Dual Function Materials for Direct Air Capture of CO_2

DE-SC0020795

Jonathan Peters and Raghubir Gupta

Susteon, Inc.

2023 Carbon Management Research Project Review Meeting
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Project Overview


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SBIR Phase II: DE-SC0020795

Funding: $1,600,000 (DOE share)

Overall Project Performance Dates

BP1: 08/23/2021 – 08/22/2022

BP2: 08/23/2022 – 08/22/2023

DOE Project Manager: Zachary Roberts

Anglo American

SoCalGas
A Sempra Energy utility

Total

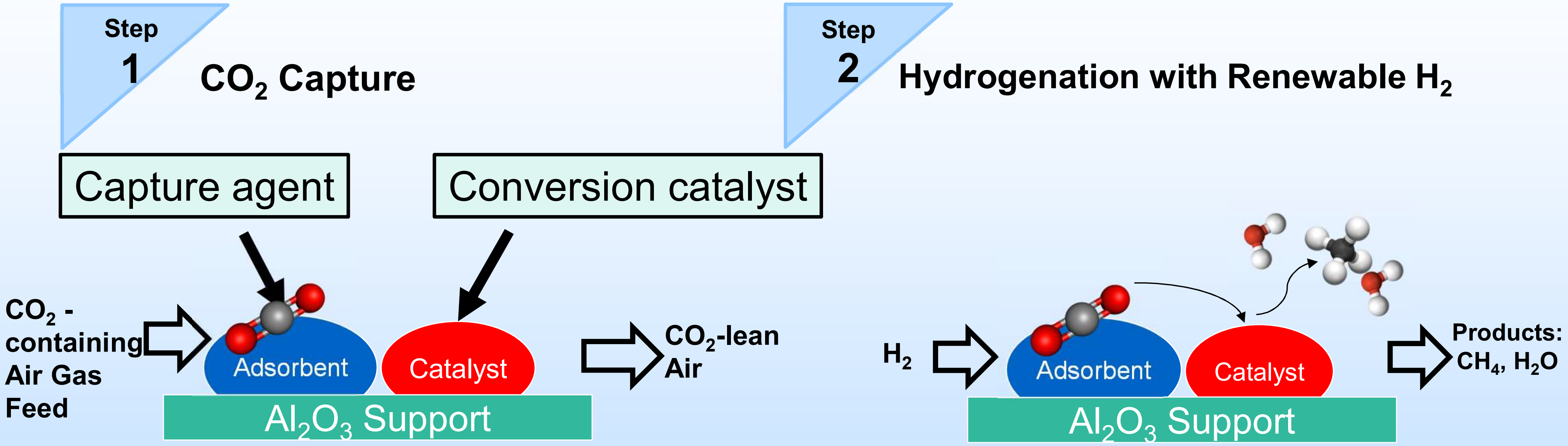
Corning

NGK Insulators, Ltd.

Industrial Partners

Reactive Direct Air Capture (DAC) of CO_2

Dual Functional Material (DFM) captures CO_2 and releases into CH_4 upon conversion



Overall reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H = -165 \text{ kJ/mol of } CO_2$$

Technology Background

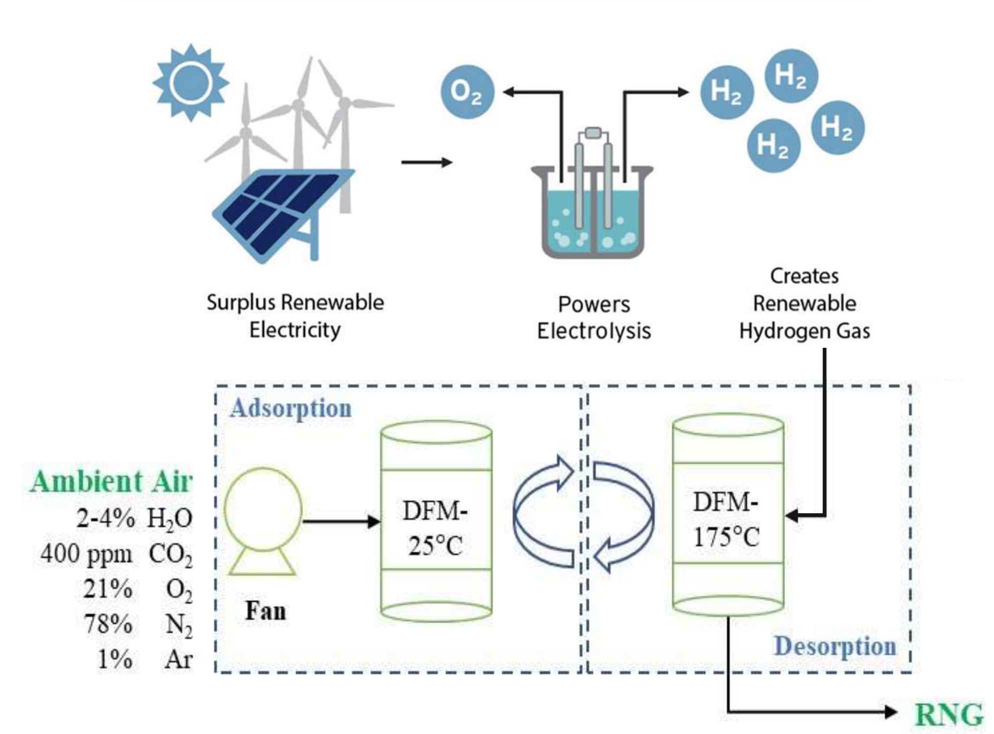
The overall objective of the project is to lower the cost of DAC through development of advanced dual-functional materials (DFM) and production of renewable natural gas (RNG) to offset the cost of DAC. DAC-DFM technology generates RNG from atmospheric CO_2.

Two Step Process Cycle

Step 1: Adsorb CO_2 from air onto DFM at ambient conditions

Step 2: Add renewable H_2 and heat to regenerate the sorbent to produce RNG

Overall Reaction: $CO_2 + 4H_2 = CH_4 + 2H_2O$



This is a **Power-to-Gas** technology using atmospheric CO_2.

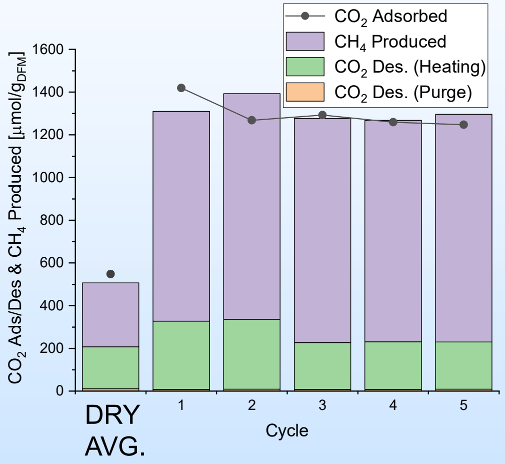
Project Objectives of SBIR Phase II

Technical Objectives

- Optimize DFMs on the selected support structures to achieve maximum CO_2 adsorption capacity, low pressure drop and CO_2 conversion to methane
- Develop an efficient heating method to minimize energy requirement
- Design and build a bench-scale unit (~ 300 g/day CO_2)
- Perform parametric and long-term testing to obtain engineering data needed for a pilot system design
- Develop a process model to accurately represent the DAC-DFM process
- Perform and refine the technoeconomic assessment (TEA) to evaluate the commercial potential of the DAC-DFM process

Summary of SBIR Phase I Results

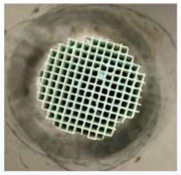
Humid vs. Dry Conditions with Granules

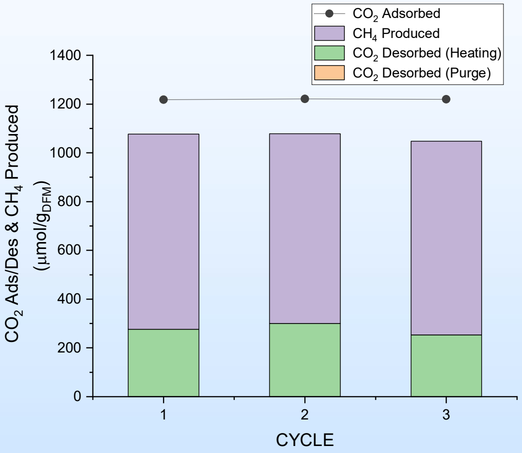


1% Ru, 10% Na_2O/Al_2O_3 granules

>6wt% CO_2 capacity in humid conditions

DFM Washcoated Monolith Performance

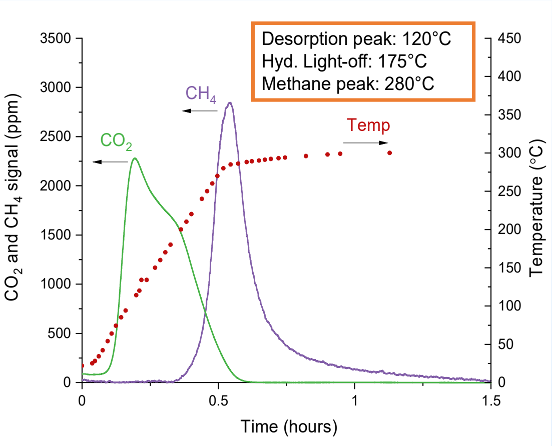




1% Ru, 10% Na_2O/Al_2O_3//TiO_2 monolith

Demonstrated washcoated monolith performance

TOS Performance With Granules



1% Ru, 10% Na_2O/Al_2O_3 granules

Methanation initiates at 175°C, peak CH_4 production at 280°C

Advantages/Challenges

Advantages

- Sorbent materials are low-cost and widely available.
- DFM performance is stable over 450 hours under various climate conditions and is enhanced by humidity in air.
- Joule-heated monolith provides fast, efficient heating for CO_2 conversion into methane.

Challenges

- Requires low-cost carbon-free hydrogen
- Requires ruthenium catalyst for methanation
- Combining capture and conversion in one unit simplifies the flowsheet, however, it adds some complexity to the reactor design

Technical Approach

Optimize the composition of Ru + Na_2O/Na_2CO_3 on alumina support DFM

1) minimize amount of Ru in the DFM
2) maximize CO_2 capture capacity
3) maximize CO_2 capture kinetics
4) maintain high dynamic capture capacity between cycles
5) lowest temperature for light-off of the methanation reaction
6) minimum degradation over 1000s of adsorption/ methanation cycles

Support the DFM on a low-pressure drop structured support

such as monolith or laminates to minimize the energy consumption due to pressure drop.

1) target is **<250 kWh/ton of CO_2 captured** for low pressure-drop
2) supporting of DFM will require optimization of the coating process to coat a uniform layer of Na_2CO_3 and Ru/alumina.

Develop a design for heating of DFM layer

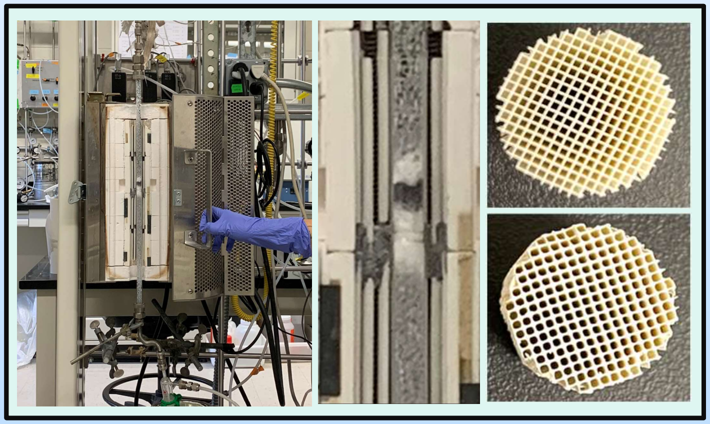
1) to initiate the methanation reaction by desorbing CO_2
2) to develop a design for a heating layer using Joule heating

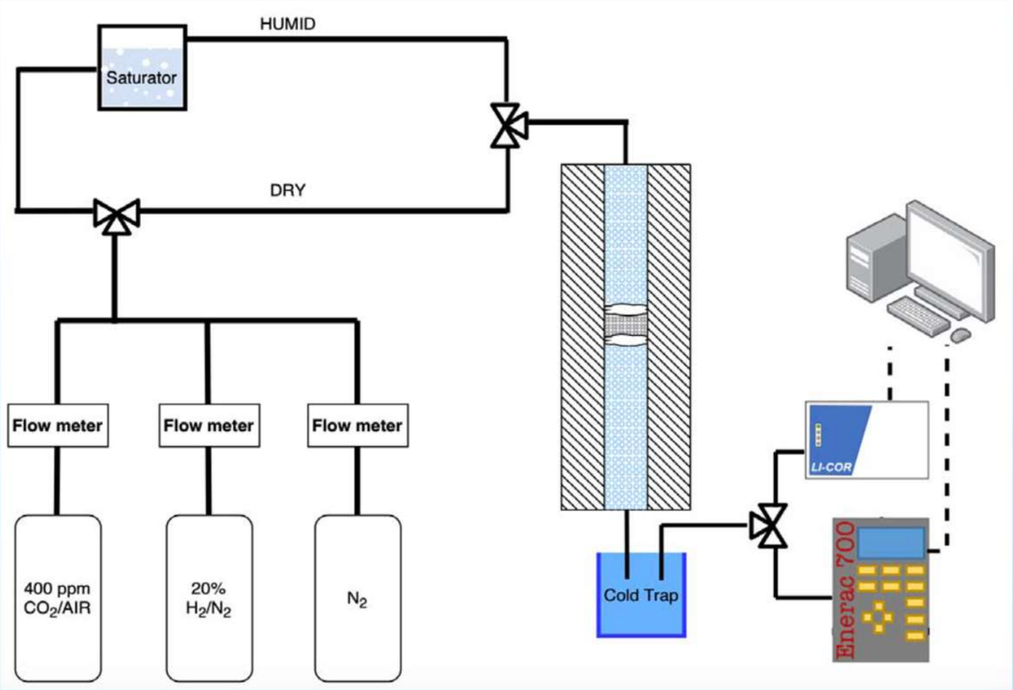
Design an efficient process cycle

for adsorption, heating, desorption, methanation, and cooling to maximize capital productivity and minimize the overall capex and opex for the technology

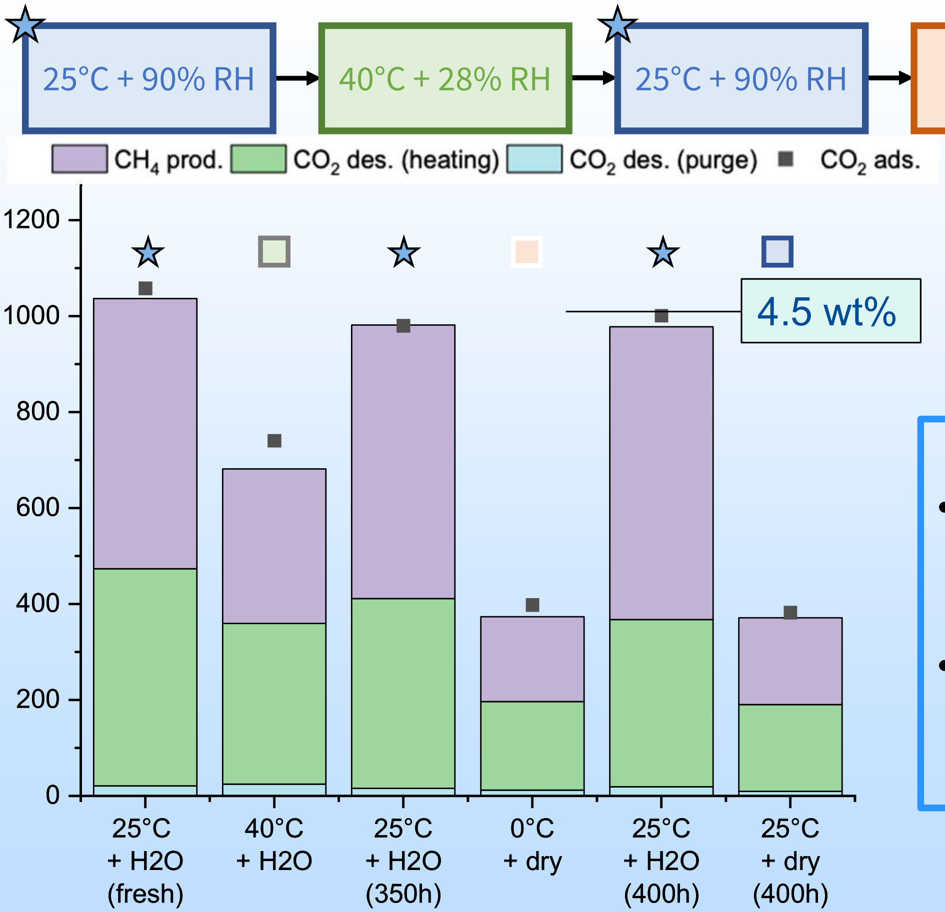
Lab Scale DAC-DFM Testing

- Reactor oriented within a tube furnace with single-zone temperature control
- Gas manifold system allows for gas switching between cycle steps
- Measure parts-per-million concentrations of CO_2 and CH_4 at the reactor outlet using NDIR gas analyzers

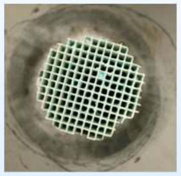




Robust Performance Under Various Climate Conditions



Sample — 1%Ru, 10%Na_2O/Al_2O_3//mo (cordierite)
1.4 g/in^3, 600 cpsi, 2 mil wall



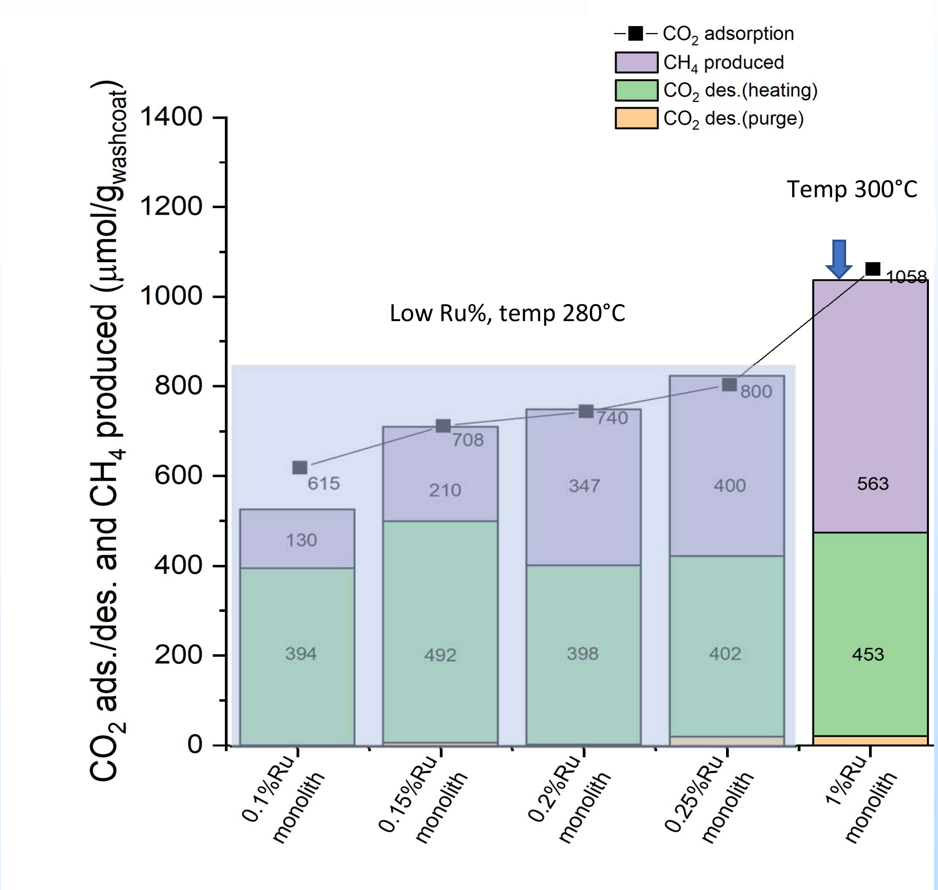
- CO$_2$ adsorption capacity returns to 4.5 wt% after exposed to extreme climate conditions
- Humidity significantly improves DFM performance

Effect of Low Ru on DFM Performance

- Ru catalyzes CO_2 methanation
- Increasing Ru has a positive impact on conversion
- Ru helps to free CO_2 adsorption sites during methanation resulting in greater effective capacity

Takeaway:

An economic optimum is near 0.25%Ru for commercial applications.



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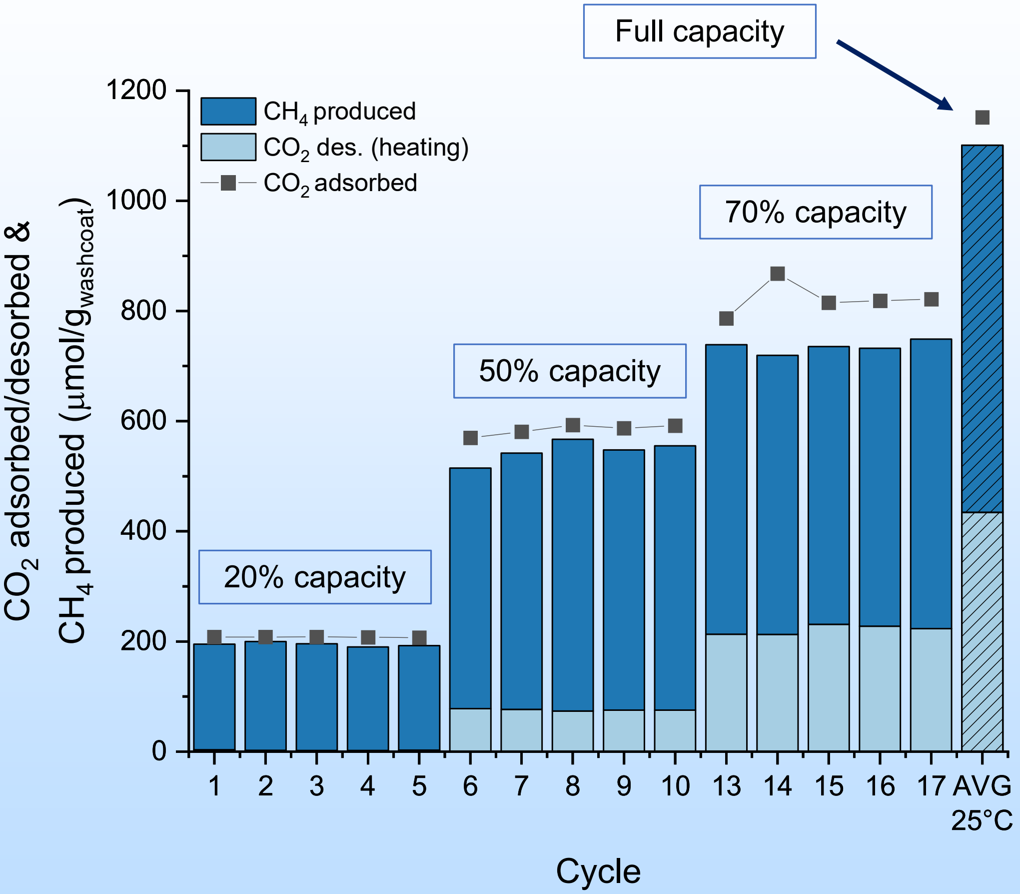
Optimized Cycle Timing Improved CO_2 to CH_4 Conversion



Sample — 1%Ru, 10%Na_2O/Al_2O_3//mo (NGK, cordierite)
1.4 g/in^3, 600 cpsi, 2 mil wall

Adsorption Times (min): 15, 50, 90, 270

By operating near 50% capacity

- Adsorption duration is reduced by 75% which results in higher CH_4 productivity in tonnes CH_4/day/m^3 DFM reactor volume.
- Near complete conversion of CO_2 into methane

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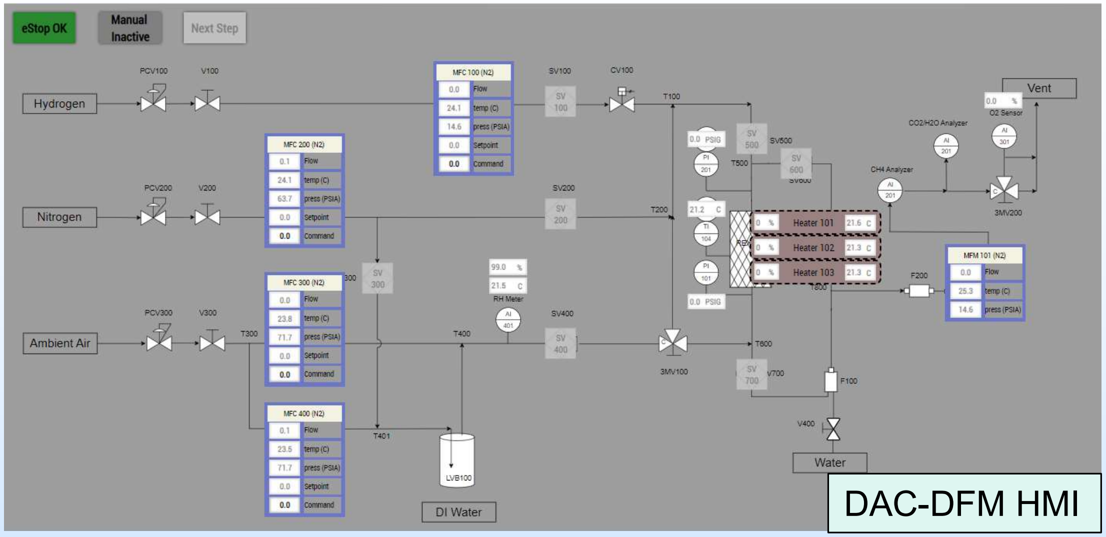
DAC-DFM Bench Scale Unit

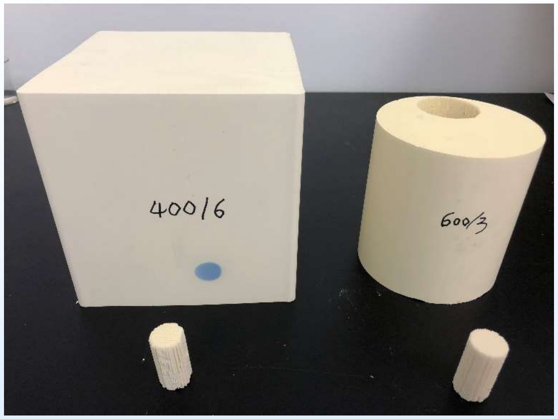


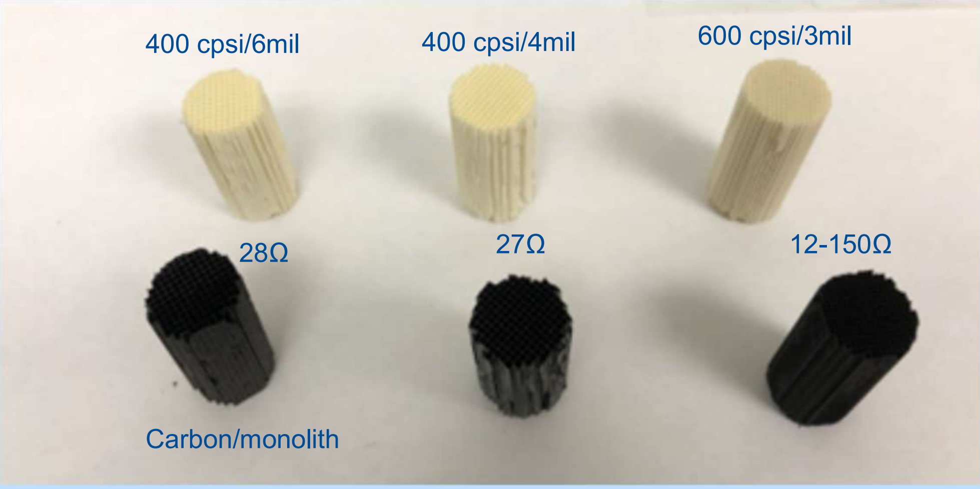
DAC-DFM HMI

- Feed gas manifold
  - Mass flow controllers
  - 0–90% RH control
  - Saturator
- Reactor
  - Isolation valves
  - Joule-heating with 30°C/min heating rate

- Gas Analysis
  - Mass flow meter
  - FTIR for methane
  - NDIR for CO_2 and RH

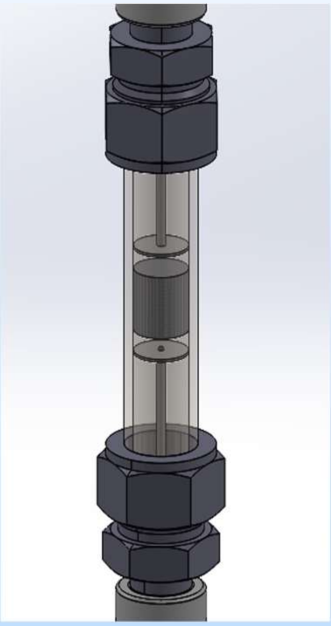
Carbon Coated Monoliths for Joule Heating

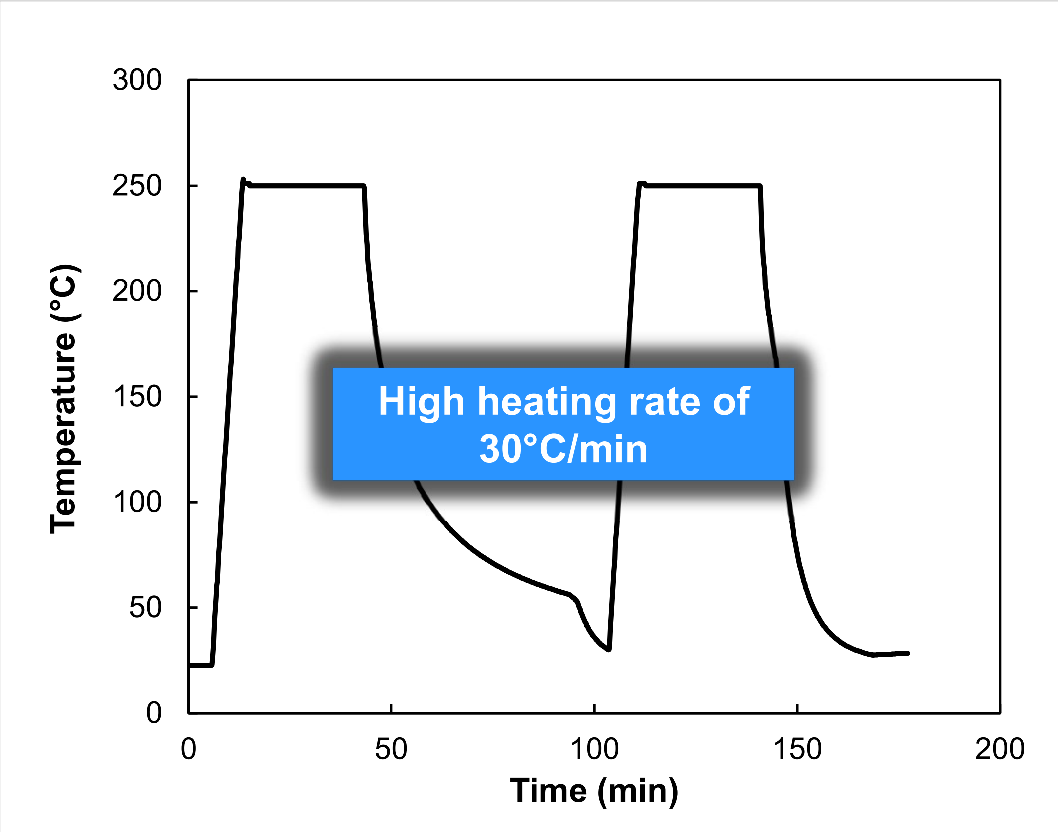




Joule Heating

- Carbon heating layer on monolith
- 400 CPSI, 7 mil wall thickness
- Heating cycles under N_2 with PID control
- Heating Temperature: 250°C
- N_2 flowrate: 100 sccm



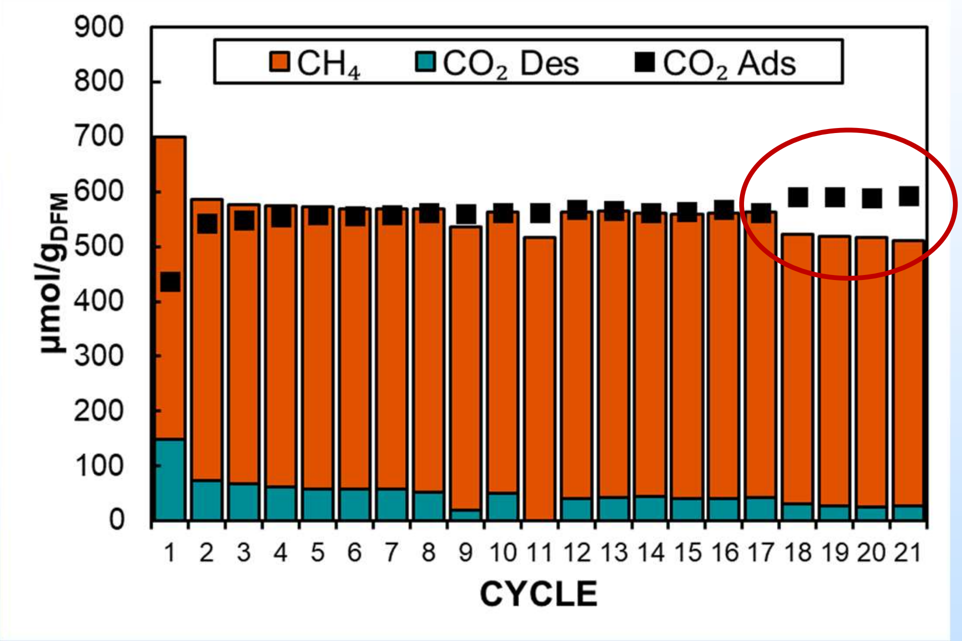


High heating rate of 30°C/min

Joule-Heated DFM Cycle Testing Results - Capacity

- 0.8 wt% Ru/ 38 wt% Na_2O/carbon//monolith
- Improved carbon heating layer (low resistance 40.8 ohms)
- 1 hr adsorption time
- 550 µmol CO_2/gDFM working capacity (1 hr)
- >90% Conversion of CO_2 to CH_4

Step	Duration	Gas	Flowrate
Adsorption (35°C)	1 hr	400 ppm CO_2/ humid air	40 L/h/g (1000 mL/min)
Purge (30°C)	10 min	N_2	4 L/h/g (100 mL/min)
Methanation (300°C)	1 hr (30°C/min heat rate)	100% H_2	4 L/h/g (100 mL/min)



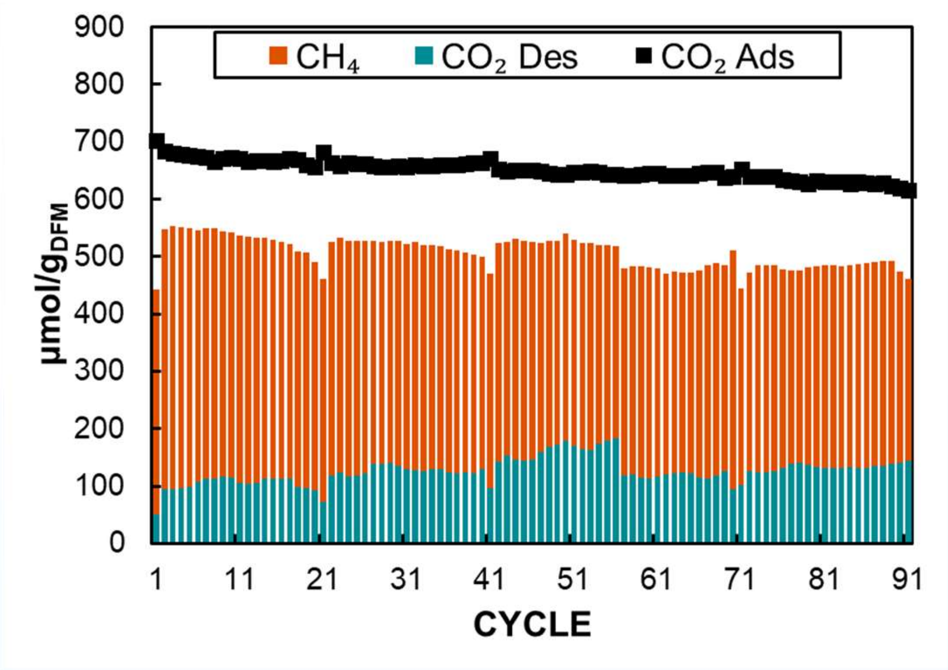
Electrode connectivity and PLC controls issues

>90% Conversion of CO_2 to CH_4

Joule-Heated DFM Cycle Testing Results - Capacity

- 0.5wt% Ru/ 30wt% Na_2O/alumina/carbon//monolith
- Improved carbon heating layer (higher resistance 228 ohms)
- 1 hr adsorption time
- ~650 μmol CO_2/g_{DFM} working capacity (1 hr)
- 72-78% conversion of CO_2 to CH_4

Step	Duration	Gas	Flowrate
Adsorption (35°C)	1 hr	400 ppm CO_2/ humid air	40 L/h/g (1000 mL/min)
Purge (30°C)	10 min	N_2	4 L/h/g (100 mL/min)
Methanation (300°C) Cycles 1- 56	1 hr (30°C/min heat rate)	100% H_2	4 L/h/g (100 mL/min)
Methanation (300°C) Cycles 57-92	1 hr (15°C/min heat rate)	100% H_2	4 L/h/g (100 mL/min)

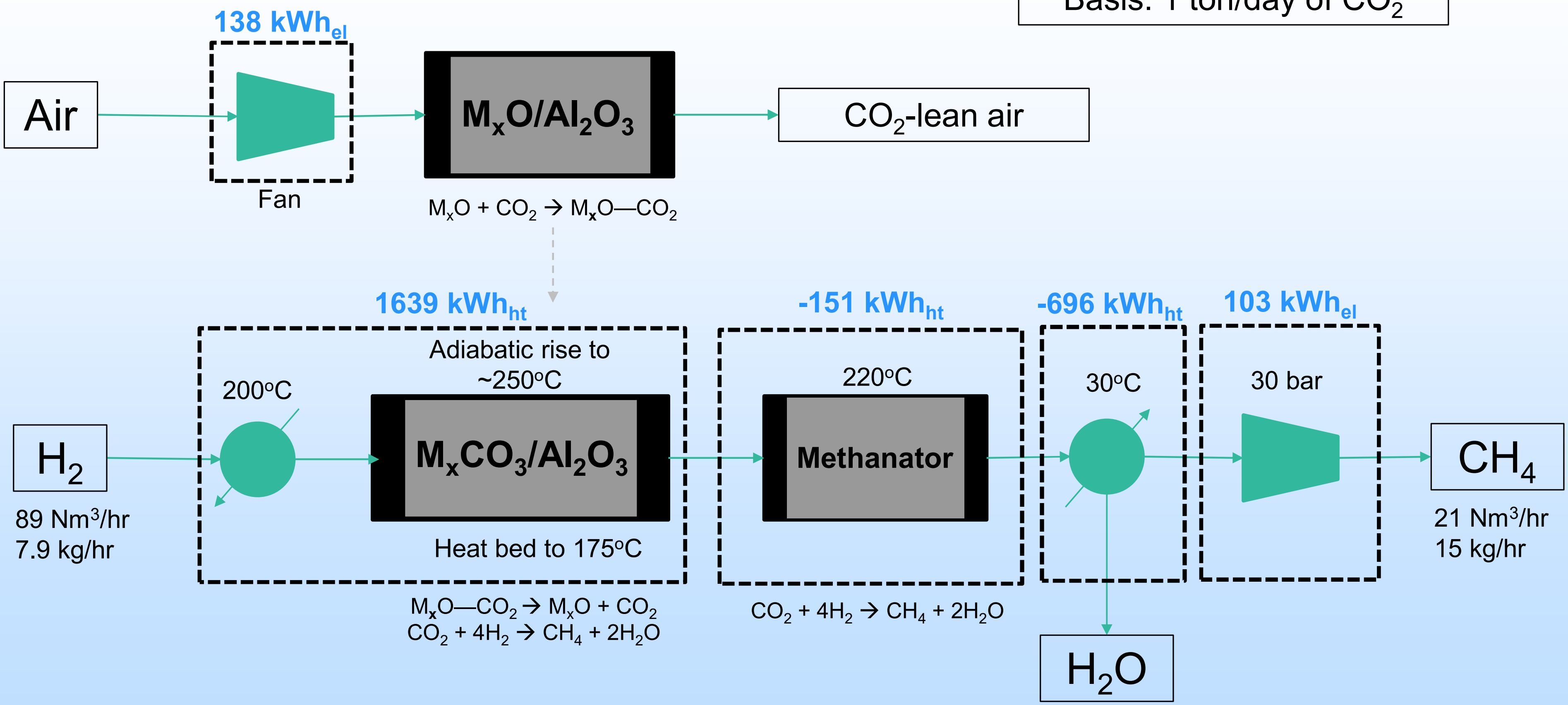


72-78% Conversion of CO_2 to CH_4

>300 Hours of continuous testing with joule heating

Process Design

Basis: 1 ton/day of CO_2



138 kWh_{el}

Air

Fan

M_xO/Al_2O_3

$M_xO + CO_2 \rightarrow M_xO—CO_2$

CO_2-lean air

1639 kWh_{ht}

-151 kWh_{ht}

-696 kWh_{ht}

103 kWh_{el}

H_2

89 Nm^3/hr
7.9 kg/hr

200°C

Adiabatic rise to ~250°C

M_xCO_3/Al_2O_3

Heat bed to 175°C

$M_xO—CO_2 \rightarrow M_xO + CO_2$
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

220°C

Methanator

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

30°C

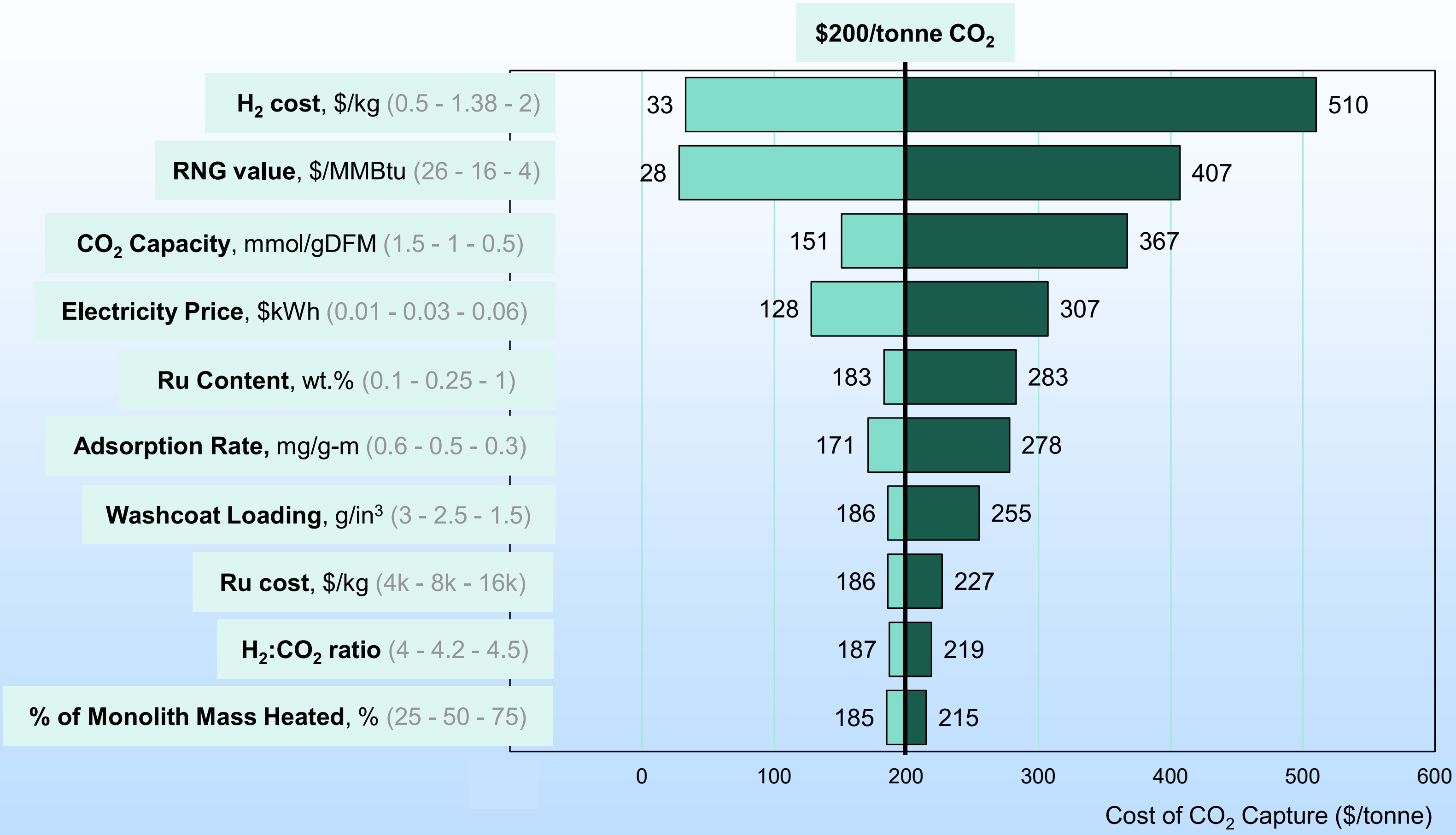
H_2O

30 bar

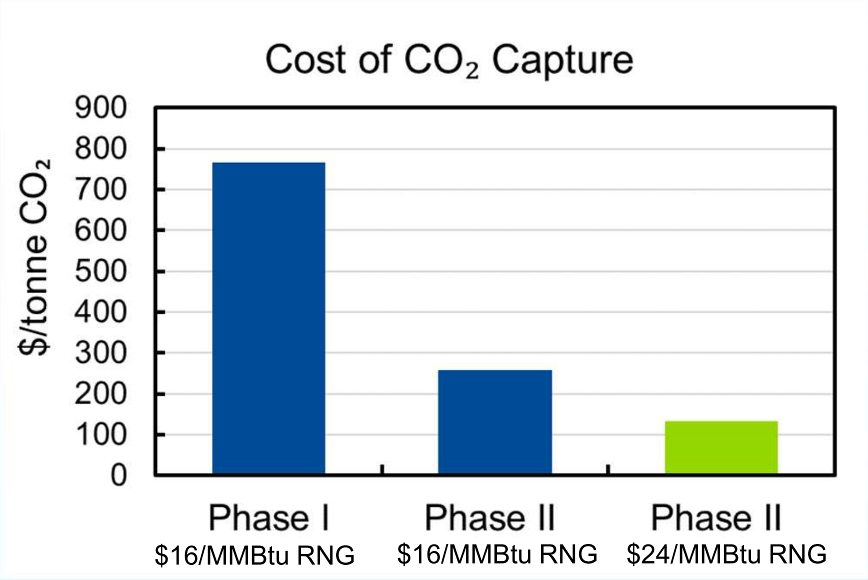
CH_4

21 Nm^3/hr
15 kg/hr

Sensitivity Analysis on Key Parameters



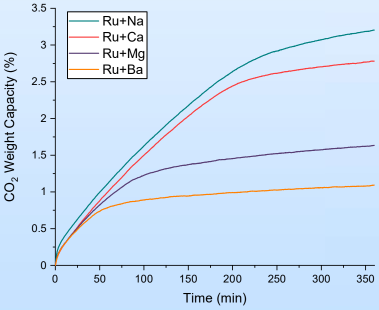
Cycle Design Impact on Process Economics



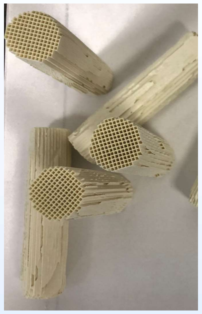
Parameter	Units	Phase I	Phase II
Ru Content	wt%	1	0.25
Adsorption Time	hrs	4	1
Capacity	mmol/gDFM	1	0.6
CO_2 Conv.	%	50	90
Product Gas Composition	mol%	CH_4 – 50% CO_2 – 50%	CH_4 – 90% CO_2 – 10%

Current lab results are now in-line with our TEA process assumptions

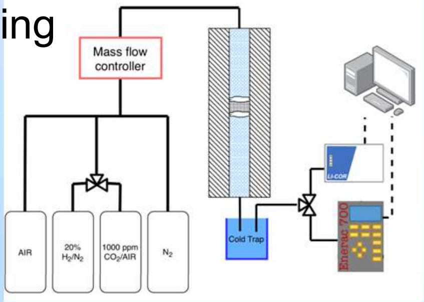
DAC-DFM Process Scale-Up

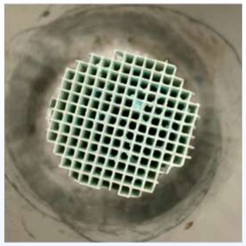


Proof of concept



DAC-DFM granules testing

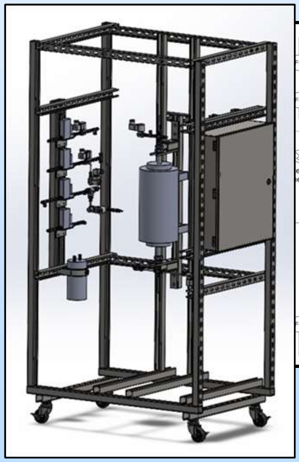


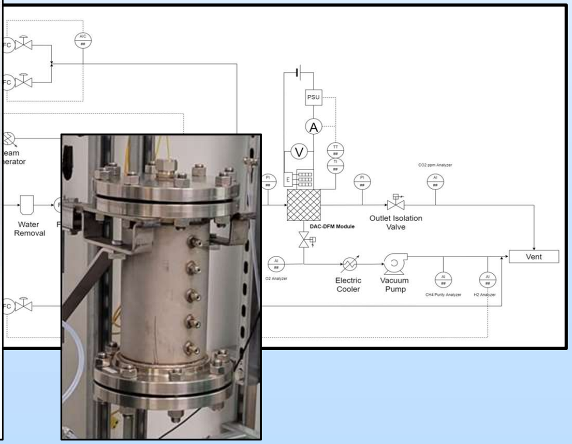


DAC-DFM washcoated monolith testing

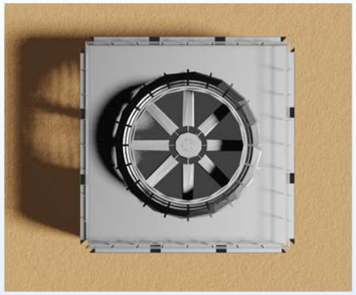
We are here

Bench-scale unit testing





Pilot-scale demo unit



Summary and Key Findings

- ✓ Demonstrated a robust DFM washcoated monolith formulation with stable performance (>450 hours of testing) that is enhanced with humidity achieving up to 1.2 mmol CO_2/g_{DFM} capacity.
- ✓ Lowered the Ru content in the DFM from 1 wt% to <0.25 wt%, thus reducing the Capex and Opex of the process and reduced the cost of RNG production.
- ✓ Learned that CO_2 preferentially adsorbs on strong sites on DFM in the beginning of adsorption step followed by weaker sites towards the end of adsorption step. This led to operating near 50% capacity via 75% shorter adsorption step resulting in >90% conversion of CO_2 into CH_4.
- ✓ Demonstrated continuous Joule-heated DFM cycle testing for over 300 hours with heating rates up to 30°C/min.
- ✓ Fully integrated monolith supported DFM and reactor scale-up by 600X from 0.5 to 300 g/day
- ✓ TEA and LCA demonstrate commercial viability while maintaining a net negative carbon emissions on a cradle-to-gate basis.

Acknowledgements

- Project Team
  - Susteon
  - Columbia University

- DOE/NETL
  - Zach Roberts
  - DE-SC0020795

- Industry Partners

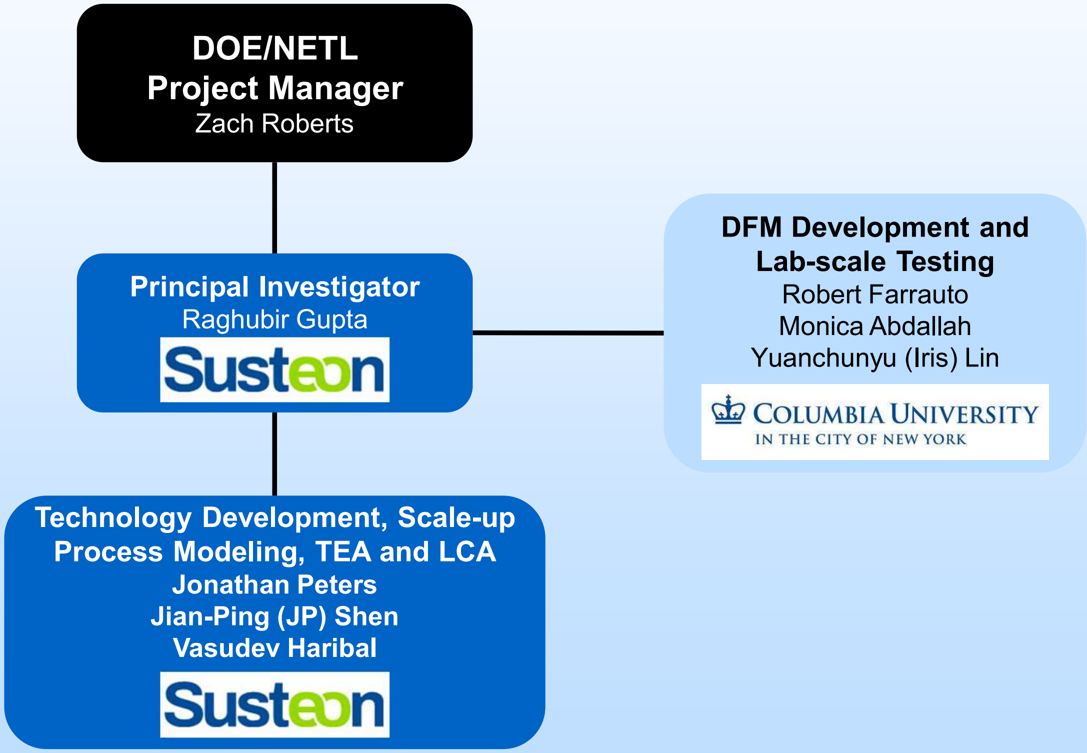
ANGLO AMERICAN TOTAL SoCalGas A Sempra Energy utility

NGK INSULATORS, LTD. CORNING

Appendix

- These slides will not be discussed during the presentation but are mandatory.

Organization Chart



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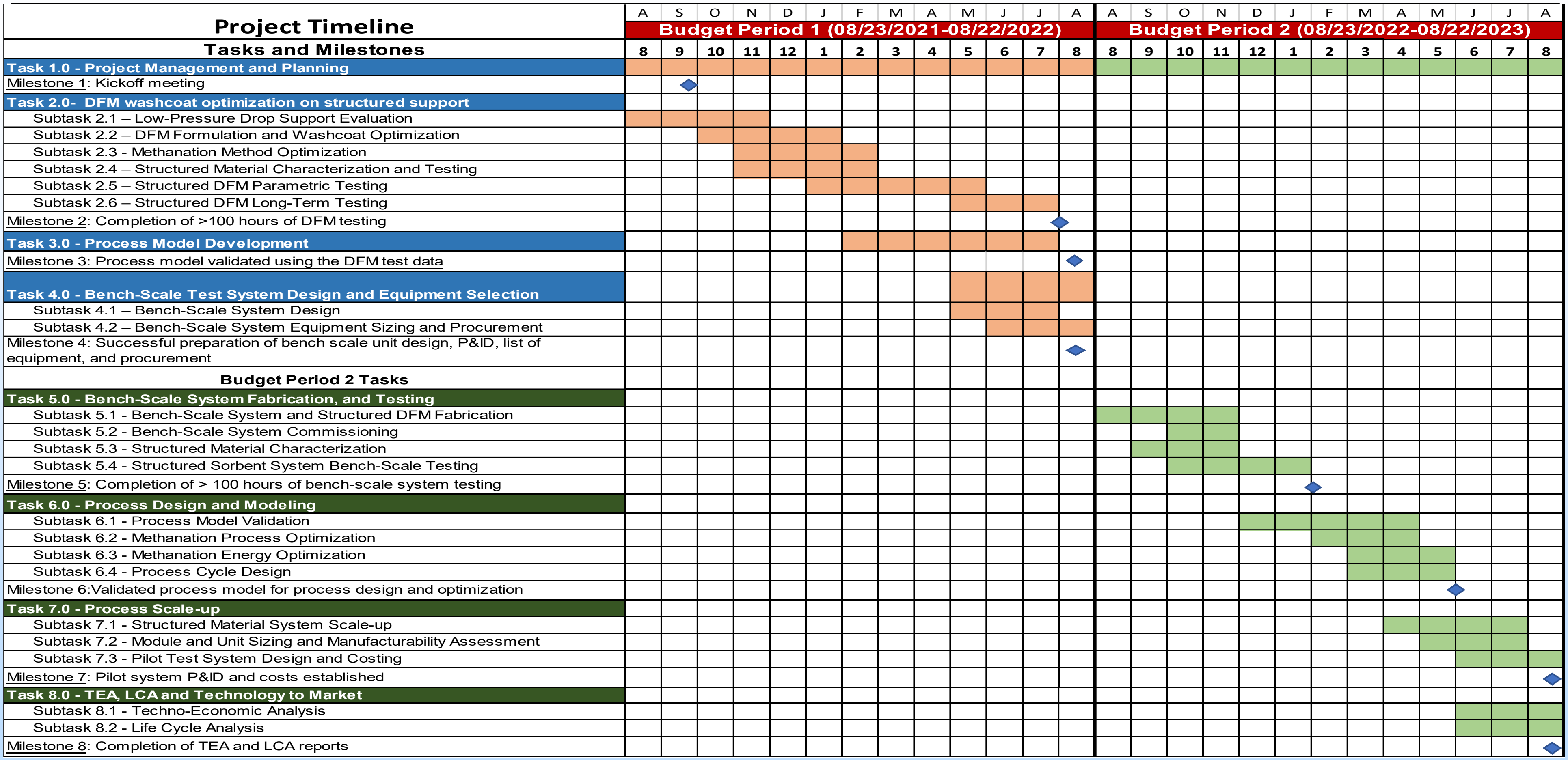
Gantt Chart



Project Timeline	A	S	O	N	D	J	F	M	A	M	J	J	A	A	S	O	N	D	J	F	M	A	M	J	J	A
	Budget Period 1 (08/23/2021-08/22/2022)													Budget Period 2 (08/23/2022-08/22/2023)												
Tasks and Milestones	**8**	**9**	**10**	**11**	**12**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**8**	**9**	**10**	**11**	**12**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Task 1.0 - Project Management and Planning	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Milestone 1: Kickoff meeting		◆																								
Task 2.0- DFM washcoat optimization on structured support																										
Subtask 2.1 – Low-Pressure Drop Support Evaluation	🟧	🟧	🟧	🟧																						
Subtask 2.2 – DFM Formulation and Washcoat Optimization			🟧	🟧	🟧	🟧																				
Subtask 2.3 - Methanation Method Optimization				🟧	🟧	🟧	🟧																			
Subtask 2.4 – Structured Material Characterization and Testing				🟧	🟧	🟧	🟧																			
Subtask 2.5 – Structured DFM Parametric Testing						🟧	🟧	🟧	🟧	🟧																
Subtask 2.6 – Structured DFM Long-Term Testing										🟧	🟧	🟧														
Milestone 2: Completion of >100 hours of DFM testing												◆														
Task 3.0 - Process Model Development							🟧	🟧	🟧	🟧	🟧	🟧														
Milestone 3: Process model validated using the DFM test data													◆													
Task 4.0 - Bench-Scale Test System Design and Equipment Selection										🟧	🟧	🟧	🟧													
Subtask 4.1 – Bench-Scale System Design										🟧	🟧	🟧														
Subtask 4.2 – Bench-Scale System Equipment Sizing and Procurement											🟧	🟧	🟧													
Milestone 4: Successful preparation of bench scale unit design, P&ID, list of equipment, and procurement													◆													
Budget Period 2 Tasks																										
Task 5.0 - Bench-Scale System Fabrication, and Testing																										
Subtask 5.1 - Bench-Scale System and Structured DFM Fabrication														🟩	🟩	🟩	🟩									
Subtask 5.2 - Bench-Scale System Commissioning																🟩	🟩									
Subtask 5.3 - Structured Material Characterization															🟩	🟩	🟩									
Subtask 5.4 - Structured Sorbent System Bench-Scale Testing																🟩	🟩	🟩	🟩							
Milestone 5: Completion of > 100 hours of bench-scale system testing																			◆							
Task 6.0 - Process Design and Modeling																										
Subtask 6.1 - Process Model Validation																		🟩	🟩	🟩	🟩	🟩				
Subtask 6.2 - Methanation Process Optimization																				🟩	🟩	🟩				
Subtask 6.3 - Methanation Energy Optimization																					🟩	🟩	🟩			
Subtask 6.4 - Process Cycle Design																					🟩	🟩	🟩			
Milestone 6:Validated process model for process design and optimization																							◆			
Task 7.0 - Process Scale-up																										
Subtask 7.1 - Structured Material System Scale-up																						🟩	🟩	🟩	🟩	
Subtask 7.2 - Module and Unit Sizing and Manufacturability Assessment																							🟩	🟩	🟩	
Subtask 7.3 - Pilot Test System Design and Costing																								🟩	🟩	🟩
Milestone 7: Pilot system P&ID and costs established																										◆
Task 8.0 - TEA, LCA and Technology to Market																										
Subtask 8.1 - Techno-Economic Analysis																								🟩	🟩	🟩
Subtask 8.2 - Life Cycle Analysis																								🟩	🟩	🟩
Milestone 8: Completion of TEA and LCA reports																										◆