Bench-Scale Testing of Monolithic PPI Structured Contactors for Direct Air Capture of CO_2

DE-FE0032094

Dr. Christopher Bertole
CORMETECH, Inc.

2023 Carbon Management Research Project Review Meeting
August 28 – September 1, 2023

Funding and Performance Dates

- Two years total period, in two budget periods.
- Total Federal Share = $1,500,000.
- Cost share = 20%.

BUDGET	Budget Period 1 9/15/2021 – 9/14/2022			Budget Period 2 9/15/2022 – 12/14/2023*			Total 9/15/2021 – 12/14/2023*		
	Federal Share	Cost Share	Total	Federal Share	Cost Share	Total	Federal Share	Cost Share	Total
Total	$882,681	$220,670	$1,103,351	$617,319	$154,330	$771,649	$1,500,000	$375,000	$1,875,000
Cost Share %	20%			20%			20%		

*90-day project NCE to 12/14/23 for completing the TEA/LCA work.

Project Participants

Georgia Tech

Overall Project Objectives

- Develop a next generation oxide monolith + amine structured contactor for DAC, based on poly(propyleneimine) (l-PPI).

- Refine, with inputs from experimental kinetic, thermodynamic and transport measurements, the following models:
  - (i) Single channel monolith model
  - (ii) DAC process model

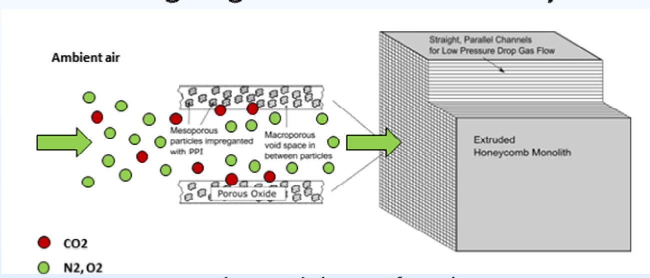
  in order to:
  - (iii) Simulate the impact of substrate textural properties (meso and macro porosity) on DAC performance, and
  - (iv) Enable contactor optimization prior to prototype synthesis and bench-scale testing validation.

- Refine the DAC process TEA and LCA.

Technology Background

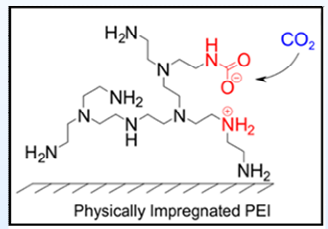
Global Thermostat DAC Platform

1. Moving Large Air Volumes Efficiently



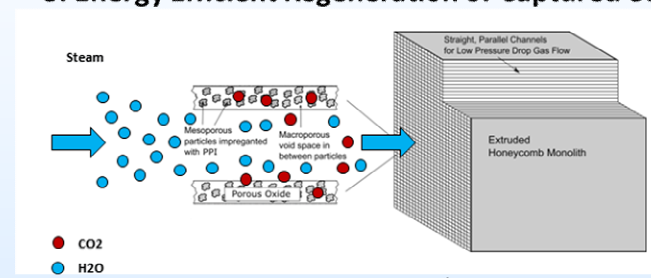
Honeycomb monoliths significantly outperform all other designs, enabling low pressure drop and minimum energy cost

2. Capturing CO_2 Selectively at 400 ppm



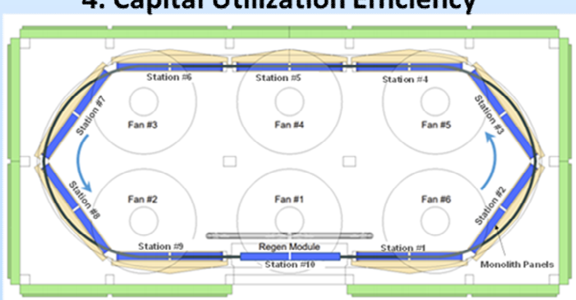
Amine-based polymers, incorporated in proprietary coatings, yield selectivity, capture efficiency, and compatibility with honeycomb monolith approach

3. Energy Efficient Regeneration of Captured CO_2



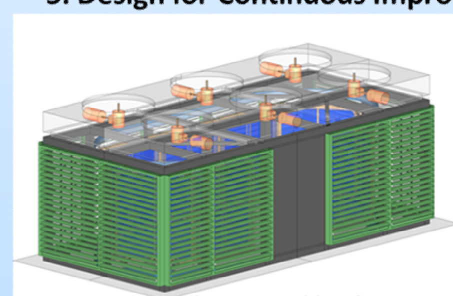
Temperature-Vacuum Swing Adsorption (TVSA) with steam as direct phase-change heat transfer fluid

4. Capital Utilization Efficiency



Process and mechanical movement design enable multi-bed adsorption configuration serviced by one regen module

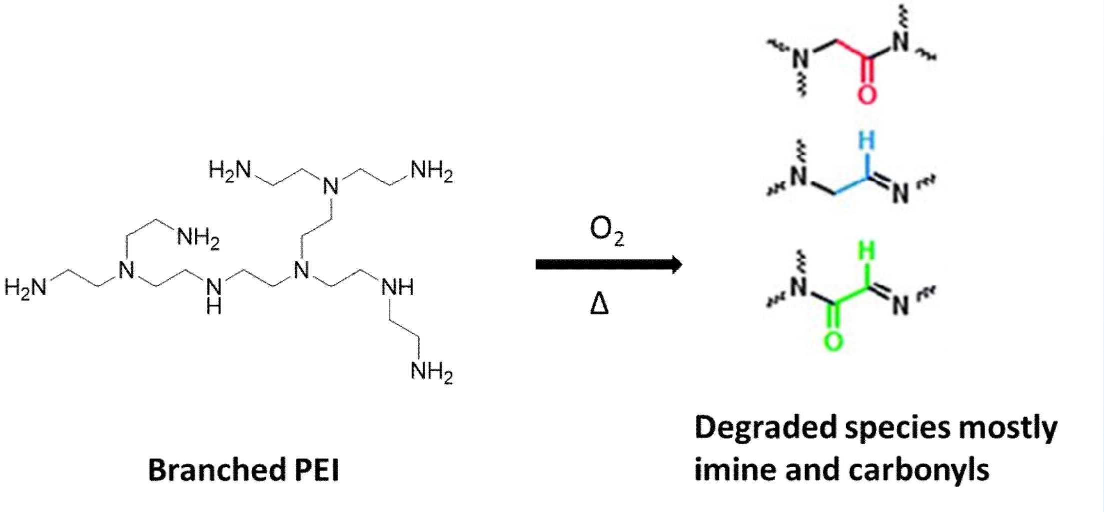
5. Design for Continuous Improvement



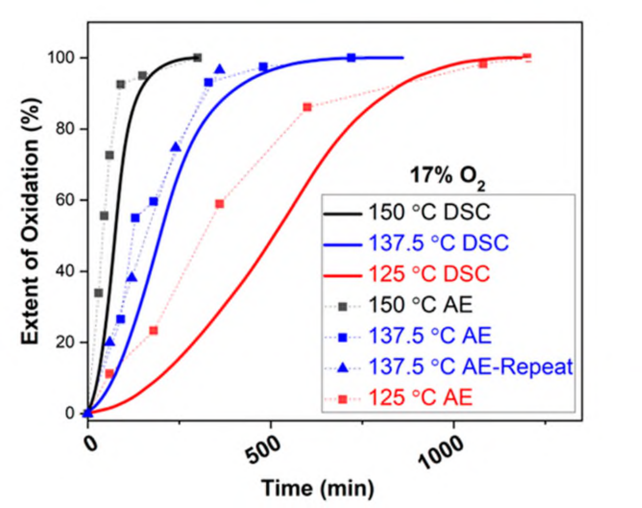
Base capital design capable of receiving new and future generations of improved adsorbent materials to regularly maximize capture capacity and extend plant capital life.

Technology Background
Oxidative Stability of Base Sorbent: PEI

- Poly(ethylenimine) is known to degrade in the presence of O_2.



Phys.Chem.Chem.Phys. 2014, 16, 1529-1535



ACS Sustainable Chem. Eng. 2021, 9, 25, 8477–8486

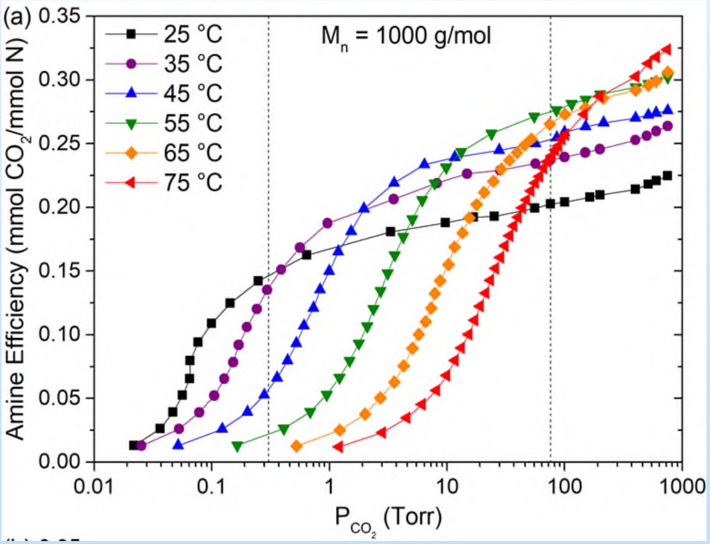
- GT's base DAC process is designed to mitigate high temp exposure.
  - Incorporating a new sorbent with enhanced oxidative stability will improve the on-stream sorbent lifetime in the base GT DAC process, and potentially enable new process paradigms.

Technology Background

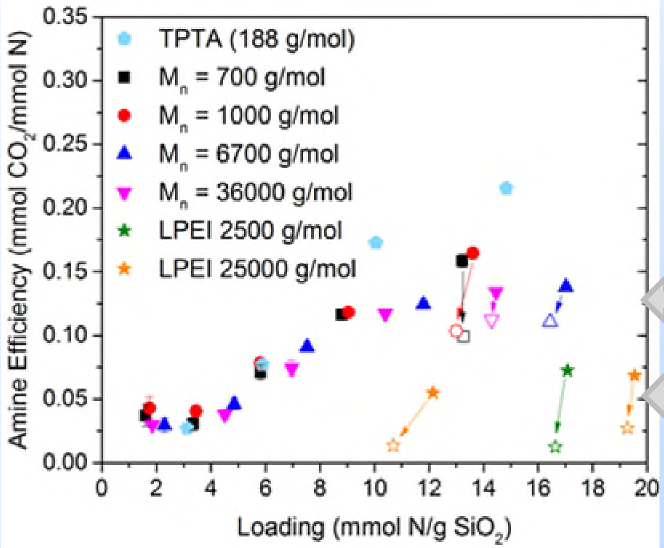
Improved Oxidative Stability Sorbent: PPI

- Poly(ethylenimine) / PEI: $-(NH-CH_2-CH_2)_{n>1}-NH_2$
- Poly(propyleneimine) / PPI: $-(NH-CH_2-CH_2-CH_2)_{n>1}-NH_2$

l-PPI has good CO_2 uptake for DAC.



l-PPI has superior oxidative stability.



Open Symbols:
Post-oxidative exposure
(24h at 110°C in 21% O_2/N_2)

l-PPI

l-PEI

Pang, S. H.; Lively, R. P.; Jones, C. W. ChemSusChem 2018, 11 (15), 2628-2637.

Technology Background
State before Start of Project

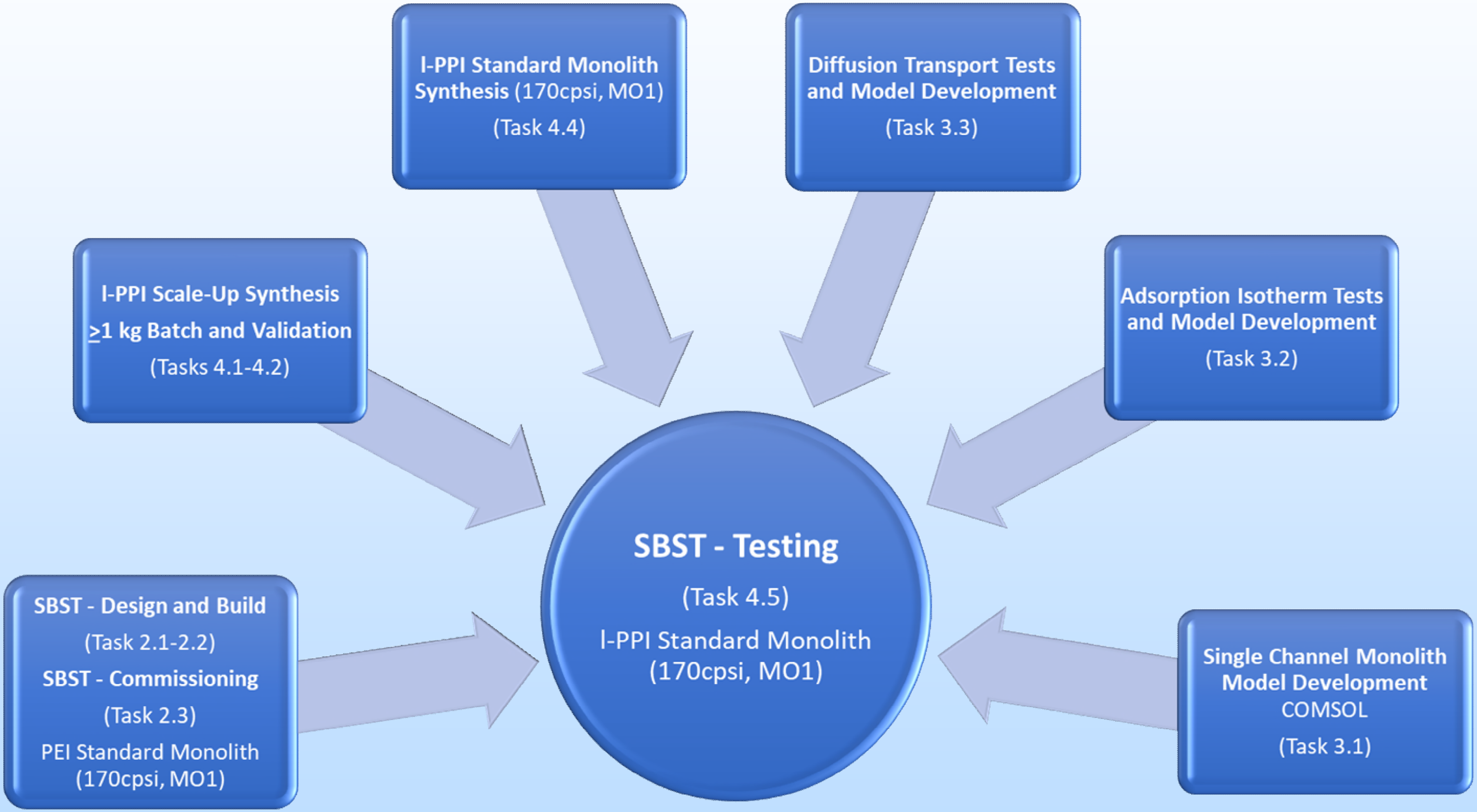
- **l-PPI performance under DAC conditions was only known:**
  - for supported powders,
  - under dry feed adsorption,
  - and thermal N_2 desorption conditions.

  Data were not available for monolith l-PPI under "real" process conditions.

- **l-PPI was not a commercially available material.**
  - Cannot order it from a catalog in sufficient quantity to run the bench-scale validation tests for a monolithic form.

Project Steps – BP1

Scale-Up of Linear-Poly(propyleneimine) (l-PPI)



MO1 = Metal Oxide–1 porous support

Project BP1 – Success Criteria

Decision Point	Date	Success Criteria
Completion of BP1	9/14/2022	❑ Adsorption data obtained under DAC relevant conditions for PEI baseline part, under at least two different operating conditions; data consistent with core sorption tester. ❑ Minimum 1 kg of I-PPI. ❑ Capacity of I-PPI > 1.00 (normalized target value basis) on single brick tester. ❑ Optimized substrate for I-PPI: min 20% adsorption capacity improved. ❑ Energy performance calculated from the process model.

Project – Risks and Mitigations

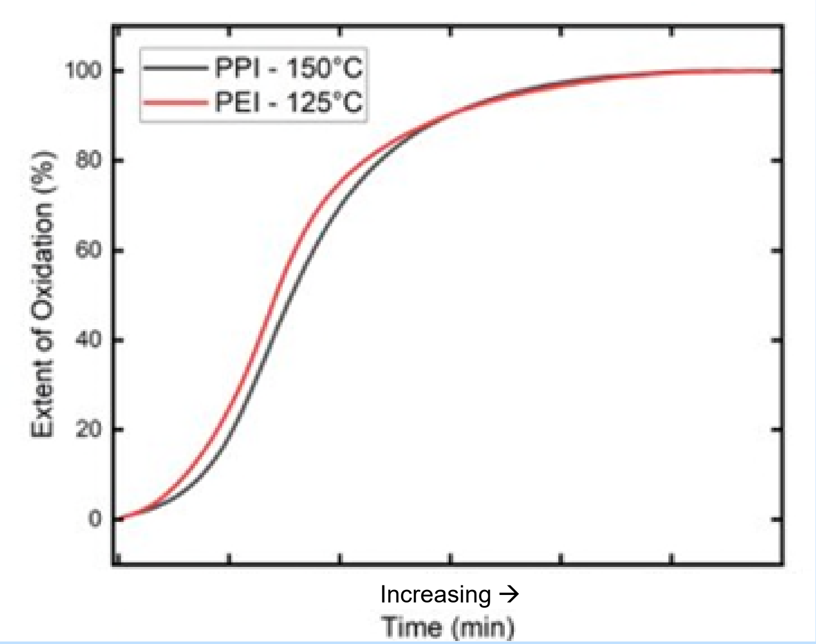
- **Risk 1: bench-scale test unit doesn't work properly.**
  - Mitigation: CORMETECH had extensive experience with unit design.
  - **Status: complete.** Data are in good agreement with core test unit.

- **Risk 2: l-PPI produced by sub-contractor is of poor quality.**
  - Mitigation: Global Thermostat set quality specifications for vendor.
  - **Status: complete.** Material produced met quality specifications.

- **Risk 3: only 1kg of l-PPI was produced by sub-contractor.**
  - Achieved target amount (min 1kg), but it's a limited, precious supply.
  - **Status: complete.** All core and full-size parts needed in the project work scope have been synthesized and tested.

Oxidative Stability Baseline Test
Completed in BP1

- **Initial testing of lab-scale l-PPI selected for scale-up:**
  - Confirmed significant oxidative stability benefit of l-PPI over PEI (+25^{o}C).

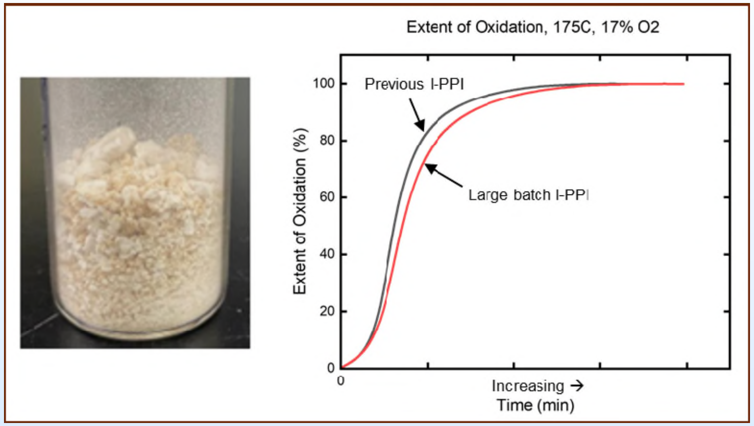


Isothermal DSC oxidative stability test

1kg L-PPI Scale-Up Batch
Completed in BP1

Table shows quality assurance tests run by vendor before shipment; all tests passed spec.

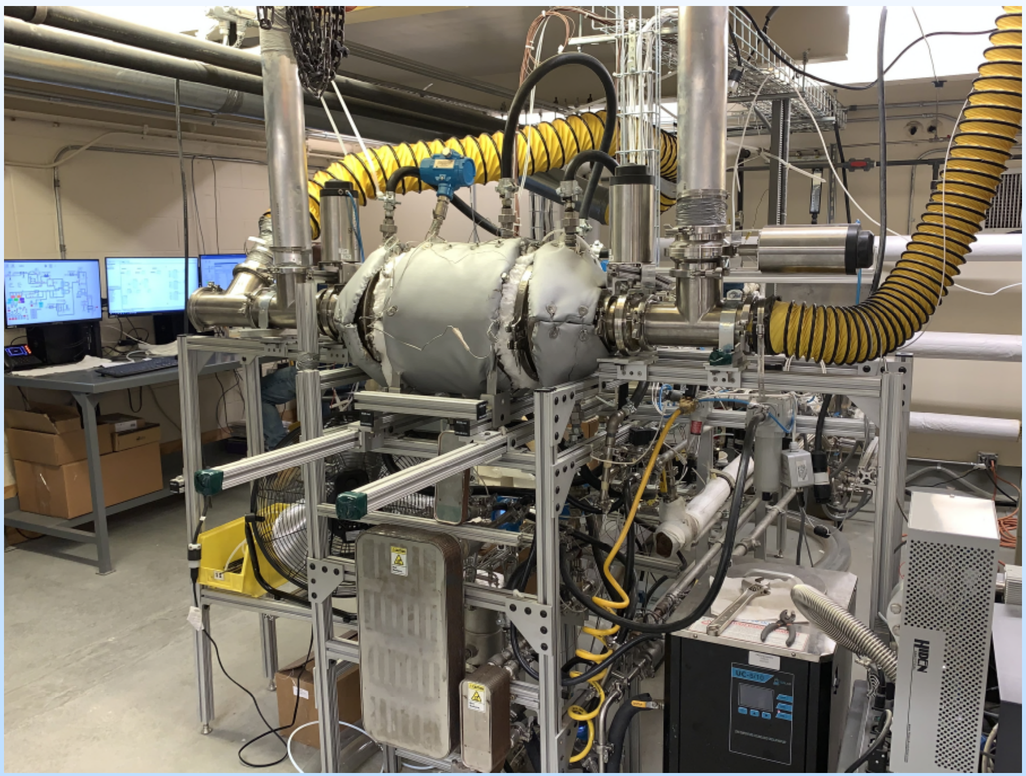
Parameter	Method
Appearance	Visual inspection
Average Molecular Weight	Calculated on NMR
Identity	^{1}H-NMR
Identity	ATR-IR
Purity	SEC-HPLC RI-Detection
Metals	ICP-MS
Amine content	Conductometric titration
Drying Loss	Extra Drying at 80°C, 5 mbar



- **GT and GTRC** performed validation tests on a small aliquot of the large batch l-PPI (ATR, CO_2 capacity, NMR, melting point, oxidative stability).
- Data comparison to the previously synthesized l-PPI indicated that the large-batch l-PPI is good material.

Single Brick Sorption Tester (SBST)
Bench-Scale Test Unit / Completed in BP1

Test Cycle: Air Adsorption → Vacuum Purge → Steam Injection → Vacuum Purge.



CORMETECH.

Fully-automated test unit.

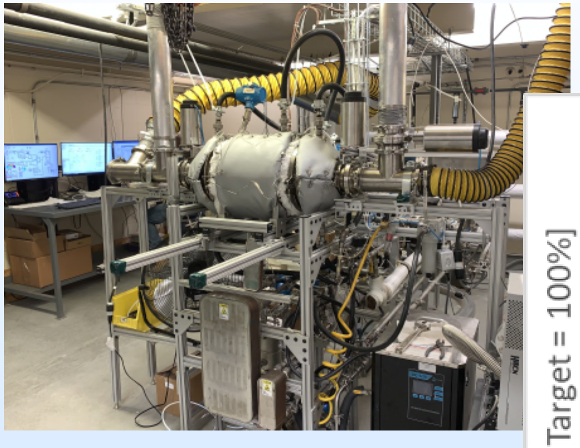
Low-range analyzers (inlet, outlet) for air stream analysis.

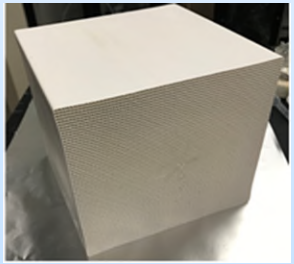
High-range analyzer for product stream analysis.

Mass spectrometer for fast transient analysis (steam out).

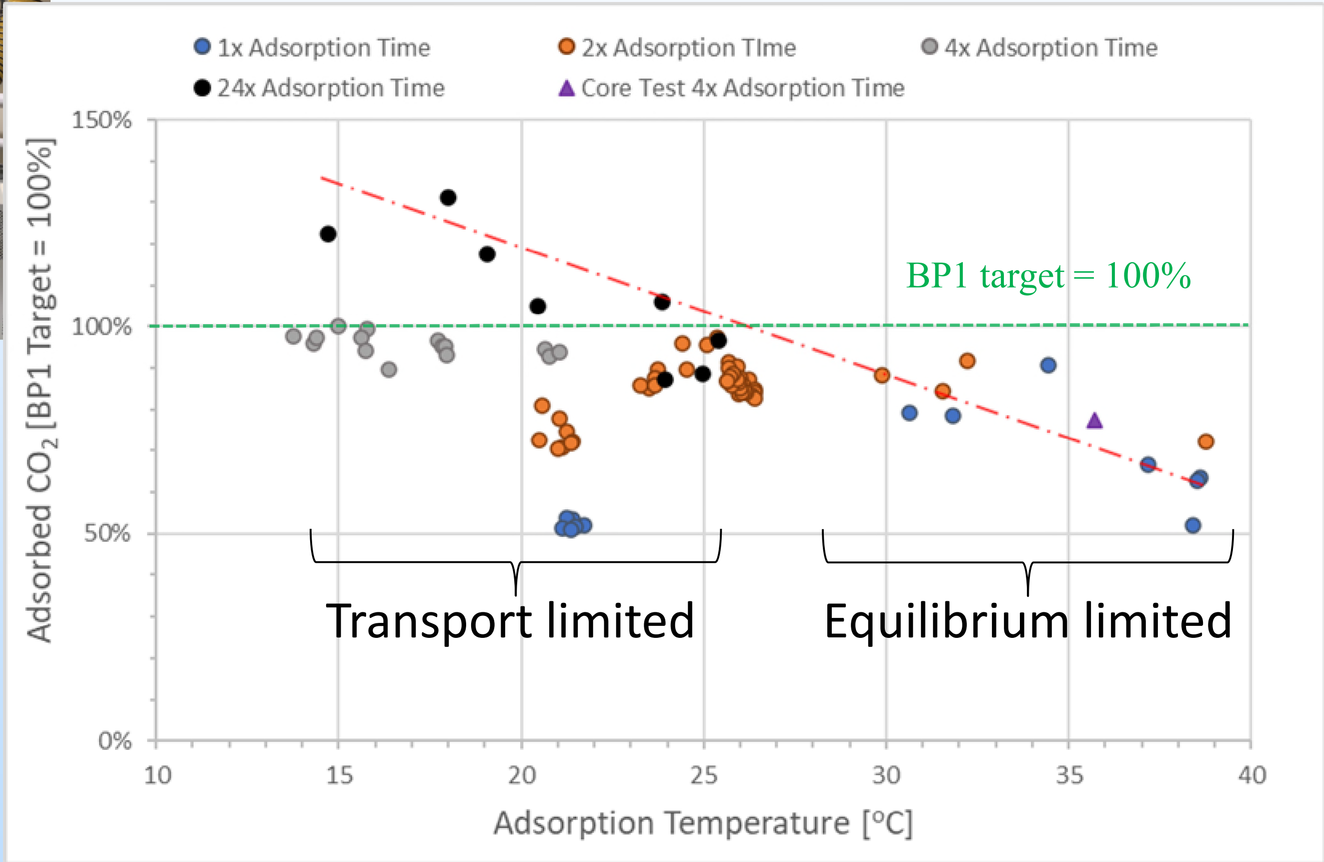
Commissioning: PEI part data agreed well with core data.

BP1 SBST Data for l-PPI Monolith
(170cpsi Standard Monolith MO1 Substrate)





BP1 performance target was achieved.
(H_2O content of air feed ranged from 1.0-1.9v%)



Clear opportunity to optimize for PPI:

- Substrate properties
- Amine loading

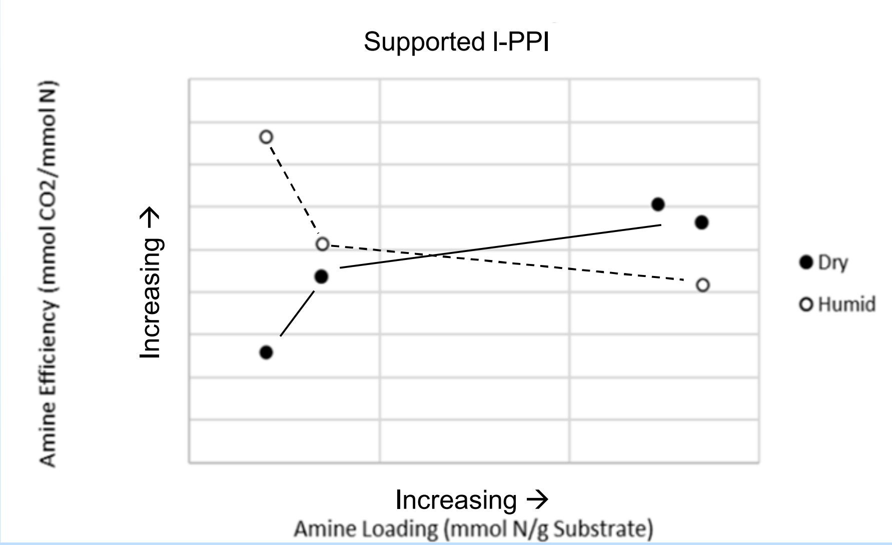
Core sample data (corrected to same PPI loading) is consistent with SBST data.

BP1 TGA and Core Test Data

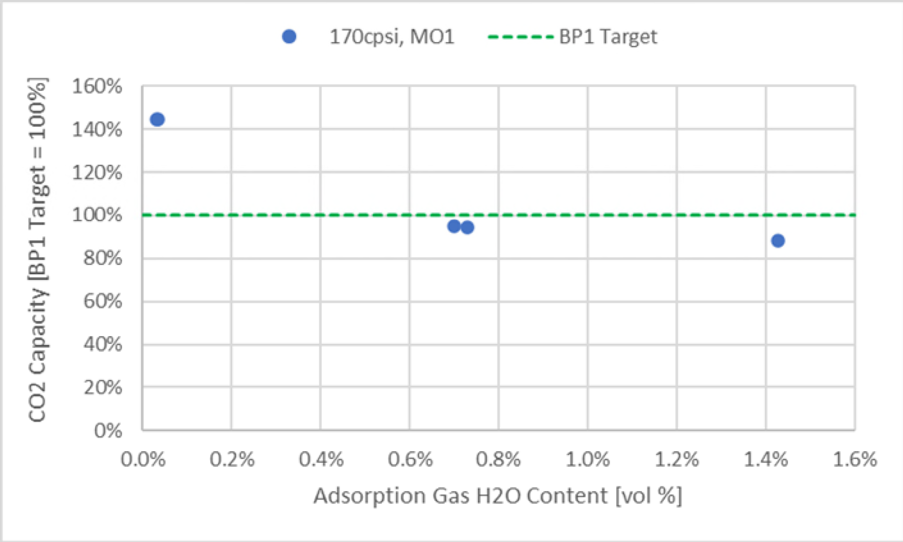
Impact of Adsorption Air Moisture Content

- **Air moisture can decrease l-PPI's CO_2 adsorption capacity.**
- **Humidity's impact depends on the l-PPI loading: it promotes at low PPI loading but inhibits at higher PPI loadings.**

Humid TGA data by Global Thermostat

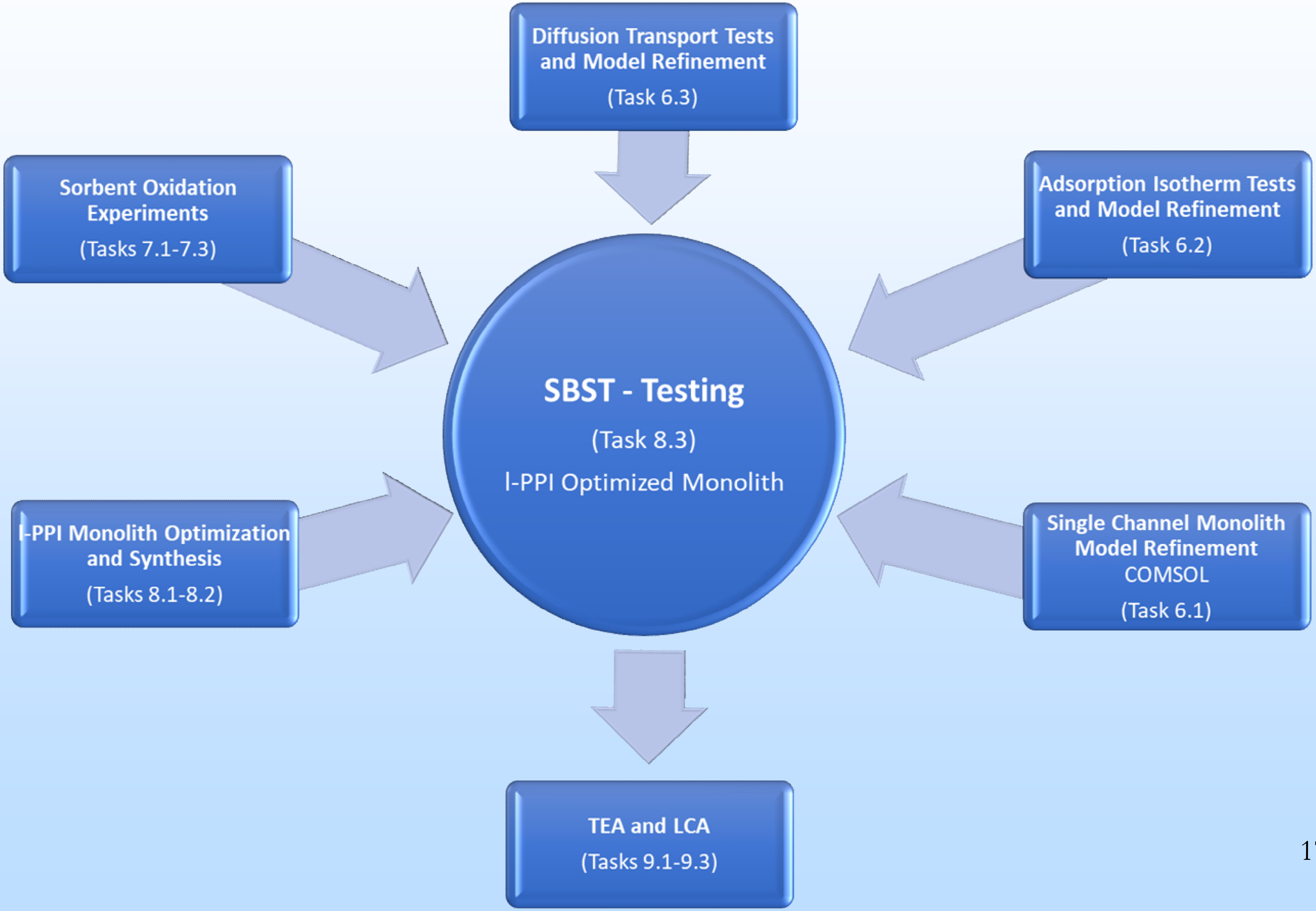


Core sample data by CORMETECH



Project Steps – BP2

Scale-Up of Linear-Poly(propyleneimine) (l-PPI)



Project BP2 – Success Criteria

Decision Point	Date	Success Criteria
Project Completion	12/14/2023	❑ Minimum of 1 full-size I-PPI loaded optimized substrate ready for testing on the single brick sorption tester. ❑ Capacity of I-PPI > 1.20 (normalized target value basis) on single brick tester. ❑ Oxidative stability of I-PPI validated, per State Point Data Table. ❑ Transport data obtained from at least 2 different methods show < 50% variation. ❑ The TEA/LCA show advantages of I-PPI-based DAC systems vs. PEI-based DAC systems.

Synergy Achieved

- **Fundamentals: Structure / Property Relationships**
  - Adsorption/desorption isotherms (Global Thermostat)
  - Diffusive transport (Georgia Tech)
  - Single-channel monolith model (CORMETECH)
- **Monolith Prototyping**
  - Batch and extrude monolith prototypes at CORMETECH, with structures optimized for l-PPI (from Fundamentals).
- **Monolith Testing**
  - Test optimized l-PPI monolith at CORMETECH on SBST.

Tasks 6.1-6.3, 8.1-8.2

Approach to Optimize Substrate for l-PPI

<u>Focus Areas for Improvement</u>

- **Increase CO_2 uptake rate.**
  - Modify size and distribution of meso / macro pores → faster diffusion
  - Increase cell density → faster transport (bulk channel to monolith wall)
- **Increase CO_2 uptake capacity.**
  - Increase pore volume → higher PPI loading
  - Lower cell density and increase wall thickness → higher PPI loading
  - Increase amine efficiency → better PPI utilization
- **Reduce H_2O inhibition effect on CO_2 uptake capacity.**
  - Modify mean size / distribution of meso / macro pores
  - Optimize PPI loading

Tasks 6.1-6.3, 8.1-8.2

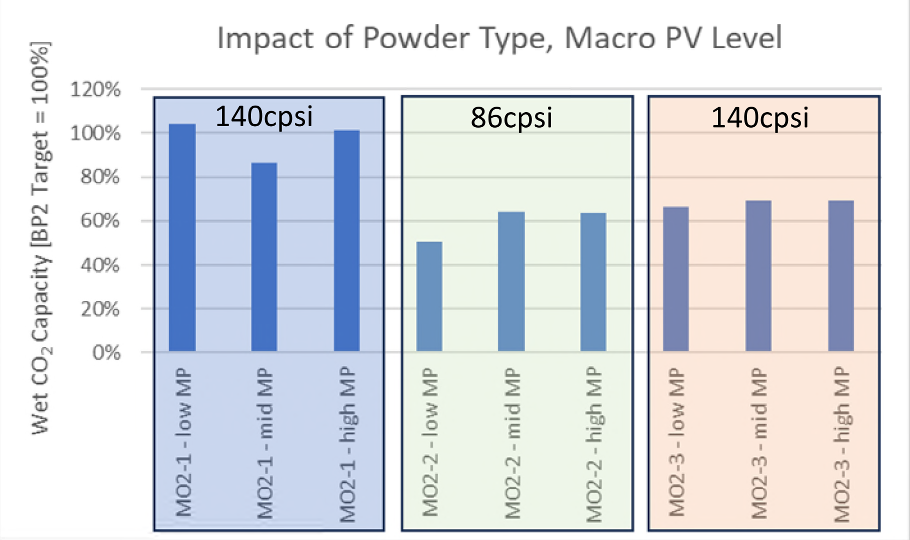
Approach to Optimize Substrate for l-PPI

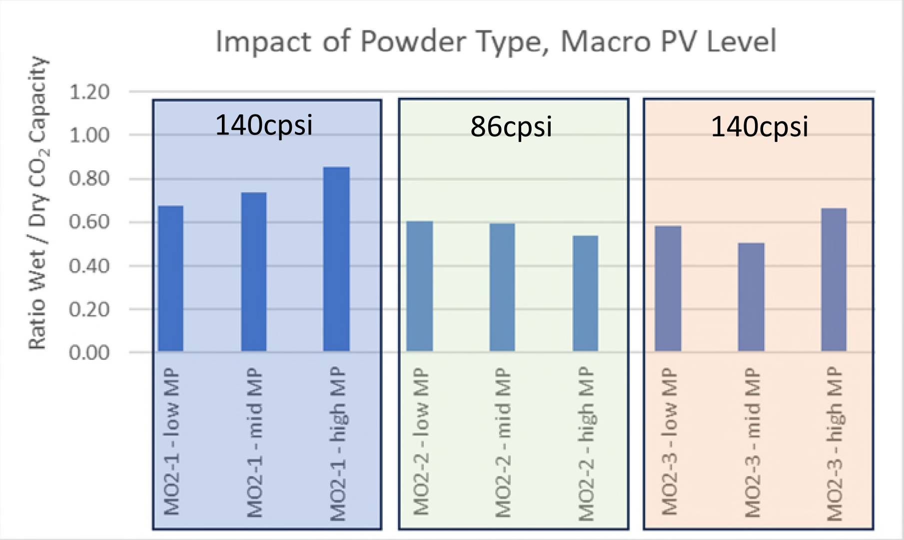
Work

- **“Set 1” monoliths.**
  - **Three MO2 powders with a range of meso-pore diameters.**
    - MO2-1: smallest diameter meso pores
    - MO2-2: middle diameter meso pores
    - MO2-3: largest diameter meso pores
  - **Three levels of macro-porosity achieved by addition of pore former.**
    - Low MP: no pore former addition
    - Mid MP: mid-level pore former addition
    - High MP: high-level pore former addition
  - **Made Set 1 samples with existing lab-process dies.**
    - MO2-1: 140 cpsi
    - MO2-2: 86 cpsi
    - MO2-3: 140 cpsi
  - **Test matrix for evaluation:**
    - 2 factors/3 levels: extruded 9 substrates and activated 9 samples.

"Set 1": PPI-Monolith Data

Adsorption = 35ºC, 450ppm CO_2, 1.3% H_2O, 20% O_2; Desorption = 105ºC, 100% N_2.





- **Best performing monolith:**
  - MO2-1 powder.
  - High MP level.

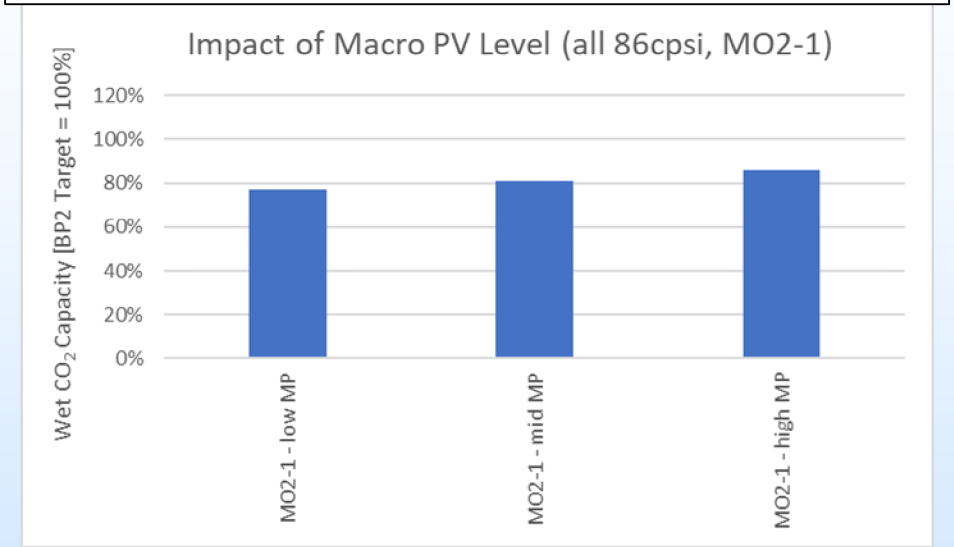
Tasks 6.1-6.3, 8.1-8.2
Approach to Optimize Substrate for l-PPI

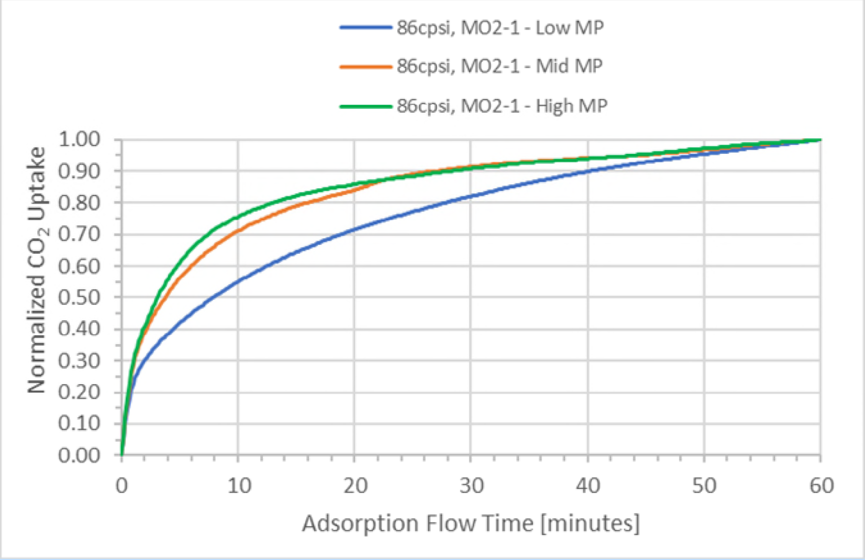
<u>Work</u>

- **"Set 2" monoliths.**
  - **Made Set 2 samples with new lab-process dies.**
    - 86 cpsi / thick wall, 170 cpsi reference, 325 cpsi.
  - **Test matrix for evaluation:**
    - Extruded 21 substrates and activated 7 samples.
    - Focus is on MO2-1-high MP (based on "Set 1" testing feedback).
  - **Confirmed MP level selection.**
    - MO2-1-low MP, MO2-1-mid MP, MO2-1-high MP: all with 86 cpsi / thick wall.
  - **Confirmed MO2 powder type selection.**
    - MO2-1, MO2-2, MO2-3: all with 86 cpsi / thick wall and high MP.
  - **Confirmed cell density selection.**
    - 86 cpsi / thick wall, 170 cpsi reference, 325 cpsi: all with MO2-1-high MP.

"Set 2": PPI-Monolith Data

Adsorption = 35°C, 450ppm CO_2, 1.3% H_2O, 20% O_2; Desorption = 105°C, 100% N_2.

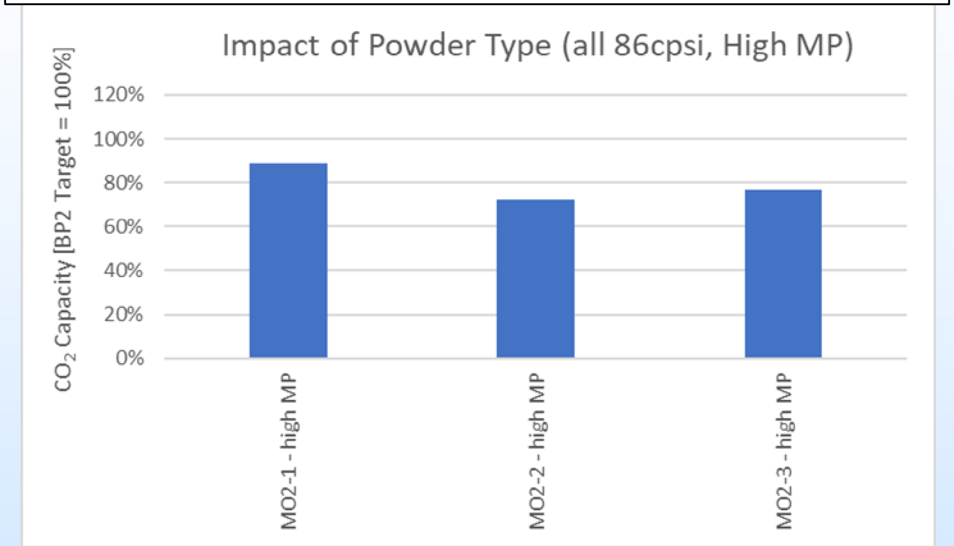


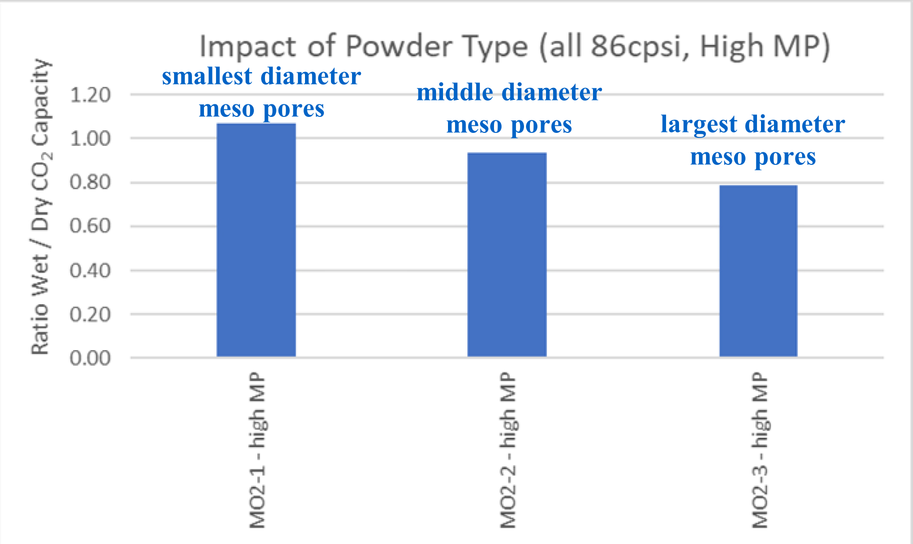


- **Best performing monolith:**
  - MO2-1 powder.
  - High MP level.

"Set 2": PPI-Monolith Data

Adsorption = 35°C, 450ppm CO_2, 1.3% H_2O, 20% O_2; Desorption = 105°C, 100% N_2.

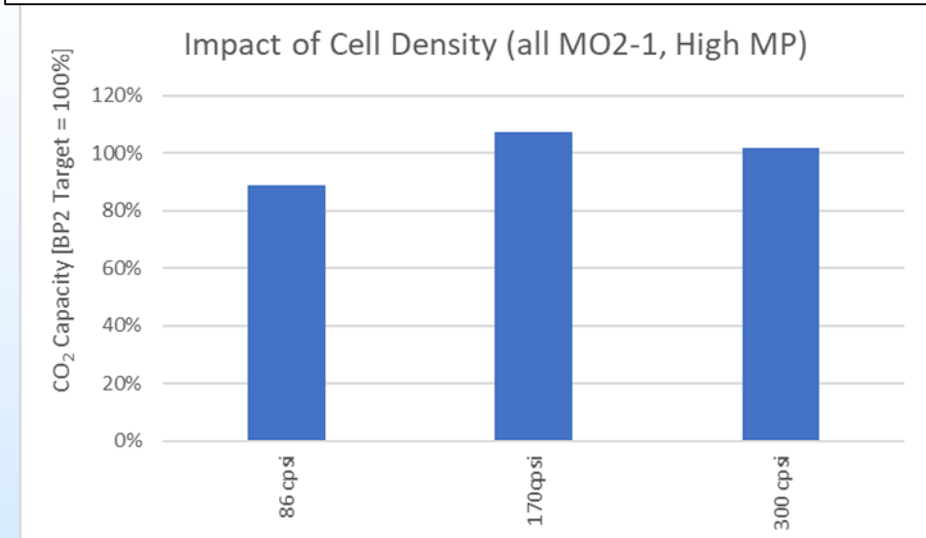


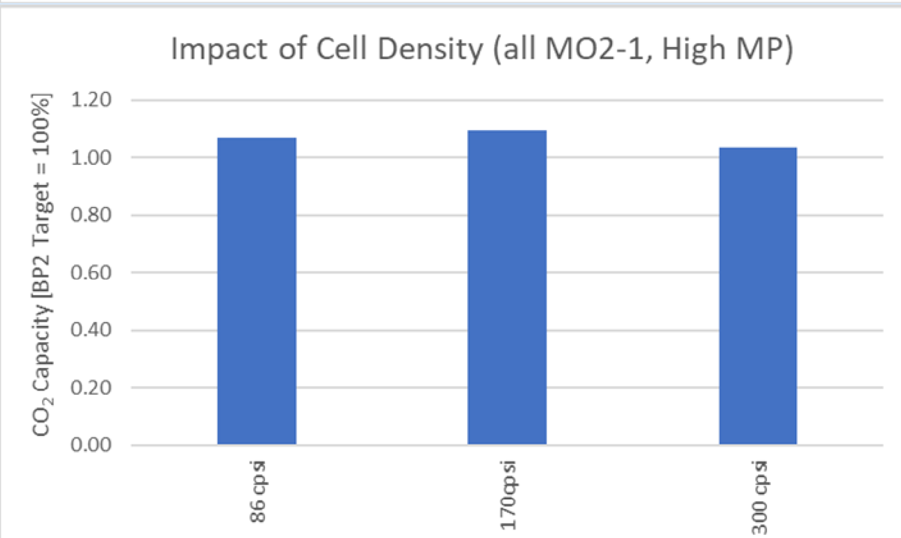


- **Best performing monolith:**
  - MO2-1 powder.
- **Water inhibition effect:**
  - Inverse relationship with pore diameter.

“Set 2”: PPI-Monolith Data

Adsorption = 35ºC, 450ppm CO_2, 1.3% H_2O, 20% O_2; Desorption = 105ºC, 100% N_2.



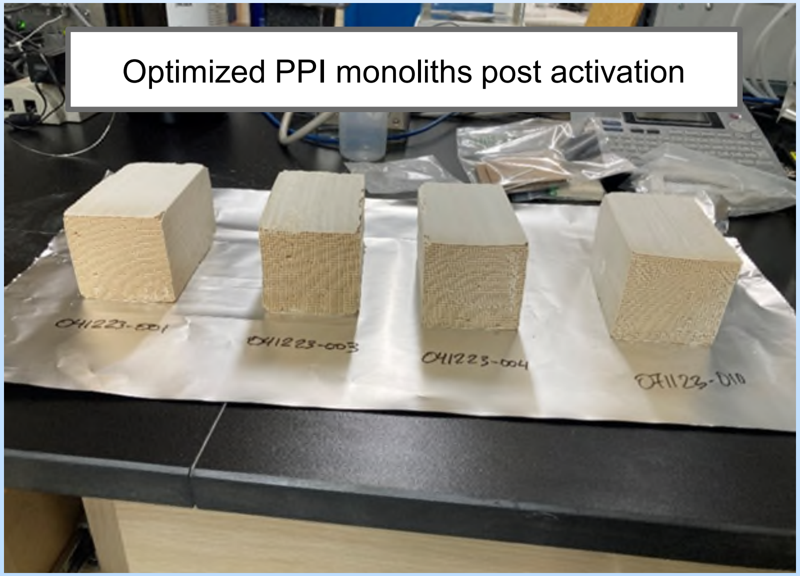


- **Best performing monolith:**
  - 170cpsi.
- **Optimal monolith selection:**
  - 170cpsi
  - MO2-1
  - High MP

Tasks 6.1-6.3, 8.1-8.2
Approach to Optimize Substrate for l-PPI

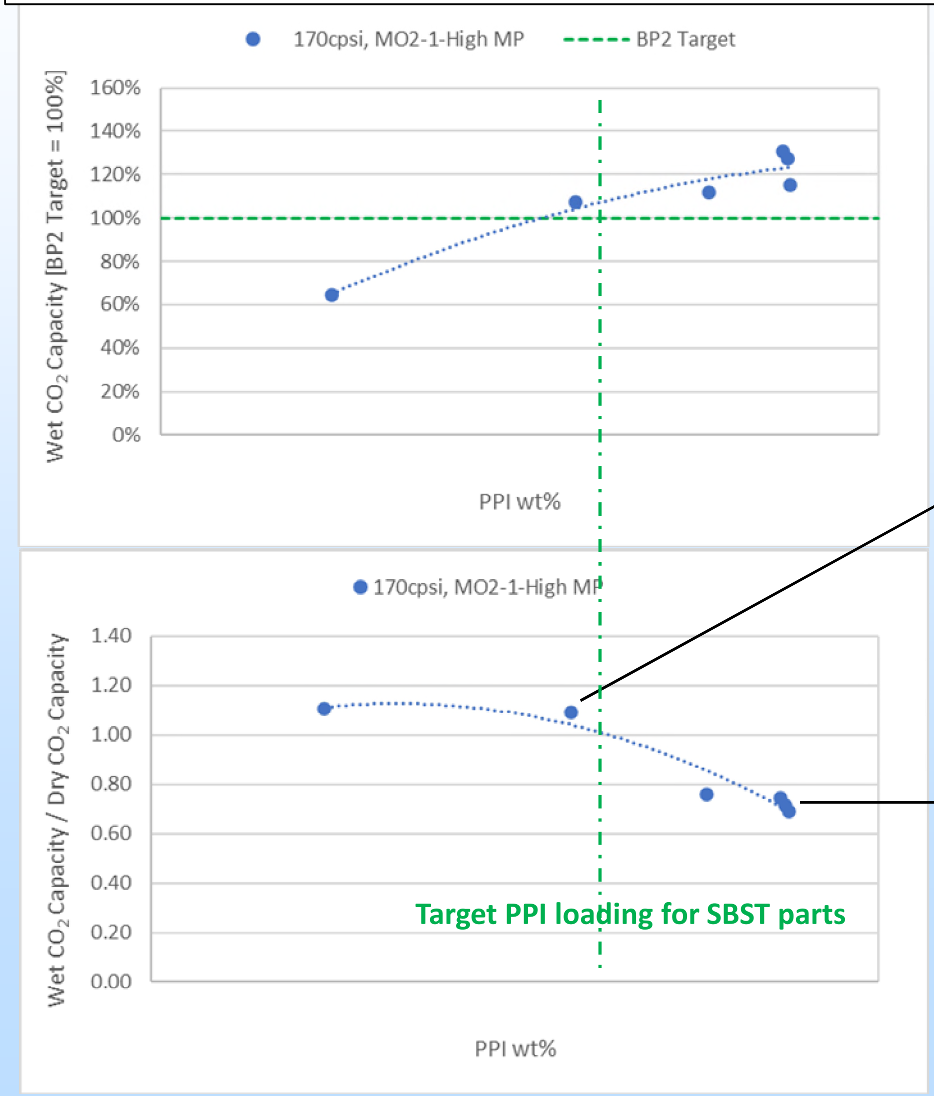
<u>Work</u>

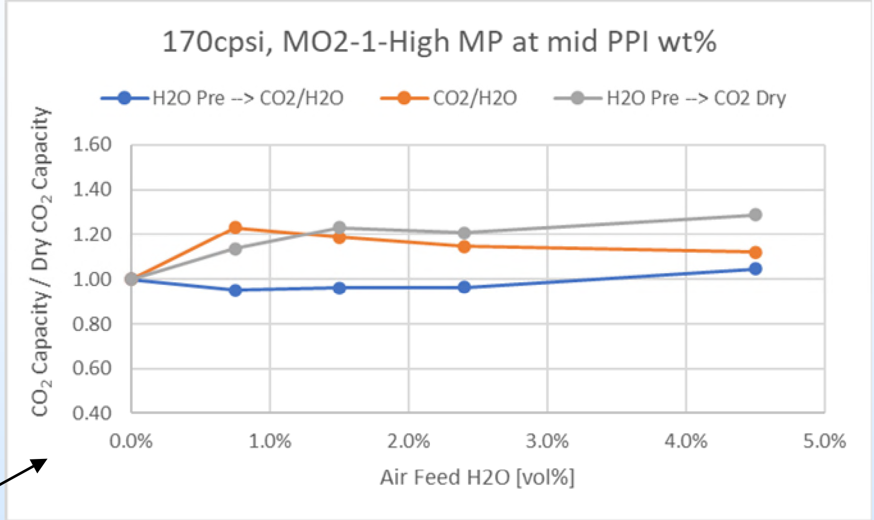
- **"Set 3" monoliths.**
  - Optimal monolith selection = 170cpsi, MO2-1, High MP
  - Confirmed optimal PPI loading for this substrate.
    - Meet BP2 capacity target, minimize water inhibition.
  - Made large PPI-monolith part (composite of 4 quadrants) for SBST testing.

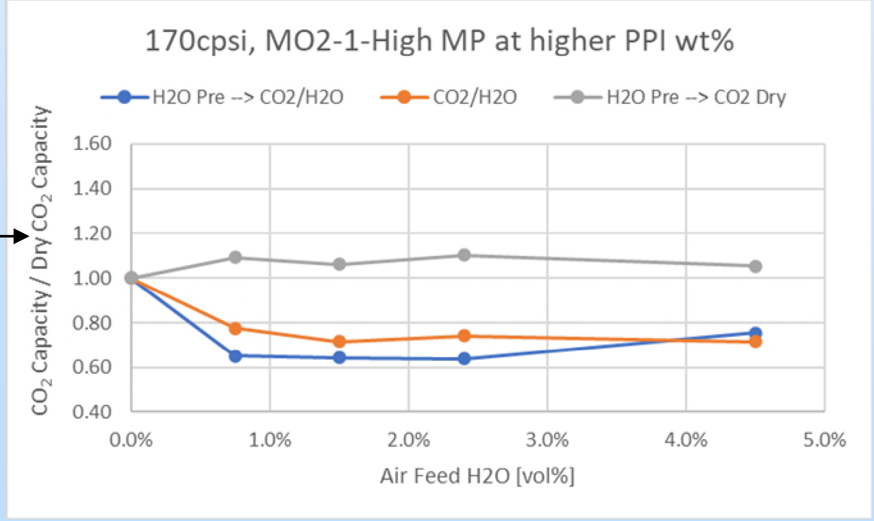


"Set 3": PPI-Monolith Data

Adsorption = 35ºC, 450ppm CO_2, 1.3% H_2O, 20% O_2; Desorption = 105ºC, 100% N_2.

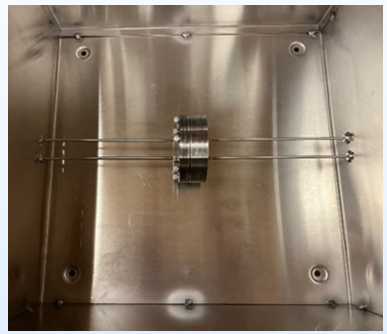


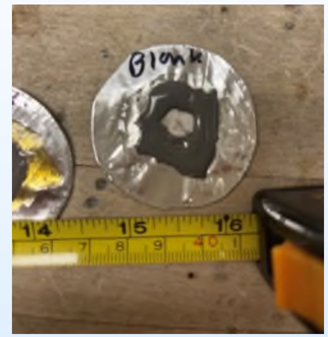


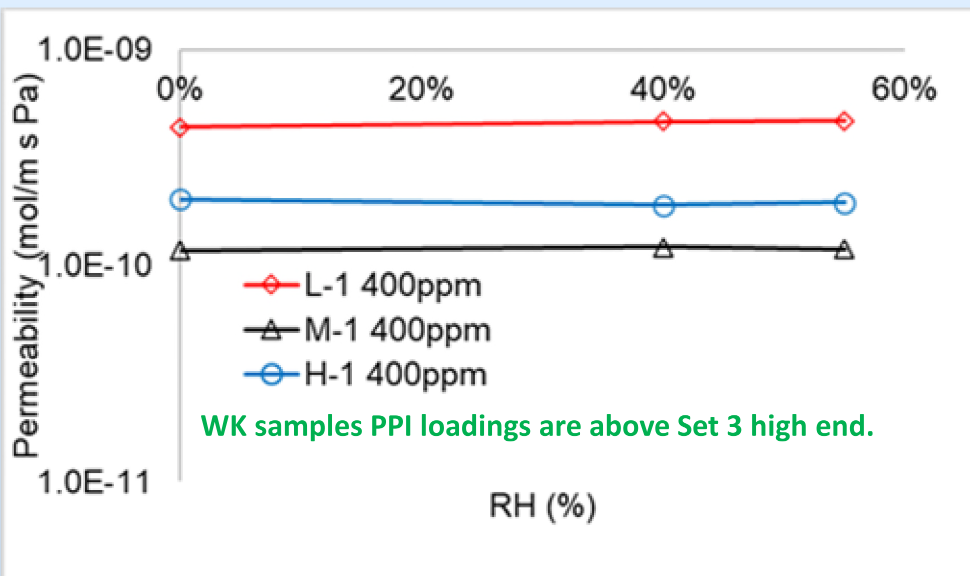


WK Data for PPI-MO2-1

Wicke-Kallenbach membrane diffusion cell

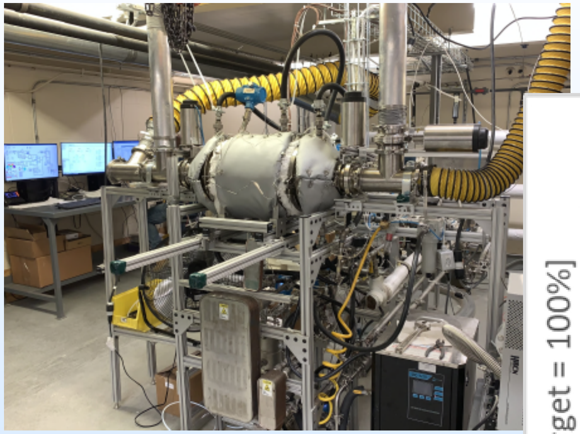




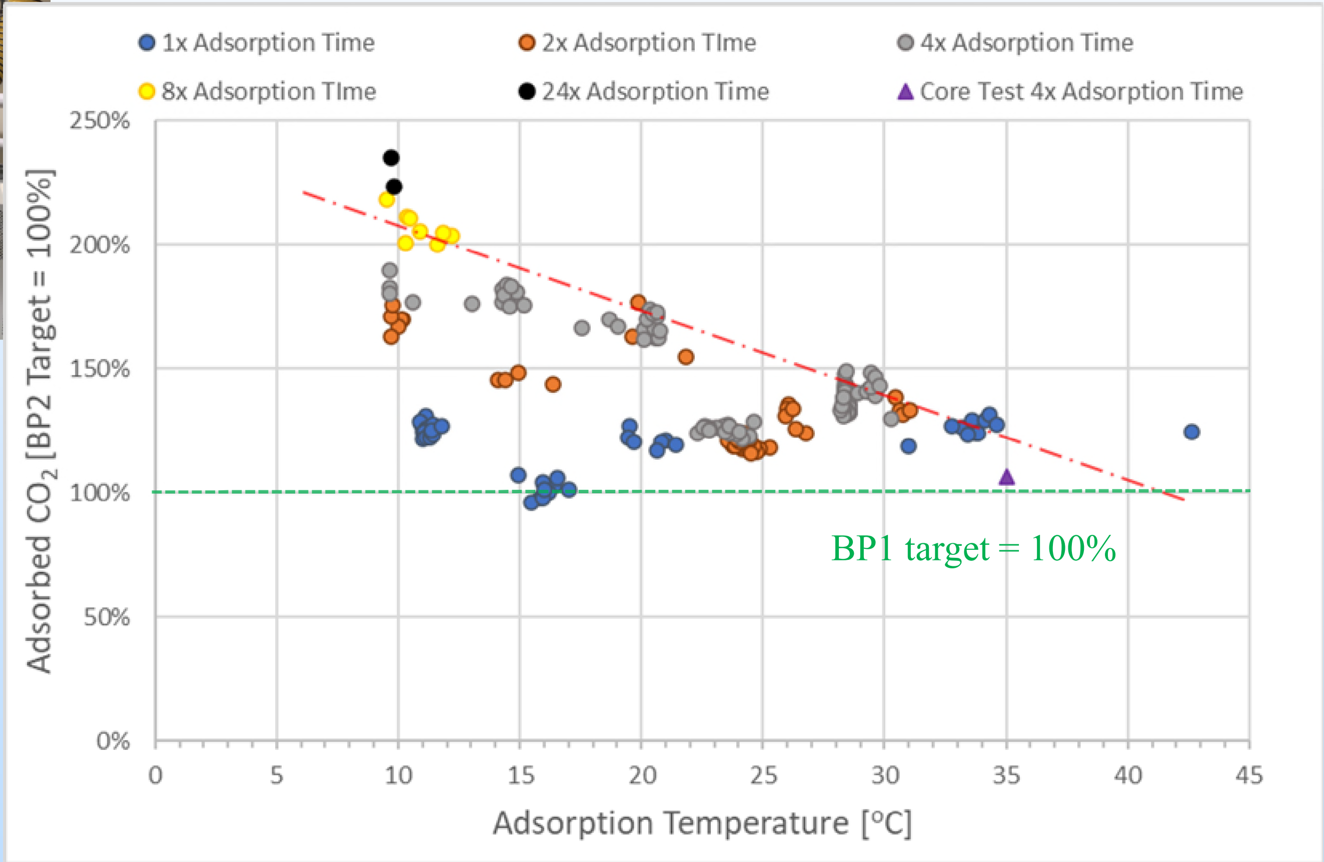


- WK testing confirms that humidity does not impact the diffusive flux of CO_2 through the PPI-loaded monolith substrate wall.
- Water inhibition effect likely originates from capillary condensation in between small PPI domains → higher loadings may increase PPI domain size.

BP2 SBST Data for 1-PPI Monolith
(170cpsi Optimized Monolith MO-2 Substrate)



BP2 performance target was exceeded!
(H_2O content of air feed ranged from 0.8-2.2v%)



~2x capacity increase relative to BP1 result.

Core sample data (corrected to same PPI loading) is consistent with SBST data.

Lessons Learned

PEI is a hydrophilic, liquid amine.

l-PPI is a hydrophobic, solid amine (melting point ~ 110^oC).

Use of l-PPI instead of PEI is not a simple substitution.

- **Impregnation protocol requires non-aqueous solvents.**
  - Scale-up consideration (powders → monolith cores → full-size monoliths).
- **Structure of the l-PPI solid domains in the porous solid monolith structure impacts performance.**
  - Humidity either promotes or inhibits CO_2 adsorption, depending on the l-PPI loading and the pore size distribution.

Next Steps
Testing/Development/Commercialization

- **In this project:**
  - Complete remaining BP2 work activities:
    - Oxidative stability testing and update models.
    - DAC process TEA and LCA for l-PPI.
  - Project closeout meeting on December 8, 2023.

- **After this project:**
  - Larger-scale demonstration of PPI.
    - Depends on feasibility & cost of upscaling l-PPI synthesis.

Summary Slide

- L-PPI supported on an optimized monolithic substrate has been synthesized and tested on the bench-scale, exceeding the BP2 CO_2 adsorption capacity target.

- Monolithic l-PPI is a promising Next Gen adsorber material for the Global Thermostat DAC process.

Organization Chart – Participants

Prime Recipient

CORMETECH.

Christopher Bertole (PI) – Sr. Director, Product and Applications Development
Gavin MacInnes – Lead Catalyst Development Engineer
Travis Jones – Manager, Product and Applications Development Laboratory
Colby Burtt – Lead Process Development Engineer
James Altizer – Sr. Director, Product and Manufacturing Development
Amanda Currie, Dilair Khara, Joe Kliwinski – Sr. R&D Technicians
Casey Huten – Lead Engineering Technician
Chris Lawson – Sr. Engineering Technician
Derick Sufczynski – Engineering Technician
John Powe, Chacko John, Kyle Kearney – Development Technicians

Sub-Recipient

Georgia Tech

Chris Jones – John F. Brock III School Chair & Professor
Ryan Lively – Associate Professor
Anthony Vallace – Postdoctoral Research Fellow

Sub-Recipient

Global Thermostat
The Carbon Negative Solution

Eric Ping – VP, Technology Development
Miles Sakwa-Novak – VP, Materials
Cassandra Hertz – Research Scientist II
Abby Clabaugh – Development Engineer
Stephanie Didas – Director, Innovation

Organization Chart – Project Efforts

Prime Recipient

CORMETECH.

- Bench-scale test unit (SBST) design, build, and commissioning
- Full-size l-PPI monolith impregnation and CO_2 capacity testing
- Single channel monolith modeling for optimization
- Monolith porous substrate optimization and prototype extrusion

Sub-Recipient

Georgia Tech

- l-PPI validation testing
- CO_2 diffusion rate measurements
- Transport modeling

Sub-Recipient

Global Thermostat
The Carbon Negative Solution

- l-PPI procurement and validation testing
- CO_2 adsorption/desorption measurements
- Adsorption modeling
- l-PPI oxidative stability testing
- TEA and LCA

Project Schedule – Gannt Chart