Next Generation Fiber-Encapsulated Nanoscale Hybrid Materials for Direct Air Capture with Selective Water Rejection

Project Number DE-FE0031963

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U.S. Department of Energy

National Energy Technology Laboratory
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Program Overview

a. Funding: $800,000 DOE + $200,000 Cost Share

b. Overall Project Performance Dates: 01/01/2021 – 10/31/2022

c. Project Participants:

   Columbia University (lead institution: Alissa Park (PI))

   Cornell University (Yong L. Joo)

   Oak Ridge National Laboratory (Michelle Kidder)

d. Overall Project Objectives

   We aim to address direct air capture (DAC) challenges by developing the **next generation fiber-encapsulated DAC sorbent** employing an electrospun, solid sorbent embedded with liquid-like Nanoparticle Organic Hybrid Materials (NOHMs) that will **selectively reject water while allowing facile CO_2 diffusion.**

Team Members

Design, Synthesis and Testing of NOHMs for CO_2 capture

COLUMBIA | ENGINEERING
The Fu Foundation School of Engineering and Applied Science


Ah-Hyung Park (PI) Annie Lee (GRA)


Jeffrey Xu (Postdoc) Dongjae Kim (Postdoc)

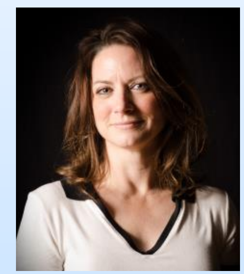
Fabrication of nanofibers via electrospinning technology

Cornell University


Kyle Kersey (GRA) Yong Joo (co-PI)

Design and characterization of polymeric materials

OAK RIDGE National Laboratory



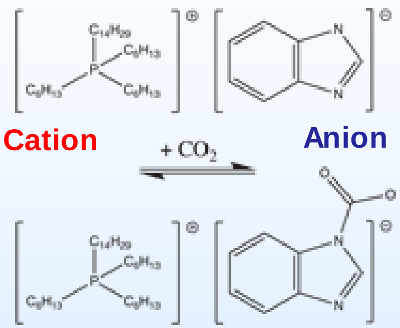
Michelle Kidder (co-PI)

Yeonshil Park (Postdoc)

Technology Background

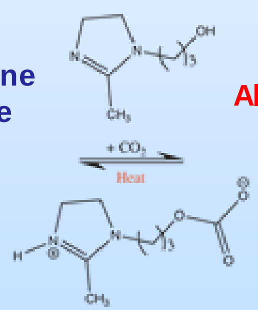
Water-lean Solvents for CO_2 Capture

Ionic Liquids

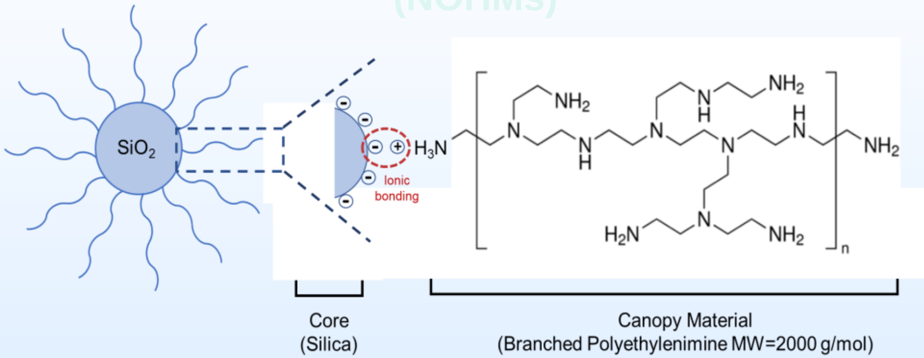


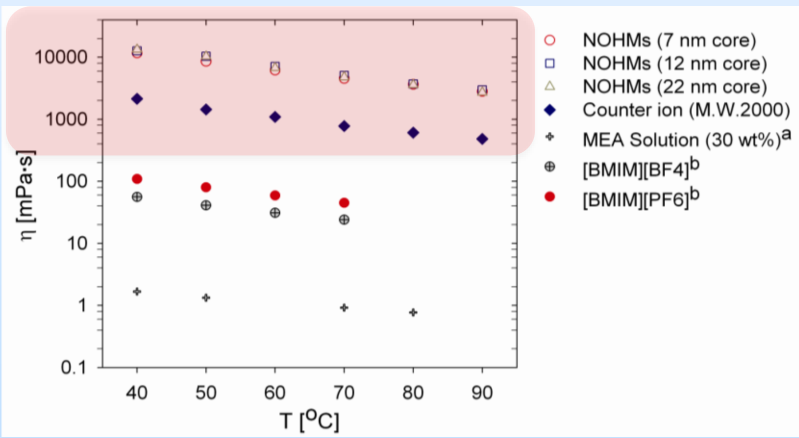
CO_2BOLs

CO_2 Binding Organic Liquids



Liquid-like Nanoparticle Organic Hybrid Materials (NOHMs)



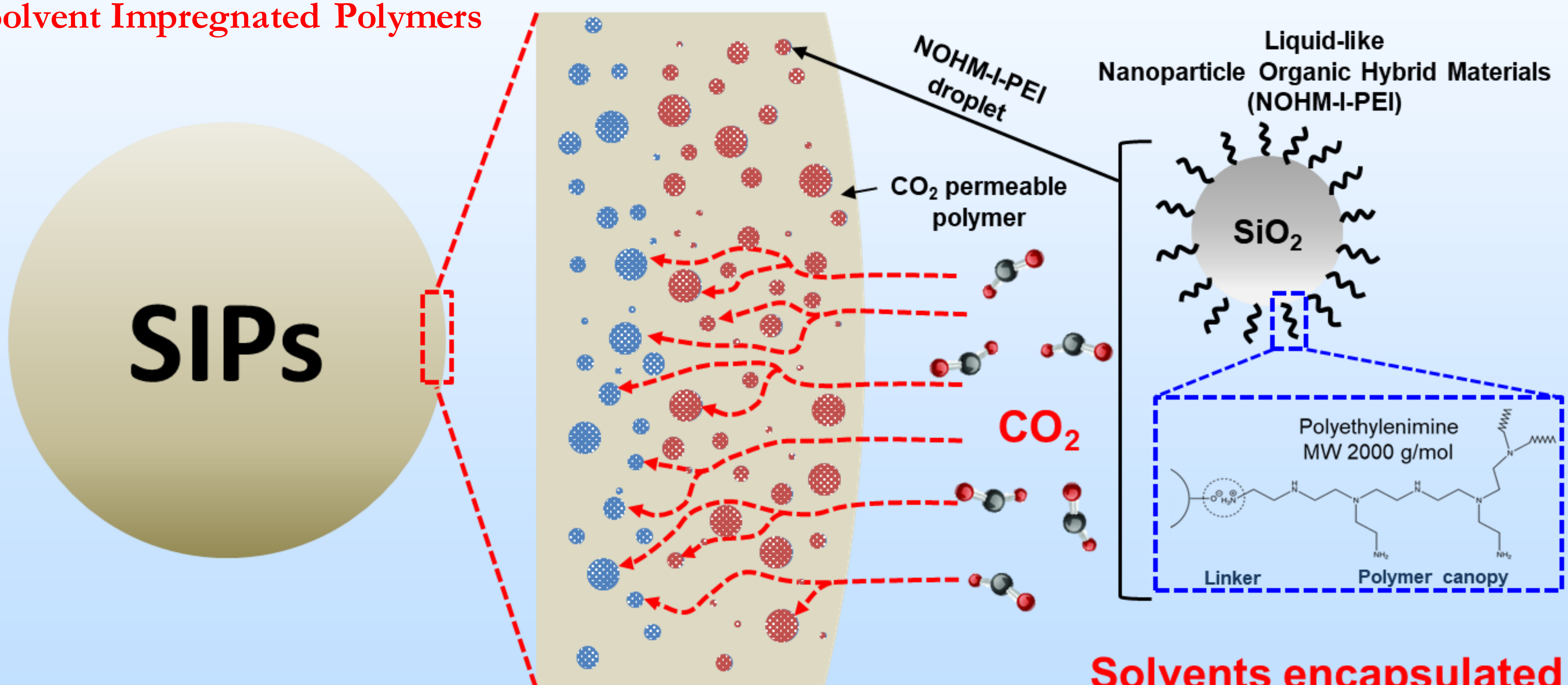


Petit, Bhatnagar & Park, *Journal of Colloid and Interface Science* (2013)

Introduction of nanoparticles increases the viscosity of the system
→ Need to develop **novel carriers** of NOHMs

Encapsulation of NOHM-I-PEI for CO_2 Capture

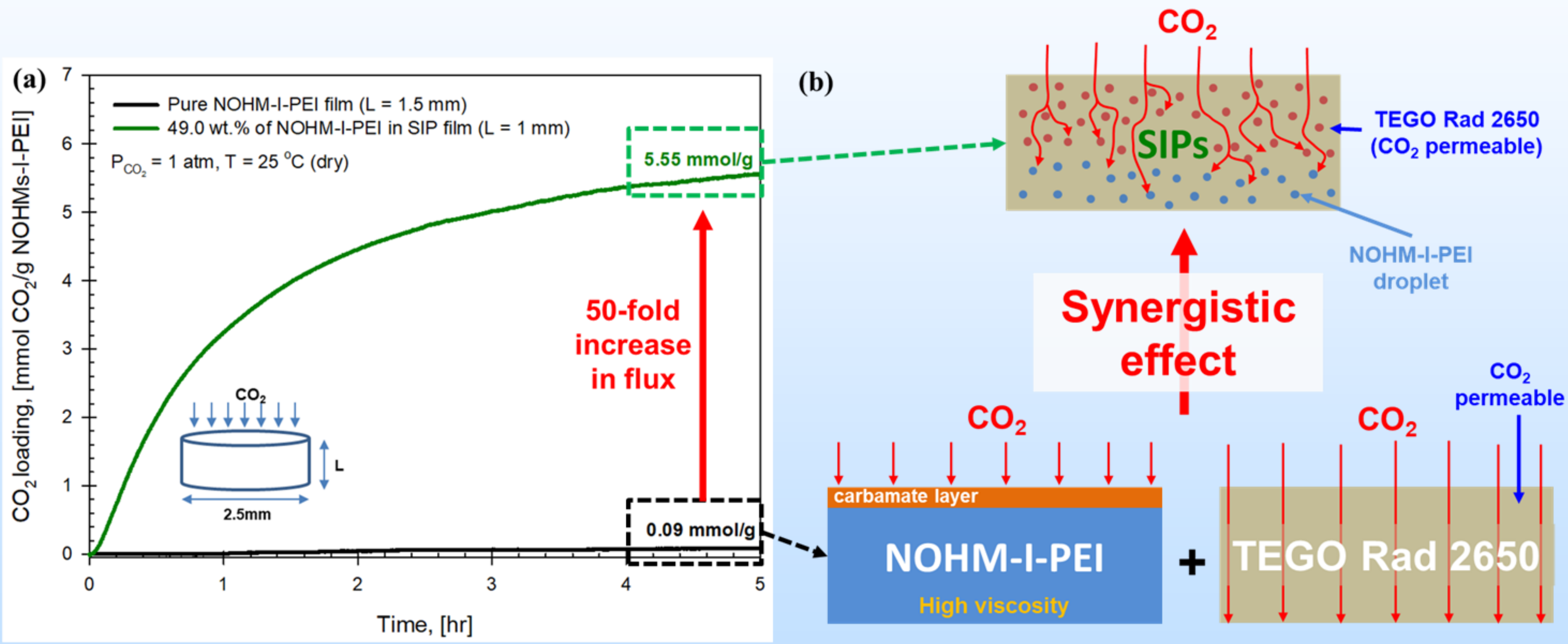
Solvent Impregnated Polymers



Solvents encapsulated <u>solid sorbents</u>

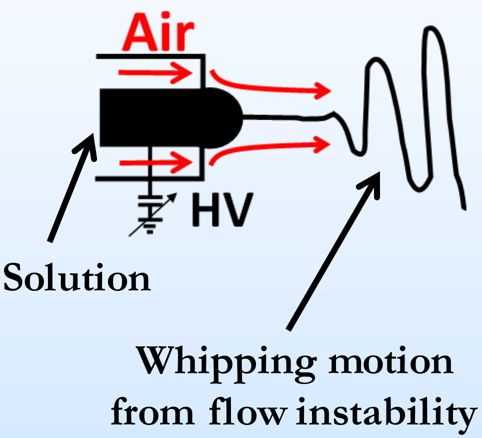
Rim et al., *Advanced Functional Materials* (2021)

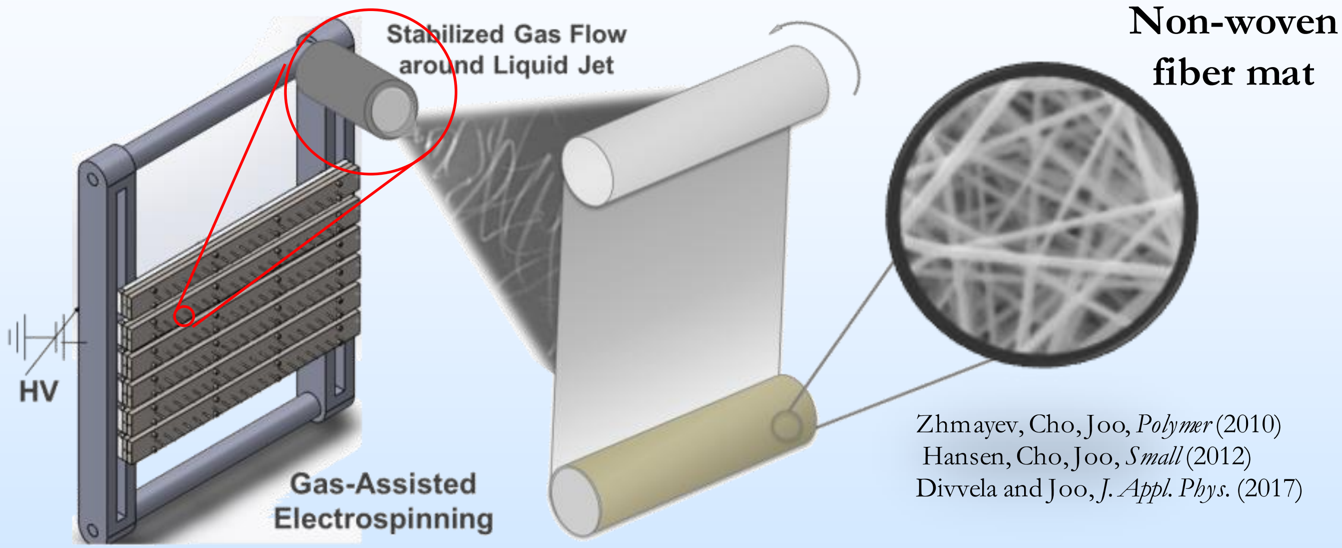
Accelerated CO_2 Sorption Kinetics of NIPEI via Increased Interfacial Area



Rim et al., *Advanced Functional Materials* (2021)

Gas-Assisted Electrospinning



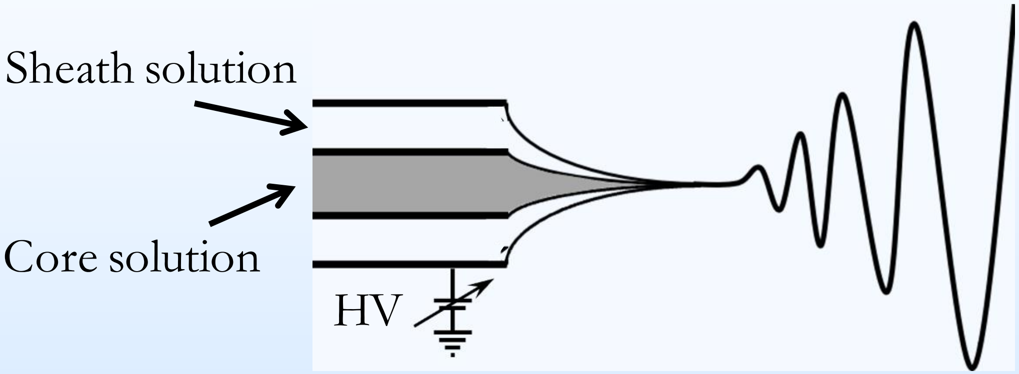


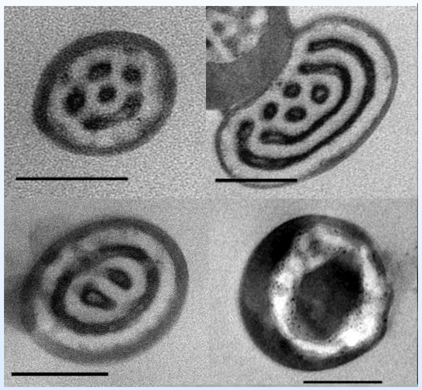
Zhmayev, Cho, Joo, *Polymer* (2010)
Hansen, Cho, Joo, *Small* (2012)
Divvela and Joo, *J. Appl. Phys.* (2017)

- Sheath of high-speed air promotes faster solvent evaporation than in traditional electrospinning
- Able to utilize faster flow rates to decrease processing time

Core-Sheath Fiber Morphology

- Coaxial electrospinning allows control of internal fiber assembly

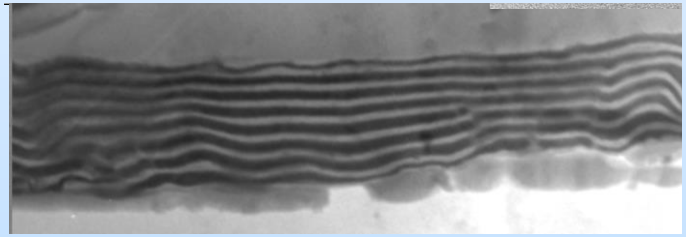




SiO_2 Nanoparticles in PI-*b*-PS Nanofibers

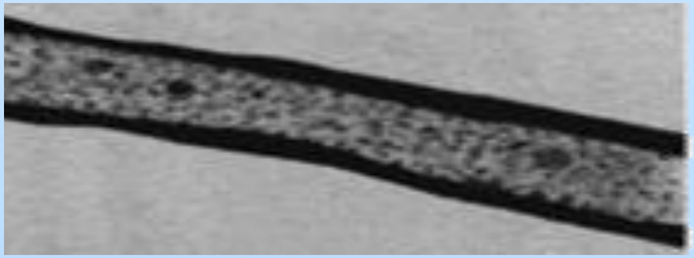
Kalra and Joo, *Small* (2008), (2009)

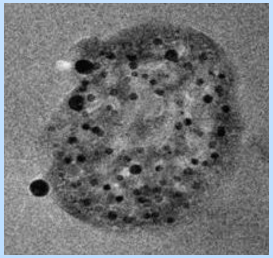
Alternating Layers of PI-*b*-PS Nanofibers



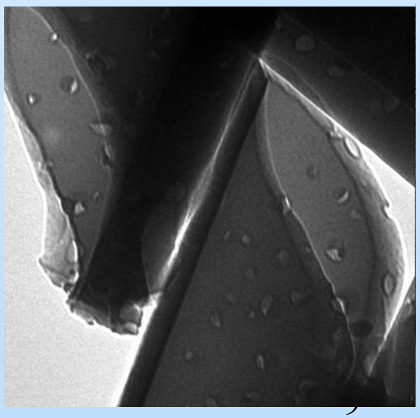
Kalra and Joo, el al., *Macromol.* (2006), *Adv. Mater.* (2006)

Core (SiO_2)/Sheath (Ni) Nanofibers

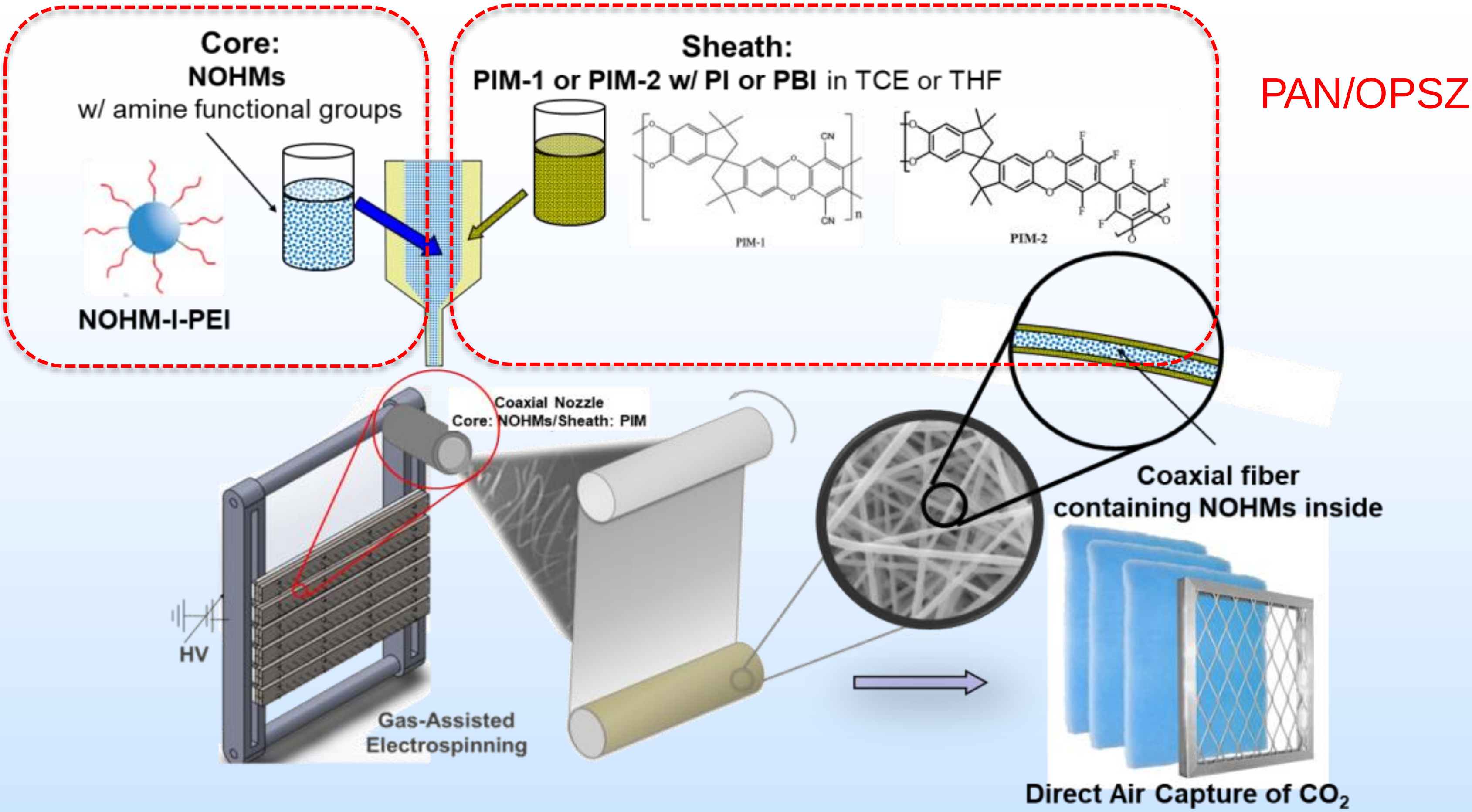




Hollow V_2O_5/SiO_2 Nanofibers



Panels and Joo, *J. Nanomater.* (2006)



Objective: To address direct air capture (DAC) challenges by developing the **next generation fiber-encapsulated DAC sorbent** employing an electrospun, solid sorbent embedded with liquid-like Nanoparticle Organic Hybrid Materials (NOHMs) that will **selectively reject water while allowing facile CO_2 diffusion**.

Technical Approach/Project Scope

Experimental design and work plan

- Q1-Q2: Design and synthesis of NOHMs and polymers for DAC
- Q2-Q5: Fabrication of NOHMs/PIM coaxial fibers and analysis
- Q2-Q5: Fabrication of NOHMs(core)/ceramic(sheath) nanofibers and analysis
- Q3-Q6: Fabrication of air filters based on deposition of NOHMs/PIM or ceramic nanofibers
- Q4-Q7: Process modeling and TEA/LCA

Decision Points	Success Criteria
Can NOHMs be synthesized for DAC?	At least **three** of the synthesized NOHMs can effectively capture CO_2 at the same levels as conventional DAC sorbents.
Can the fiber-encapsulated NOHMs capture CO_2 faster?	The developed fiber-encapsulated NOHMs should be able to capture CO_2 at a rate **50% faster** than that of NOHMs.
Can the fiber-encapsulated NOHMs sorbent selectively reject water?	The developed fiber-encapsulated NOHMs should reject at least **30% of water** in the system.
Are fibers impregnated with NOHMs stable for multiple cycles?	The first generation of fiber-encapsulated NOHMs generated from this project should be stable at least **10 DAC cycles**.

Progress and Current Status of Project

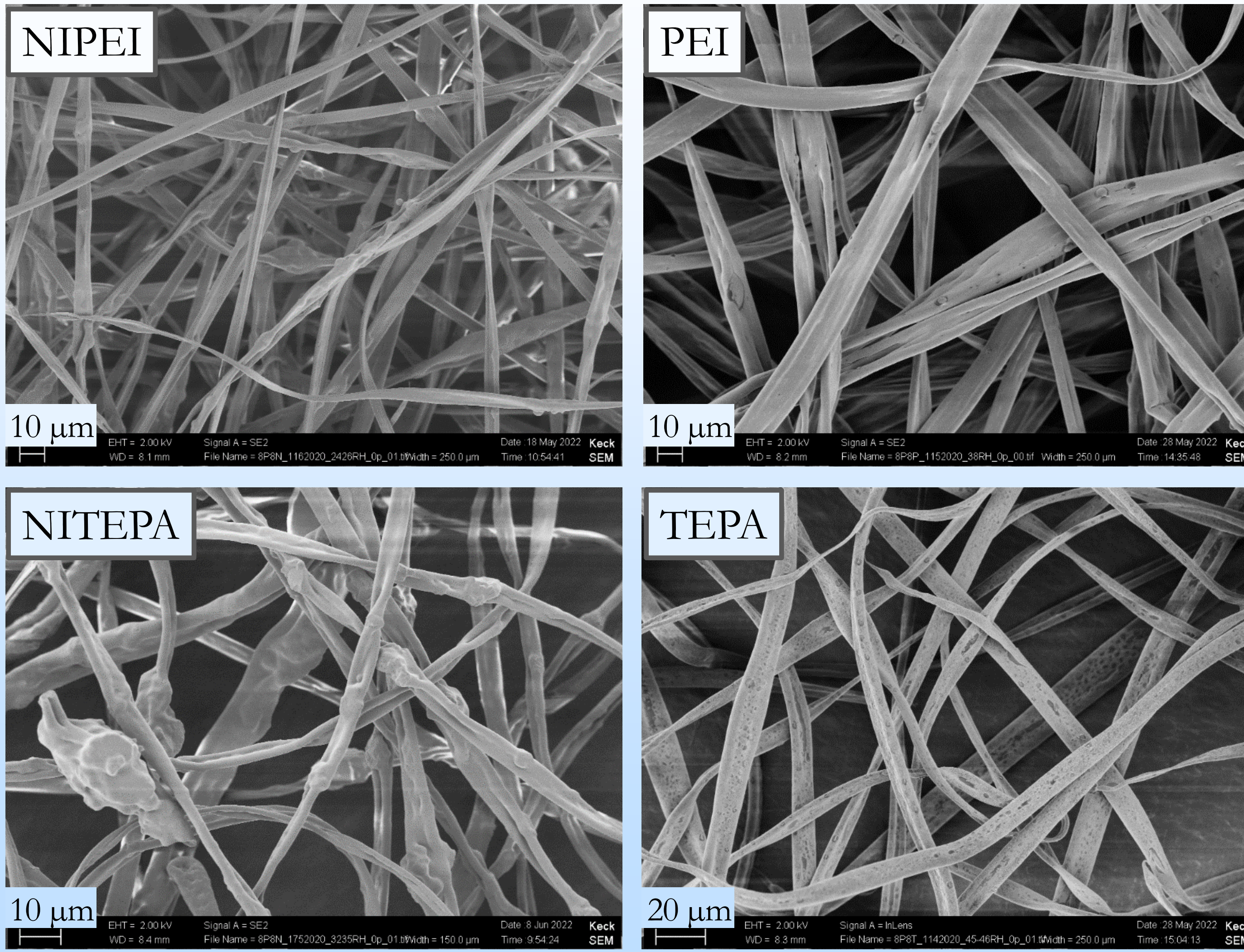
PIM-1 based NOHMs electrospun fibers

Incorporation of Amine Solvent into PIM-1 Electrospun Fibers

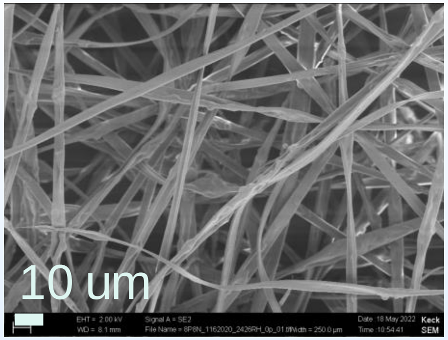
Developed procedures to electrospin uniform PIM-1 composite fibers at high flow rate

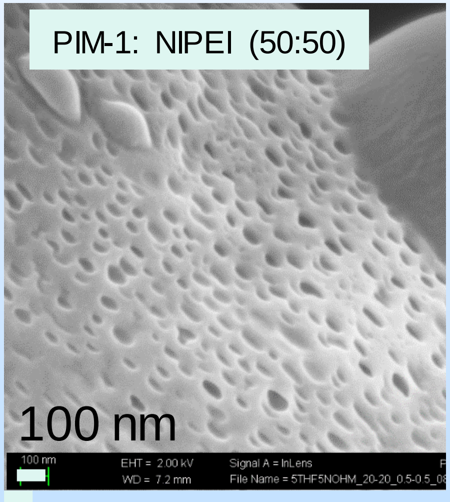
Able to incorporate amine sorbents, both tethered (i.e., NOHMs) and untethered (free polymers)

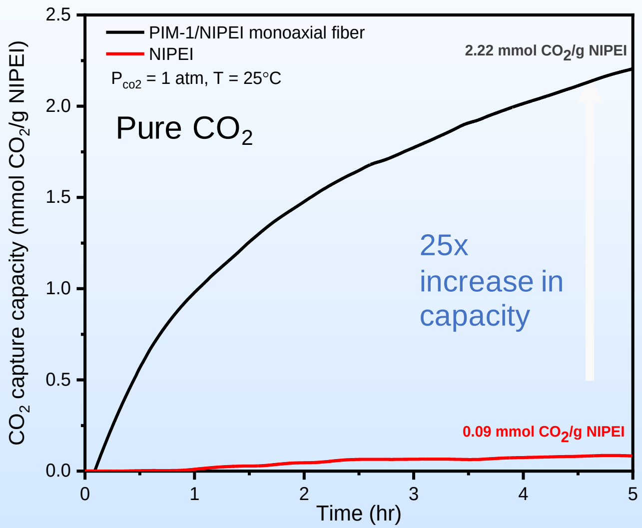
Morphology shows **flat fibers with 5-15 μm width and 1-1.5 μm thickness**



PIM-1 Encapsulated NIPEI : Improved Capacity & Kinetics of CO_2 Capture



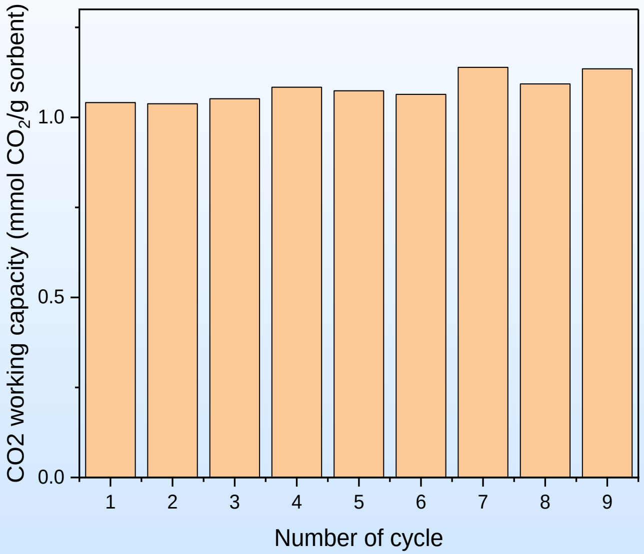




- Sonication and mixing of electrospinning solution
  → **Smaller NIPEI droplets**

- Encapsulation by highly-permeable polymer
  → **Significantly reduced mass transfer limitation**

Average: 1.1 mmol CO_2 /g sorbent ±0.04

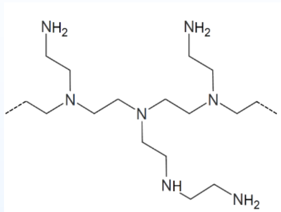


Stable Cycling of CO_2 capture and release

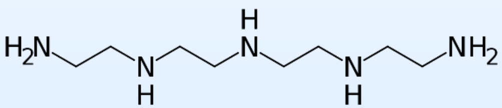
Capture: 1 atm CO_2, 25 °C
Regeneration: 1 atm N_2, 120 °C

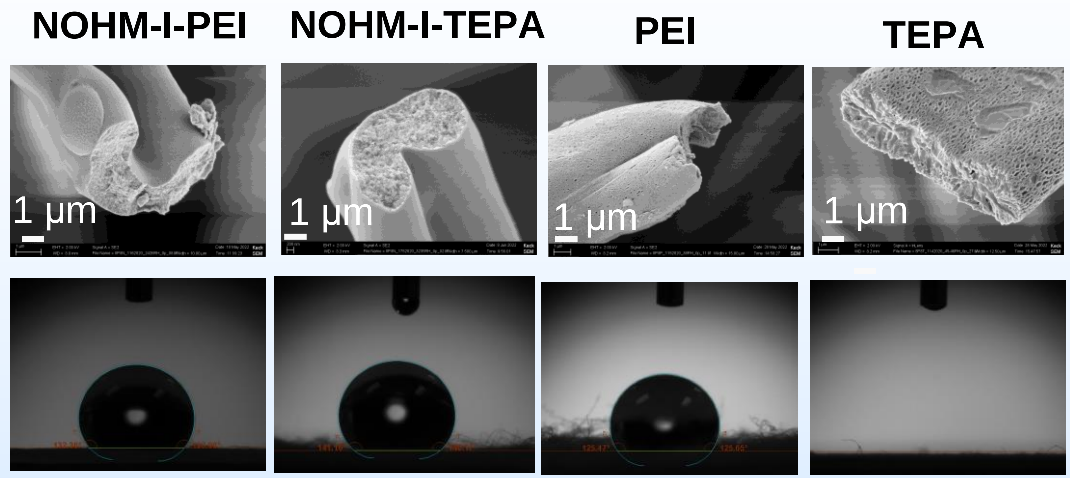
PIM-1 Encapsulation of Different Types of Amines and NOHMs

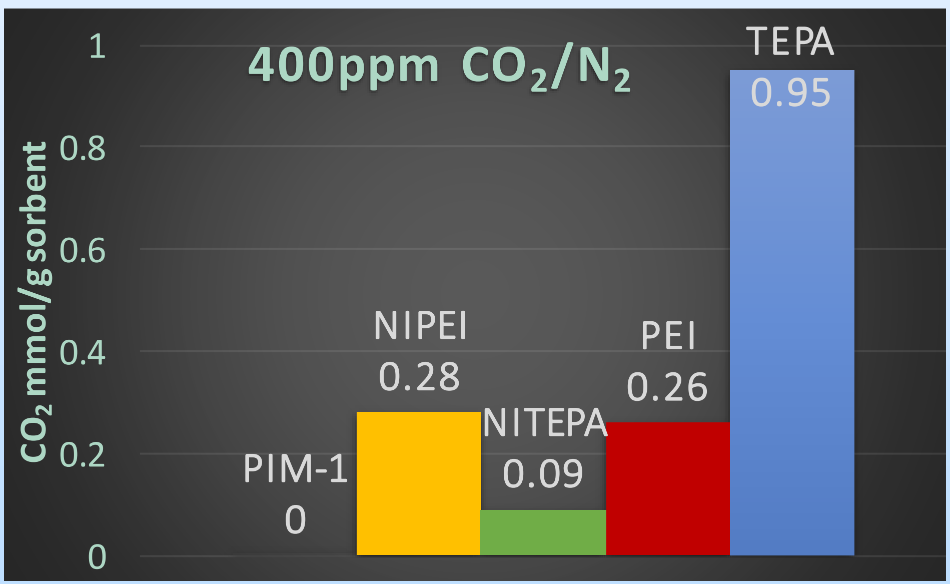
PEI: MW 2000 Polyethylenimine

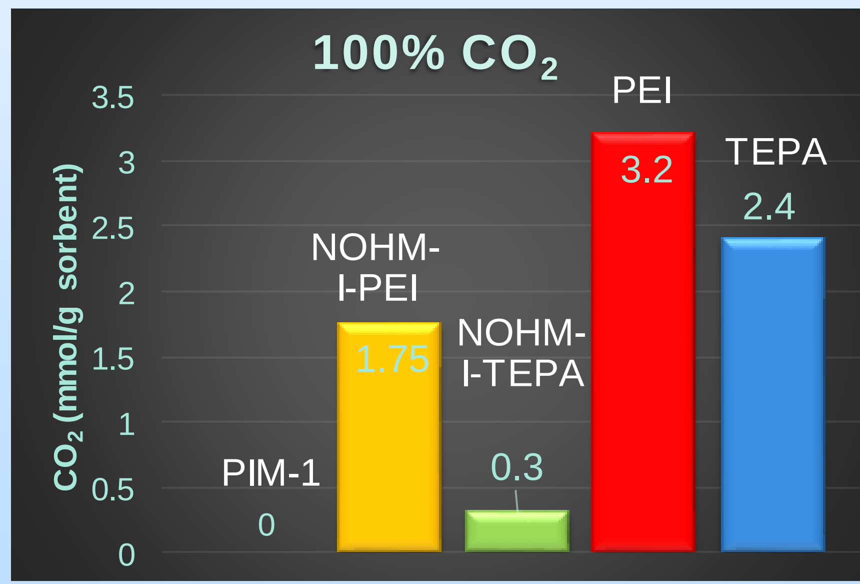


TEPA: Tetraethylenepentamine







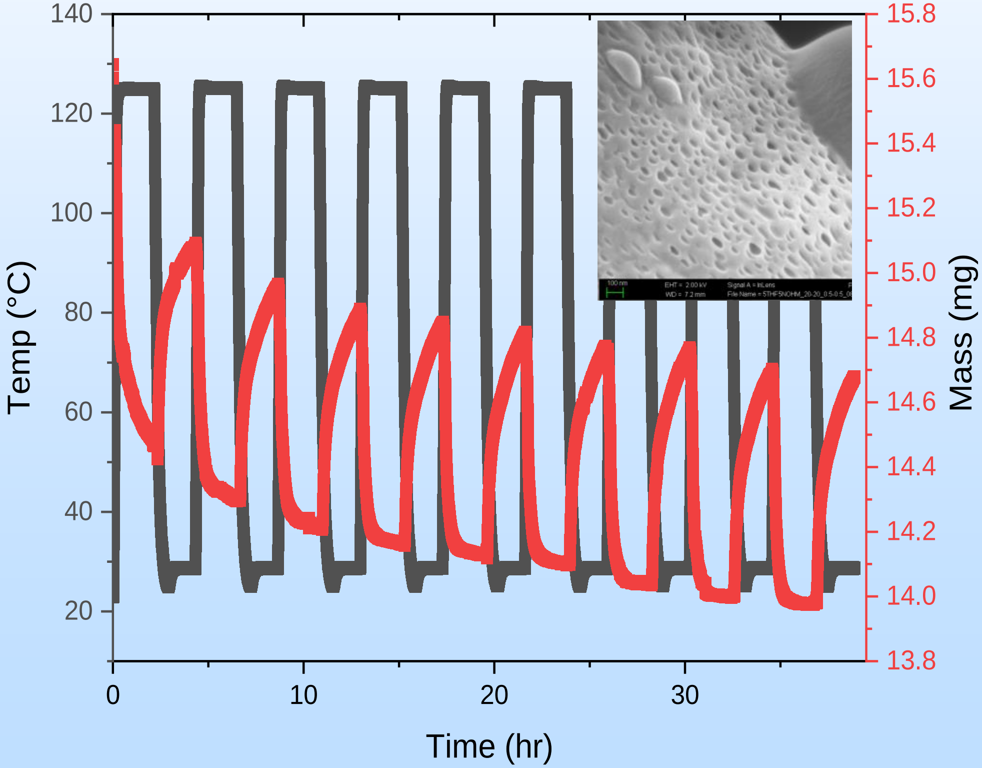


PIM-1/TEPA fibers offer highest porosity and capture capacity under dry air conditions

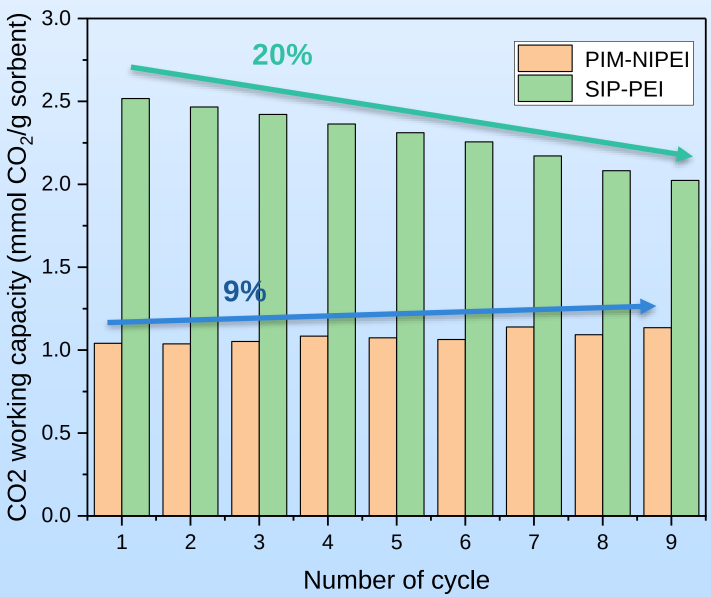
Recyclability of 50:50 NIPEI:PIM

2 hr recycle sorption time
average 1.08 mmol CO_2/g sorbent ±0.04

Initial activation with N_2 at 120 °C for 2 hours
Sorption: 1 atm CO_2, 25 °C – 2hr
Desorption: 1 atm N_2, 120 °C 2hr

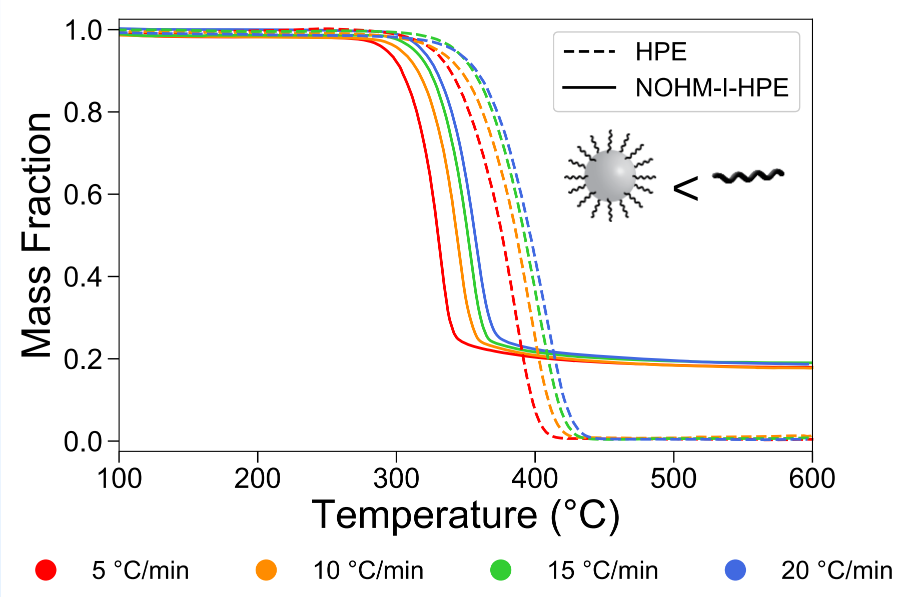


1 hr sorption, 1 hr desorption for SIP-PEI /
49 wt% PEI loading onto SIP
Rim et al., **2021**

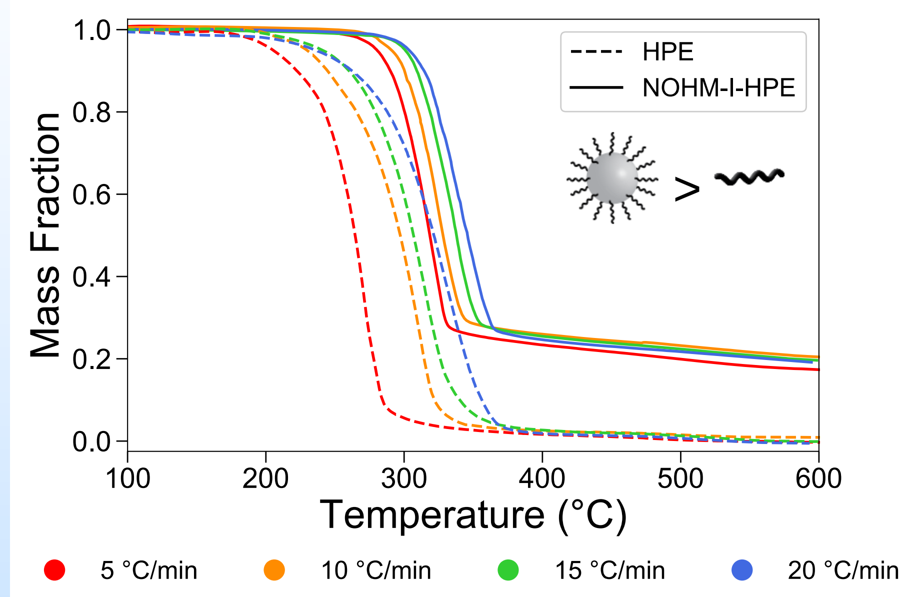


Recyclability of 50:50 NIPEI:PIM

N_2 Atmosphere



Air Atmosphere



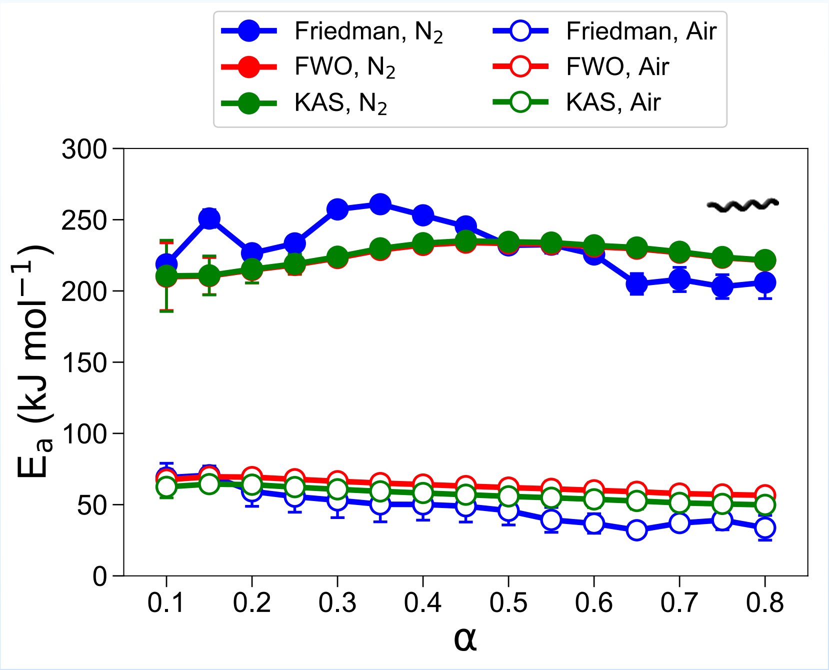
Thermal stability of NOHM-I-HPE is lower than HPE in N_2, but higher in air

Experimental conditions: 20-600 °C,
HR = 5-20 °C/min, flowrate = 40
mL/min

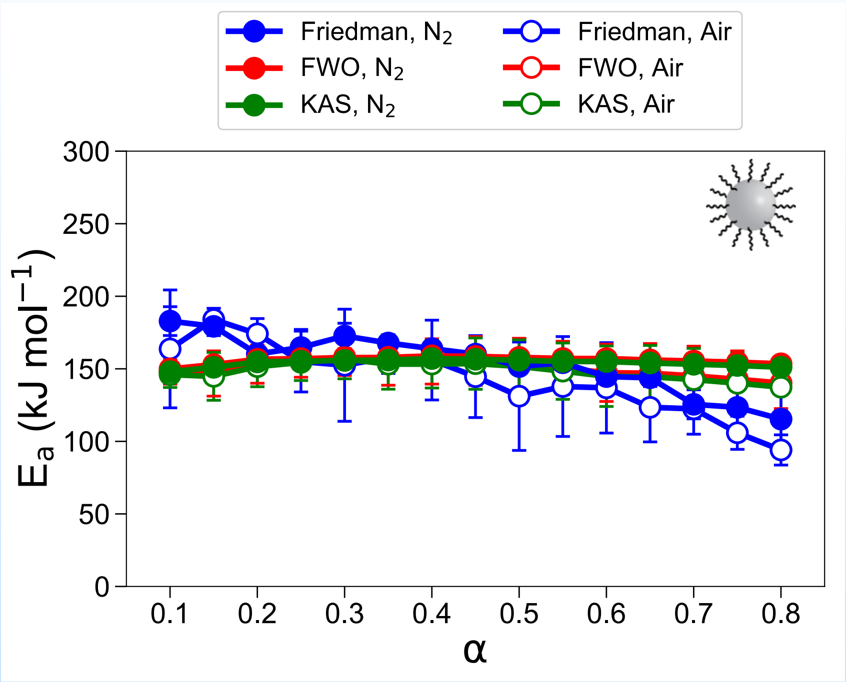
Feric *et al*. *Energy Fuels*, **2021**. 35 (23), pp. 19592-19605.

Presence of O_2 does not affect activation energy of NIHPE thermal degradation

HPE



NOHM-I-HPE



Free polymer stability is significantly reduced in the presence of O_2, while that of NOHM-I-HPE remains relatively unchanged

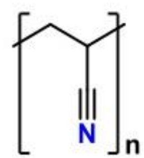
Feric *et al*. *Energy Fuels,* **2021**. 35 (23), pp. 19592-19605.

PAN/OPSZ based NOHMs electrospun fibers

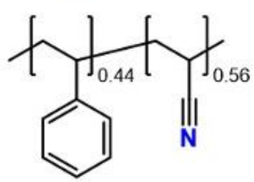
Using Commercially-available Polymers/Ceramics as Shell Materials

Polymer Core + **Ceramic Sheath**

Polyacrylonitrile (PAN)

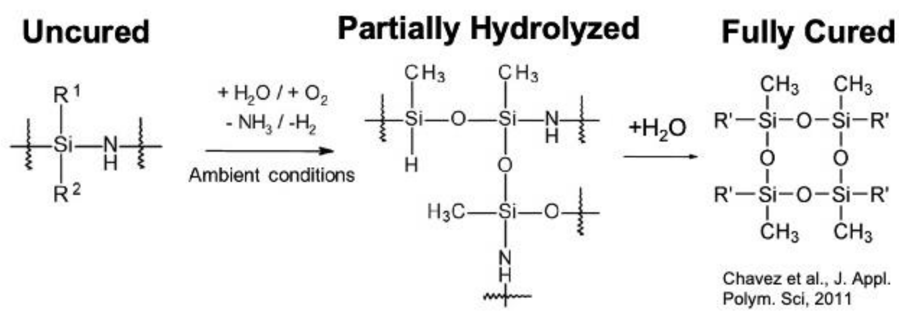


Poly(styrene-co-acrylonitrile) (Ps-co-PAN)



- Common, low-cost polymers
- Mutually soluble with NOHM-I-PEI in DMF solvent

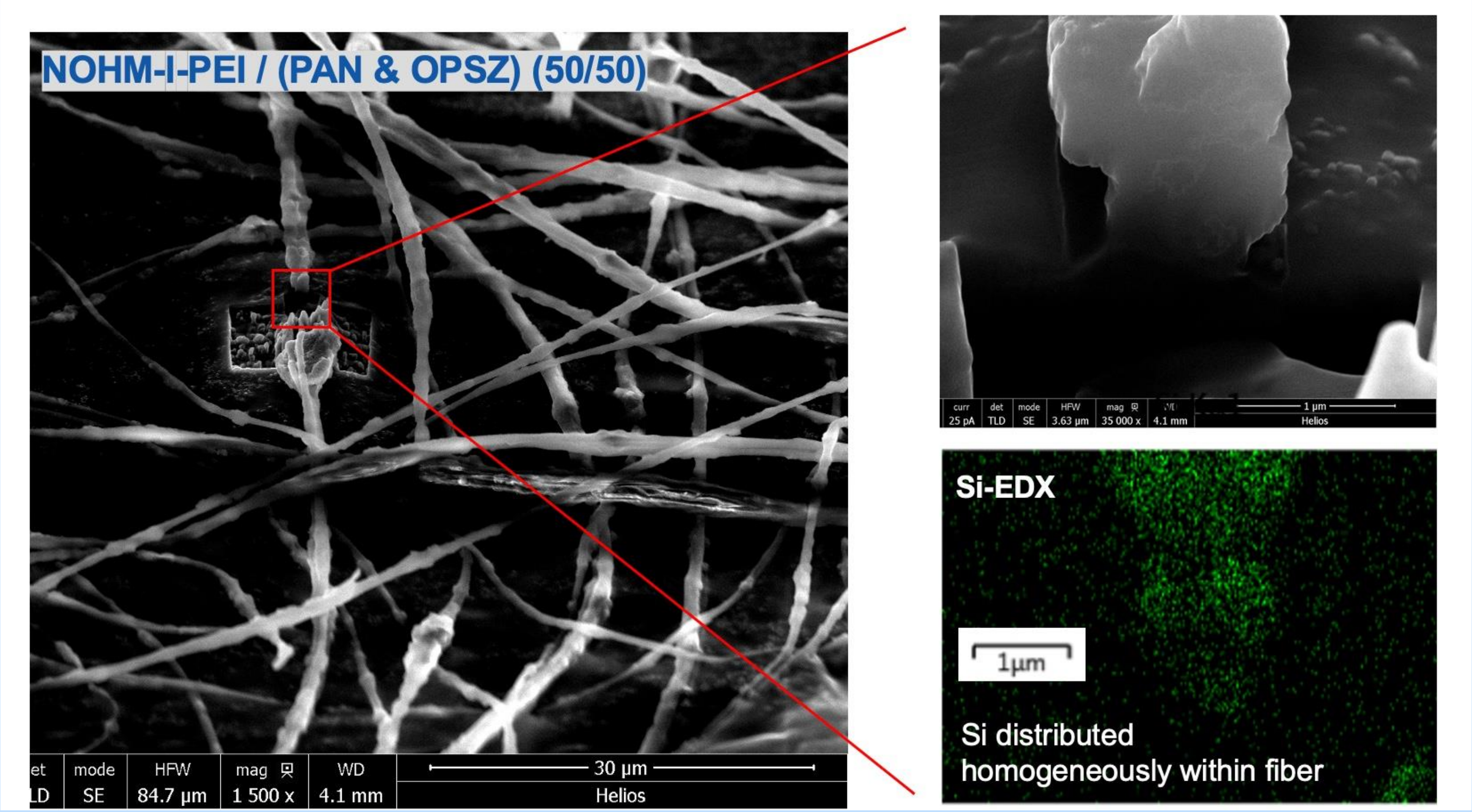
Organopolysilazane (OPSZ)



Chavez et al., J. Appl. Polym. Sci, 2011

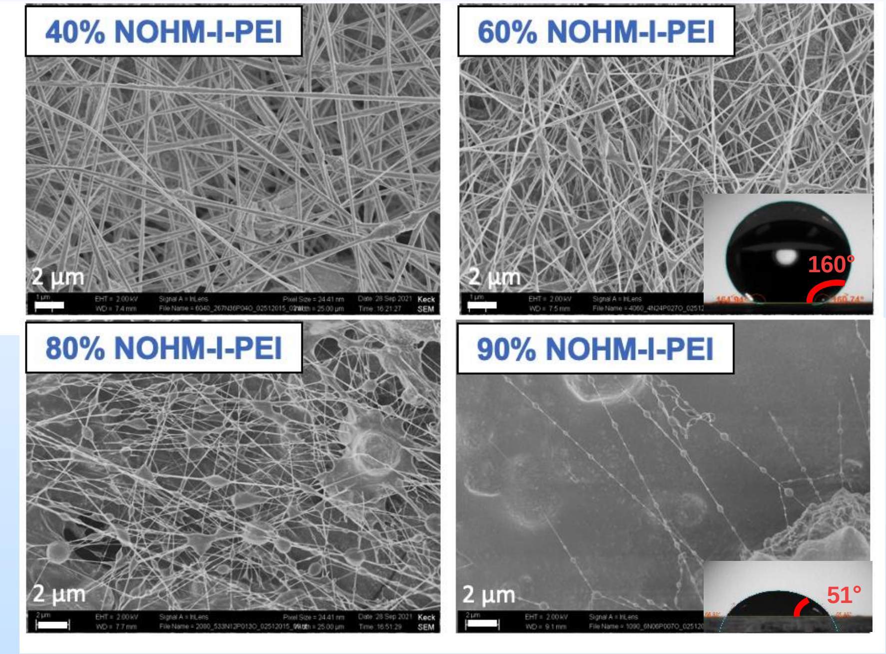
- A commercial anti-corrosion hydrophobic coating material
- Low viscosity and low surface tension -> naturally migrates to fiber surface during processing and cures to SiO_2 in air

PAN/OPSZ-Encapsulated NIPEI: Distribution of NIPEI within Nanofibers

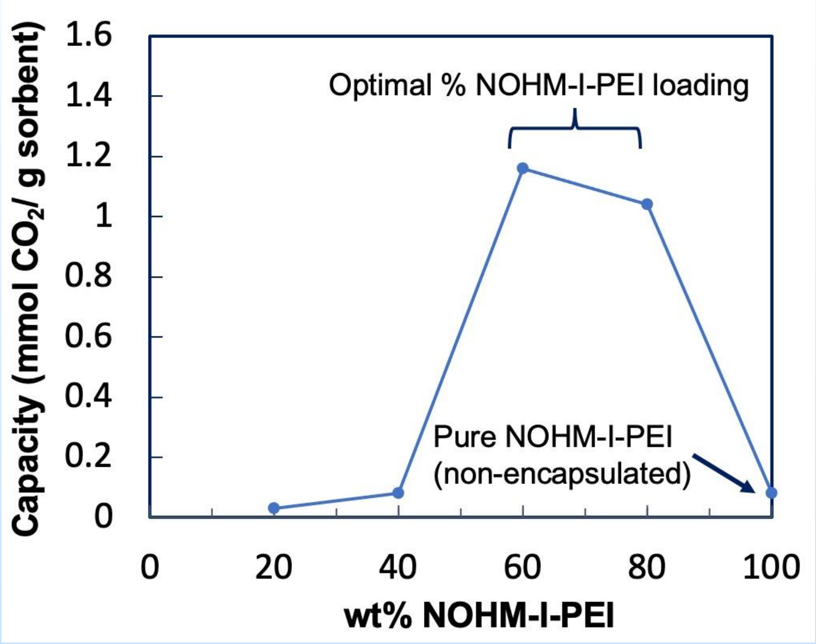


PAN/OPSZ-encapsulated NIPEI Fibers: Sorbent Loading vs. Capture Capacity

NOHM-I-PEI / (PAN & OPSZ) Fibers



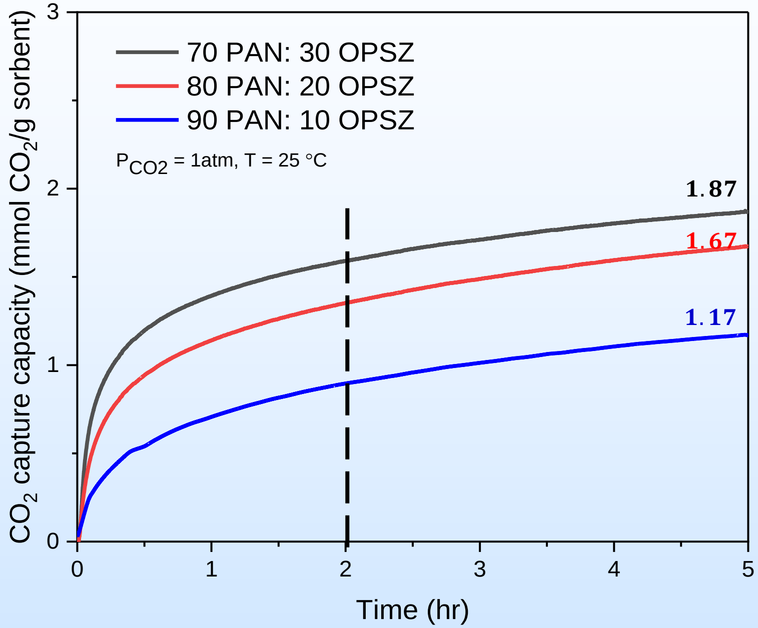
(400 ppm CO_2, Adsorption T=30 ℃)

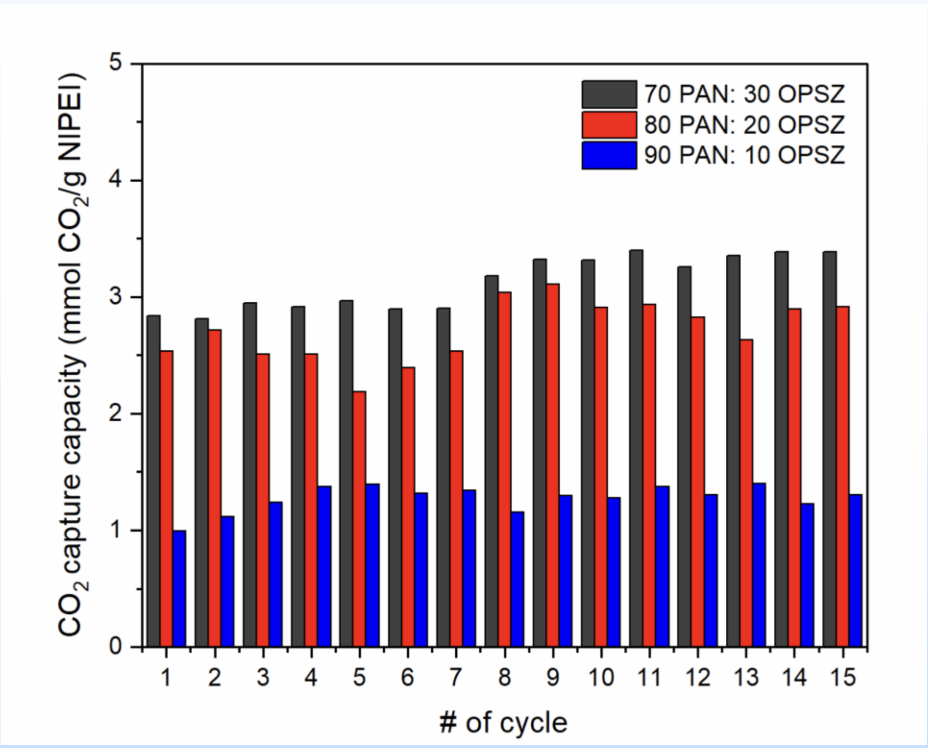


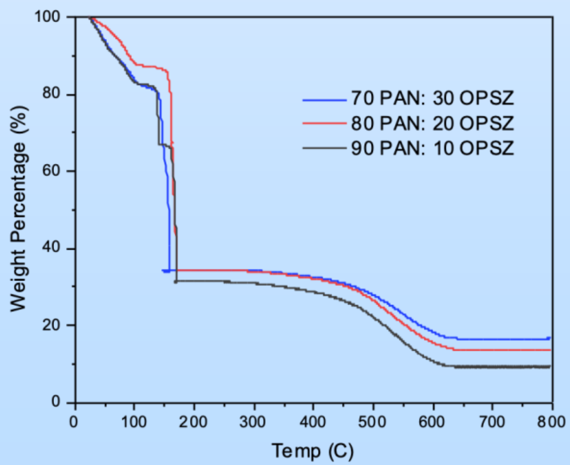
Fiber morphology

→ trade-off b/t **higher sorbent loading** vs. **gas transport** & **capacity**

CO_2 capture capacity and cyclability of PAN/OPSZ/NIPEI fibers







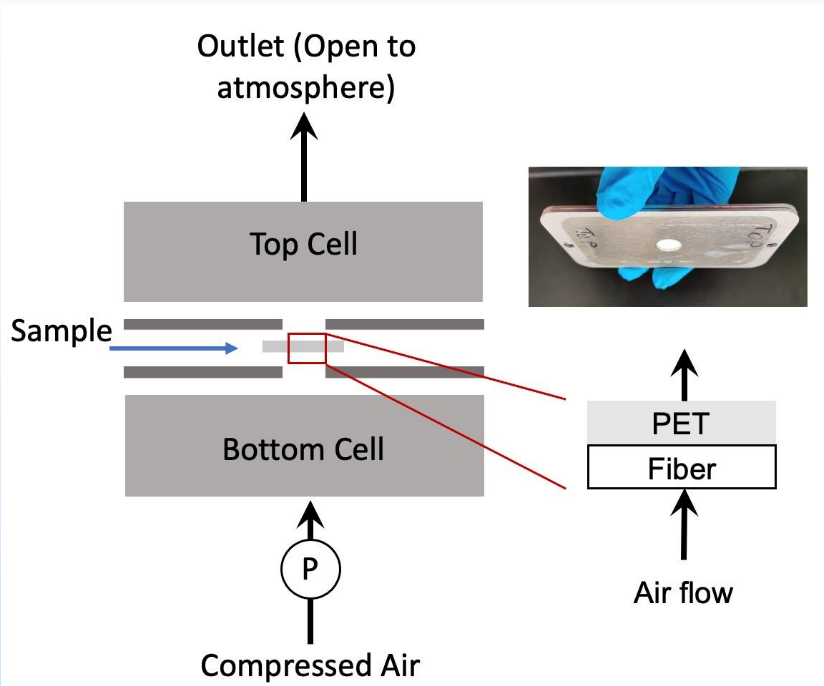
58% NIPEI

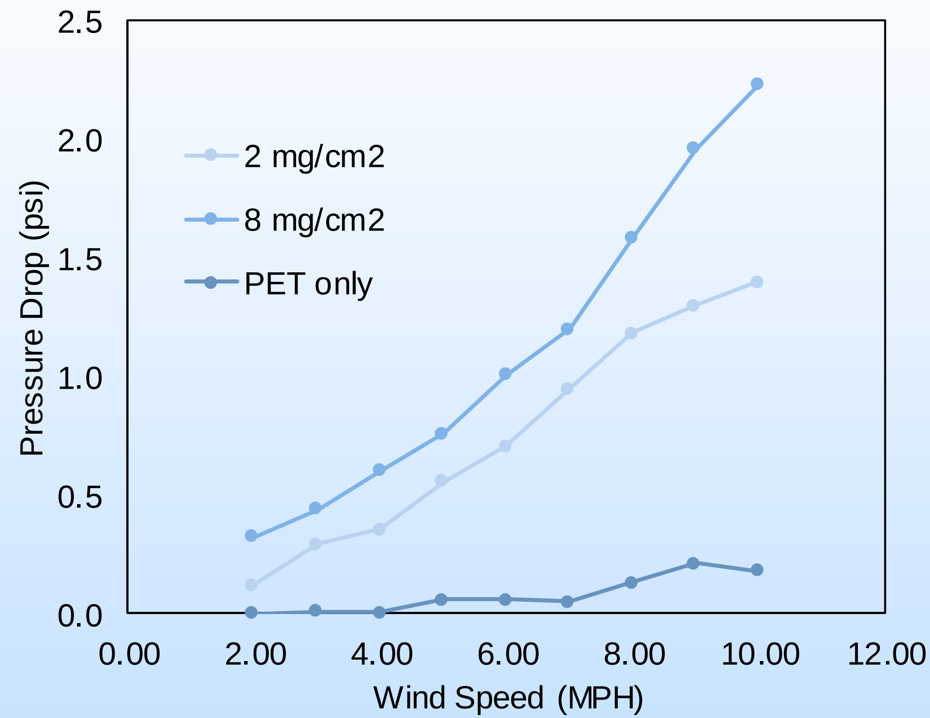
60% NIPEI

62% NIPEI

70 PAN: 30 OPSZ: 3.12 $\pm$ 0.13 mmol CO_2/g NIPEI
80 PAN: 20 OPSZ: 2.71 $\pm$ 0.16 mmol CO_2/g NIPEI
90 PAN: 10 OPSZ: 1.28 $\pm$ 0.07 mmol CO_2/g NIPEI

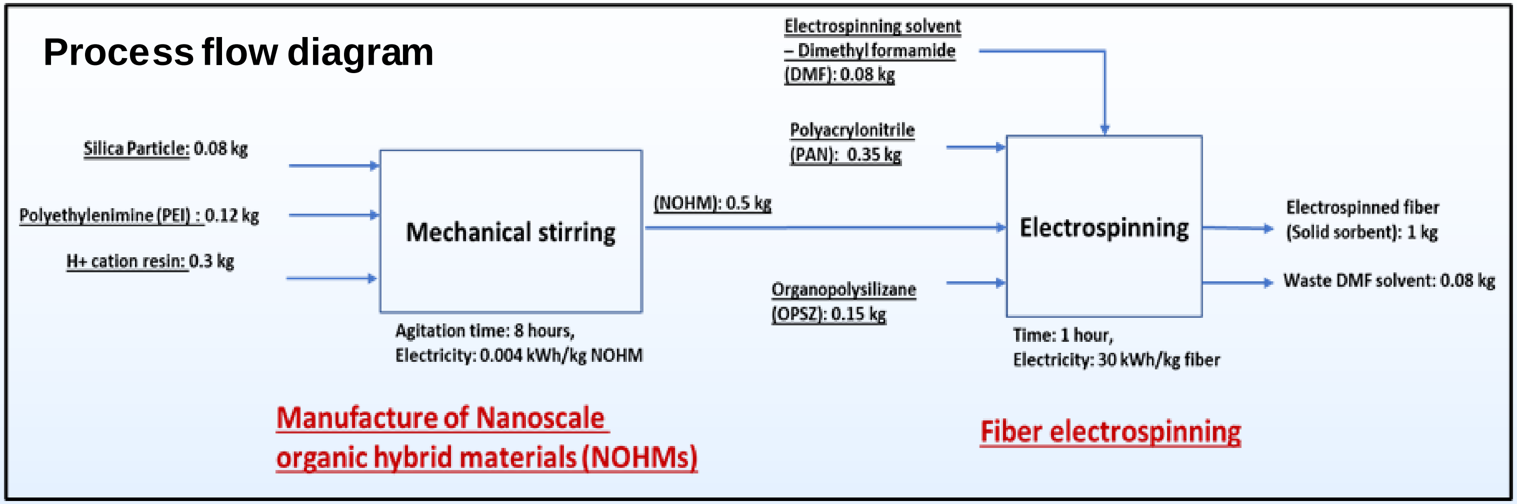
PAN/OPSZ Fiber Mats Exhibit Low Pressure Drop

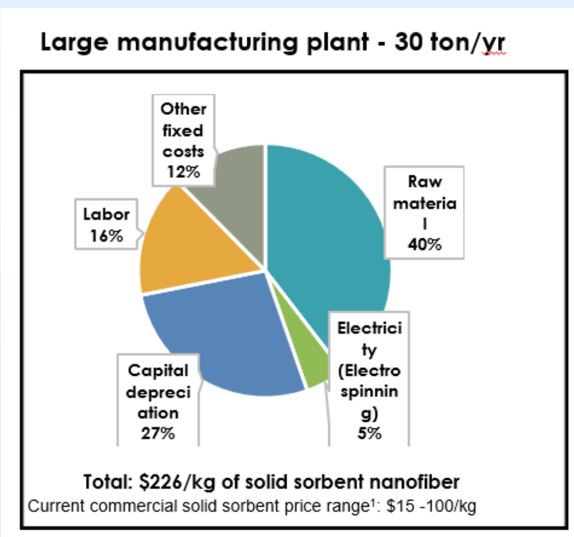




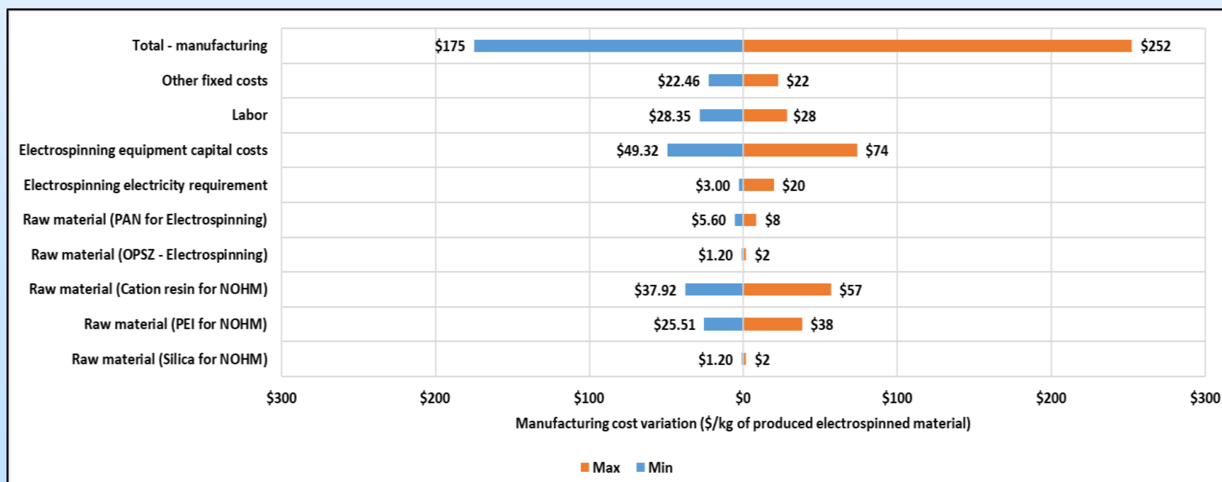
Fiber mats can be engineered to have lower pressure drops compared to traditional contactors

TEA of Sorbent Manufacturing Process





Sensitivity analysis of solid sorbent manufacture process from base cost - $226/kg



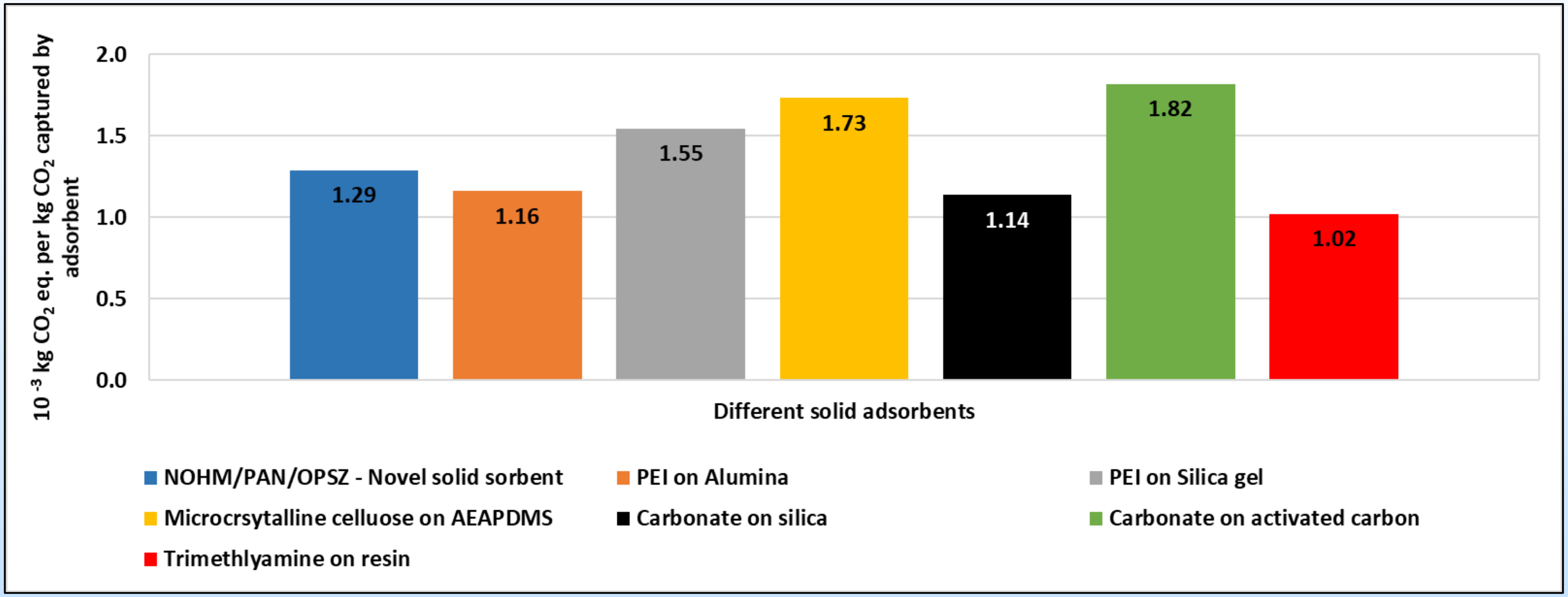
Scaling up solid sorbent manufacture process from **1 ton/yr to 30 ton/yr** decreases cost by nearly **50%** depicting economies of scale effect (**$525/kg vs $226/kg**)

[1]National Academies of Sciences, Engineering, and Medicine 2019. Negative Emissions Technologies and Reliable Sequestration: A Research Agenda. Washington, DC: The National Academies Press. https://doi.org/10.17226/25259

Other fixed costs include Maintenance, taxes, miscellaneous, etc.

LCA of Sorbent Manufacturing Process

Comparing the environmental impacts (cradle to gate) of manufacturing: Novel solid sorbent vs. existing solid sorbent in literature



Based on ISO 14040 series guidelines

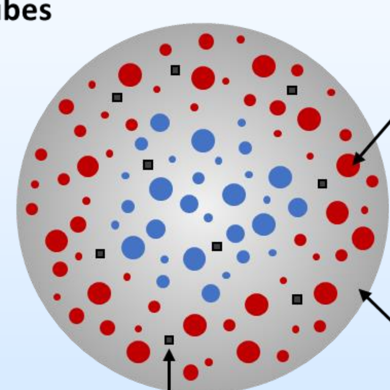
- The value of the **global warming potential** of the novel sorbent (1.29 x 10^{-3} kg CO_2 per kg CO_2 captured by adsorbent) lied between those shown by other solid sorbents.

Sorbent regeneration using non-thermal energy transfer

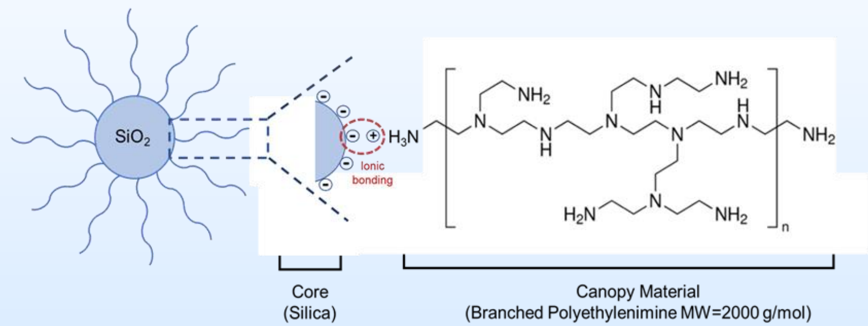
Schematic design of mag-NPEI-SIPs for Non-Thermal Energy Transfer

CO_2 adsorbed
CO_2 free
Fe_3O_4 nanocubes

SIPs

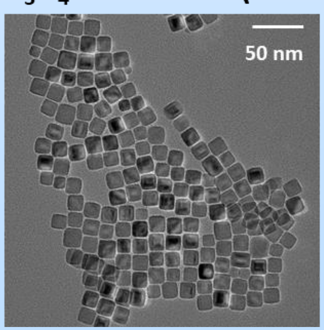


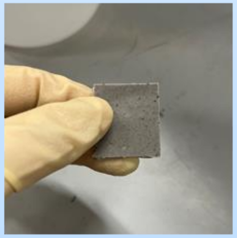
Nanoparticle Organic Hybrid Materials (NOHMs)

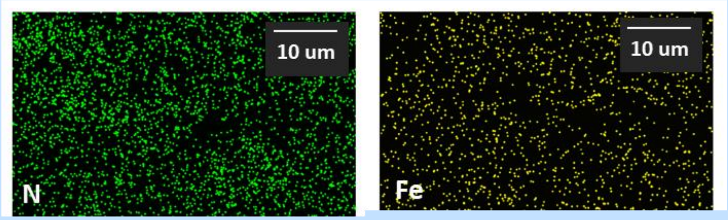


CO_2 permeable polymer TEGO Rad 2650

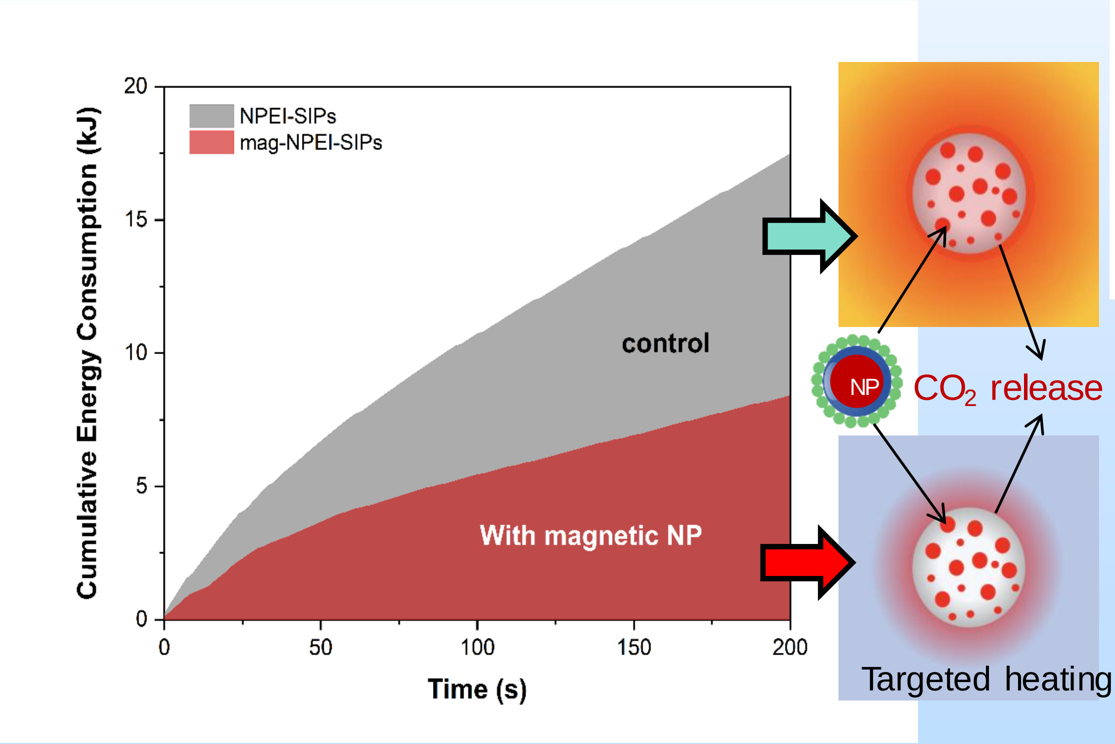
Fe_3O_4 nanocubes (15 nm)

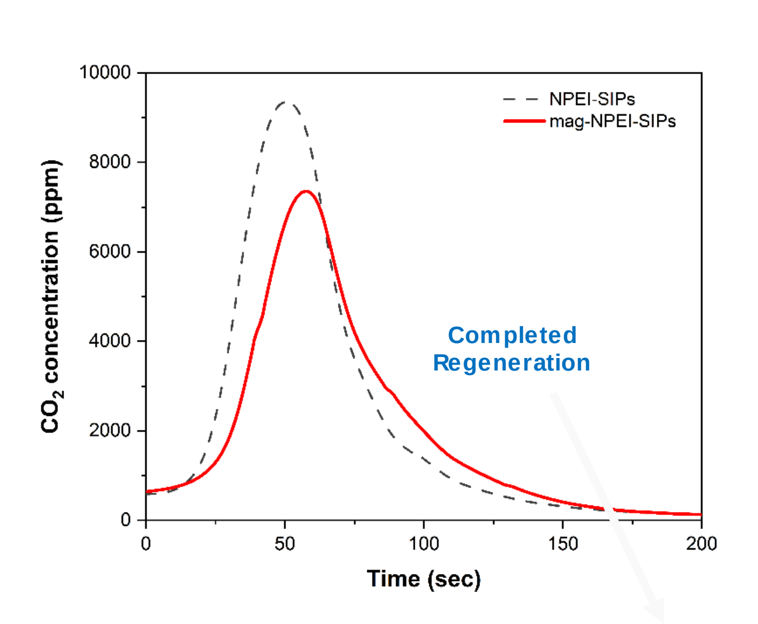






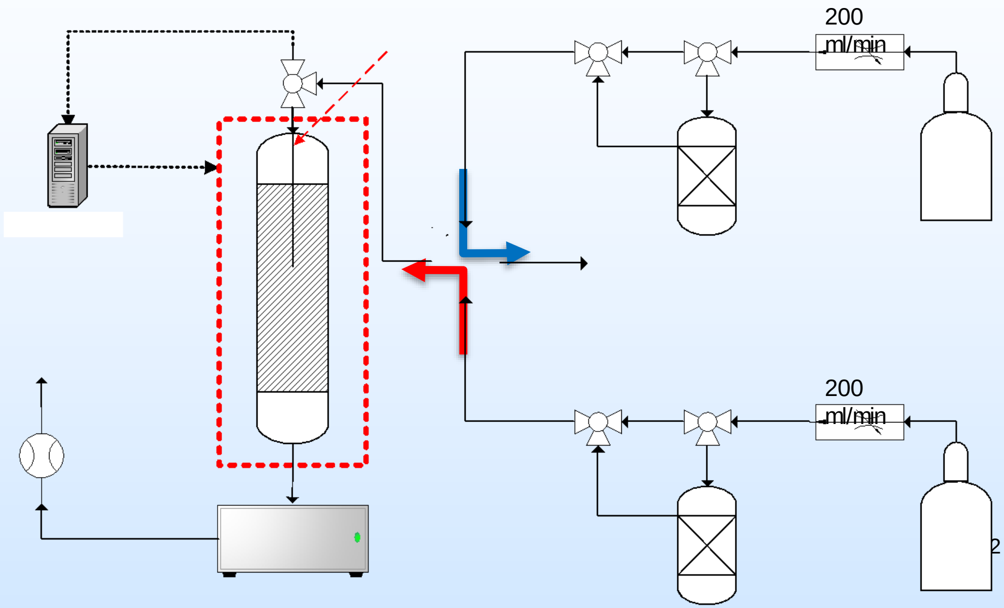
Regeneration of CO_2 using microwave and the effect of magnetic particles

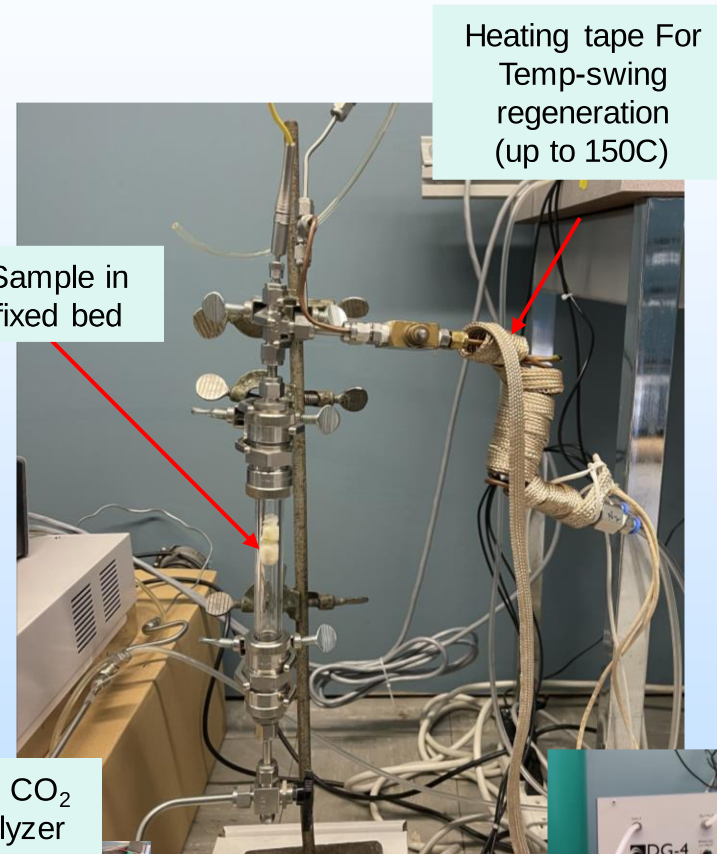




Plans for future testing

Experimental setup for Breakthrough Testing

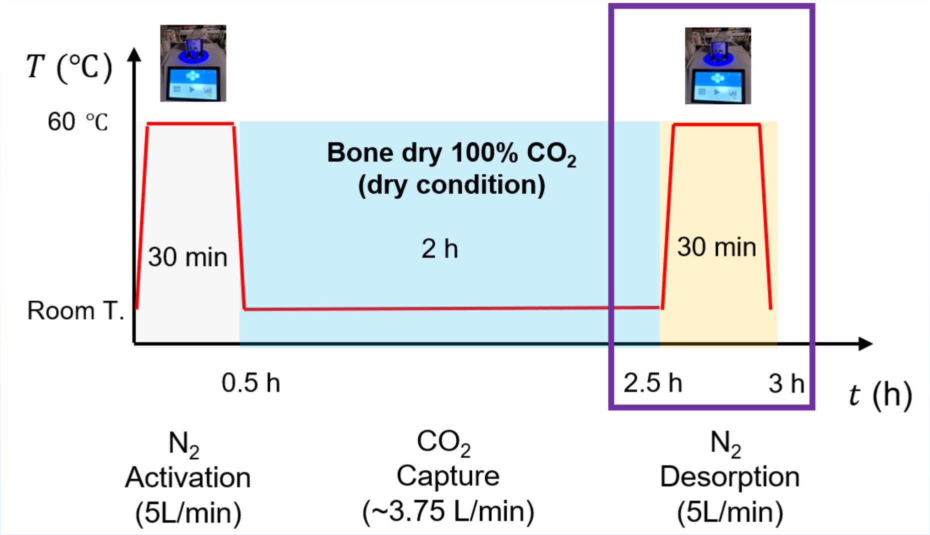




Goal: Test the effect of humidity and multiple cycles under DAC condition

Current optimization:
Reactor size, flowrate, and sample loading

Rapid Regeneration Using Microwave desorption



Microwave-transparent silica reactor

Energy consumption

Summary

- Successfully synthesized NOHMs with oxidative thermal stability
- Electrospinning process and parameters have been optimized for PIM-1 or PAN/OPSZ + amine hybrid fibers
- Morphological control gives uniform fiber dimensions with consistent incorporation of liquid/liquid-like amine sorbents
- Tested encapsulated NOHMs and shown promising thermal cyclability and CO_2 capture performance across multiple loading/regeneration cycles
- High-level TEA estimates that a large manufacturing plant (30 ton/yr) for electrospun PAN/OPSZ/NIPEI fiber sorbents yields $226/kg sorbent
- Non-thermal energy transfer (e.g., microwave) can be used to increase desorption kinetics, which could be further enhanced via adding magnetic particles to NOHMs

Acknowledgements

- Students and Collaborators
- **Tony Feric at DOE**
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- Ming Gao, Wei Yu, Sara Hamilton
- Junfeng Wang
- Youngjune Park (Gwangju Institute of Science and Technology, Korea)
- Andrew Lin (National Chung Hsing University, Taiwan)
- Camille Petit (Imperial College London, UK)

U.S. DEPARTMENT OF ENERGY

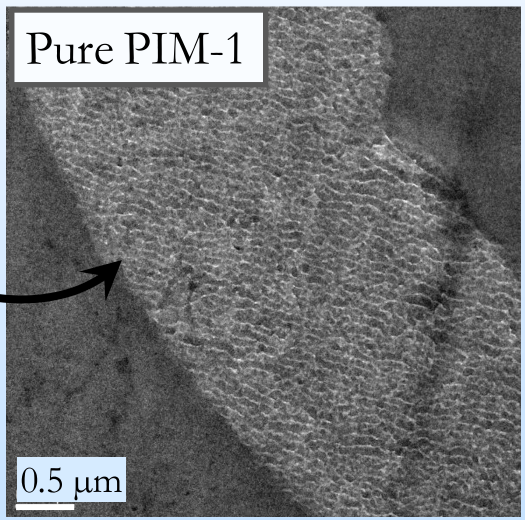
Appendix

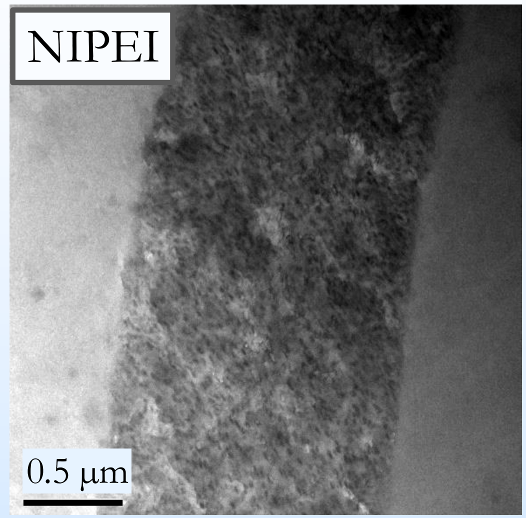
Incorporation of Amine Solvents into PIM-1 Electrospun Fibers

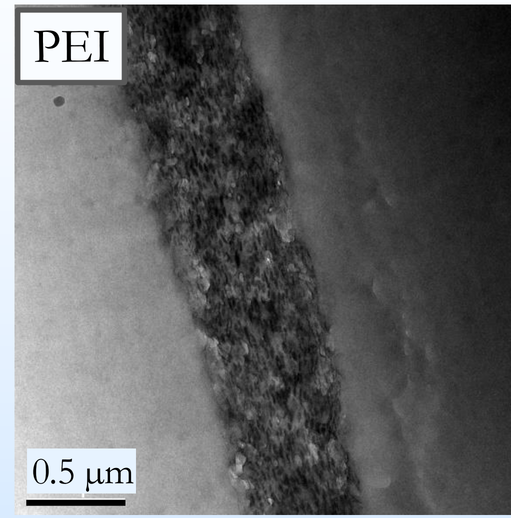
Internal mesoporosity visible inside fibers containing NIPEI or PEI

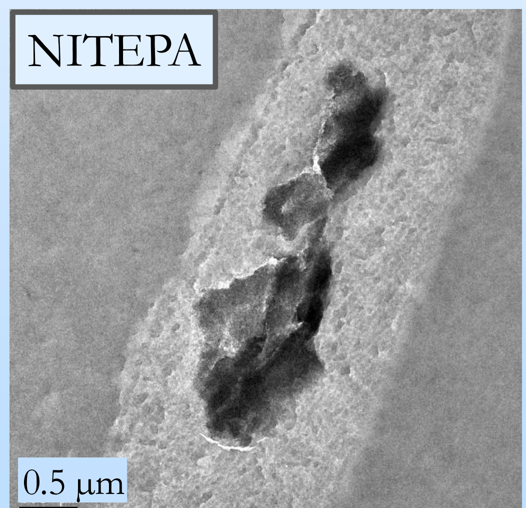
High contrast with background suggests uniform NIPEI and PEI incorporation

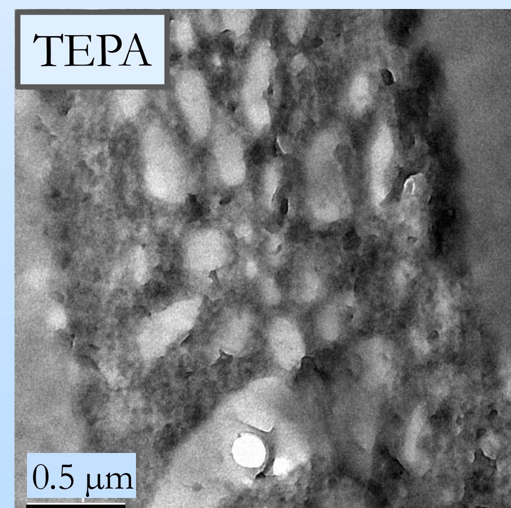
Uniform, microporous internal structure of pure PIM-1









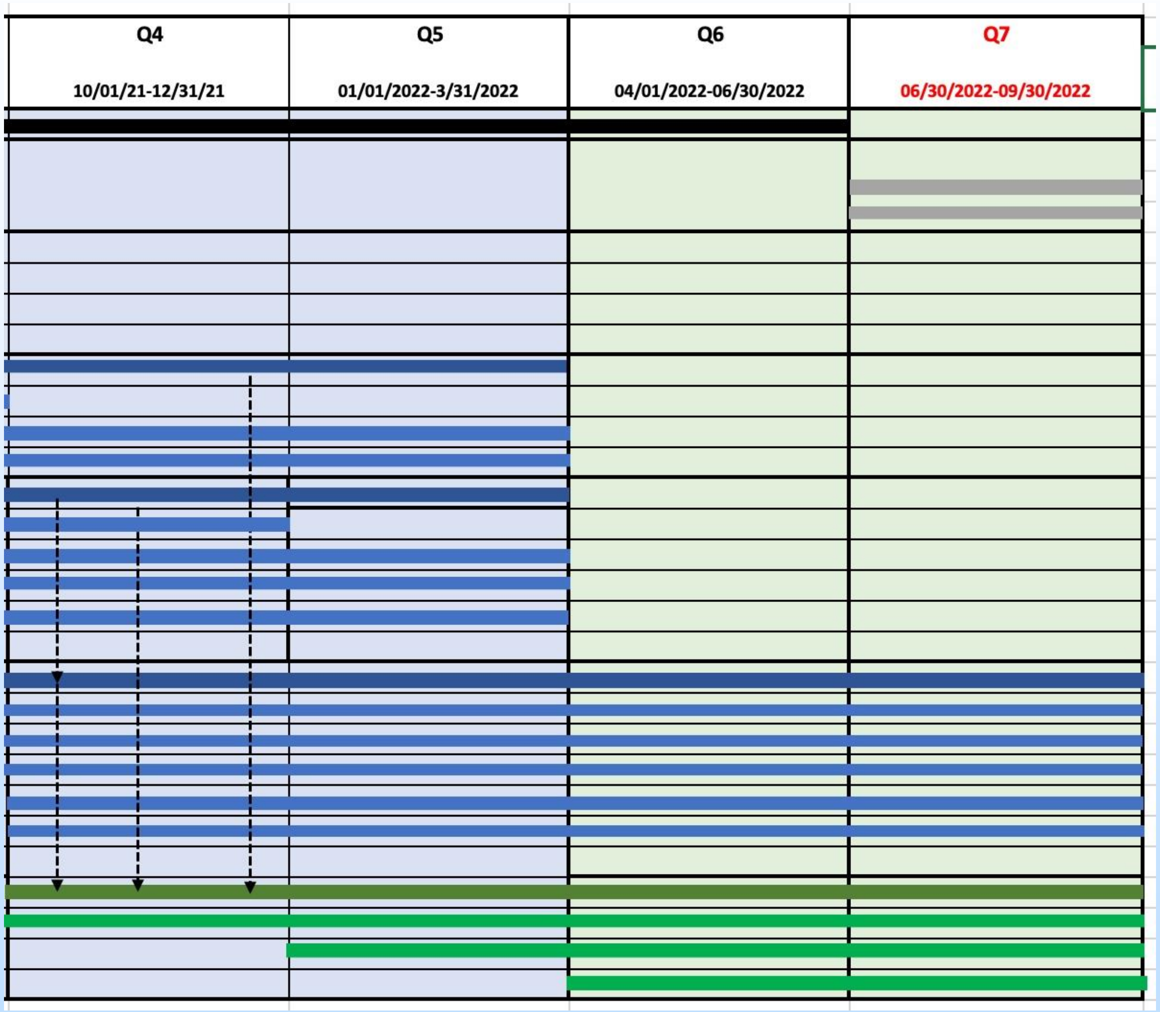


Solid-phase NITEPA apparent as isolated crystals, whereas untethered TEPA shows internal voids due to low viscosity and leaching

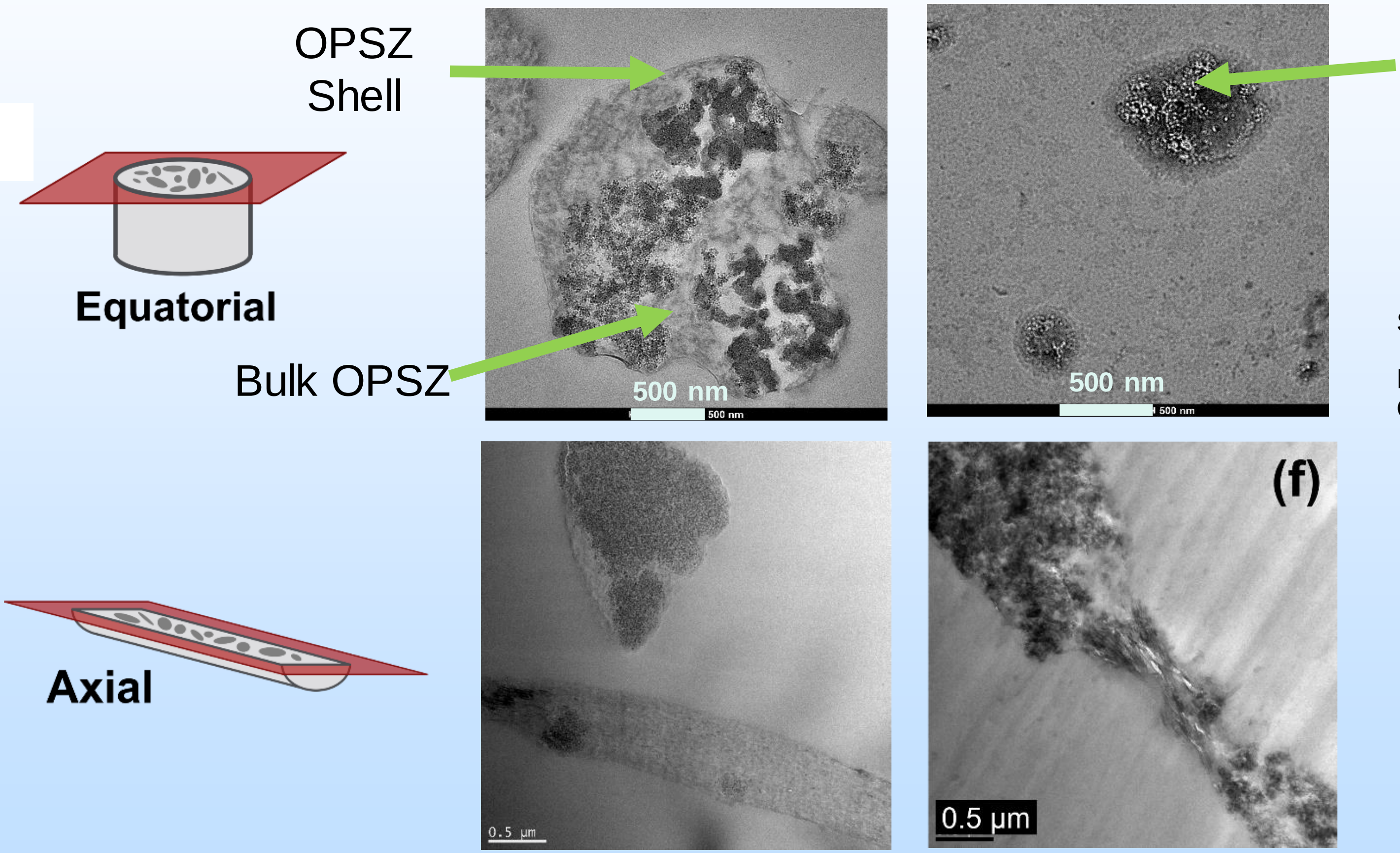
Gantt Chart

			Start date	End date	Q1 01/01/-2021-03/31/21	Q2 04/01/21-06/30/21	Q3 07/01/21-09/30/21
Columbia	Task 1	**Project management and planning**					
		ST 1.1 – Project Management Plan	1/1/21	3/31/21			
		ST 1.2 – Technology Maturation Plan	6/30/22	9/30/22			
		ST 1.3 – Technology EH&S Risk Assessment	6/30/22	9/30/22			
Columbia ORNL Cornell	Task 2	**Design and Synthesis of NOHMs for CO2 Capture**	1/1/21	3/31/21			
		ST 2.1. Synthesis of NOHMs with different amine group	1/1/21	9/30/22			
		ST 2.2. Optimization between CO2 capture capacity and viscosity of NOHMs	1/1/21	3/31/21			
		ST 2.3. Characterization and evaluation of pure NOHMs for encapsulation and CO2 capture	1/1/21	3/31/21			
ORNL Cornell Columbia	Task 3	**Fabrication of NOHMs/PIM coaxial nanofibers**	4/1/21	3/31/22			
		ST 3.1. Enhancement of PIM's hydrophobicity, thermal stability, and mechanical properties	4/1/21	9/30/22			
		ST 3.2. Electrospining of NOHMs/PIM coaxial nanofibers	7/1/21	9/30/22			
		ST 3.3. Charaterization of NOHMs/PIM coaxial nanofibers	7/1/21	9/30/22			
Cornell ORNL Columbia	Task 4	**Fabrication of NOHMs (core)/ceramic (sheath) nanofibers**	4/1/21	3/31/22			
		ST 4.1. Control hydrophobicity of ceramic (OPSZ)	2/1/21	9/30/21			
		ST 4.2. Conventional monoaxial electrospining of NOHMs and OPSZ mixture	7/1/21	3/31/22			
		ST 4.3. Coaxial electrospining of NOHMs (core) and OPSZ (sheath)	7/1/21	3/31/22			
		ST 4.4. Characterization of NOHMs/ceramic nanofibers	7/1/21	3/31/22			
		ST 4.5 Compare perma-selectivity of composite PIM-1/NIPEI membranes vs. fiber-encapsulated air filter	1/1/22	9/30/22			
Cornell Columbia ORNL	Task 5	**Fabrication of air filters with NOHMs/(PIM or ceramic) nanofibers**	7/1/21	9/30/22			
		ST 5.1. Deposition of nanofibers on a coarse filter media	7/1/21	9/30/22			
		ST 5.2. Characterization of nanofibers bearing air filter media	6/30/22	9/30/22			
		ST 5.3. CO2 capture using air filters - fixed bed testing	6/30/22	9/30/22			
		ST 5.4. Long term CO2 capture testing in a lab scale unit with simulated air (with moisture)	6/30/22	9/30/22			
		ST 5.5. Develop thermodynamic and kinetic models for laboratory phase equilibria results	10/1/21	9/30/22			
		ST 5.6 Test sorbent regeneration using microwave non-thermal energy coupled with fluidized bed	1/1/22	9/30/22			
ORNL Columbia Cornell	Task 6	**Process Modeling and TEA/LCA**	10/1/21	9/30/22			
		ST 6.1. Development of full-scale process models for direct air capture	10/1/21	9/30/22			
		ST 6.2. Operation of process models to achieve DOE targets	1/1/22	9/30/22			
		ST 6.3. Economic Analysis and Life Cycle Analysis	4/1/22	9/30/22			

Gantt Chart


Q4
10/01/21-12/31/21
Q5
01/01/2022-3/31/2022
Q6
04/01/2022-06/30/2022
Q7
06/30/2022-09/30/2022

PAN/OPSZ-Encapsulated NIPEI: Distribution of NIPEI within Nanofibers



Sample:

NOHM-I-PEI / (PAN & OPSZ) (50/50)

Fiber cross-section via Epoxy, Microtome and TEM (Lead Citrate Stain)

Kersey, K. et al., Manuscript in Review

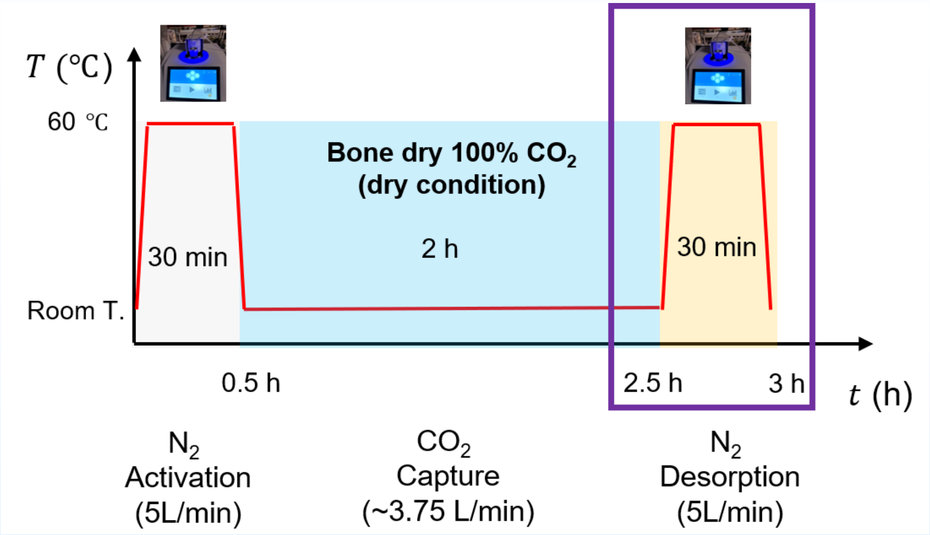
Opportunities for Collaboration

Collaboration among team members: PIs have distinct expertise (Park: CO_2 capture materials and mechanistic studies, Kidder: Material development, advanced characterizations and mechanistic understanding in capture and conversion, Joo: electrospinning and device fabrication) and have a long history of strong collaborations. The proposed hybrid DAC materials require the expertise from all three areas.

List potential areas of complementary work that others may contribute to this technology

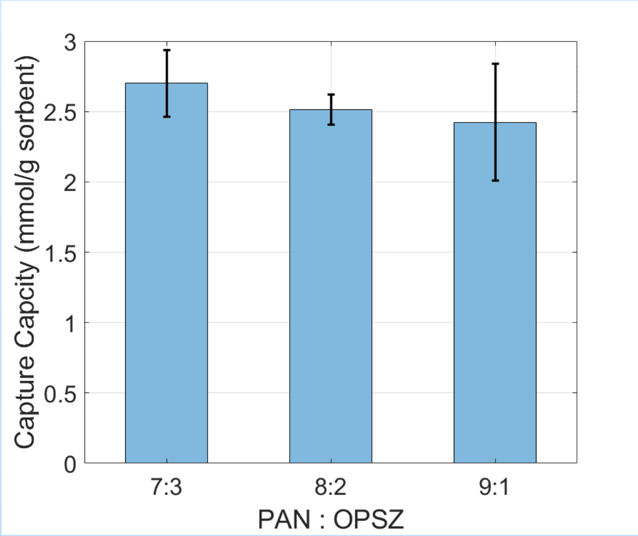
- **Scale-up:** DAC companies (e.g., Climeworks, Global Thermostat), Energy companies (e.g., Shell, TOTALEnergies, Saudi Aramco)
- **Engineering design and fabrication:** HVAC technology companies
- **The utilization of captured CO_2**: Conversion R&D groups

Rapid Regeneration Using Microwave desorption

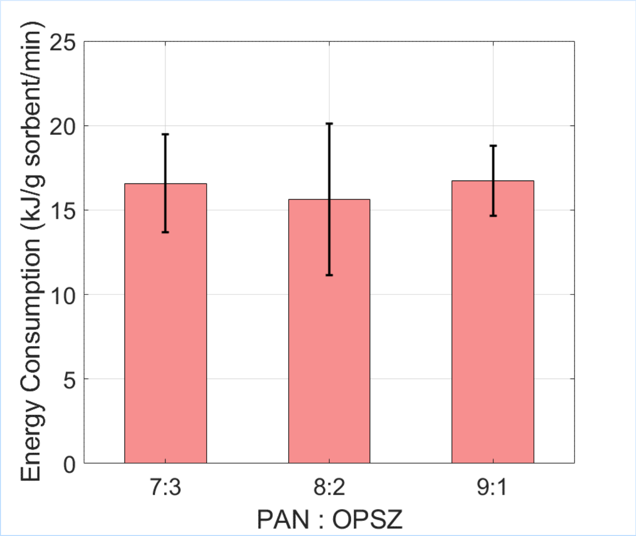


Microwave-transparent silica reactor

Capture capacity

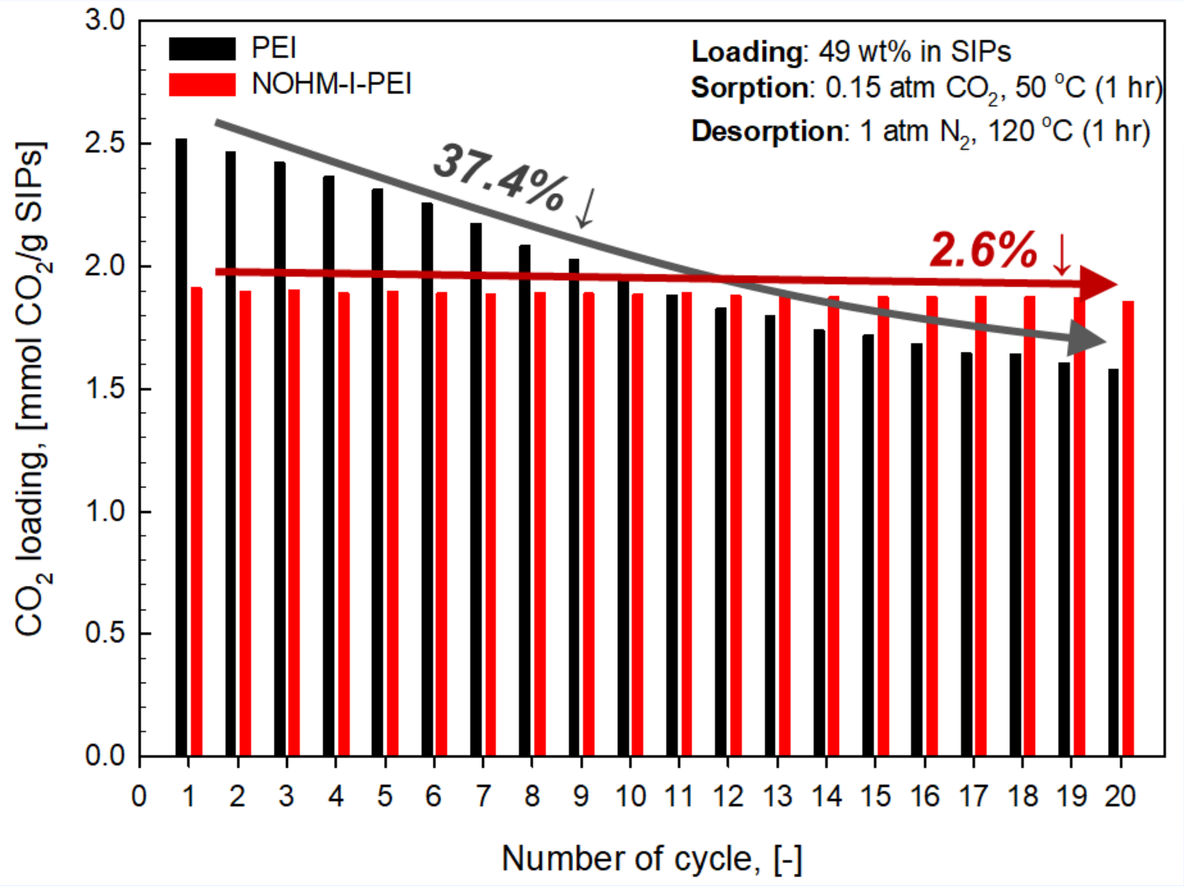


Energy consumption



Microwave regeneration process could be further enhanced via adding magnetic particles

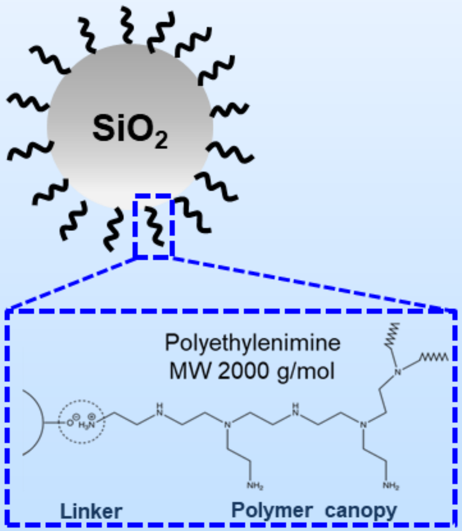
Recyclability of Thermally Stabile NIPEI-SIPs



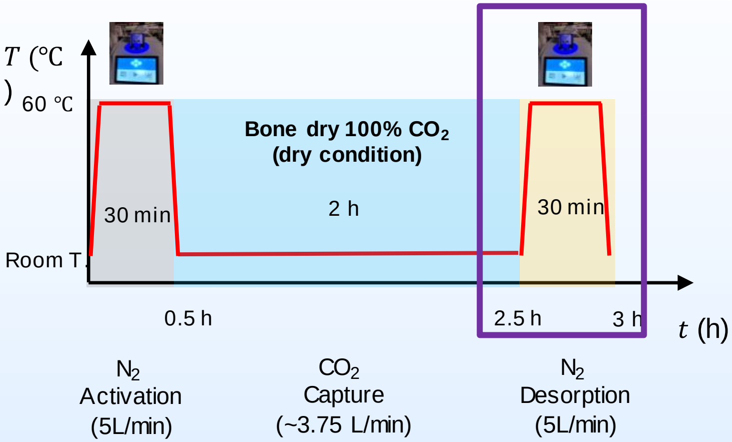
1^{st} cycle

PEI-SIPs > NPEI-SIPs

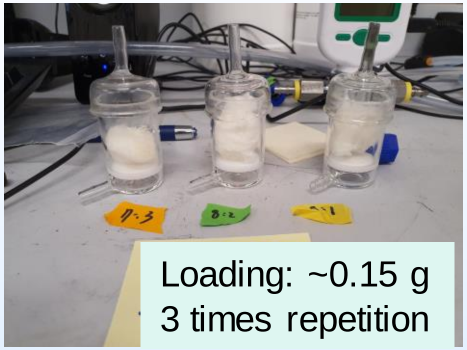
→ 20 wt% of inert silica nanoparticles



1 atm CO_2 capture and microwave desorption (PAN:OPSZ - NIPEI)



PAN-OPSZ-NIPEI

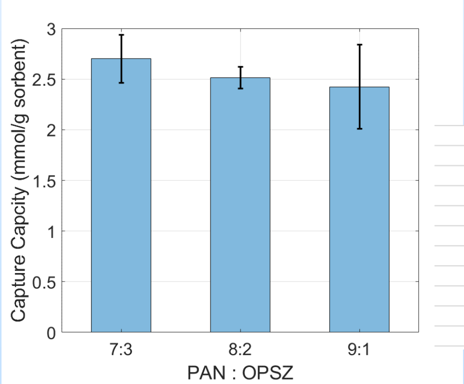


Microwave
hot spots
burn some region
Even at 60℃
(standing wave)

→ Need solutions
to enhance
heat transfer

Loading: ~ 150 mg (× 10 times)
Capture: 2 hr, 1 atm CO_2, 25 °C
Regeneration: **30 min**, 1 atm N_2, 60 °C
Flowrate: ~ 5 L / min (× 100 times)

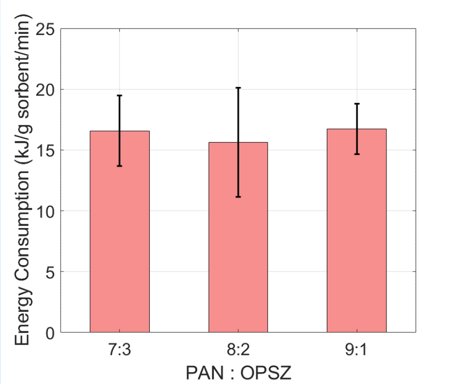
Capture capacity



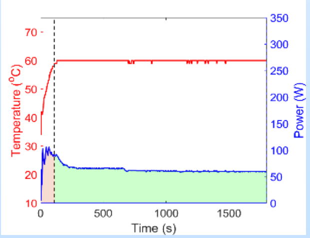
Weight measurement

Unit: (g)	1st
empty rxtor	34.9644
after loading	35.2341
after activation	35.1496
after capture	35.1727
after desorption	35.1454
loading (g sorbent)	0.1852
captured CO2 (g)	0.0231
capacity (mmol/gsorbent)	2.8348
diff (act - des)	0.0042

Energy consumption



Area under the curve



- Capture capacity is in order of 7:3 → 8:2 → 9:1.
- Energy consumption very similar but still very high! → can be improved by putting magnetic particles