# Hollow Fiber-Supported Designer Ionic Liquid Sponges for Post-combustion $CO_2$ Scrubbing


**Jong Suk Lee[a]**
**William J. Koros[a,‡]**
**Patrick C. Hillesheim[b]**
**Sheng Dai[b,‡]**



July 11, 2012
NETL $CO_2$ Capture Technology Meeting



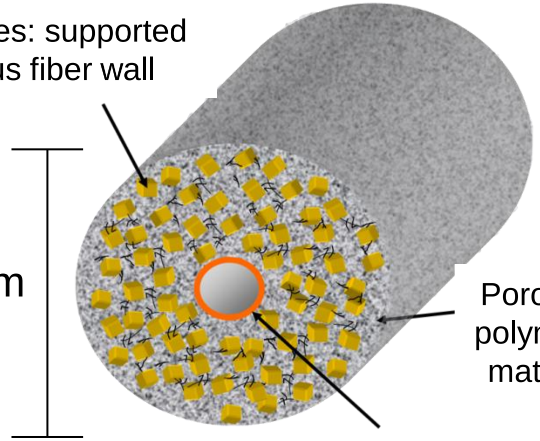
a; Georgia Institute of Technology
b; Oak Ridge National Laboratory

# Overview

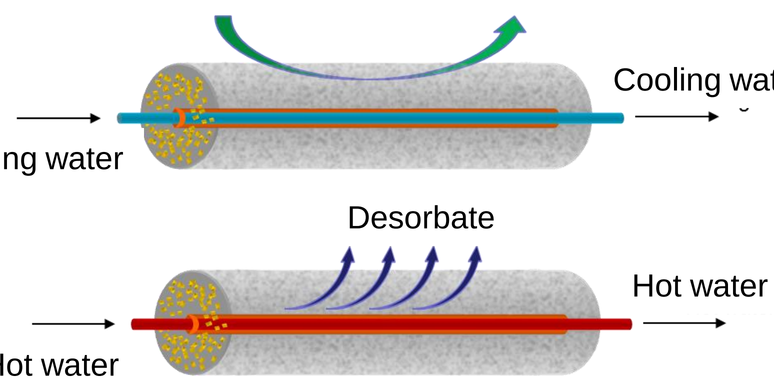
**Goal: To develop ionic liquid hollow fiber sorbents for post-combustion $CO_2$ capture.**

- Oak Ridge National Laboratory (Dai Group)
  - Increase efficiency of $CO_2$ capture via molecular design of alcohol-functionalized ionic liquids (ILs).
  - Develop next generation task-specific ionic liquids (TSILs) with $CO_2$ binding bases attached.
- Georgia Institute of Technology (Koros Group)
  - Integrate TSILs into high surface-to-volume hollow fiber modules.
- Sci-Tec
  - Evaluate feasibility of large scale synthesis, cost analysis, and future implementation of binary IL/superbase systems.

# Background – Hollow Fiber Sorbents




Schematic of hollow fiber sorbents
(Ind. Eng. Chem. Res. 2009)

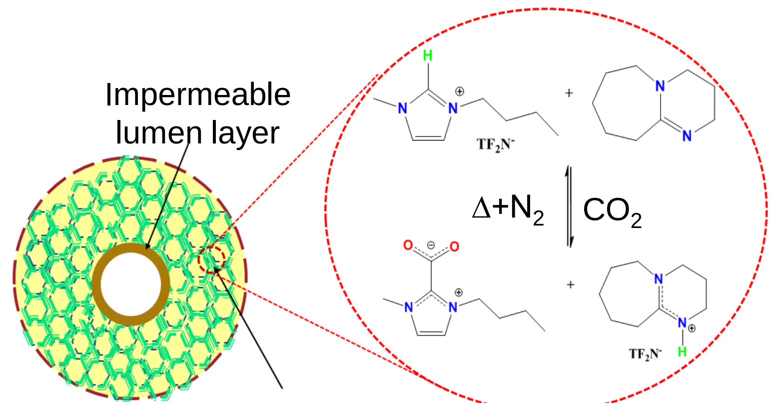



Rapid Temperature Swing Adsorption Process

## Advantage of Hollow Fiber Sorbents

Hollow fiber configuration with impermeable barrier layers creates "adsorbing heat exchangers," enabling many options not available to pellets or monoliths

## Next generation hollow fiber sorbents



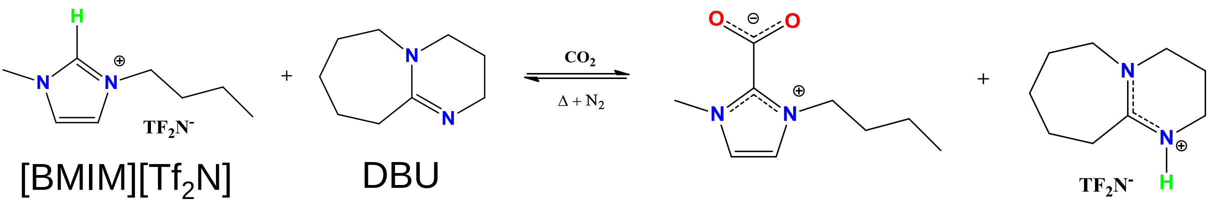

Ionic liquid & super base imbibed into CELL WALLS of pores in fiber wall (<1 µm)

*Key concept: Imbibe ionic liquid and superbase into highly interconnected CELL WALLS of open porous network for rapid kinetics and high sorption uptake*.

(Lee et al. Polymer 53 2012)

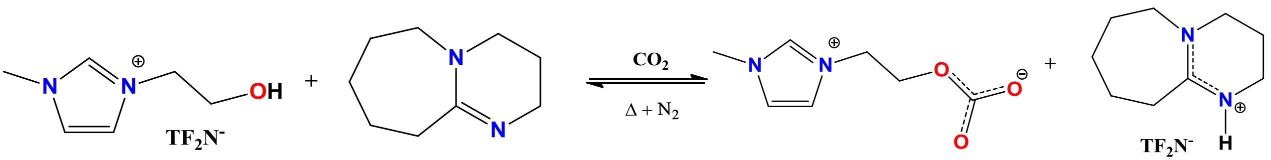
# Integrated Ionic Liquid-Superbase for $CO_2$ Capture

1. $CO_2$ binding via deprotonation of acidic proton in C2

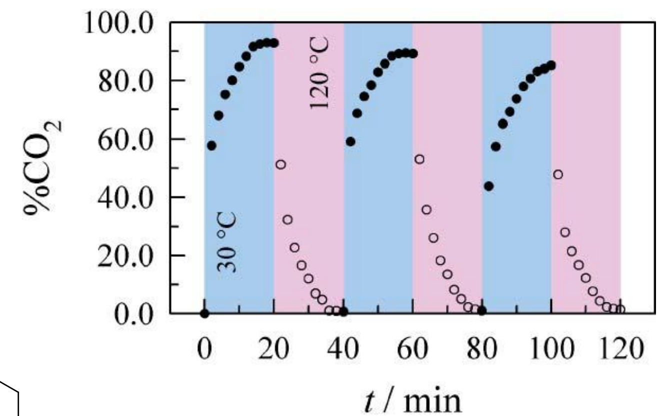



[BMIM][$Tf_2N$] DBU

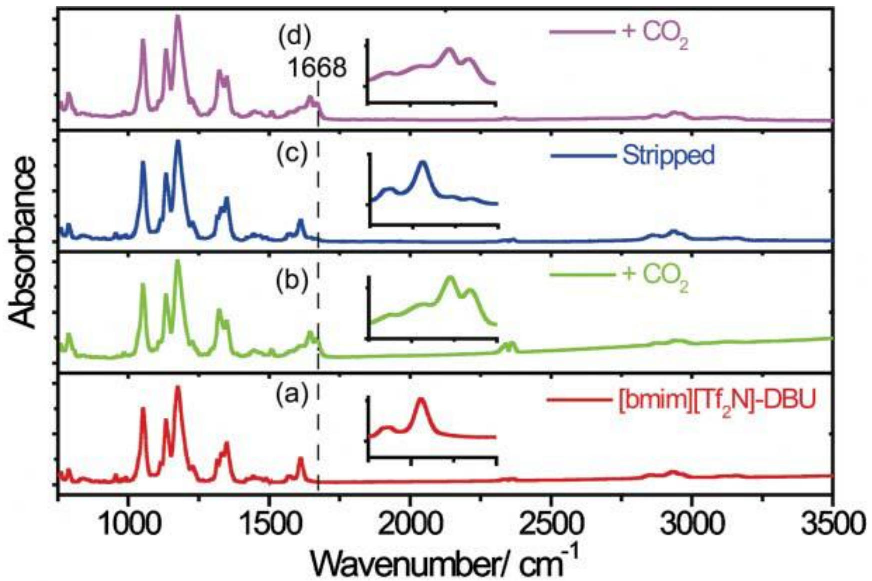
2. $CO_2$ binding via deprotonation of hydroxyl group




[$Im_{21}$OH][$Tf_2N$] DBU



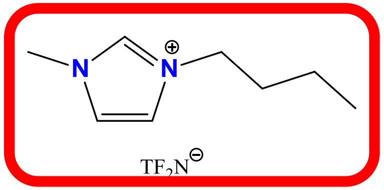

Long term stability of [$Im_{21}$OH][$Tf_2N$]-DBU



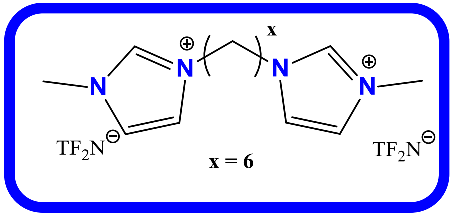

- Reversible binding of 1 mol of $CO_2$ per mol of IL-Superbase
- Equimolar capture of $CO_2$ in 8-12 minutes
- Thermally and chemically stable binding platform

(Wang et al. Green Chemistry 12 2010)

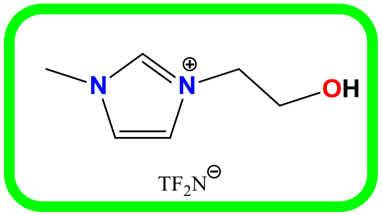
# Development of Ionic Liquid Sorbents



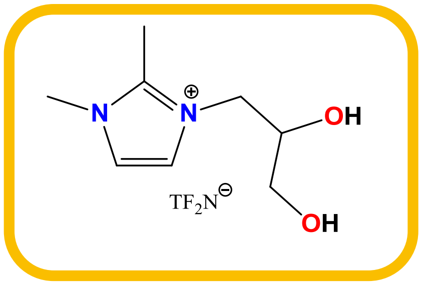

[BMIM][$Tf_2N$]



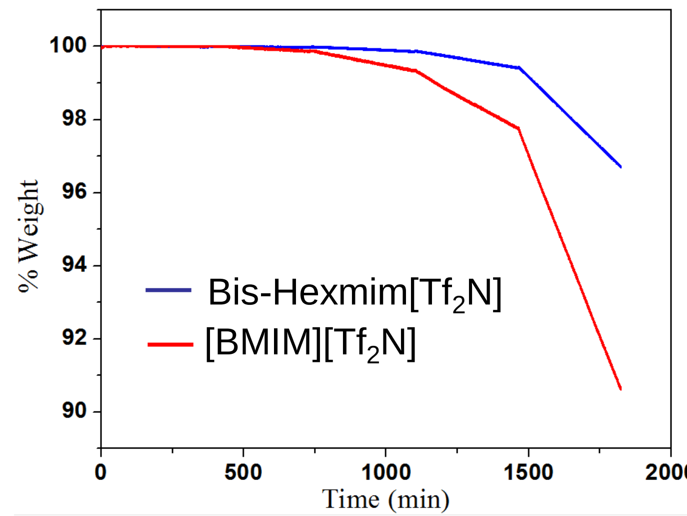

Bis-Hexmim[$Tf_2N$]



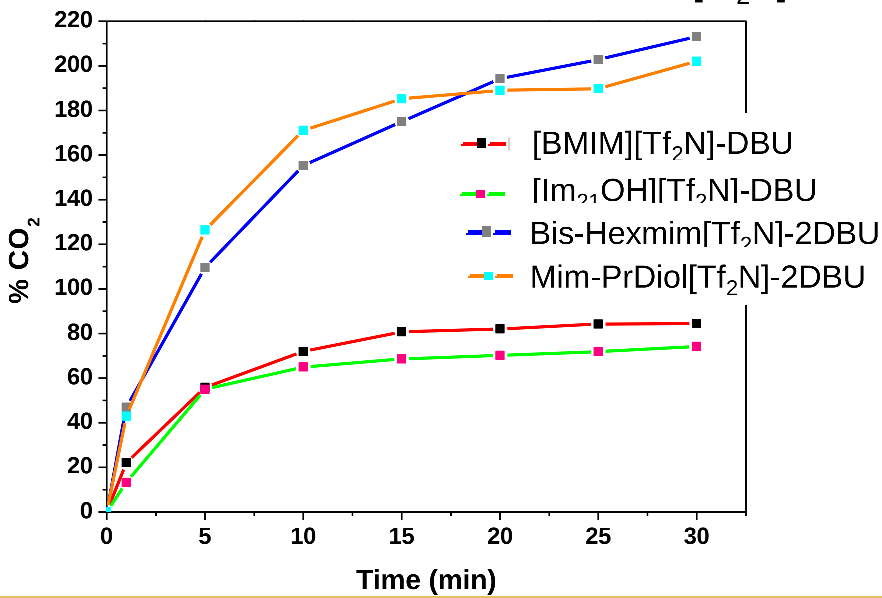

[$Im_{21}OH$][$Tf_2N$]




Mim-PrDiol[$Tf_2N$]




Thermal stability of ionic liquids

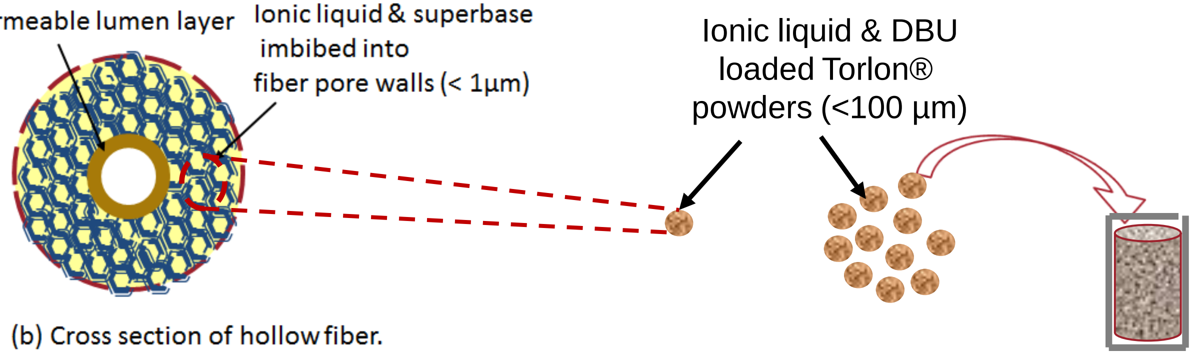



- ❑ Increase in long-term thermal stability for temperatures up to 250 °C
- ❑ Improved kinetics
- ❑ Increased maximum $CO_2$ capacity (~9 wt%)

Working capacity; $$wt\% \equiv \frac{M_{\text{sorbed CO2}}}{M_{\text{sorbed CO2}} + M_{\text{sorbents}}} \times 100\%$$

# Benefits of Ionic Liquid/Superbase Containing Polymer Sorbents

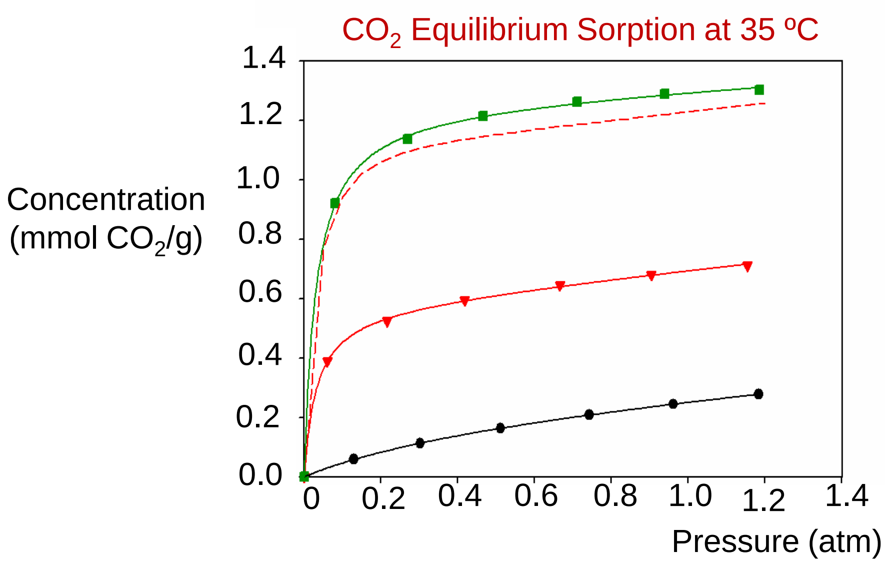

(a) A film layer formed in absorption column. Substantial diffusion resistance.

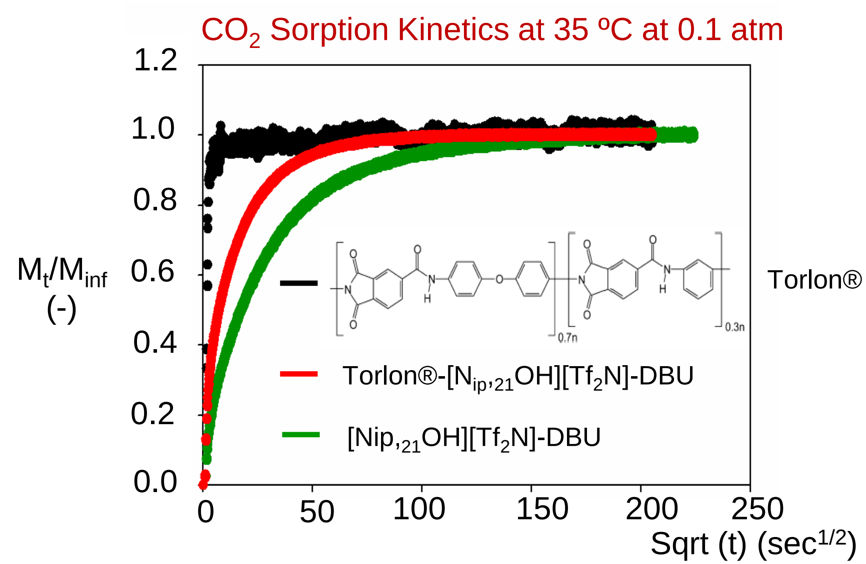



(b) Cross section of hollow fiber. Very rapid kinetics.

0.5 μm filter element powder holder

**Fine sized Torlon® powders simulate thin pore walls typically formed in fiber supports!**

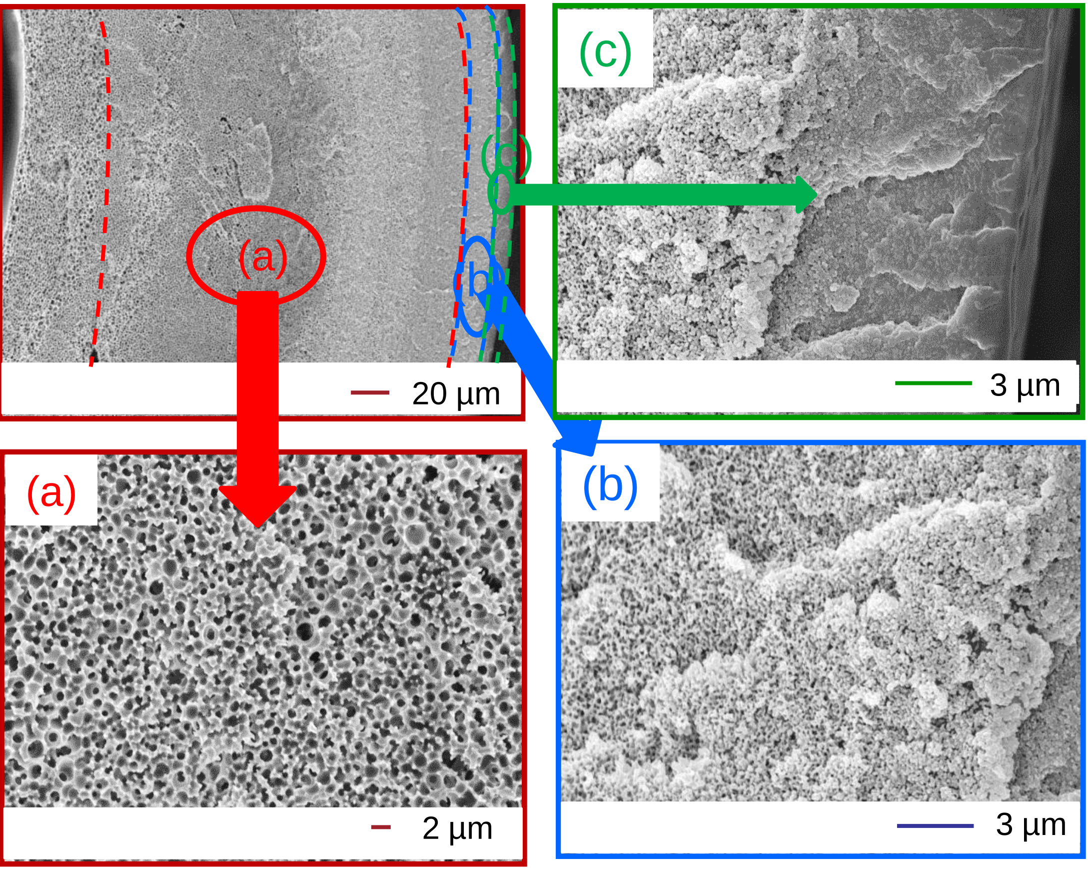



**Ionic liquid-superbase loaded Torlon® powders improved both $CO_2$ equilibrium and kinetic sorption!**

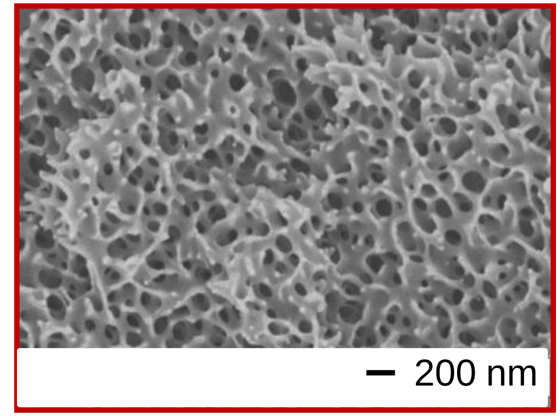
(Lee et al. Polymer 53 2012)

# Development of Ionic Liquid Hollow Fiber Sorbents




SEM images for the cross section of Torlon®-[BMIM][$Tf_2N$]-DBU fibers;

**[BMIM][$Tf_2N$]-DBU swells polymer walls**, **closing pore cells in outer region and results in slow sorption kinetics!**

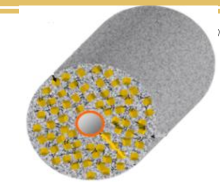



SEM image for [BMIM][$Tf_2N$]-DBU loaded Torlon® fibers

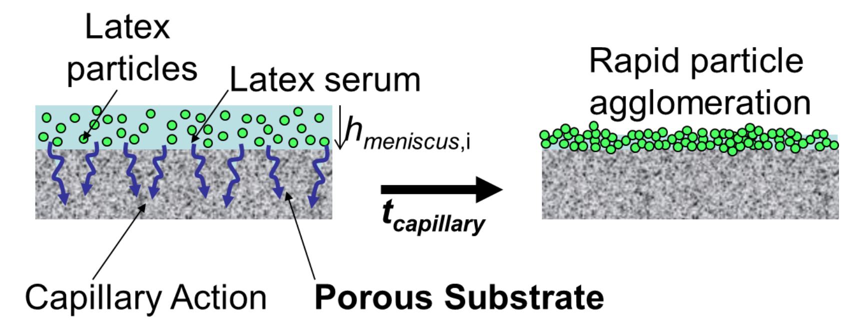
**Optimized two-step non-solvent infusion of ionic liquid & superbase maintains open celled porous walls for improved sorption kinetics.**

1. Two step non-solvent infusion technique (i.e. (1) IL/MeOH & (2) DBU/Hexane) allows effective loading levels of ionic liquid/superbase.
2. <u>Concentration level and infusion time of ionic liquid and DBU</u> were optimized to avoid pore collapse.

# Defect-free Lumen Side Barrier Layer Formation



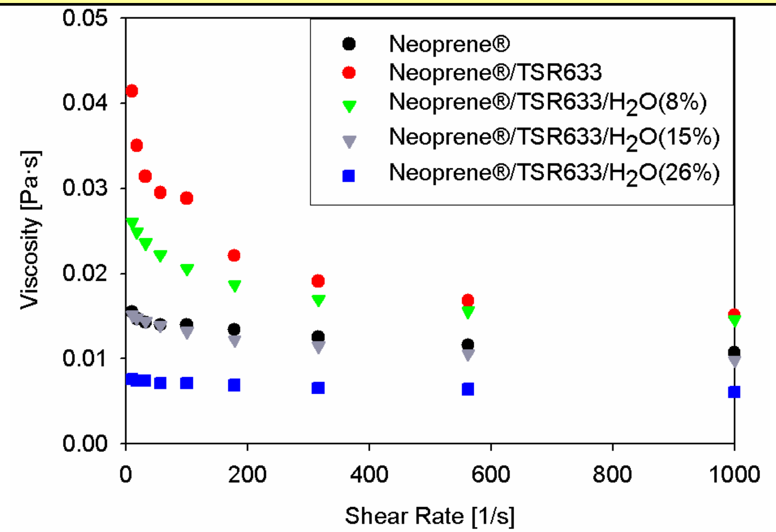
A fiber lumen layer prevents contact between flue gas and bore side hot & cold water used to control temperature during rapid cycle sorption and desorption.



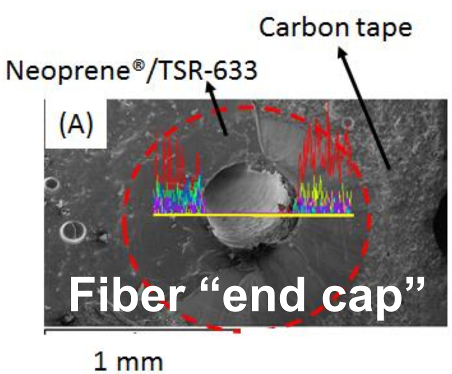

**"Toluene-assisted" drying creates defect-free fiber lumen layers, nearly impermeable to water**

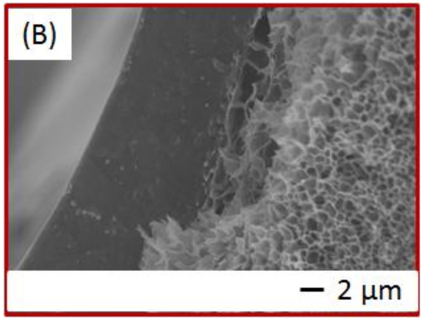
(ACS Appl. Mater. Interfaces, 2011)

➔ **Neoprene®+crosslinking agents (TSR-633)** provides lumen side barrier layer!




Diluting lumen coating latex with 8% $H_2O$ avoids clogging during post-treatment.




**"Toluene-assisted" drying creates defect-free fiber lumen layers with a He permeance of < 2 GPU and He/$N_2$ selectivity of ~5.**

Note that GPU refers to $1\times10^{-6}$ ccSTP/cm²/s/cmHg.

# Path Forward/Development/Commercialization

1. Develop “single-component” (ionic liquid-superbase) to avoid evaporation.

   - Synthesis of new single-component IL-superbase compounds is under way.

2. Evaluate long-term *chemical stability* of ionic liquid/base systems with simulated flue gas conditions.

   - Investigate effects of $H_2O$ on $CO_2$ multicycle sorption stability.

3. Pursue fiber sorbents with both fast kinetics & high sorption uptake.

   - Either: (a) incorporate single-component compounds, or (b) functionalize Torlon® fibers with superbase, to eliminate 2-stage infusion and superbase loss.

4. Evaluate feasibility of integrated hollow fiber sorbents under realistic conditions.

   - Investigate effects of $H_2O$ on $CO_2$ multicycle sorption stability *in actual modules.*

# Conclusions

- Ionic liquid/base systems are efficient reversible carbon capture media.
- The synergistic benefits of combining ionic liquid/superbase with porous polymer hollow fibers were demonstrated.
- Delicate morphological features in the open-celled porous wall can be maintained by the *two-step non-solvent infusion protocol*.
- A defect free crosslinked Neoprene® lumen layer was created to allow temperature control during rapid cycle sorption and desorption.

**Acknowledgement**: Innovative Materials & Processes for Advanced Carbon Capture Technology (IMPACCT) DE-FOA-0000208: Award: DE- AR0000104
ARPA-E Solvent Development for Carbon Capture