

Enhanced Biomimetic Three-Dimensional Nanoporous Gyroid Membrane for High Efficiency Carbon Dioxide Absorption

Juergen Biener / TCF-21-24965

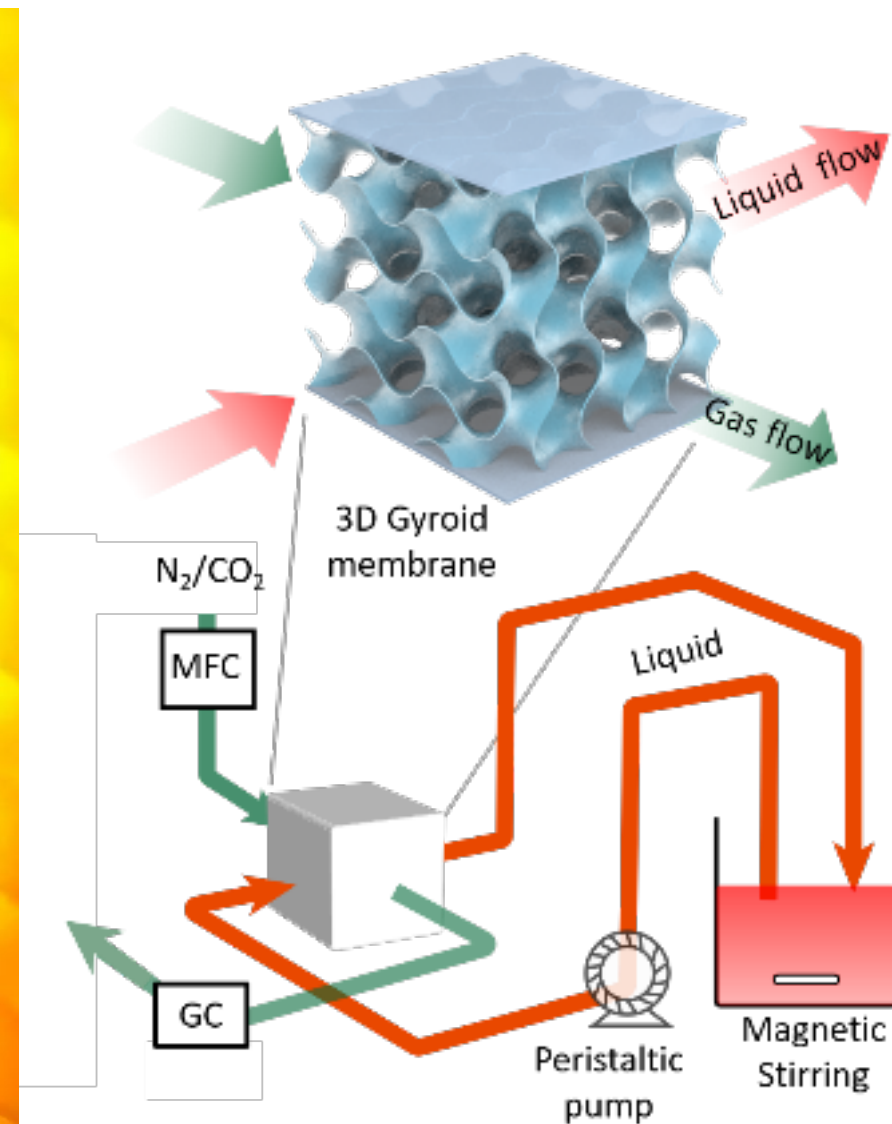
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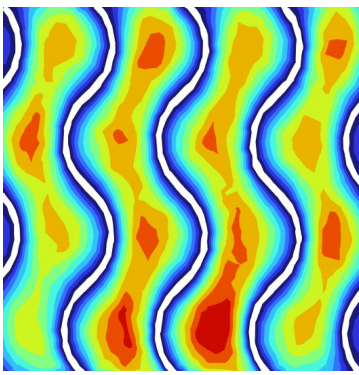
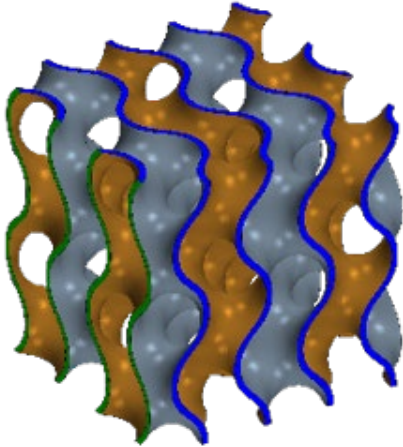
Work at LLNL was performed under the auspices of the U.S. Department of Energy under Contract IM release number: LLNL-PRES-867746



Benefits of our 3D Gyroid Membrane Contactor technology

3D Gyroid membrane contractor morphology:

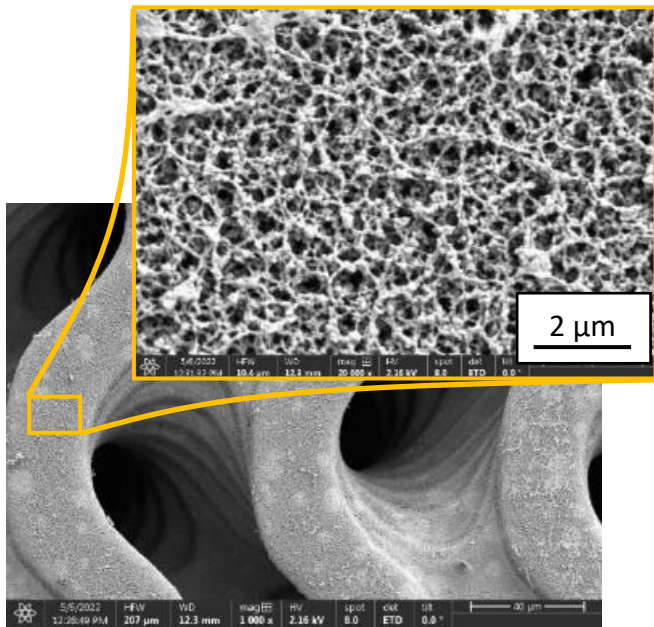
- Two separate interwoven flow channel systems
- High membrane surface area packing density
- Reduced membrane polarization due to curved flow channels



Flow velocity map

Tunable high permeance membrane wall

- Thin (10-100 micron)
- High porosity (up to 95%)
- Pore size tunability



$$-\frac{d(CO_2)}{dt} \propto \frac{dC_{CO_2}}{dx} \times A$$

CO₂ removal rate

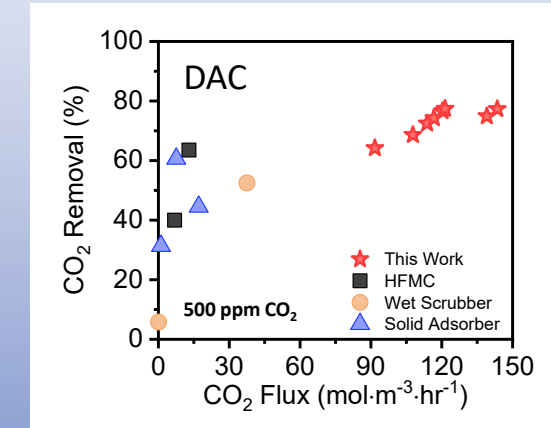
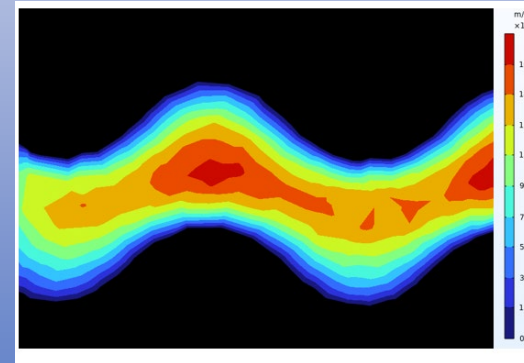
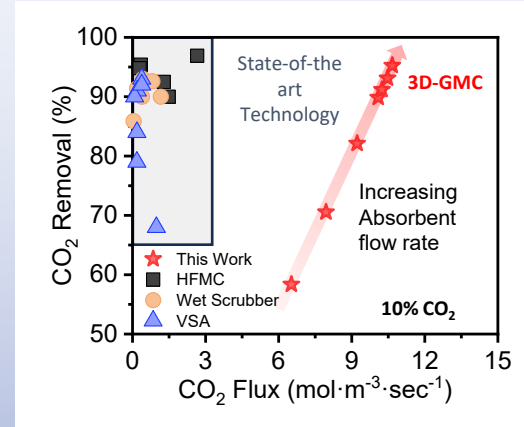
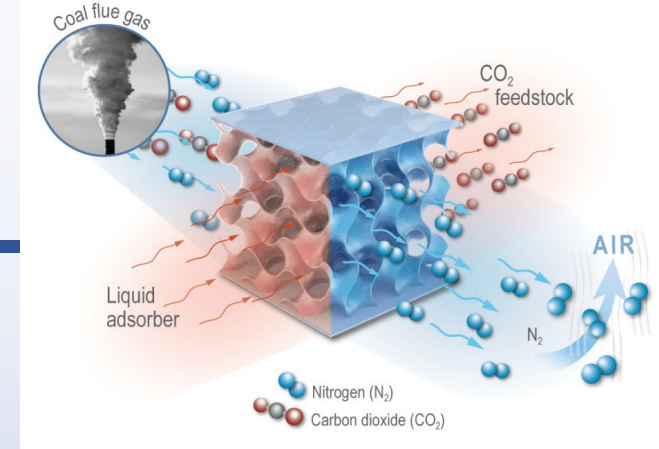
High membrane area packing density provided by gyroid architecture

Forced mixing maximizes CO₂ concentration gradient across membrane

Goal: Demonstrate 10x smaller device volume compared to current state-of-the-art membrane designs

3D Gyroid Membrane Contactor (3D-GMC) highlights

- Ultra fast (< 1 s contact time) and ultra compact (< 1 cm contact path)
- $>90\%$ CO_2 from flue gas at a 6-times higher CO_2 flux per unit size compared to conventional hollow fiber membrane contactors
- $>80\%$ removal of CO_2 from air at 12-fold higher CO_2 flux
- Only 2% decrease in CO_2 removal rate during 100 h tests

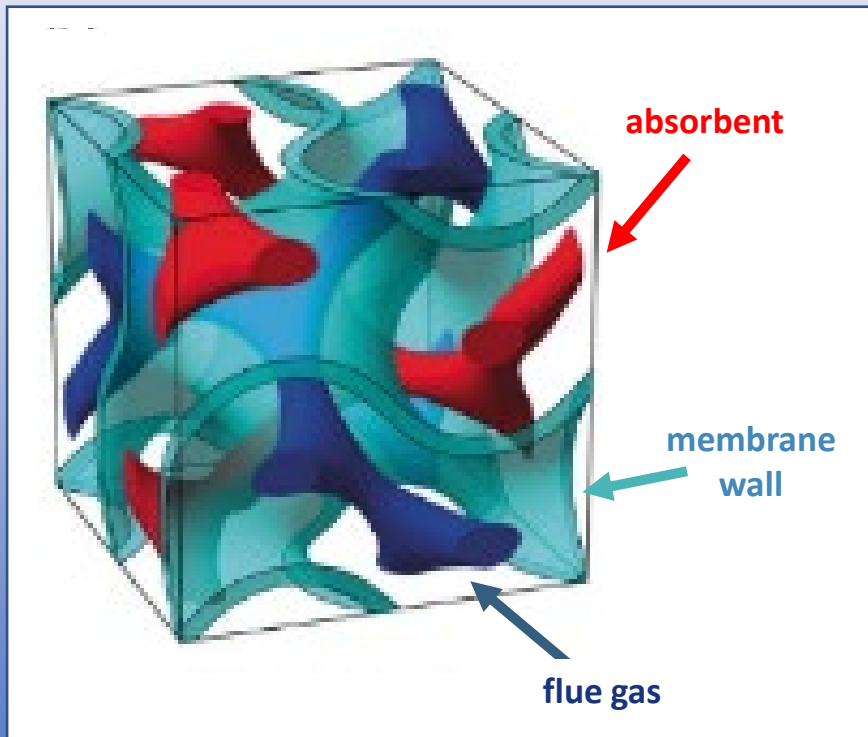


COMSOL velocity profile of gas stream at 40ml/min

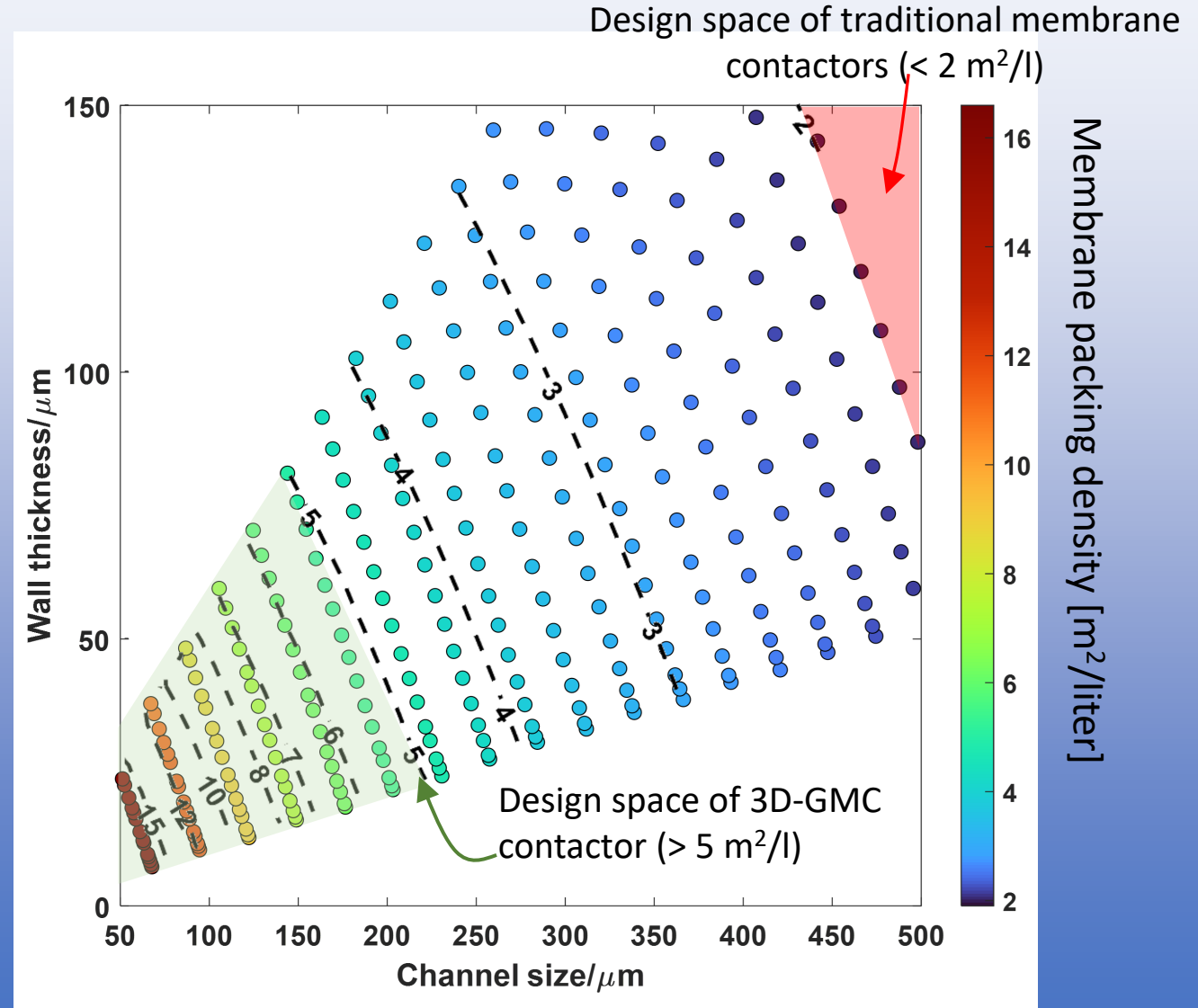
The excellent performance of the 3D-GMC can be attributed to the system's high membrane packing density in combination with its flow channel architecture which suppresses membrane concentration polarization.

3D-GMCs offer ultra high packing densities

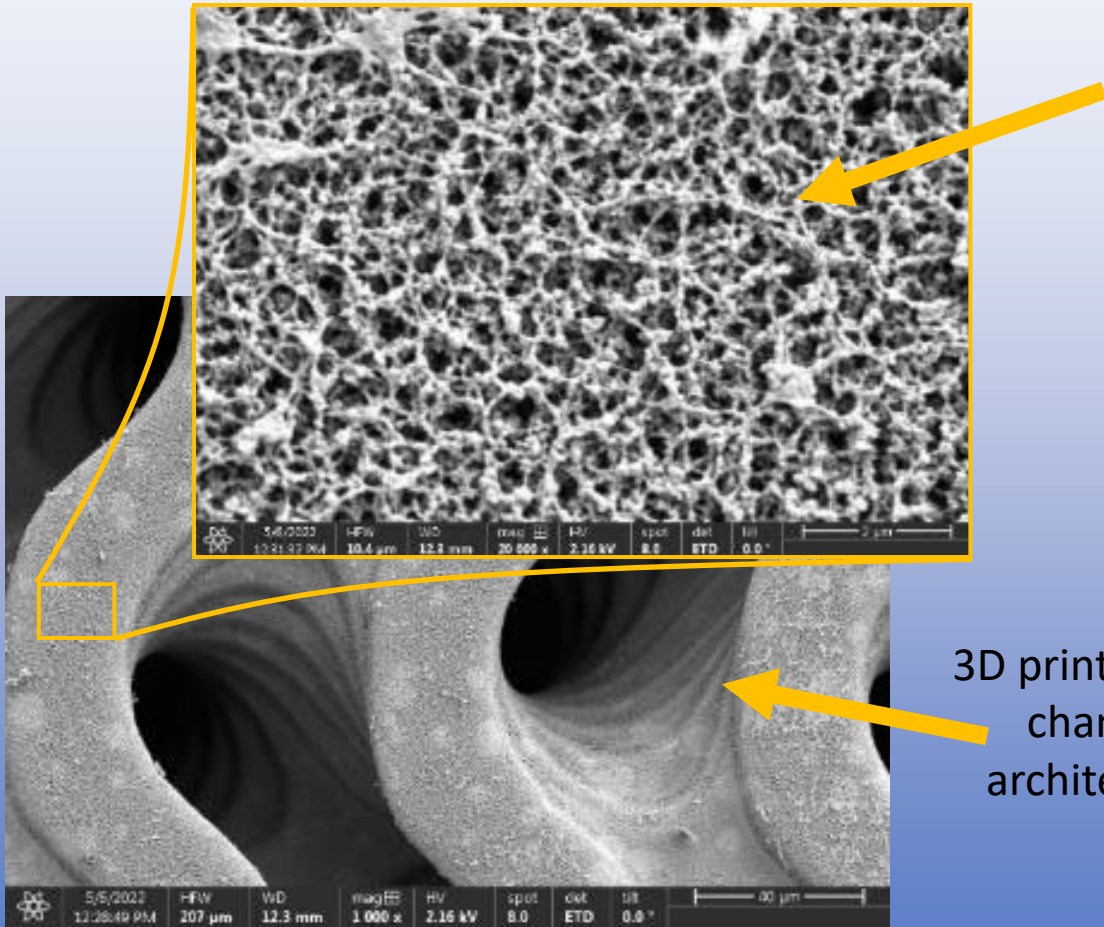
3D Gyroid membrane contractor morphology



Membrane packing density $>5 \text{ m}^2/\text{l}$

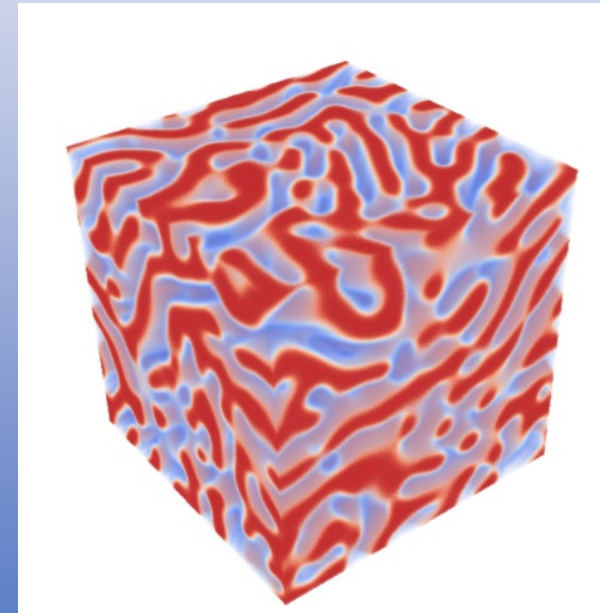


Fabrication of 3D-GMCs combines 3D printing with a self-organization process



Bicontinuous nanoscale ligament-pore architecture resulting of nanoporous membrane wall from polymerization induced phase separation (PIPS)

3D printed flow channel architecture

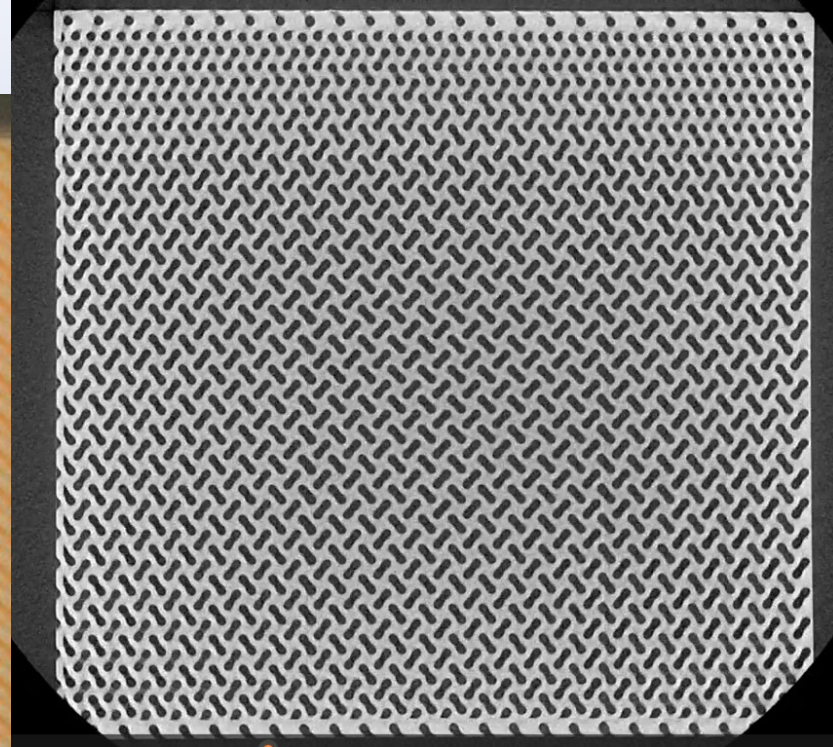


Predicting the nanoscale morphology resulting by 3D phase field simulations

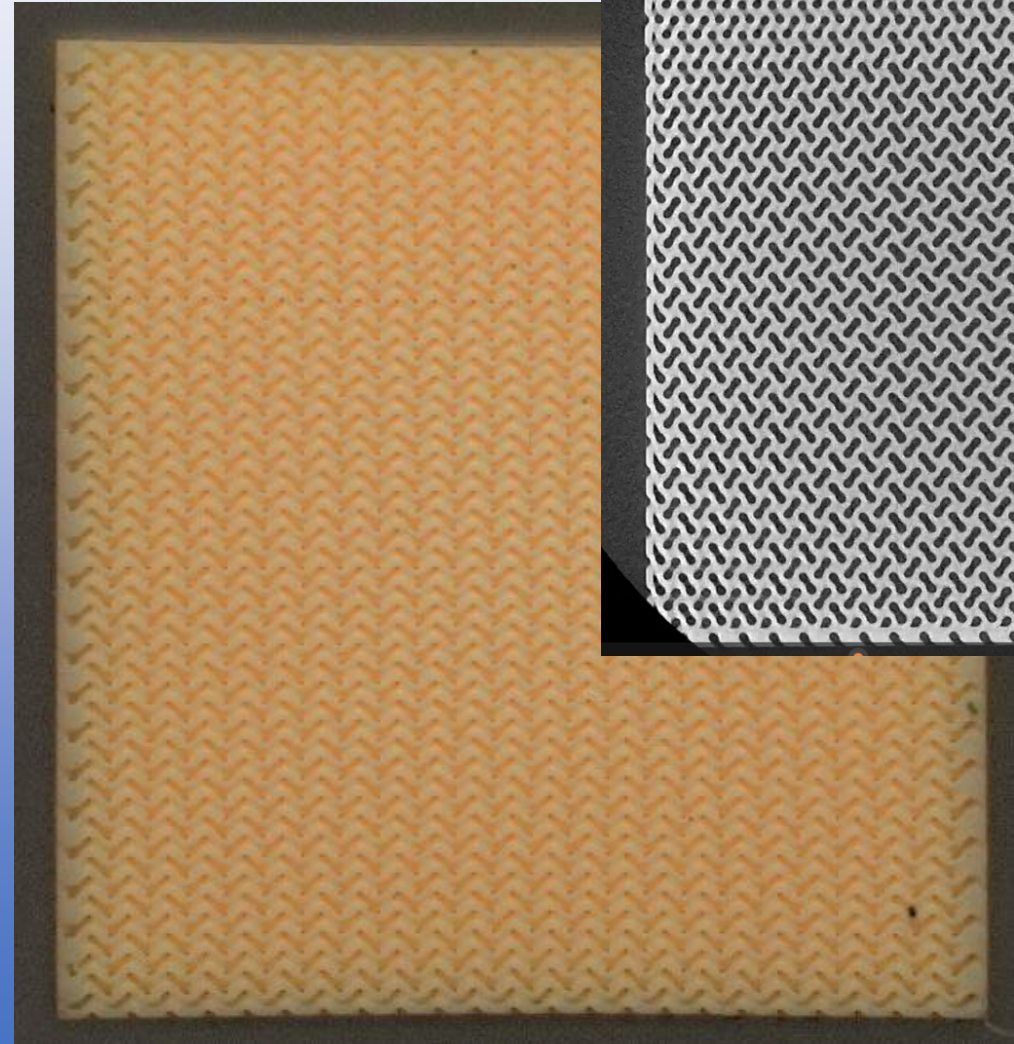
ACS Applied Materials & Interfaces
16 (2024) 38442-38457

Combining 3D printing with self-organization allows fabrication of 3D membranes with controlled macroscopic architectures and integrated nanoscale porosity

Characterization confirms the fabrication of defect free 3D-GMCs with integrated nanoscale porosity

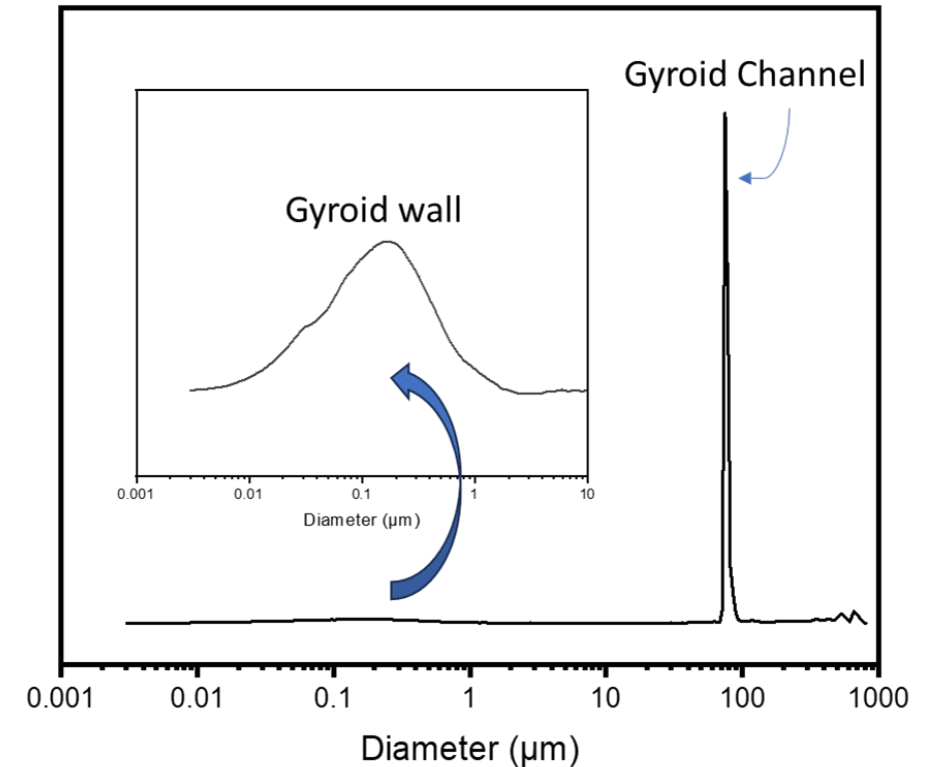


X-ray CT slice of 3D-GMC



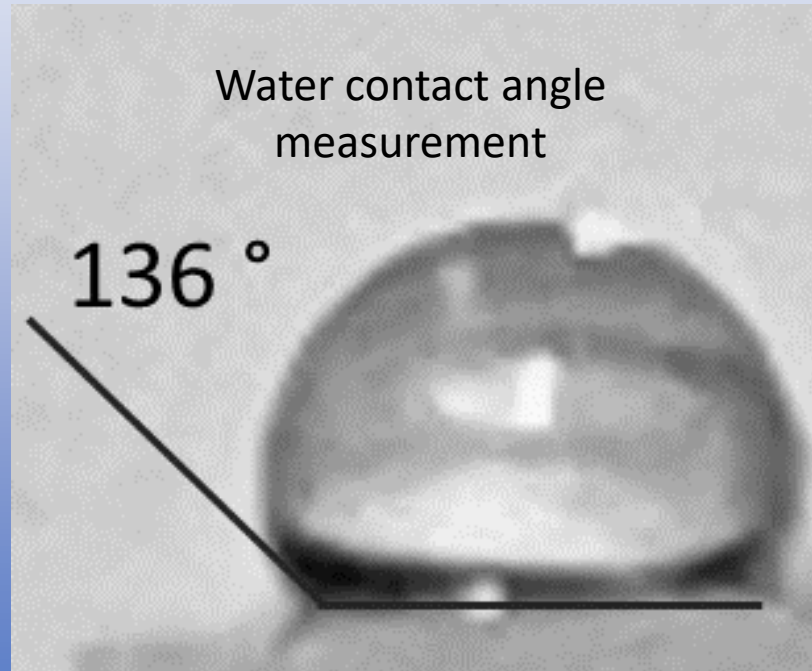
Optical image of the tested 3D-GMC

Mercury porosimetry



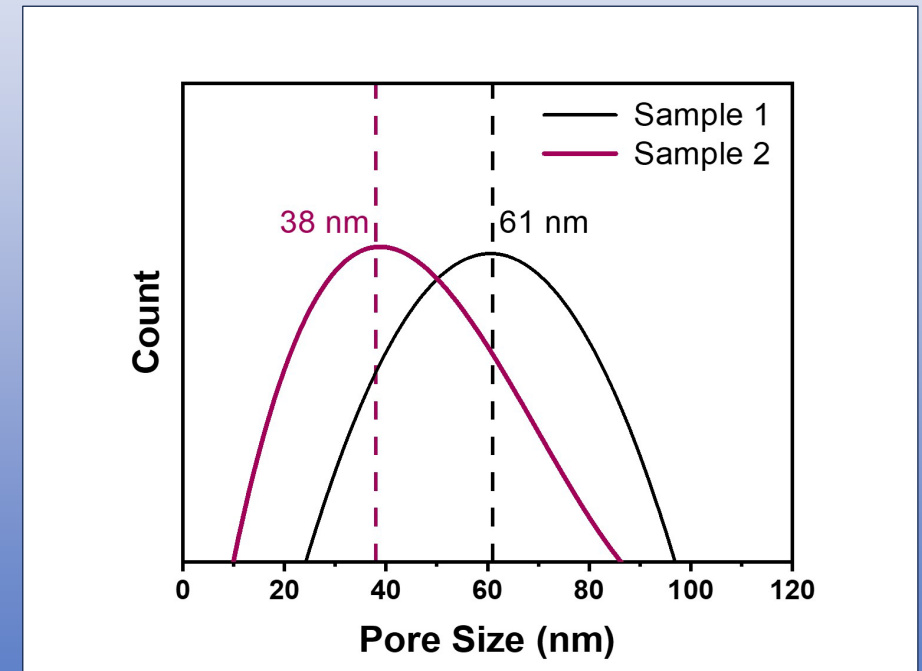
Optimization of the membrane wall transport properties

Hydrophobic membrane for fast gas-phase trans-membrane CO₂ transport



Diffusion coefficient of CO₂ in air is 4 orders of magnitude higher than in water

Controlling the pore size distribution through the polymerization kinetics

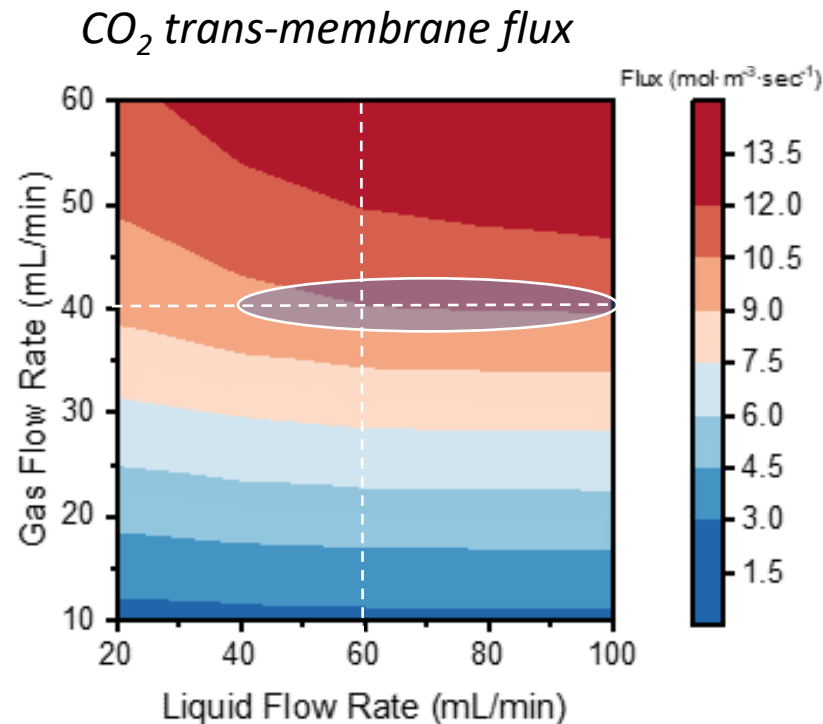
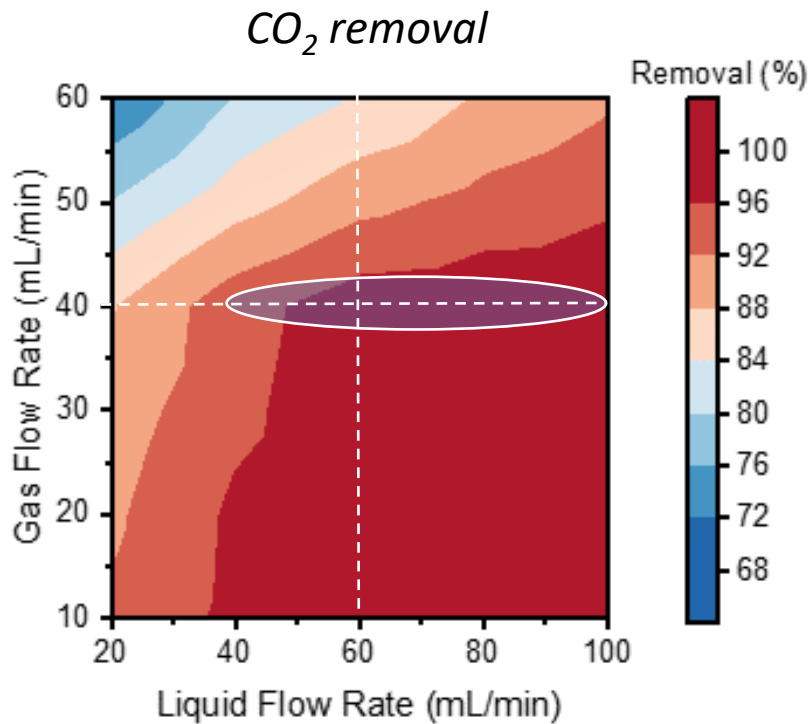
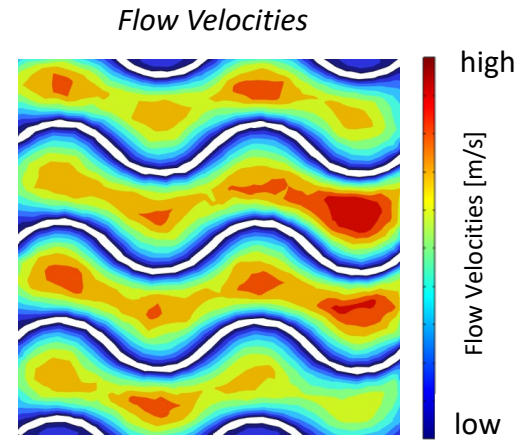


Process optimization using COMSOL multiphysics simulations

Characteristic diffusion length scales:
CO₂ in air ~ 6 mm/s vs. CO₂ in water ~ 60 μm/s

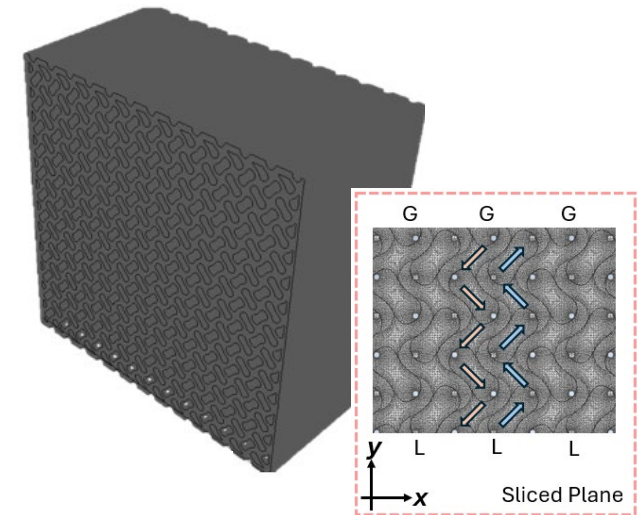


CO₂ diffusion in liquid absorbent is removal rate limiting



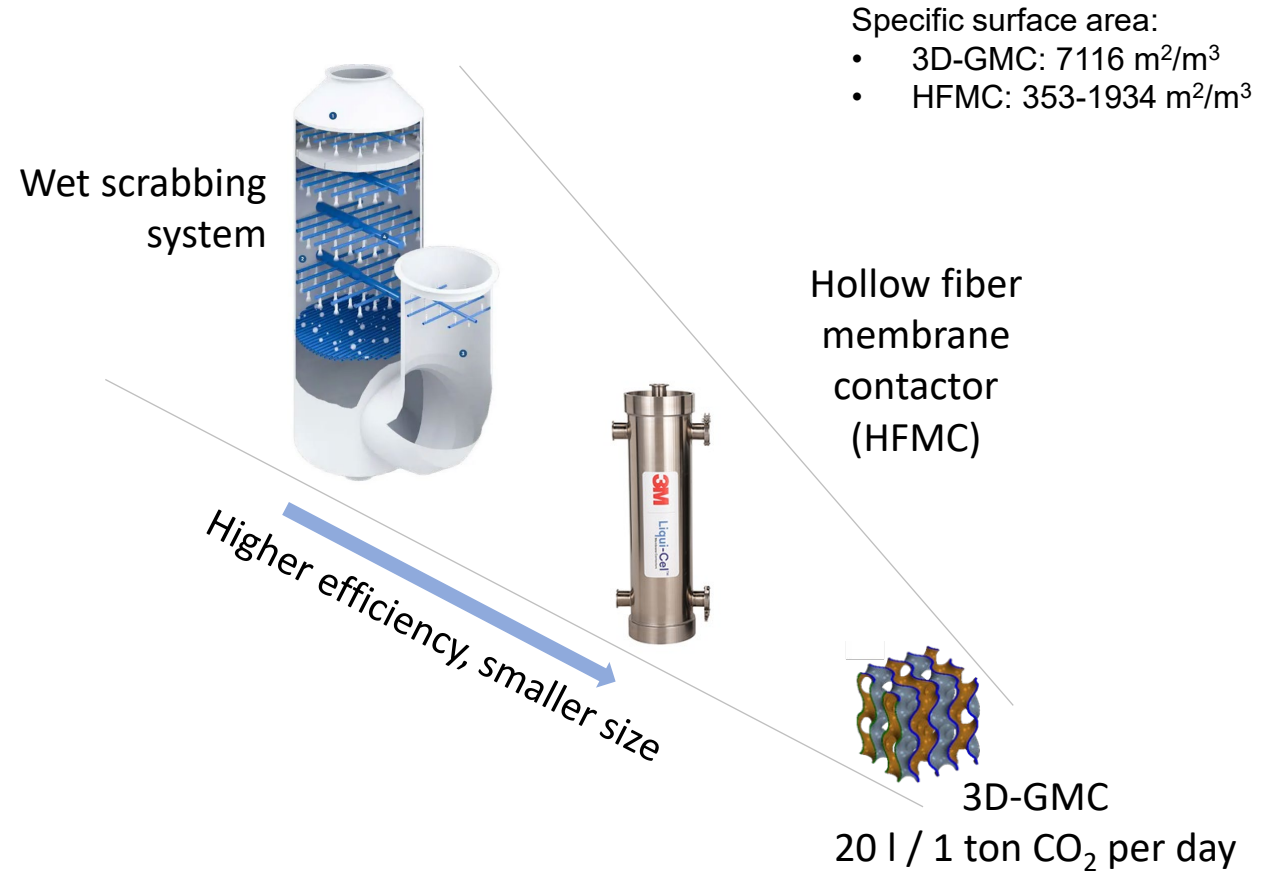
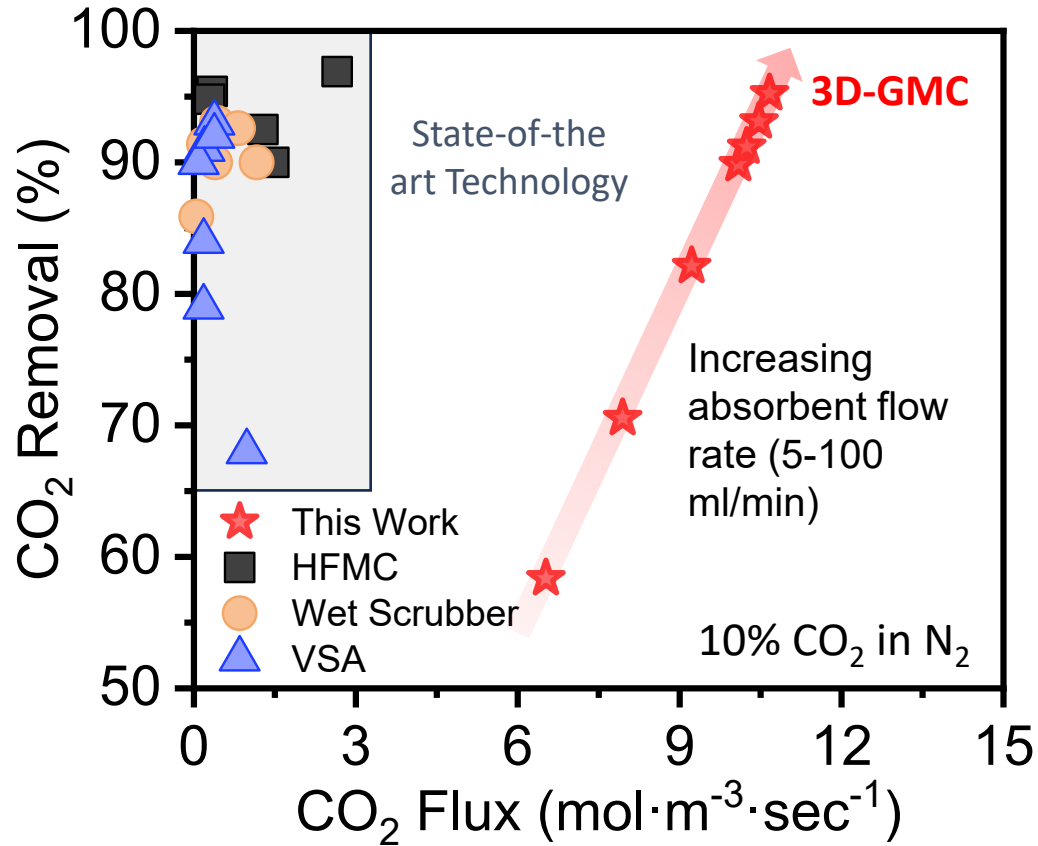
1 cm³ simulation cell

➤ Contact times on 1s time scale



Using high liquid flow rates helps to overcome limiting liquid phase CO₂ mass transport
Compromise between CO₂ removal and CO₂ trans-membrane flux

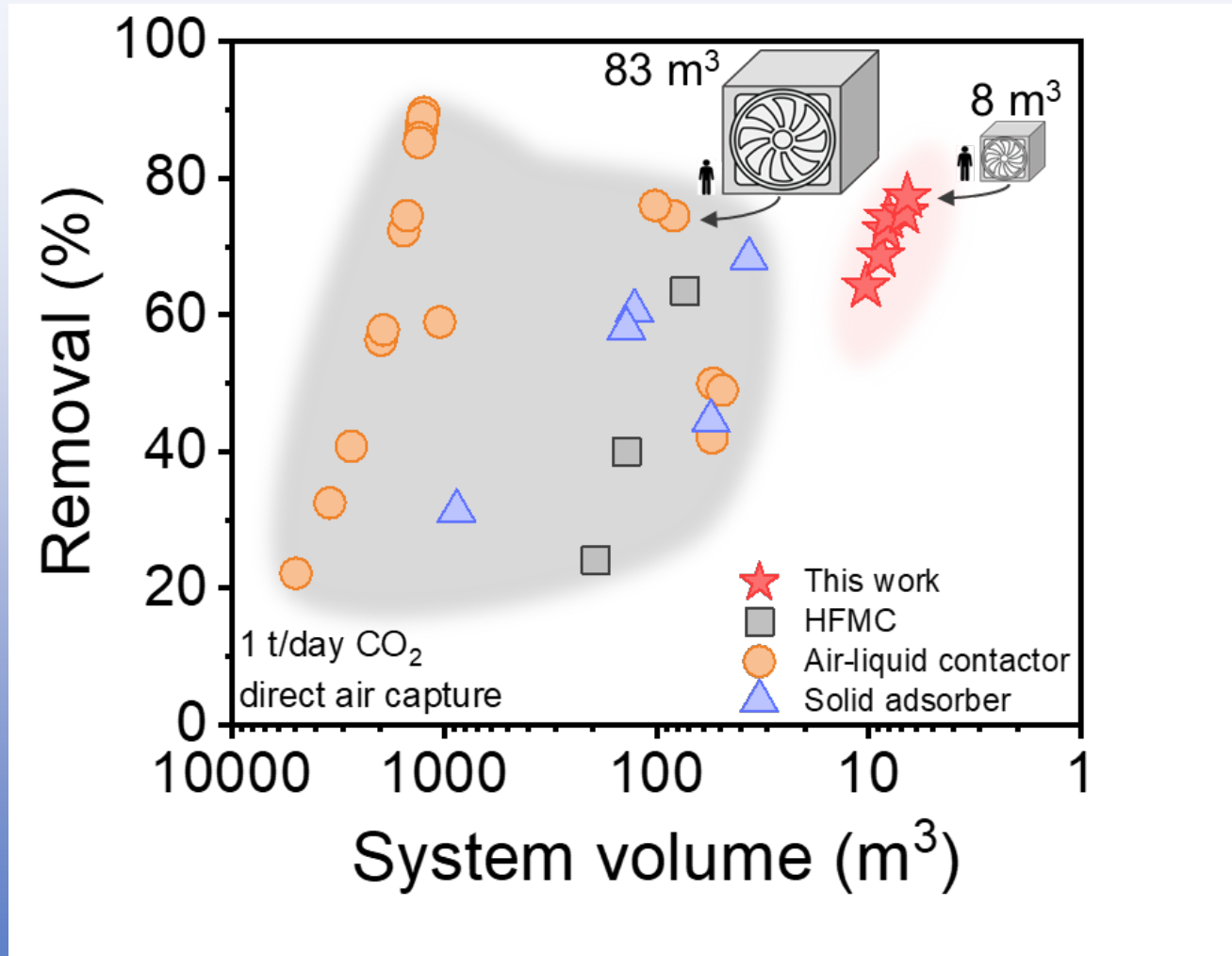
3D-GMC enables process intensification



The 3D-GMC technology enables at least a six times higher CO₂ trans-membrane flux per unit size compared to a conventional hollow fiber membrane contactor (HFMC)

The excellent performance can be attributed to the combination of a higher packing density and a more turbulent flow pattern

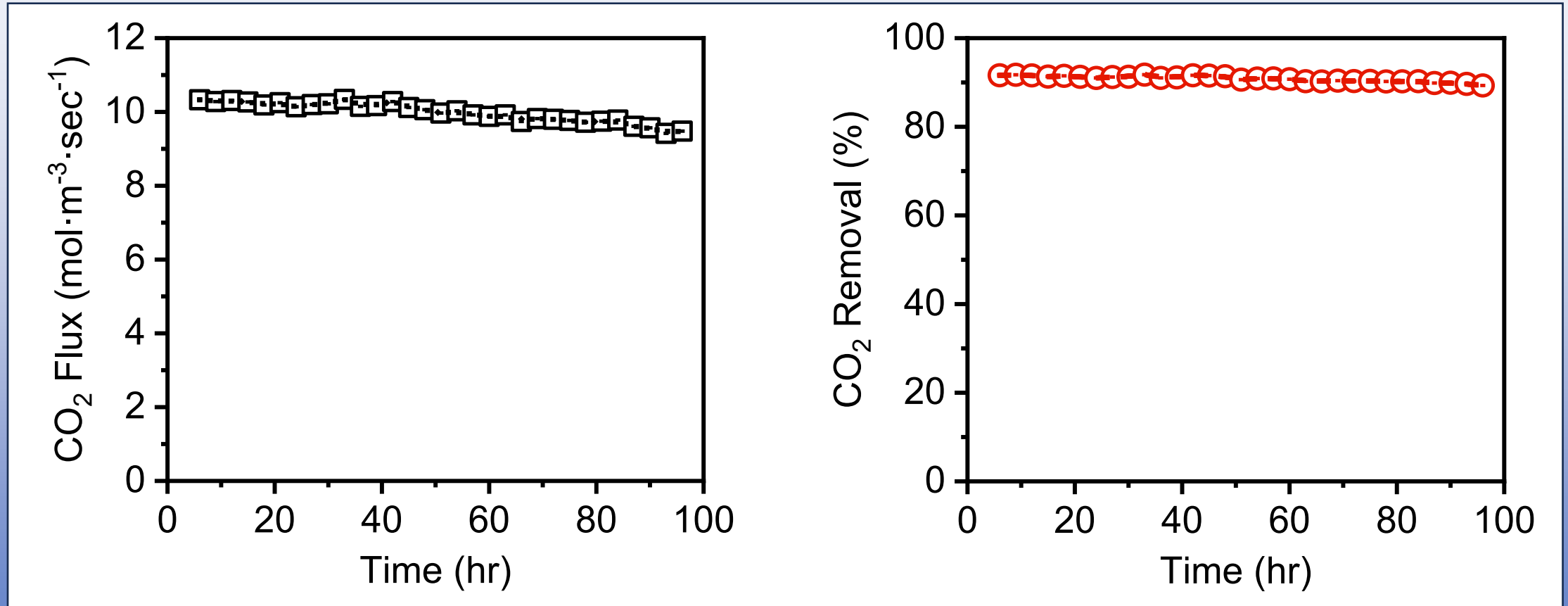
Direct Air Capture



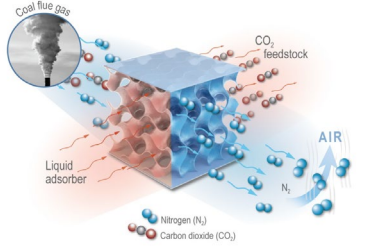
500 ppm CO₂ feed
0.8 M NaOH absorber

3D-GMC offers 10 times smaller system size for direct air capture compared to reported methods.

Long-term stability

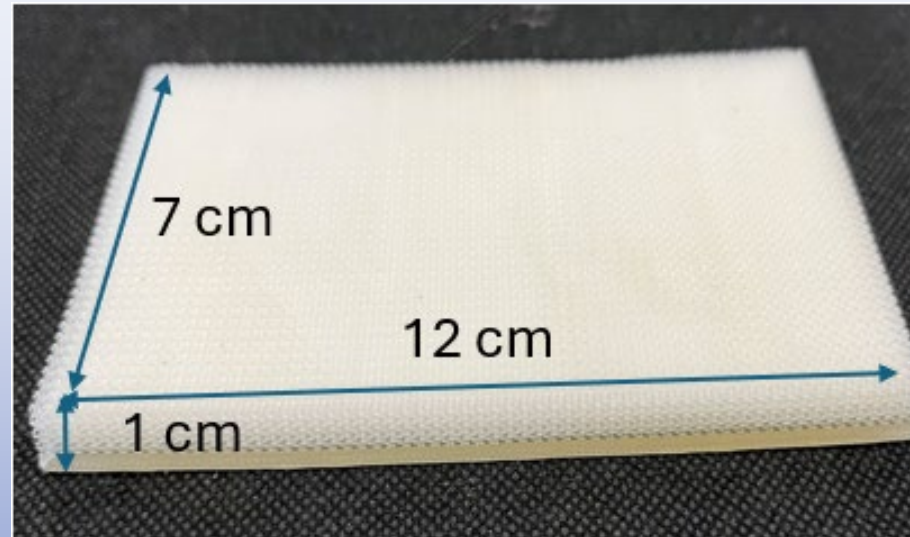
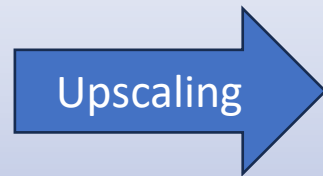
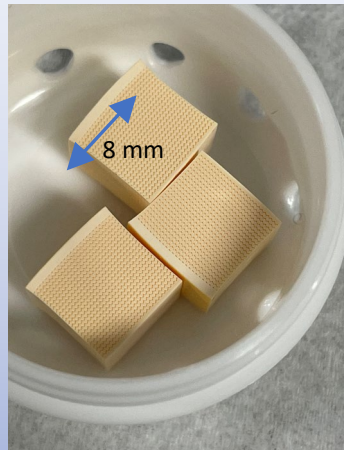


only 2% decrease in CO₂ removal rate during 100 h tests

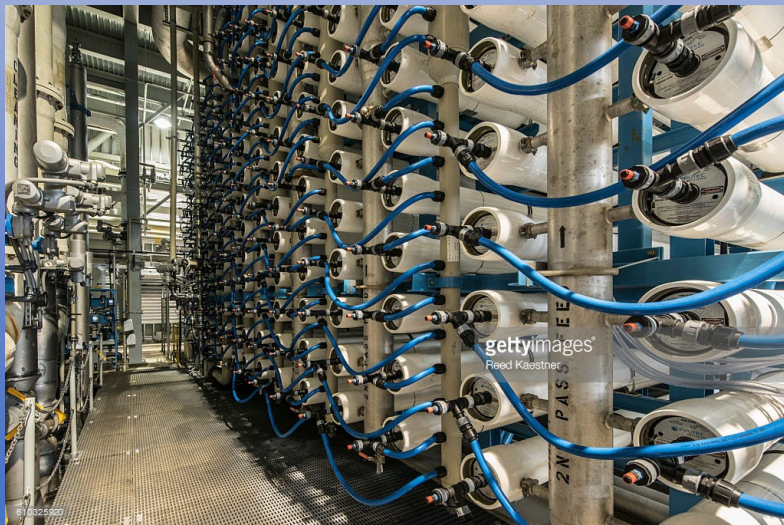
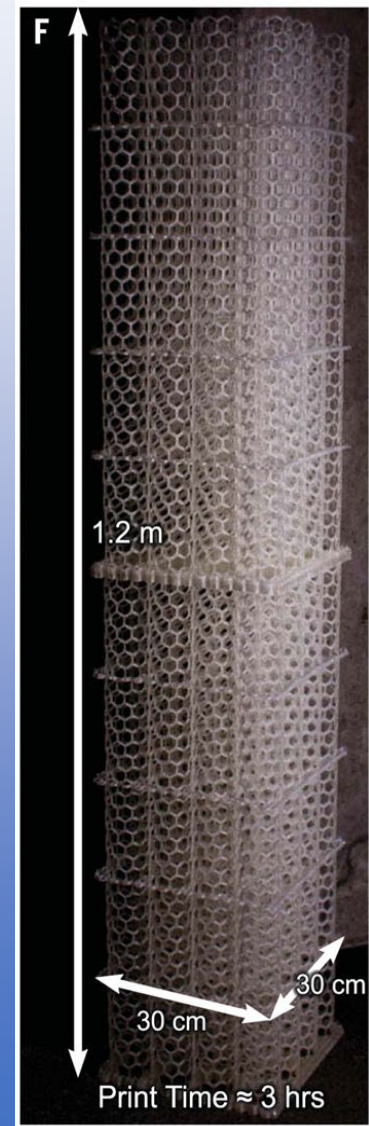


Upscaling of the 3D-GMC technology

D.A. Walker, J.L. Hedrick,
C.A. Mirkin, Rapid, Science
366 (2019) 360-364.



Preliminary 3D-GMC panel test prints



Modular Membrane technology is highly scalable
Reverse Osmosis Desalination plant Carlsbad, California
 The largest saltwater desalination plant in the Western Hemisphere providing 50 million gallons of desalinated seawater per day.

Comparison of CO₂ Capture Systems

Category	3D-GMC	HFMC	Wet Scrubber
CO ₂ Capture Efficiency (CE)	95 %	70 – 95 %	70 – 95%
CO ₂ Absorption Flux ¹	10.71 mol·m ⁻³ ·s ⁻¹	0.2 – 1.5 mol·m ⁻³ ·s ⁻¹	0.2 – 0.5 mol·m ⁻³ ·s ⁻¹
CO ₂ Volumetric Productivity ²	40.71 ton·m ⁻³ ·s ⁻¹	0.7 – 5.4 ton·m ⁻³ ·s ⁻¹	0.7 – 1.7 ton·m ⁻³ ·s ⁻¹
Specific Surface Area ³	7116 m ² ·m ⁻³	600 – 3000 m ² ·m ⁻³	100 – 200 m ² ·m ⁻³
Volume for 1t CO ₂ /d Capture	0.02 m ³	0.2 – 1.4 m ³	0.6 – 1.4 m ³
Pressure Drop	Negligible	2000 ⁴	Negligible
Absorbent Volume ⁵	2.5 m ³	57.35 m ³	-

Assumptions:

- 1: Characterized by the transmembrane flux (3D-GMC and HFMC) or CO₂ content in the product stream (wet scrubber).
- 2: The volumetric productivity is normalized by the volume of the absorber.
- 3: The specific surface area (SSA) is calculated by:

$$SSA = \frac{\text{Total Surface Area}}{\text{Volume of the Absorber}}$$

- 4: The HFMC module is set as 0.5 mm diameter, and 1 m length.
- 5: The absorbent volume is proportional to the absorber volume.

Cost savings from process intensification (CAPEX + smaller absorbent volume) and lower operational costs (low pressure drop, lower rate of absorber loss due to non-contact design)

Well suited for mobile applications due to small system size (~20 l/ton CO₂ per day)

Broader impact beyond gas-phase CO₂ separation

■ Purification and Separation:

- Water/antibody/protein/rare earth purification

■ Hemodialysis membrane

- 400,000+ Americans with permanent kidney failure
- >50 million dialysis procedures performed annually in the US

■ Artificial membrane lung

- Over 150,000 Americans die every year from lung failure
- only 2000 lung transplants available

■ Filtration:

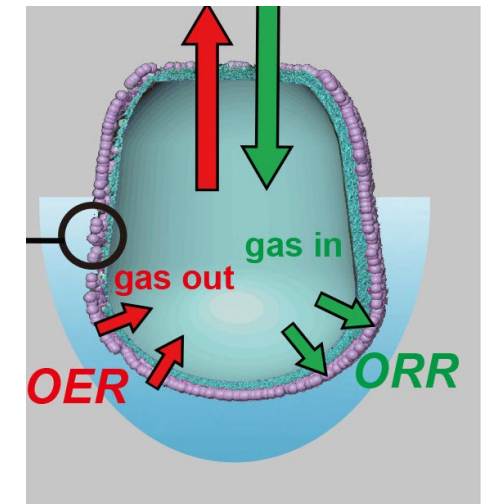
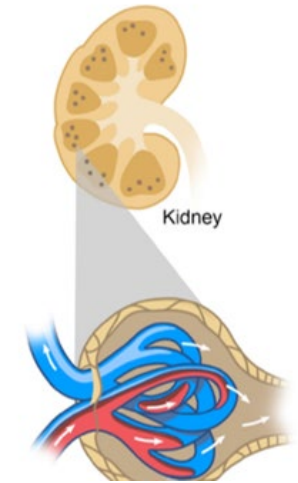
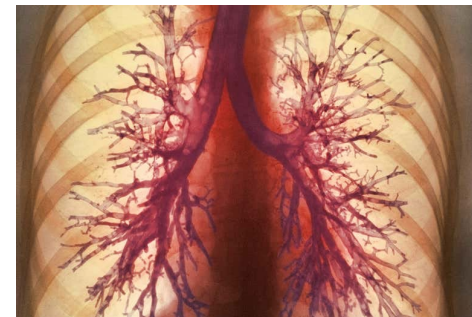
- low resistance filters (COVID-19)

■ Catalysis:

- Chemistry at liquid-liquid / liquid-gas interfaces

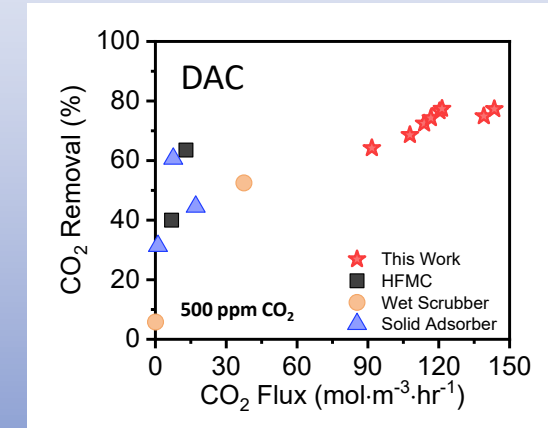
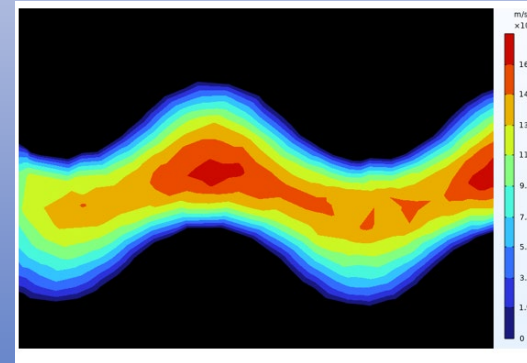
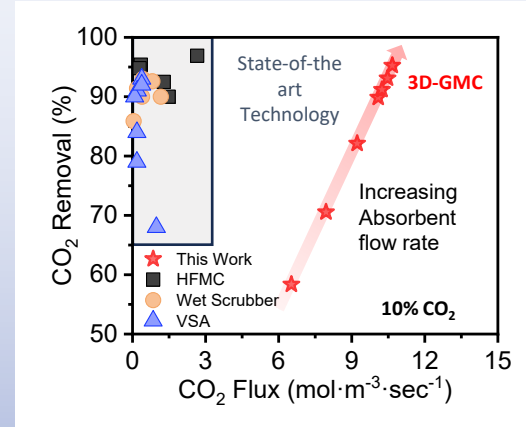
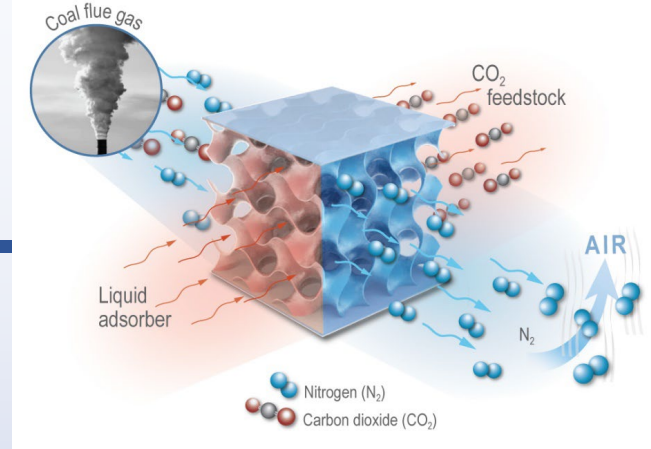
■ Energy storage:

- 3D batteries



3D Gyroid Membrane Contactor (3D-GMC) highlights

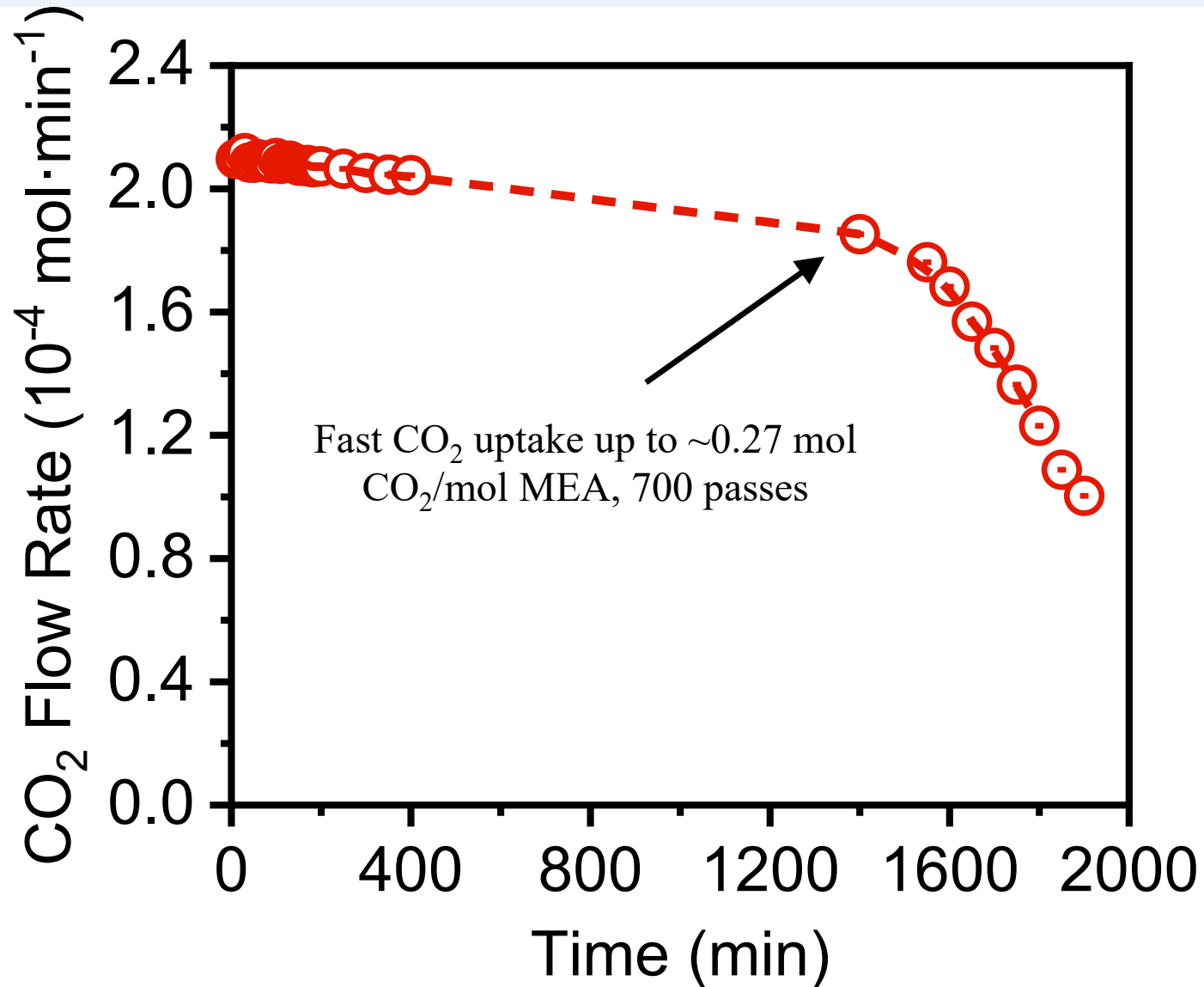
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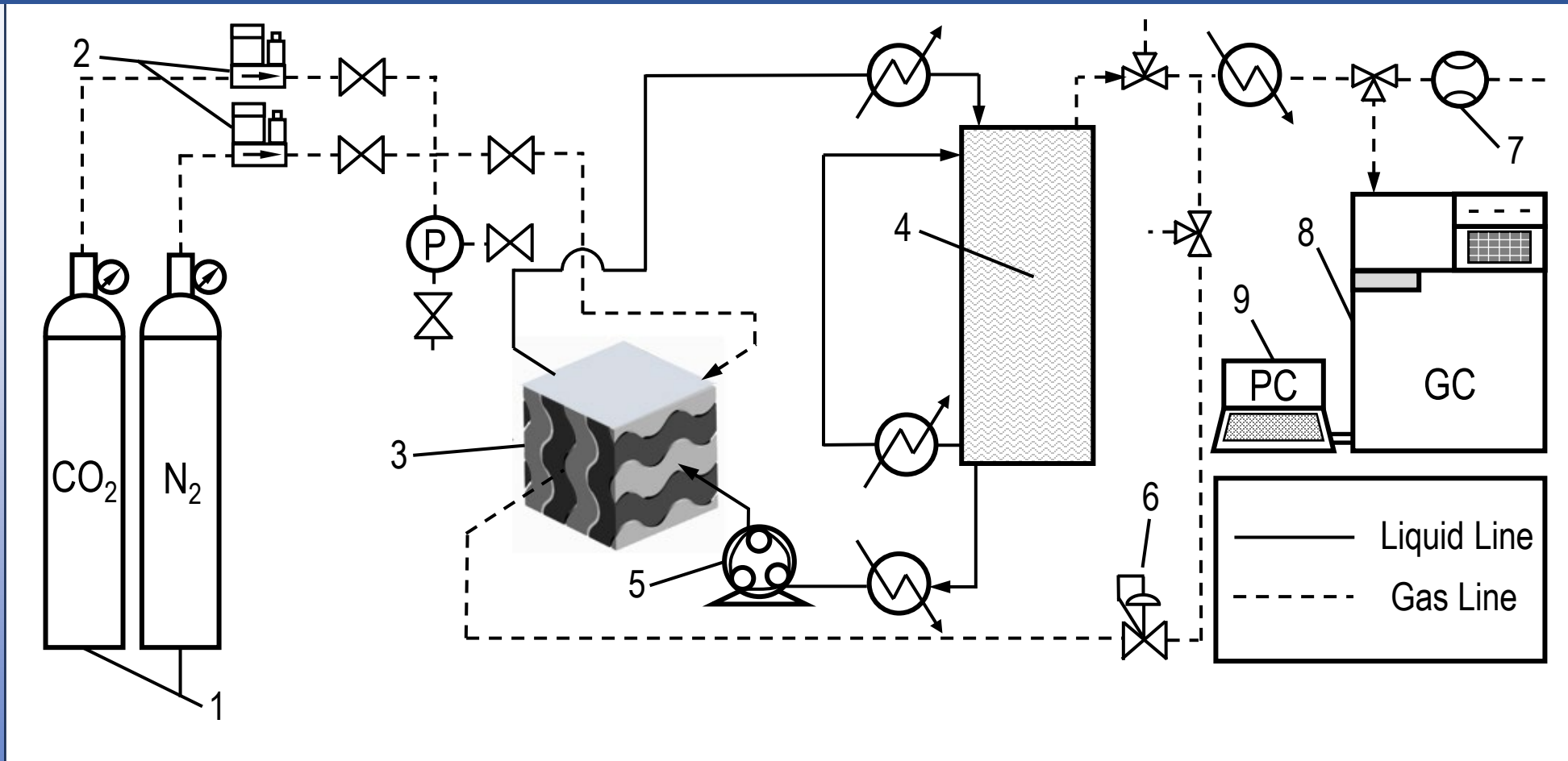
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Multi-pass performance



LFR: 60 mL/min
GFR: 40 mL/min

3D-GMC performance test setup



Schematic representation of the experimental setup: 1-N₂ and CO₂ Gas Cylinders, 2-Mass Flow Controllers, 3-3D Gyroid Membrane, 4-Desorption Column, 5-Peristaltic Pump, 6-Back Flow Regulator, 7-Bubble Flow Meter, 8-Gas Chromatography, 9-Computer connected to 8.