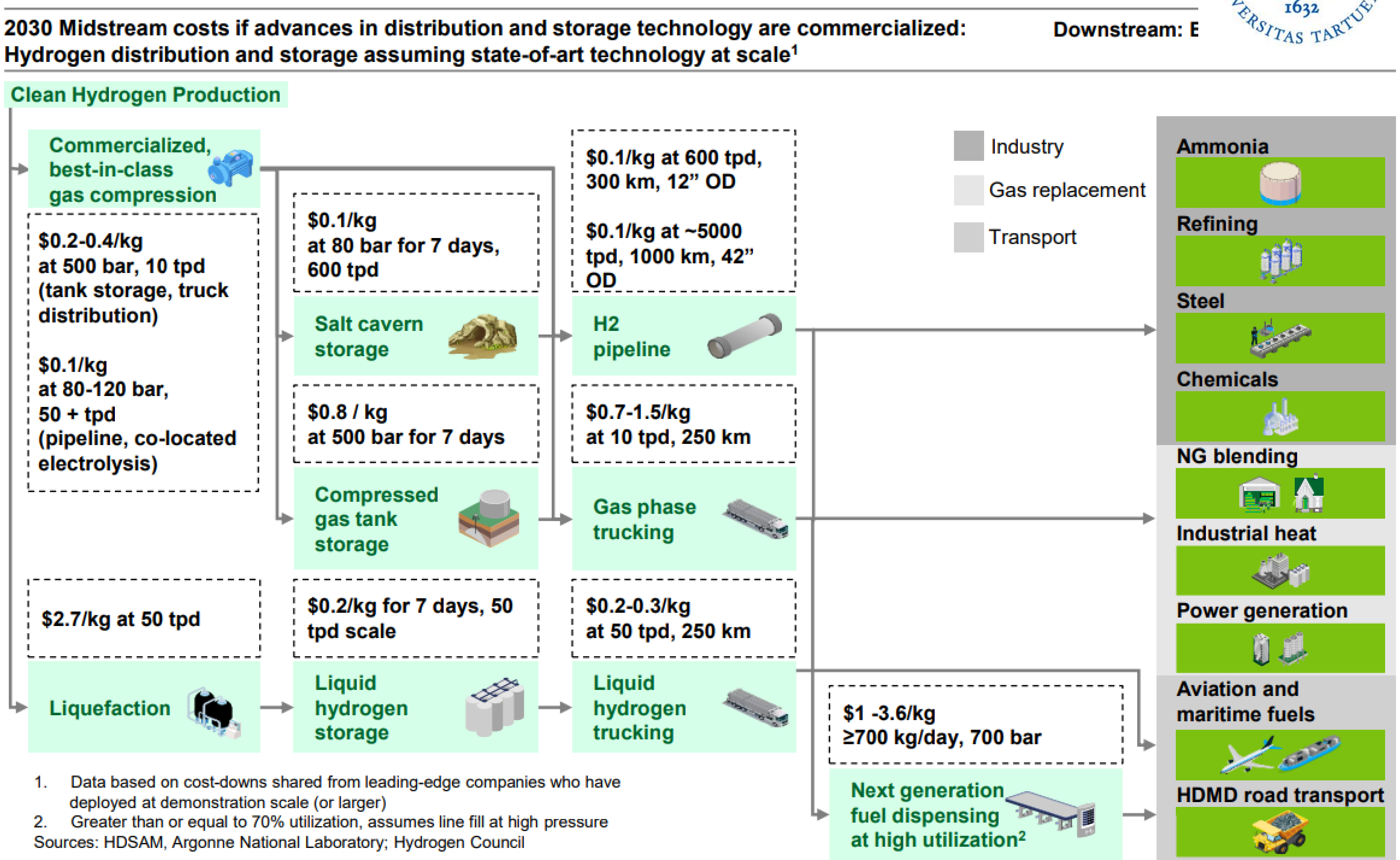
Current H_2 storage situation:

- „Cheap“ solutions are localized
- Mobile solutions with high H_2 density are expensive



Cost breakdown of a Type 4 700 bar H_2 tank

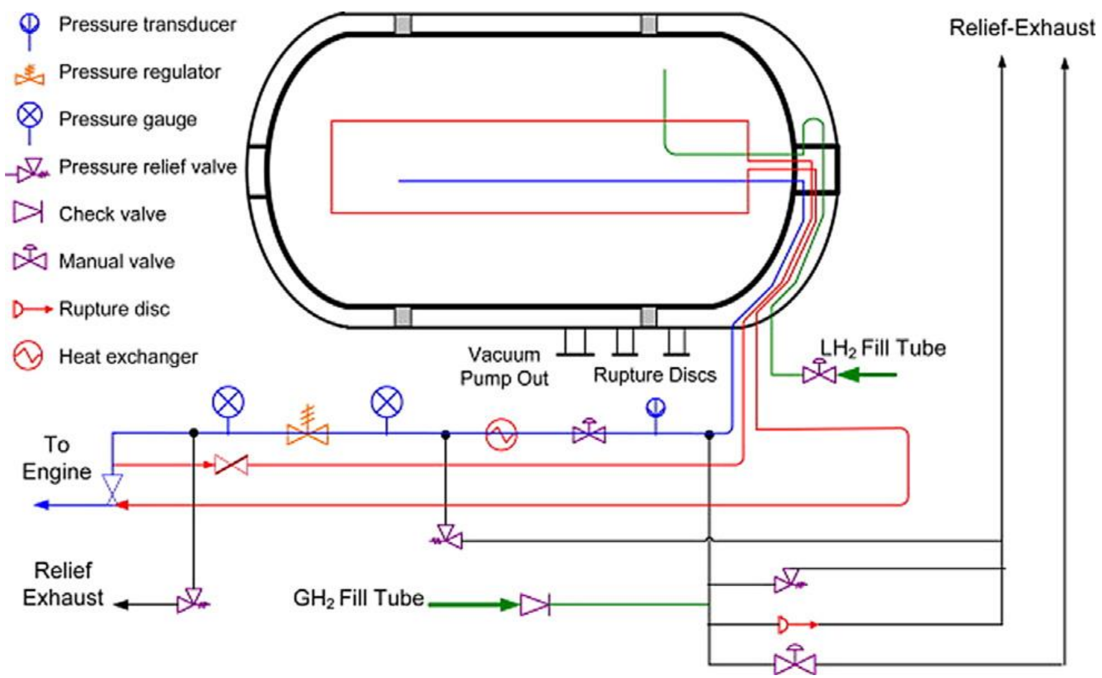
C. Houchins et al., Hydrogen Storage Cost Analysis, 2022



U.S. National Clean Hydrogen Strategy and Roadmap, 2023

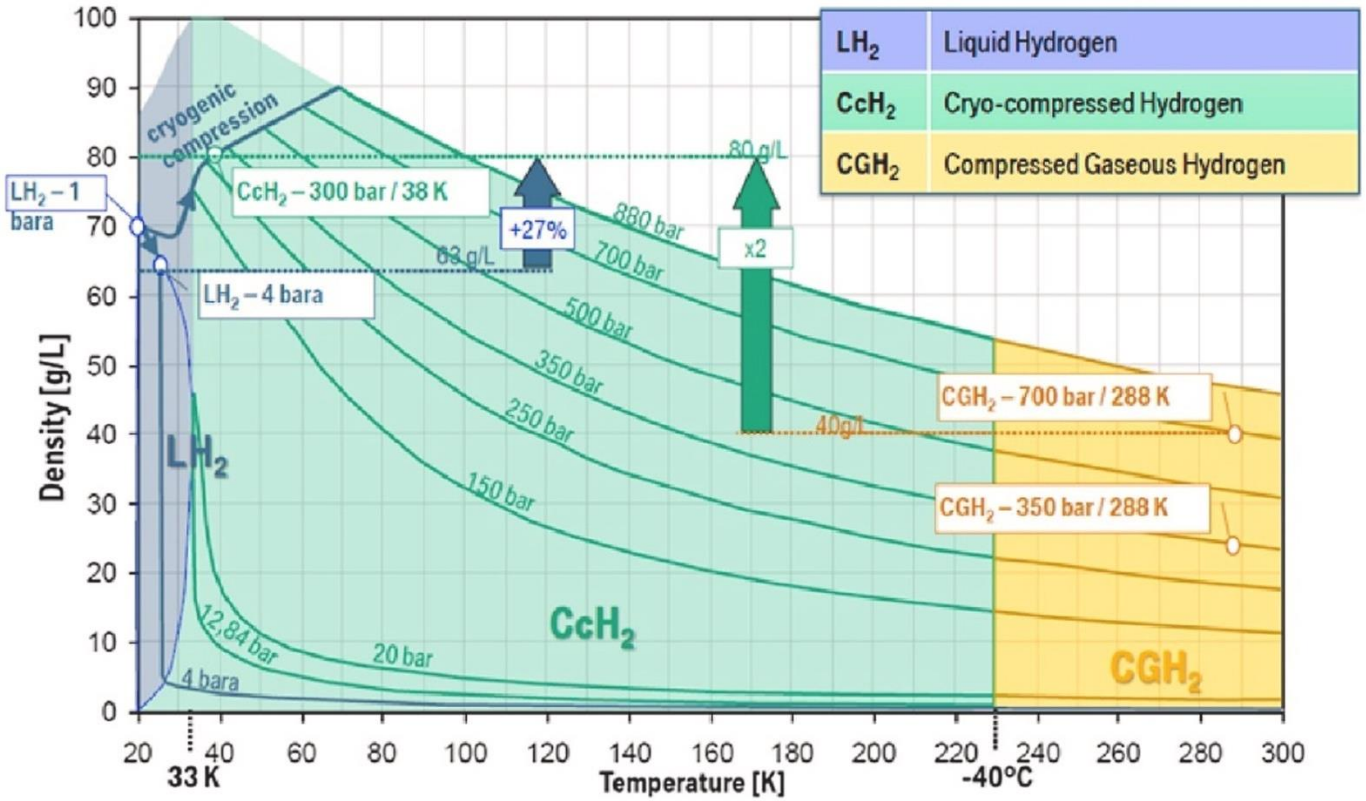
Cryoompression of H_2

- Combination of compression and cooled-down H_2
- Up to 80 g_{H2} L^{-1}
- Needs additional cooling over time or venting



Design schematic of a cryo-compressed H_2 storage system

G. Petitpas et al., Int. J. Hydrogen Energy 39, **2014**, 10564

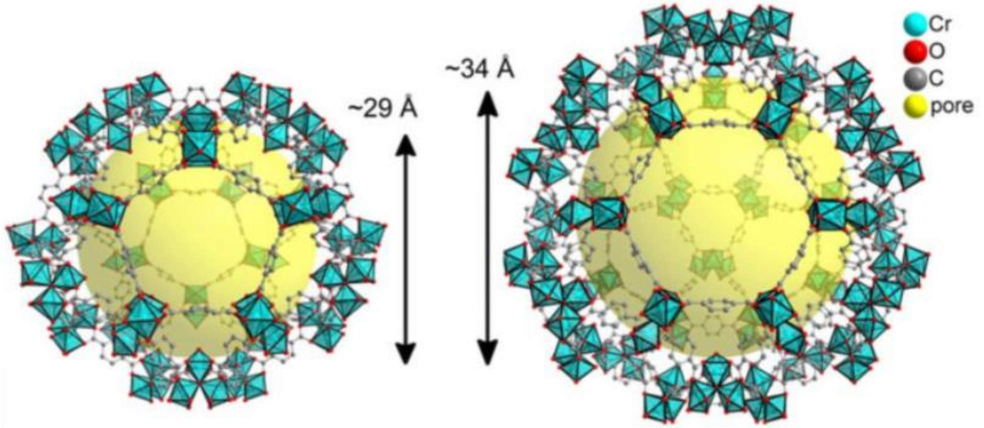


H_2 density vs pressure and temperature and regions corresponding to storage methods with pressure limits claimed by BMW in 2012

T. Zhang et al., Renewable Sustainable Energy Rev. 176, **2023**, 113204

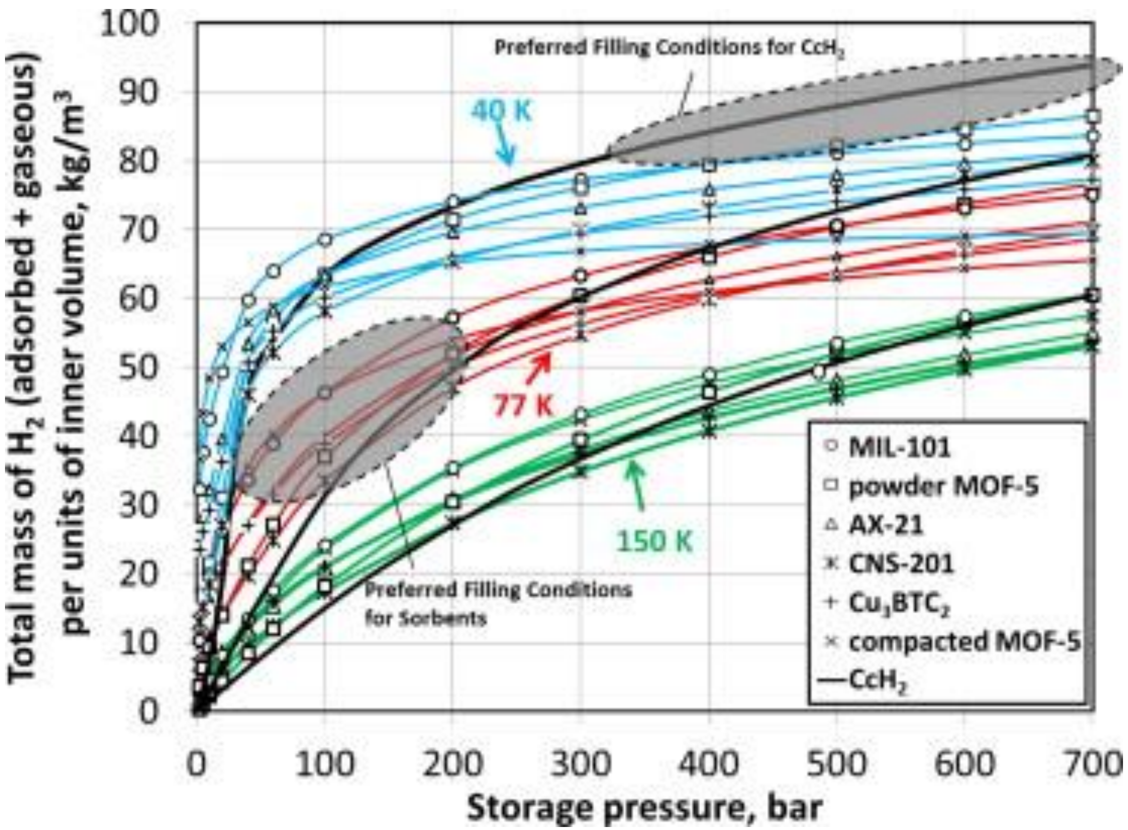
Cryoadsorption of H_2

- Enhanced H_2 density from adsorption inside pores of a solid material
- Effect scales with temperature and pressure, like for compression
- Amount and characteristic of pores of critical importance for H_2 density



Two variety of crystalline structures of MIL-101

M. Zou et al., Int. J. Mol. Sci. 23(16), **2022**, 9396



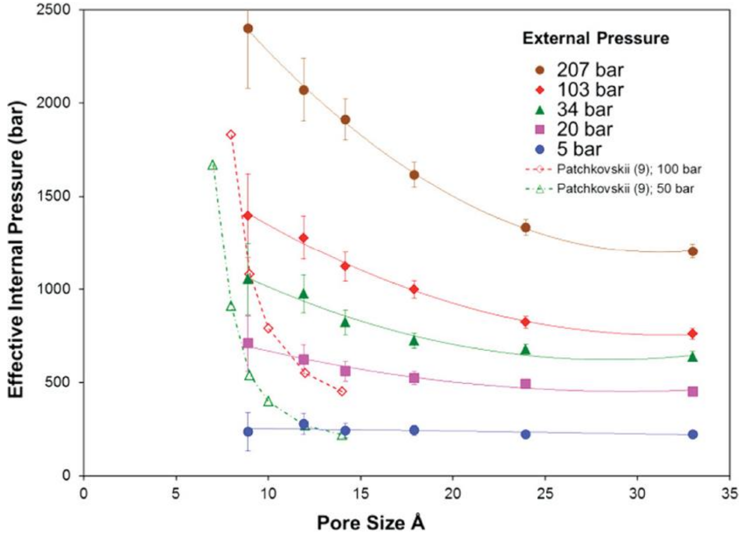
Volumetric H_2 density at different T and p conditions for cryocompression (CcH_2) and –adsorption systems

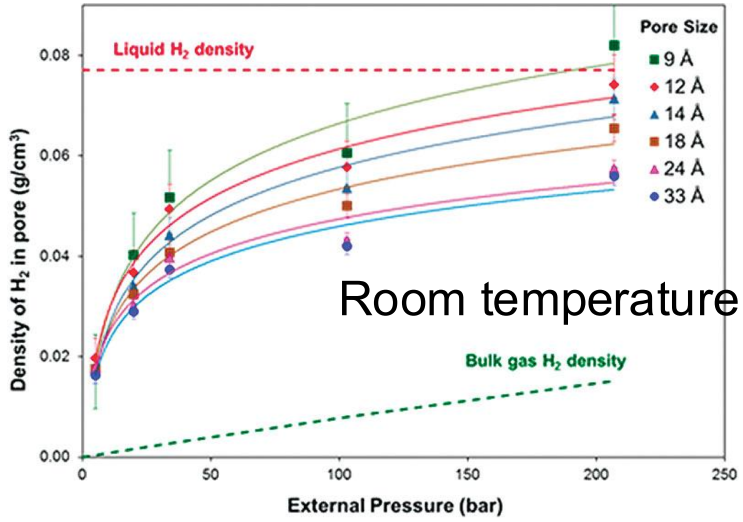
G. Petitpas et al., Int. J. Hydrogen Energy 39(20), **2014**, 10564

Cryoadsorption of H_2

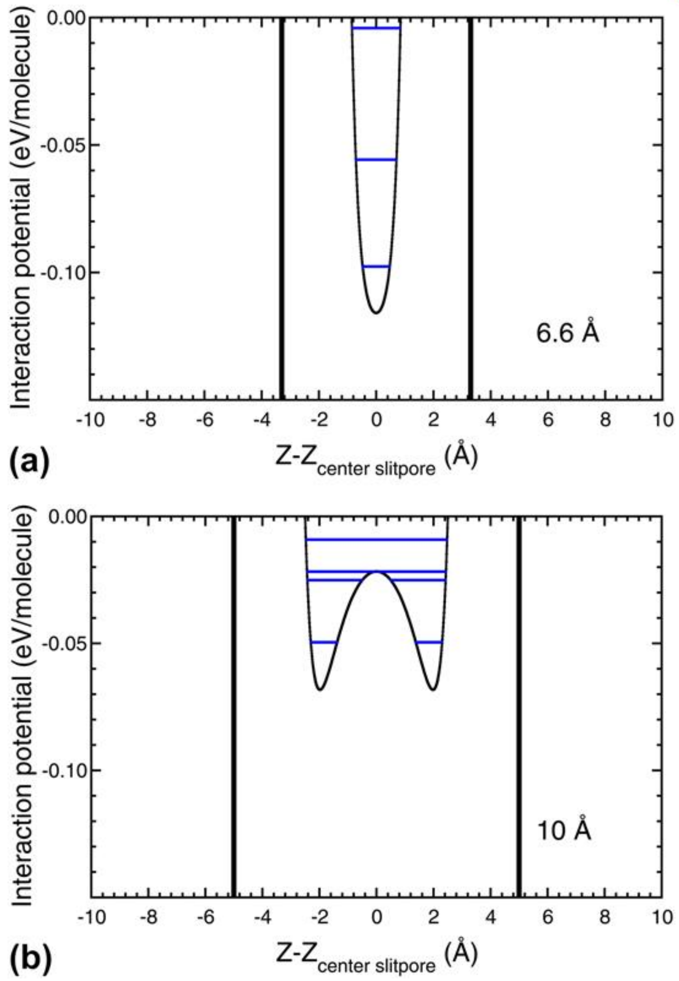
- Pores with optimal size:
  - Confine H_2 effectively
  - Yield high H_2 densities at increased temperatuures

- Densities beyond that of liquid H_2 have been shown at room temperature
- Current limitations:
  - Nonscalable and noneconomic adsorbents
  - Nonuniform optimaal porosity throughout adsorbent





N. C. Gallego et al., J. Am. Chem. Soc. 133, **2011**, 13794



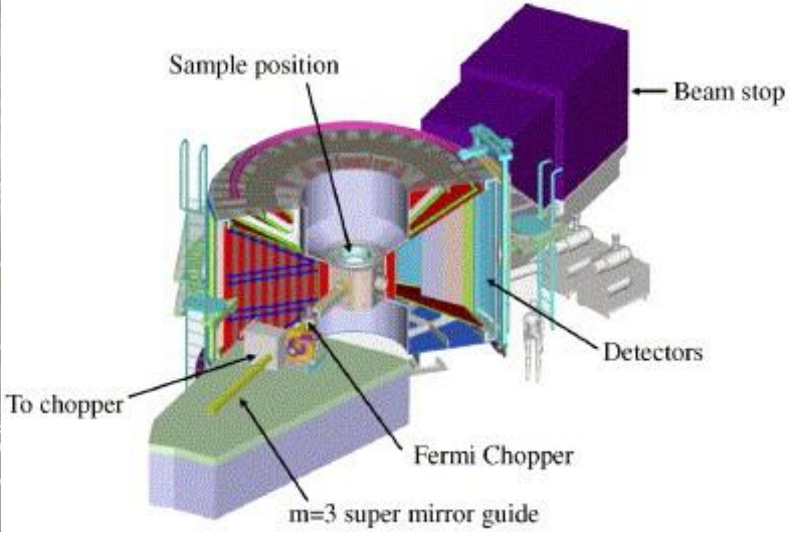
H_2 interaction potential modelled for pores with different widths

I. Cabria et al., Int. J. Hydrogen Energy 36(17), **2011**, 10748

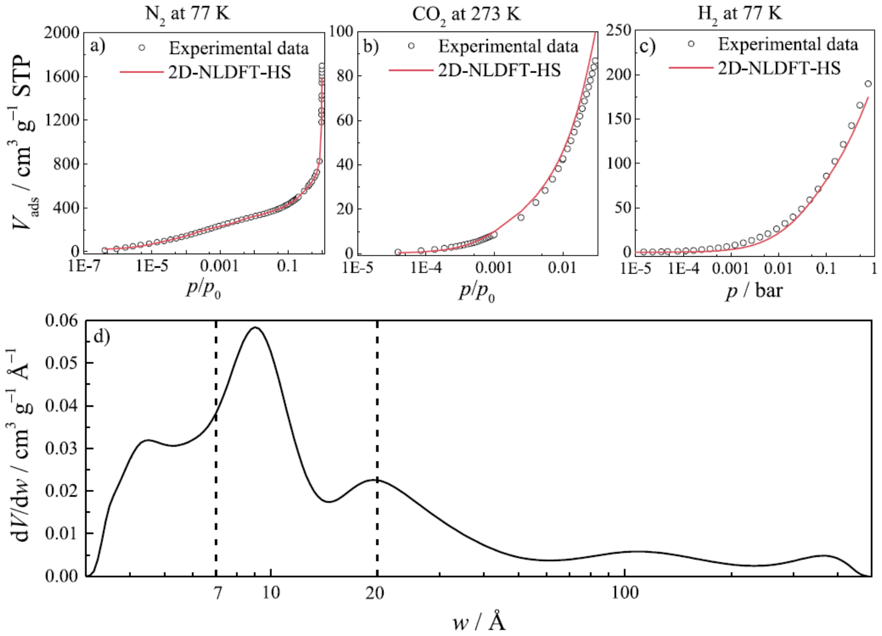
Looking for the solution

- Fundamental investigation of H_2 dynamics in different porous structure
  - Labsale and neutron scattering methods for full charaterisation

ISIS Neutron and Muon Source, UK



Merlin neutron spectrometer at ISIS



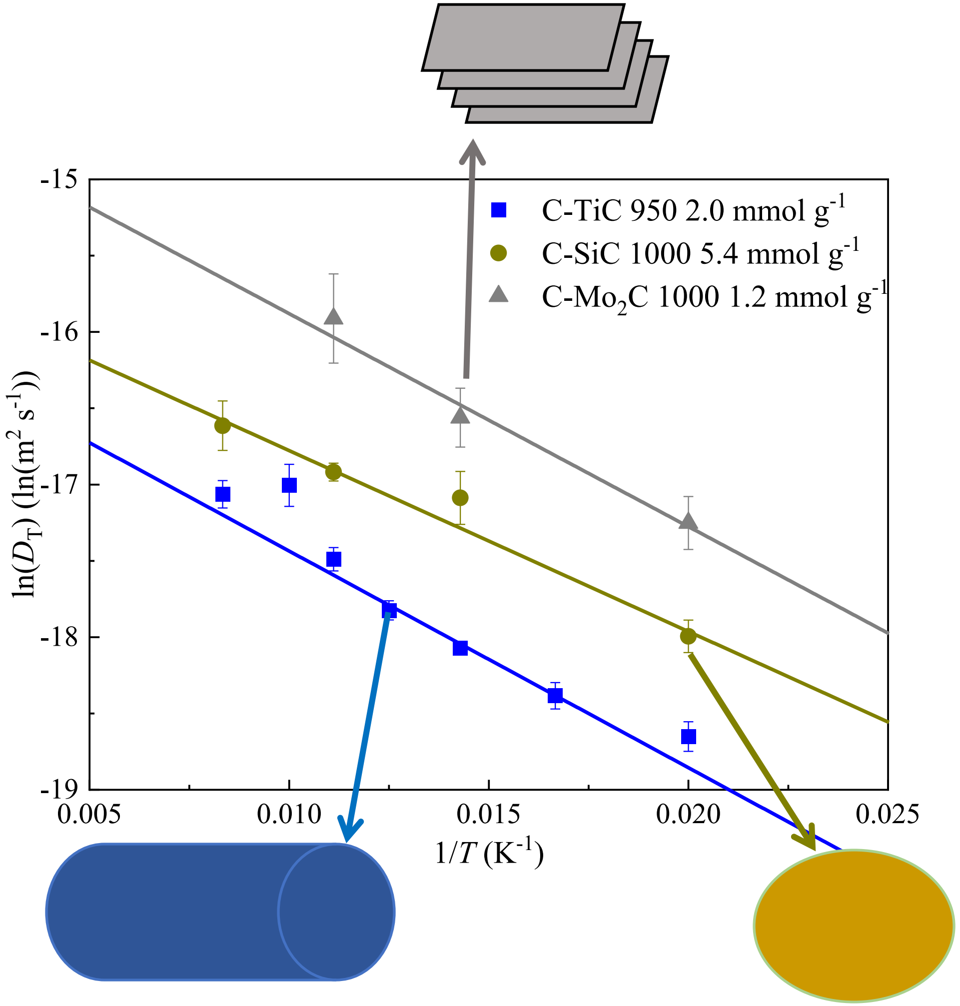
Combined modelling of three gas adsorption isotherms

M. Koppel, et al., Carbon 219, **2024**, 118799

- Development of synthesis processes:
  - Use of sustainable carbon sources
  - Optimization of synthesis routines for optimal porosity

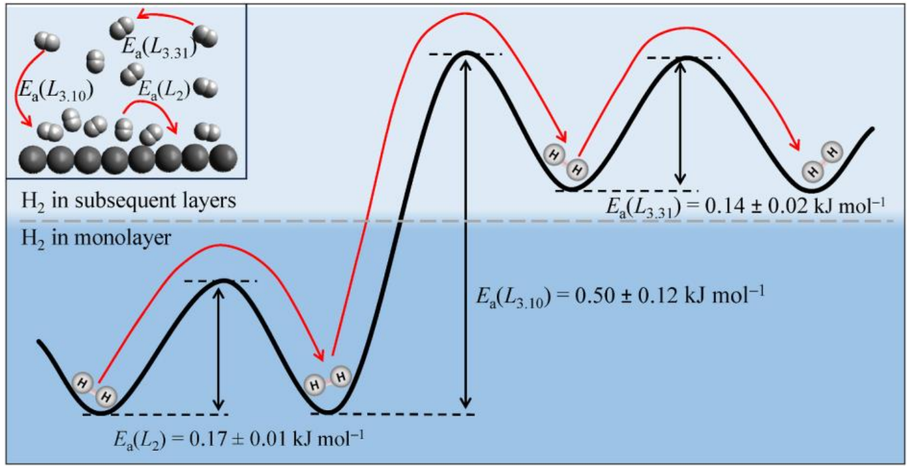
Different pores effect on H_2 confinement

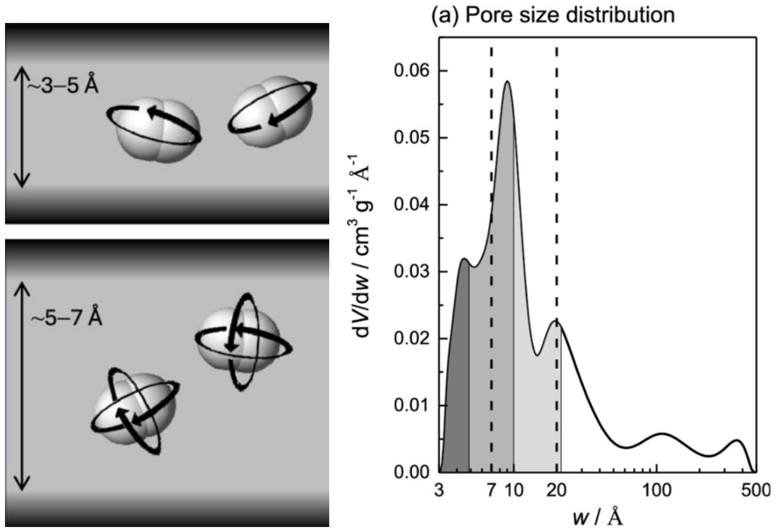
Effect of pore geometry on H_2 confinement



R. Härmas, et al., Carbon 155, **2019**, 122

H_2 mobility in between adsorption layers

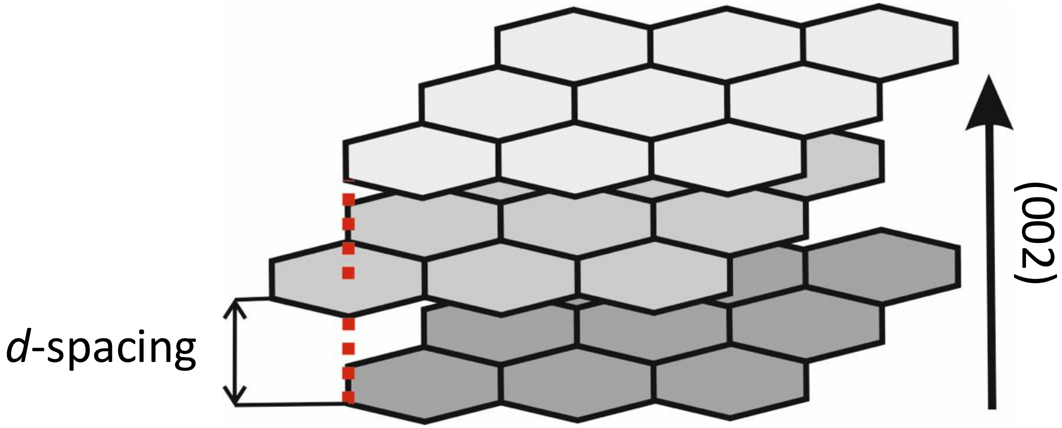


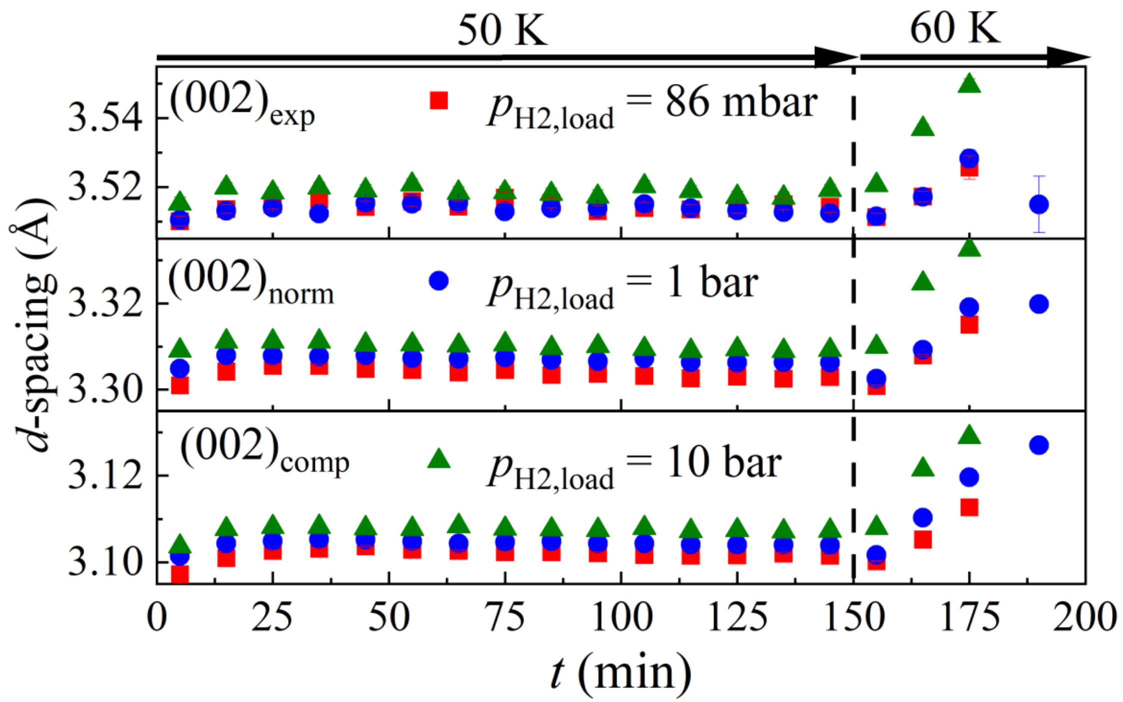


M. Koppel, et al., Carbon 219, **2024**, 118799
M. Koppel, et al., J. Phys. Chem. C 129, **2025**, 4789

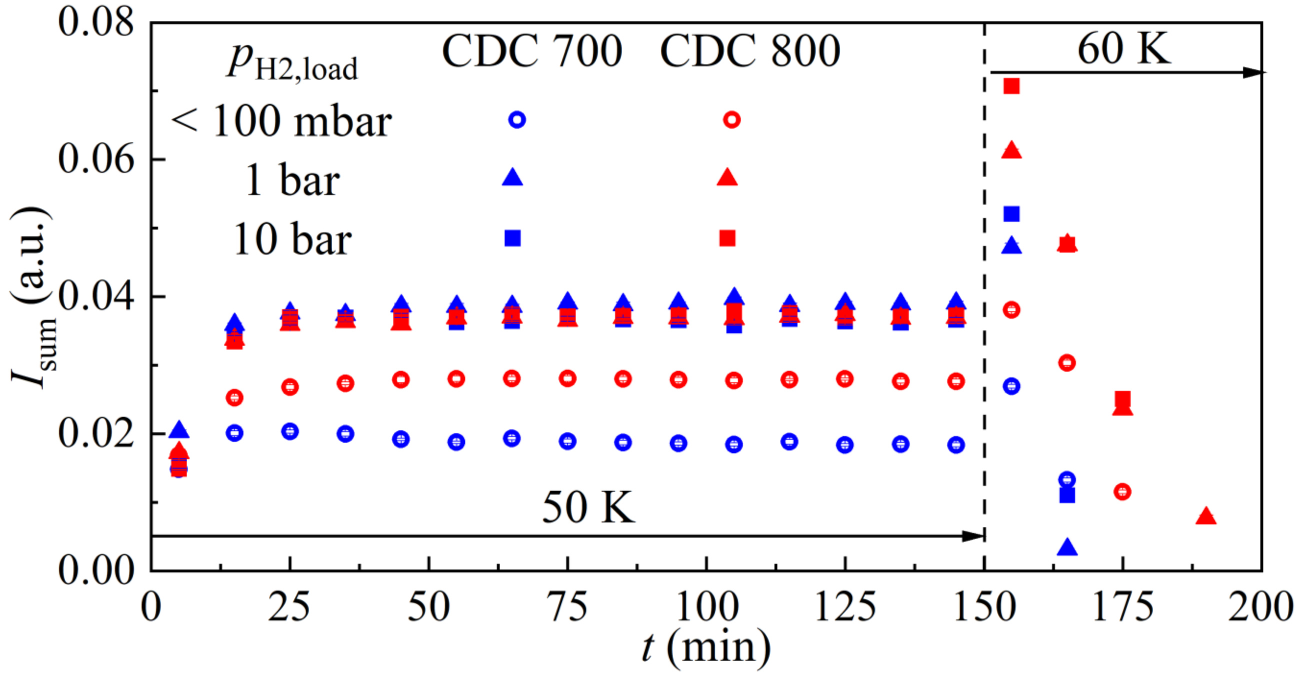
Effect of strong H_2 confinement on adsorbent

- The graphenic carbon structure orders:
  - At 50 K and under H_2 loading
  - Original graphenic structure restored at 60 K
  - Formed structure possible through internal H_2 pressure





d-spacing of the three Bragg peaks Under H_2 loading



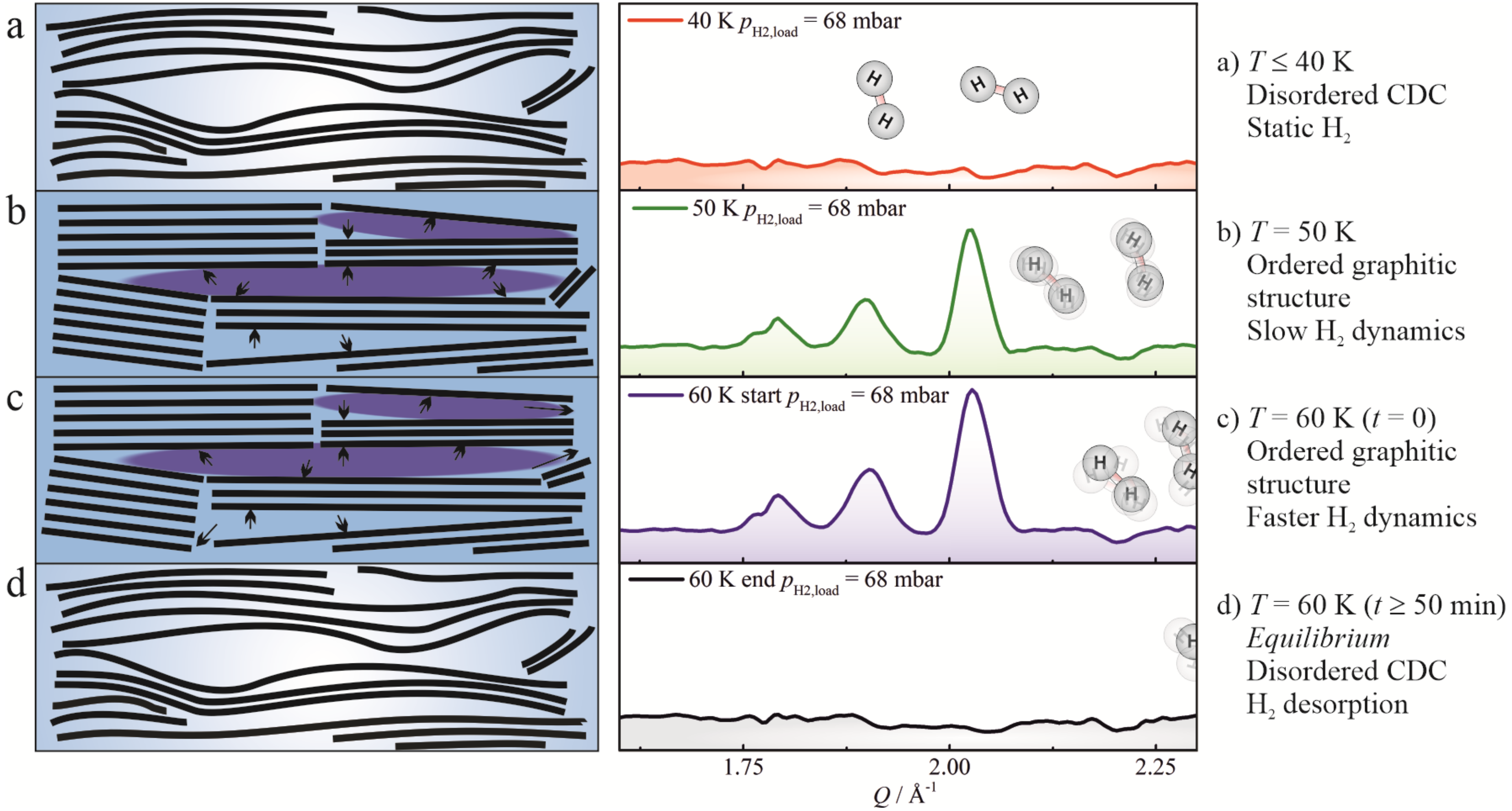
Summed up integrated intensities of the three Bragg peaks

M. Koppel, et al., Carbon 174, **2021**, 190

Effect of strong H_2 confinement on adsorbent

Reversible structural changes of adsorbent under H_2 loading:

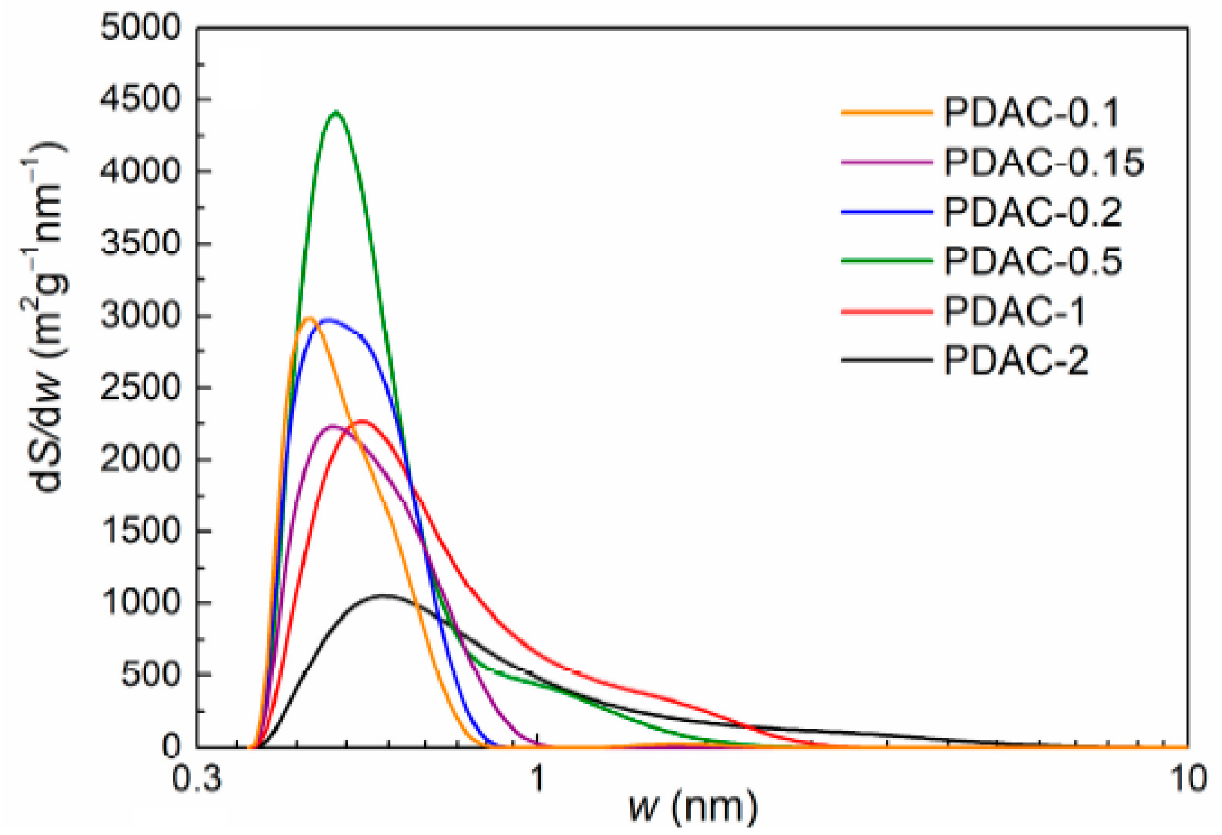
- High density adsorbed H_2 phase at 20 K
- Kinetically limited desorption upon heating
- H_2 confined in ultramicropores causes internal pressure
- Upon further heating, additional internal pressure causes H_2 release and restoration of original structure



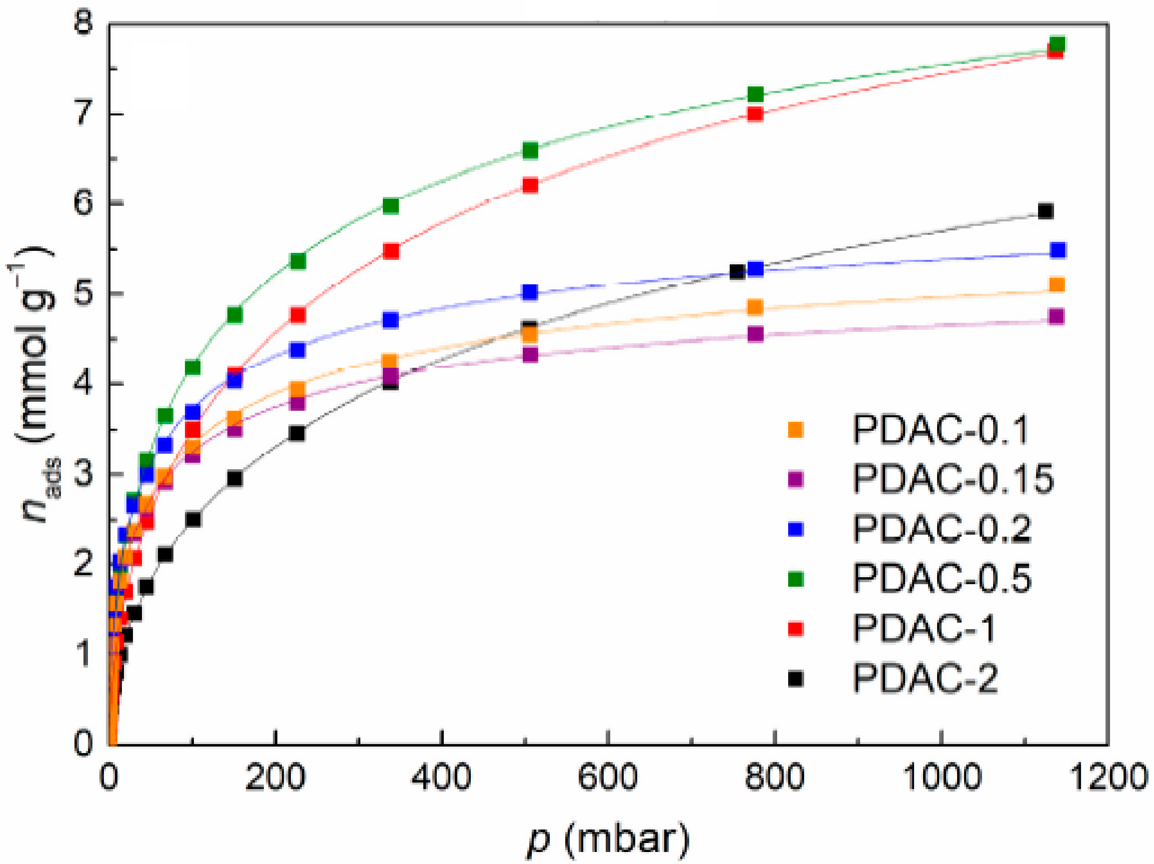
M. Koppel, et al., Carbon 174, **2021**, 190

Synthesis of carbon-based H_2 adsorbents

- Dominantly ultramicroporous carbons
- Ultramicroporous carbons achieve surface fillment at lower pressure



Pore size distributions by specific surface area



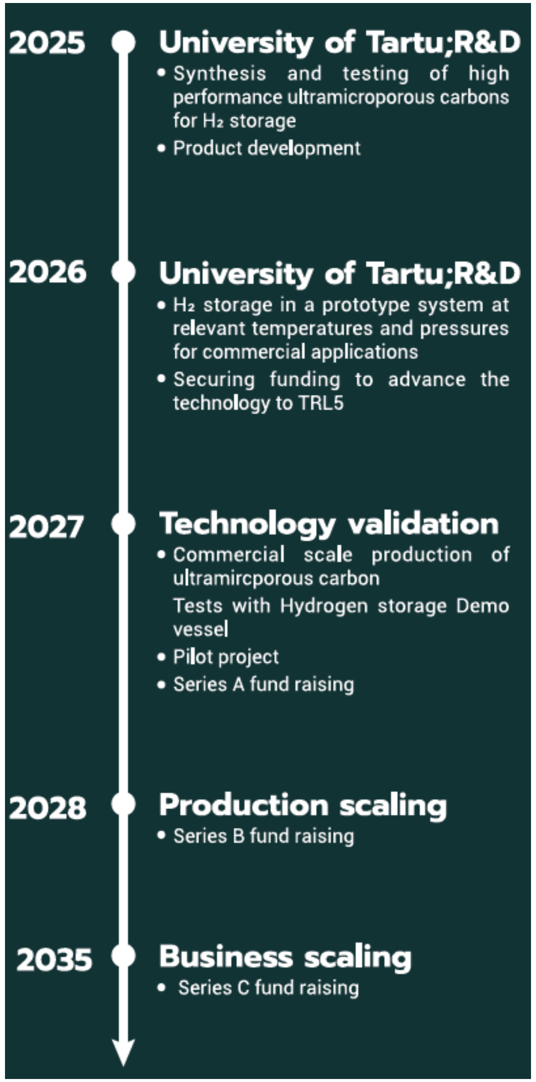
H_2 adsorption isotherms obtained at 77 K

E. Möller, et al., Nanomaterials 13, **2023**, 2883

Making ideas into reality

- Collaboration between Estanc AS and University of Tartu towards developing cryoadsorption based H_2 storage solutions
- Sub-enterprise H2Adsorb formed under Estanc AS for commercialization
- Goal of achieving H_2 storage density equivalent to 350 bar pressurization at:
  - 40 bar and -80 °C
- Lowered pressurization and tank requirements thank to ultramicroporous adosrbent
- Sustainable carbon-based adsorbents

https://h2adsorb.eu/



Prototype H_2 storage system by Renee Kauler, Christen Haamer, and Sander Kahk

Thank you for listening!

Would not be possible without wonderful collaborations

UNIVERSITY OF TARTU
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