High performance MOF/polymer composite membranes for carbon dioxide capture

Postdocs: Taku Watanabe, Yougui Huang, Ying Dai, Sangil Han; *Undergrads*: Chris Kim, CW Wang, Madison Barre, Stella Kinnaird, Megan DeWitt, Victor Manrique
Profs. David Sholl, Krista Walton, Christopher Jones, Sankar Nair, Carson Meredith, & William Koros
School of Chemical & Biomolecular Engineering, Georgia Institute of Technology

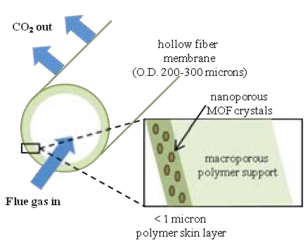
Acknowledgement: This work is supported by the ARPA-E IMPACCT Program.

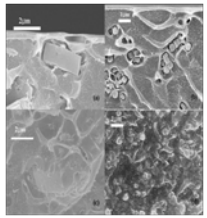
Economics of CO_2 capture with membranes

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.

Core concept: MOF-polymer composite hollow fiber membranes

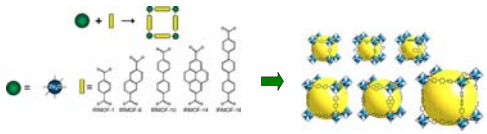




Zeolite/Ultem composite membranes (Koros, Jones, Nair et al., JACS 2009)

Metal-organic frameworks (MOFs)

Crystalline, nanoporous materials with high surface area and "designable" pore topology and functionality

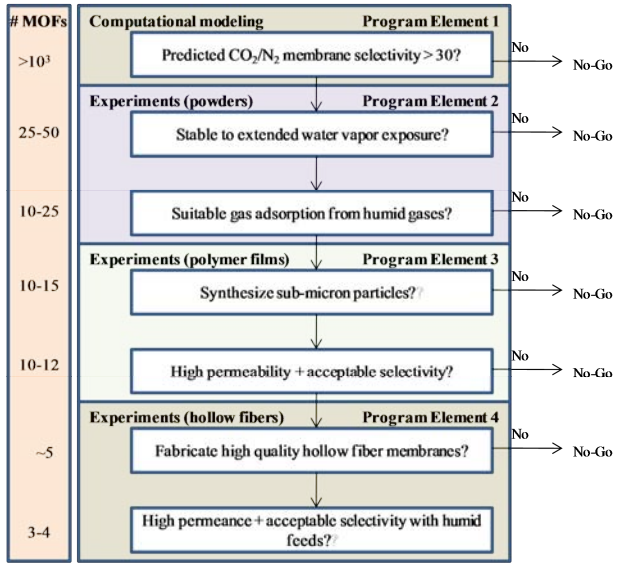


4000+ distinct crystal structures are known

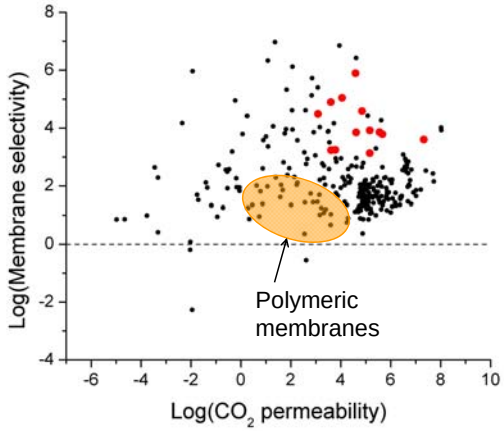
M. Eddaoudi, *et al.*, *Proc. Nat. Acad. Sci.* **2002**, *99*, 4900.; O.M. Yaghi, *et al.*, *Nature* **2003**, *423*, 705.; H.M. El-Kadari, *et al.*, *Science* **2007**, *316*, 268.

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



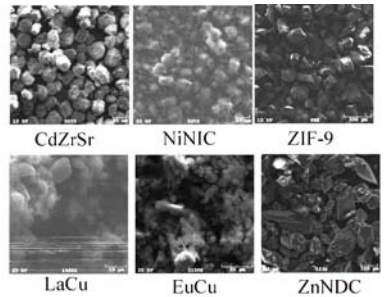
Computational Screening



- >30,000 MOFs screened by pore analysis → 378 MOFs examined by detailed molecular simulations
- A number of MOFs predicted to exceed the performance of polymeric membranes.
- ~20 MOFs suggested for experimental evaluation.

MOF nanoparticles

- We have developed syntheses that generate size-controlled particles (0.2-300 μm) of candidate MOFs

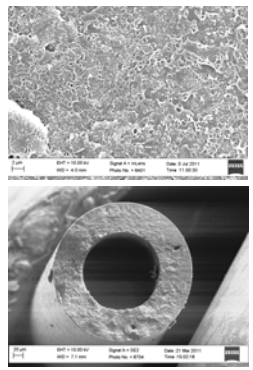


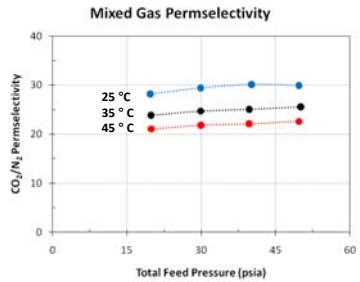
High-Throughput parallel screening of MOFs

	CO_2 (mmol/g)	S. D. (%)	N_2 (mmol/g)	S. D. (%)	Selectivity		$P_{equilibrium}$ (psi)		S x D
					Sorption	Diffusion	CO_2	N_2	
ZIF-90	0.28	1.3	0.08	6.3	9.9	2.3	3.8	10.7	22.6
ZIF-8	0.22	6.3	0.07	3.7	9.4	1.6	3.6	10.8	14.9
ZIF-7	0.24	4.6	0.05	4.3	12.3	2.2	4.7	12	26.8
Conic	0.24	3.8	0.04	3.3	17.2	9	4.3	12.3	154.5
Ni-HF	0.2	7.5	0.04	1.9	9.3	3.6	6.8	12.7	34.1
Zn/Co-BTEC	0.14	11.7	0.04	0.7	5.4	3.8	7.9	12.3	20.4
Zn-TTC	0.19	10.2	0.05	3.9	7.5	3.6	5.9	11.7	26.3
Cu-PCN	0.27	10.3	0.086	2.9	14.7	5.7	2.2	10.2	83.4

- A high-throughput screening device constructed in-house allows the identification of promising MOFs via gas sorption, gas diffusion, and $H_2O/SO_x/NO_x$ stability measurements.

MOF/Polymer films and Hollow fibers





- Promising candidate MOFs like ZIF-8 have successfully been incorporated into polymeric films and hollow fiber membranes, which show favorable separation properties.