High performance MOF/polymer composite membranes for carbon dioxide capture

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Economics of CO$_2$ Capture With Membranes

Merkel, Lin, Wei, Baker (J. Membrane Sci. 2010) process modeling

Analysis based on 600MW coal-fired power plant and sequestration-ready CO$_2$ at 140 bar Designs based on > 95% purity in delivered CO$_2$

- Single stage membrane processes not feasible
- 2-stage processes are feasible
- 2-step countercurrent sweep process gave 16% parasitic power, $23/ton capture cost
- Membrane area of 1.3 million m$^2$ for a membrane with CO$_2$ permeance of 1000 GPU and CO$_2$/N$_2$ selectivity of 50.
- Increasing permeance of membranes is more critical than selectivity as long as selectivity larger than ~30-40.

Requirements for practical membrane based solution
1. Must be highly scalable $\rightarrow$ base on polymeric hollow fibers
2. Must be robust under real conditions (water, SOx, NOx)
3. Cost per unit membrane area must be reasonable
Core Concept: MOF-polymer composite hollow fiber membranes

Zeolite/Ultem composite membranes (Koros, Jones, Nair et al., JACS 2009)
Crystalline, nanoporous materials with high surface area and “designable” pore topology and functionality

4000+ distinct crystal structures are known

Much attention has focused on “large pore” materials that will not be useful in our application.

Challenge #1: How do we rationally screen a large number of MOFs to find candidates that are well suited for CO$_2$/N$_2$ membranes?
Challenge #2: How do we establish the robustness/stability of MOFs?
Challenge #3: How do we synthesize MOFs in the nanoparticle form required for thin film membrane applications?
Challenge #4: How do we incorporate MOF particles into hollow fibers during fiber spinning?
## Project Outline

### Computational modeling (Program Element 1)
- Predicted CO₂/N₂ membrane selectivity > 30?
  - No → No-Go

### Experiments (powders) (Program Element 2)
- Stable to extended water vapor exposure?
  - No → No-Go
- Suitable gas adsorption from humid gases?
  - No → No-Go

### Experiments (polymer films) (Program Element 3)
- Synthesize sub-micron particles?
  - No → No-Go
- High permeability + acceptable selectivity?
  - No → No-Go

### Experiments (hollow fibers) (Program Element 4)
- Fabricate high quality hollow fiber membranes?
  - No → No-Go
- High permeance + acceptable selectivity with humid feeds?
  - No → No-Go

### Number of MOFs
- >10³
- 25-50
- 10-25
- 10-15
- 10-12
- ~5
- 3-4

### Values
- >10³
- 10³
- 10²
- ~10¹
- ~10⁰
- 3-4
Pore structure of MOFs are examined by fitting spheres of different sizes

- Largest sphere that can fit = Largest cavity diameter (LCD)
- Collection of spheres filling the pore forms a spanning cluster
- Largest sphere that doesn’t break the spanning cluster = Pore limiting diameter (PLD)

E. Haldoupis, S. Nair, and D.S. Sholl, JACS (2010) 132, 7526
• ~1000 metal-organic structures analyzed (out of ~30,000 compounds from CSD)
• Range of interest contains 128 structures (contains 25 compounds reported 1999)
  → **103 structures** left for further analysis
We have developed syntheses that generate size controlled MOF nanoparticles.

ZIFs are known to be highly stable in water (e.g. stable in boiling water).

Cuhfb is highly hydrophobic, and is synthesized in aqueous solution.
Our team has extensive experience with fabrication of composite membranes in cast films and hollow fibers.


Applications & Capabilities

This new system will allow us to expand production and our current capabilities. Greater flexibility will promote further exploration of fiber materials.

Applications:
1. Asymmetric Hollow Fiber Membranes
2. Hollow Fiber Sorbents
3. Hollow Fiber Substrates
4. Solid Core Fibers
5. Pseudo-Melt Spun Fibers

Capabilities:
1. Improved quench and rinse bath temperature control with heat exchangers (HE). [0°C < T < 80°C]
2. Greater air gap flexibility for improved skin formation and draw ratio optimization
3. High temperature delivery pumps for high viscosity solutions and pseudo-melt spinning
4. Rinse and re-wetting sprayers to promote defect-free skin layer formation
5. Deeper quench bath will enhance phase separation rates
6. Variable take-up drum sizes will allow for the production of longer fibers – pilot-scale implications
7. Solvent exchange station will allow user to keep delicate materials straight during the solvent exchange process. Also has applications for carbon membrane precursor materials.