Hydrogen molecular sieves for marine decarbonisation

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1 Need for Sustainable Marine Fuels

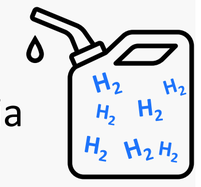
International Maritime Organisation greenhouse gas strategy *checkpoints* to achieve net-zero GHG emissions from *international shipping* by 2050 [1]:

- Reduce total annual GHG emissions by 20-30% from 2008 to **2030**
- Reduce total annual GHG emissions by 70-80% from 2008 to **2040**

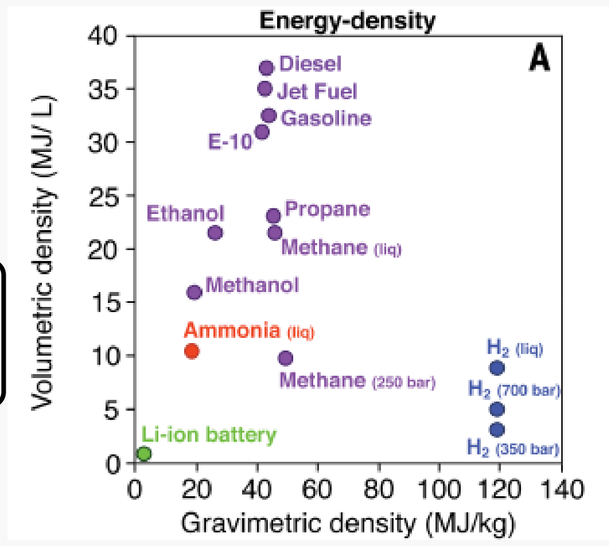
Need to implement uptake of near-zero GHG emission fuels e.g. low and zero-carbon renewable fuels, such as hydrogen, green ammonia, green methanol

2 Hydrogen as a Sustainable Fuel

- **High gravimetric density** which is almost 3x that of traditional fuels
- **Green hydrogen** is producible via electrolysis of water!



- Burns cleanly, **producing H_2O** (not GHG)



Volumetric density against gravimetric density for a range of fuels [2]

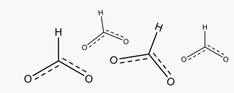
Low volumetric density means hydrogen is not yet a viable fuel
- More research is required to ensure a better storage solution

3 Storage solution – Metal-Organic Frameworks (MOFs)

- MOFs are built from **metal ions or clusters** and **organic linkers**
- They have a large porous structure with high surface areas
- MOFs are attractive material for **gas separation and storage**!

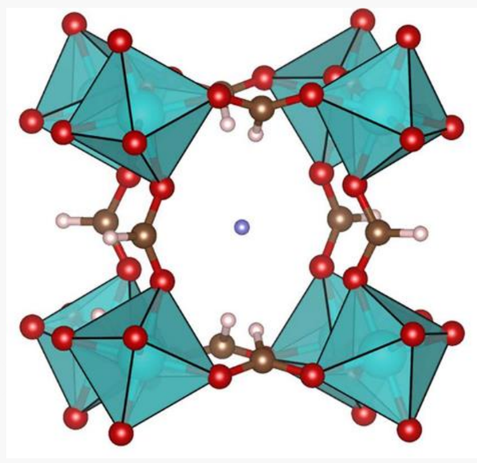
[3]	MOF type 1	MOF type 2	MOF type 3
Representative MOFs	MOF-5, HKUST-1, UiO-67, ZIF-8, MIL-100, etc	Ni2(m-dobdc), V-btdd	**ALF**
Target operation condition	77K, 5-200 bar	Near ambient temperatures (**298K** and 100 bar: Ni MOF: ~11.9 g/L, V MOF: ~10.7 g/L)	Sub-ambient and low pressure (120K, **25 bar**: ~15 g/L)
Main desirable nature of MOFs	High **surface area**	**Open metal sites**	**Small pores** and uses economical raw materials
Current status	Abundant experiments and models available	Moderate experiments and models available	Limited experiments and models

4 ALF MOF structure [4]



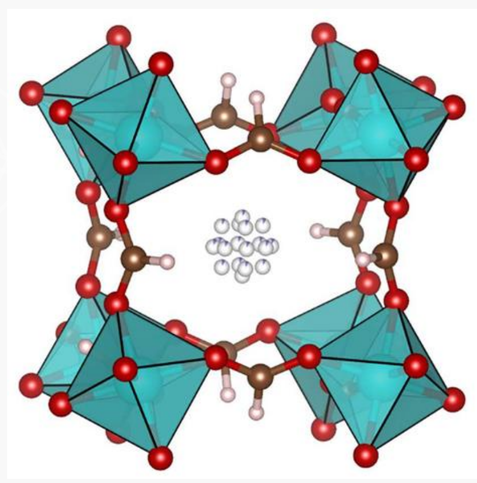
- ALF consists of Al metal nodes and formate linkers to create a microporous framework containing 2 crystallographically distinct cavities.

Small pore structure



The small pore:
- Hydrogen populates centre of cavity
  - 4 out of 12 formate hydrogens face inward
- Pore volume ~43 Å^3 at 300K
- DFT calculated heat of adsorption of H_2: 11.66kJ/ mol

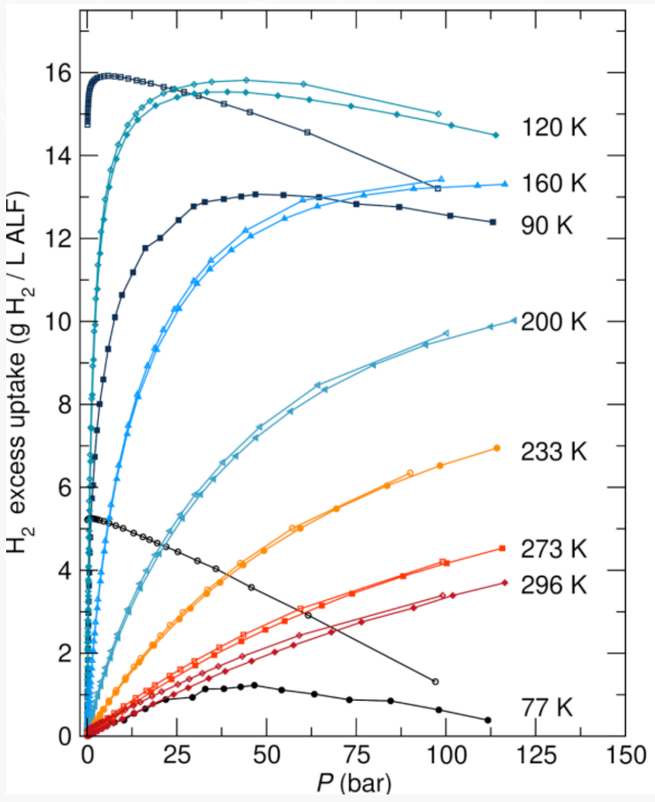
Large pore structure



The large pore:
- Hydrogen populates cavity walls
  - No inward facing formate hydrogens
- Pore volume ~79 Å^3 at 300K
- DFT calculated heat of adsorption of H_2: 12.54kJ/ mol

5 ALF MOF qualities and hydrogen storage capability [4]

- Shows best adsorption of hydrogen (~15g of H_2/ L ALF) around **120K and ~25 bar**
  Lower energetic cost compared to traditional cryogenic (77K) or compressed gas storage (up to 700 bar)!
- ALF can withstand pelletisation
- ALF is produced using abundant and cheap material, making the production cost as cheap as ~$2/kg
- Utilises non-toxic, inexpensive and abundant (8.3% of earth's crust) aluminium as its metal node [5]



Excess H_2 gas adsorption/desorption isotherm measurements on ALF between 120 K and 296 K.
Closed symbols = adsorption,
Open symbols = desorption.

6 Conclusions and future work

- The ALF MOF has shown promise toward low pressure hydrogen storage
- This could mitigate the necessity for high pressure on-board storage
- The optimum heat of adsorption for hydrogen is 15-25 kJ/mol. [4] ALF shows lower heats of adsorption (~12 kJ/mol) therefore, modification of ALF may lead to reaching this optimum.

References
[1] 2023 IMO STRATEGY ON REDUCTION OF GHG EMISSIONS FROM SHIPS, **2023,** Annex 15
[2] S. J. Davies et al., Science, **2018**, 360, 6396
[3] P. Peng et al., ACS Energy Lett. **2024**, 9, 6, 2727–2735
[4] H. A. Evans et al., J. Am. Chem. Soc., **2023**, 145, 40, 22150–22157
[5] W. Fan et al., Coordination Chemistry Reviews, **2023**, 489, 215175

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