PIM-MOF Composites for Use in Hybrid High Pressure Hydrogen Storage Tanks

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Introduction

- Hydrogen has been proposed as a potential long term sustainable energy storage solution, particularly in light duty vehicles.
- The current industrial state of the art in hydrogen storage for vehicles is compression [1]. However this technology presents some major issues :
  - Relies on pressures as high as 70 MPa to store enough hydrogen for a 500 km range [1].
  - Uses very expensive materials to achieve the lightness and pressure resistance required.
  - Fails to meet the U.S. DoE's On-board Hydrogen Storage Goals [2].

***Figure 1**: 70 MPa hydrogen tank used in the Toyota Mirai fuel cell vehicle [3]*

- One of the routes to hydrogen storage that is being pursued is storage by adsorption, which uses nanoporous materials to physically bond hydrogen, so increasing the volumetric density.
- The aim of this project is to determine whether a composite material of the well known adsorbents PIM-1 and MOF-5 is feasible, and if so, if a hybrid tank featuring this material as a liner could provide a benefit over current hydrogen storage solutions.

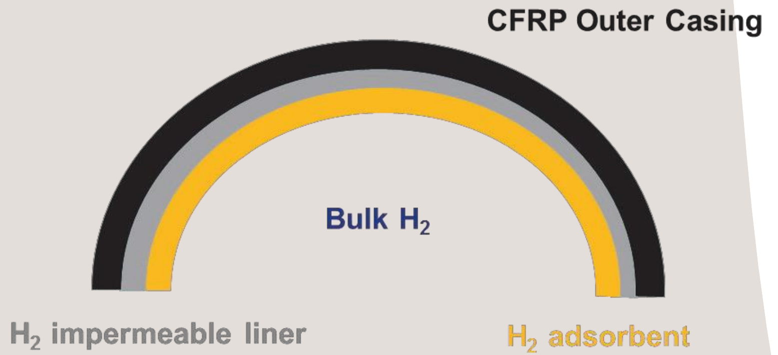

***Figure 2**: Schematic of a hybrid high pressure tank featuring an adsorbent liner*

Metal Organic Framework (MOF-5)

- MOF-5 is composed of ZnO_4 clusters attached by 1,4-benzenedicarboxylate linkers.
- Has isoreticular topology (alternatively known as IRMOF-1).
- Industrial interest from Ford, General Motors, BASF [4].
- Rouquerol BET surface area of 3508 ± 129 $m^2\ g^{-1}$ (N_2 isotherm at 77 K).

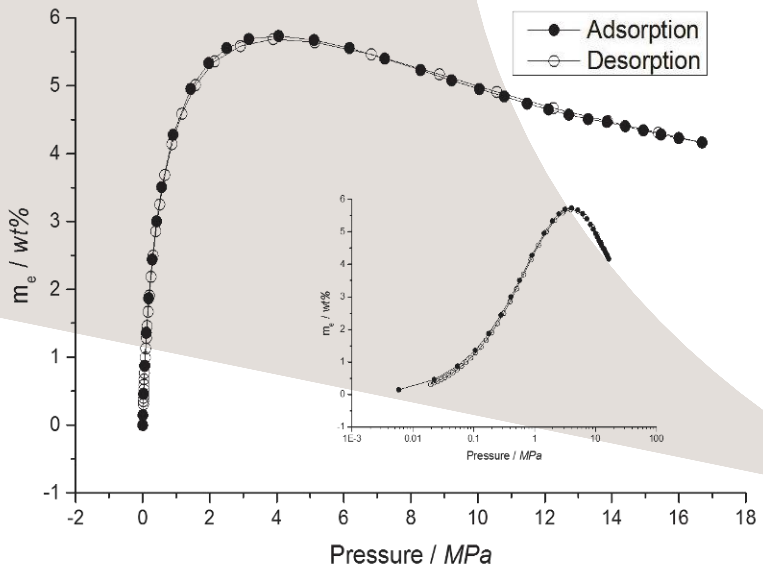

***Figure 3**: Hydrogen adsorption isotherm at 77 K for MOF-5*

- Highly microporous pore size distribution; Horvath-Kawazoe (HK) model gives a modal pore size of 0.9 nm.

Polymer of Intrinsic Microporosity (PIM-1)

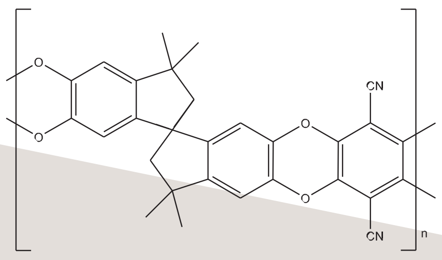

***Figure 4**: Chemical structure of PIM-1*

PIM-1 Powder

- Bright yellow powder is soluble in polar aprotic solvents (e.g. chloroform, THF).
- Initially synthesised using the optimised method of Song et al. [5], although this resulted in a material that formed brittle, cracked films (M_n = 9765 g mol^{-1}, PDI = 2.66).
- Synthesis using the original method of Budd et al. [6] resulted in a better quality PIM (M_n = 76261 g mol^{-1}, PDI = 2.53).
- TGA under N_2 flow determines thermal stability up to ~ 430 °C.
- Helium pycnometry gives skeletal density of 1.24 g cm^{-3}.
- Rouquerol BET surface area = 621.2 ± 3.0 $m^2\ g^{-1}$ (N_2 isotherm at 77 K).
- Pore size distribution reveals more than half the pore volume is microporous (HK total pore volume = 0.463 $cm^3\ g^{-1}$).

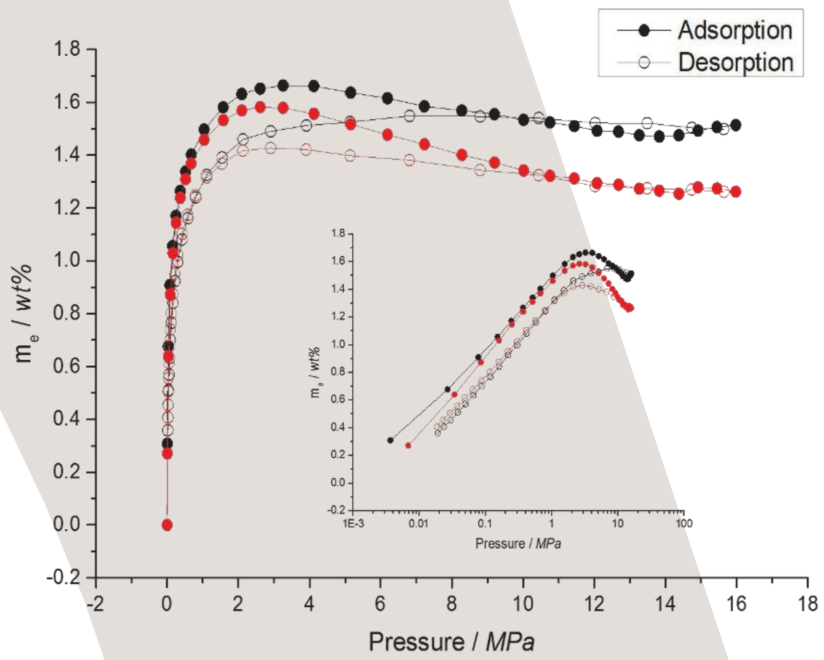

***Figure 5**: High Pressure (160 bar) Hydrogen adsorption isotherms at 77 K for PIM-1 powder (black) and PIM-1 film (red)*

PIM-1 Film

- Synthesised through solvent casting of PIM-1 in chloroform.
- Rouquerol BET surface area of 330.9 ± 5.2 $m^2\ g^{-1}$ (CO_2 isotherm at 273 K).
- Microporous analysis with N_2 difficult due to mass transfer limitations (slow equilibration).

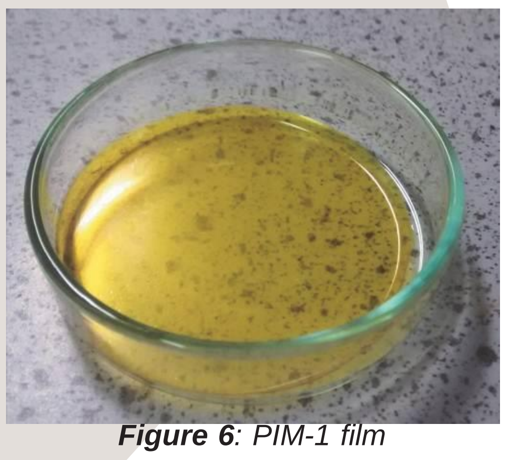

***Figure 6**: PIM-1 film*

Future Work

- Synthesis of PIM-1/MOF-5 composite (in progress).
- Continued analysis of adsorbent properties of materials, including fitting to a model developed at the University of Bath to determine parameters such as adsorbate density and pore volume.
- Analysis of mechanical (tensile and flexural moduli), thermal (specific heat capacity, thermal conductivity) and binding properties of materials.
- Develop 'rule of mixtures'-style correlations between composite content and properties.
- Design of hybrid hydrogen storage tank with a composite liner.

References

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