High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

Award No: DE-FE0031634

Jerry Y.S. Lin
Arizona State University
Tempe, Arizona

Kevin Huang
University of South Carolina
Columbia, SC

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Overview

Timeline

- ✓ Project start date:
  Oct. 1, 2018
- ✓ Project end date:
  Sep. 30, 2021
- ✓ Budget Periods:
  I: 10/1/2018-3/31/2020
  II: 4/1/2020-9/30/2021

Research Area 1

- ✓ Lab-Scale CO_2 Capture Development and Testing on Simulated Syngas

Budget

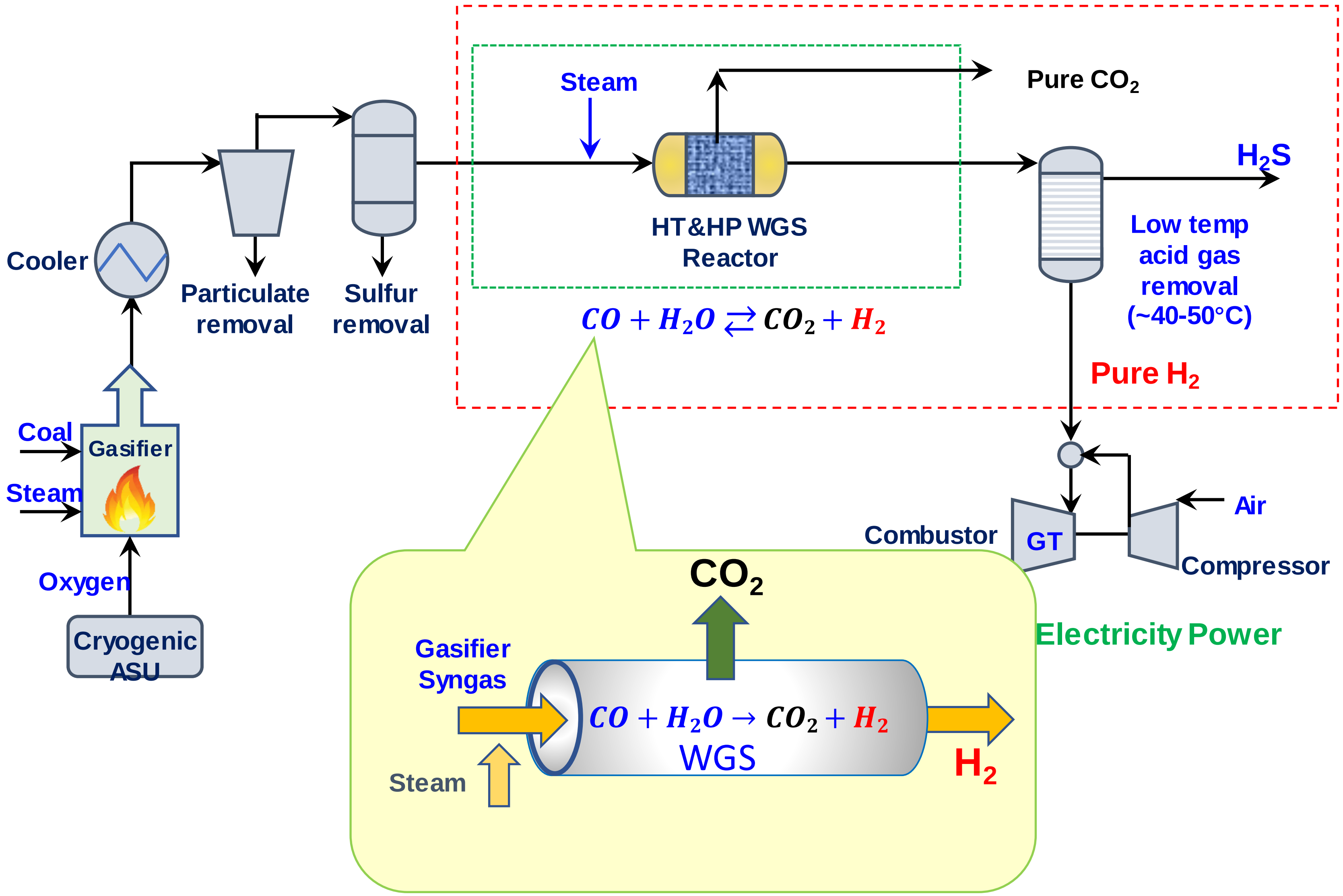
- ✓ Total project funding
  - ❑ DOE **$800,000**
  - ❑ Cost-share: **$200,007**
  - ❑ Total**: $1,000,007**

Partners

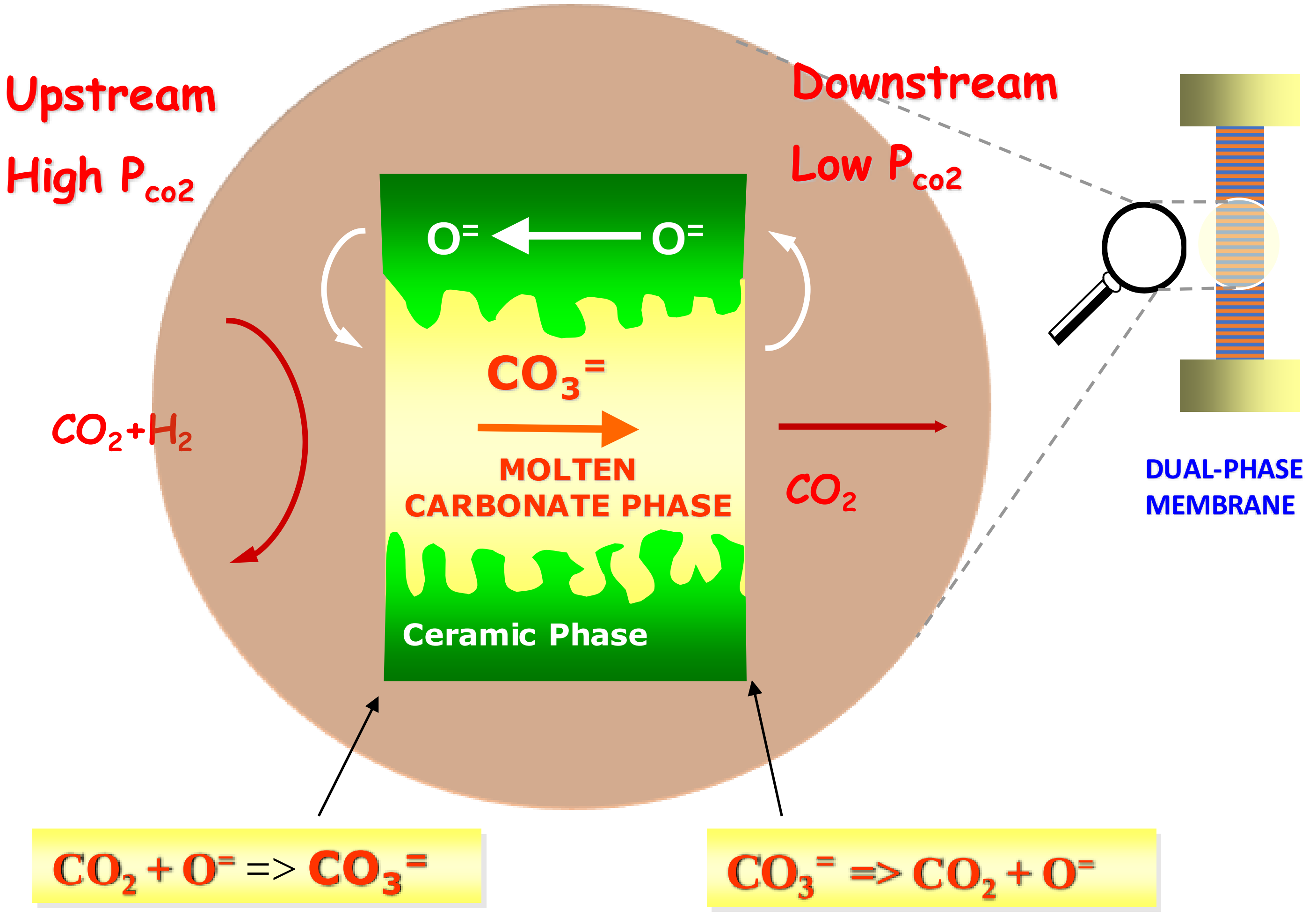
- ✓ Arizona State University (ASU)
- ✓ University of South Carolina (USC)

Membrane Reactor for IGCC process with Pre-combustion CO_2 Capture

- One single reactor
- Improvement of kinetic of WGSR at 900°C
- Improvement of thermodynamics by separating CO_2



Concept of Ceramic-Carbonate Dual-Phase (CCDP) Membrane



M Anderson & YS Lin, Proc. *ICIM2006*, pp. 678-681 *(2006)*; *J. Membr. Sci*. 357, 122*(2010)*

Project Objectives

- To synthesize the chemically/thermally stable Ceramic Carbonate Dual-Phase (CCDP) membranes.
  - ✓ CO_2 permeance > 2000 GPU ($6.5x10^{-7}$ $mol/m^2{\cdot}s{\cdot}Pa$)
  - ✓ Selectivity > 500
  - ✓ Resistant to H_2S
- To fabricate tubular CCDP membrane reactor modules.
  - ✓ High-temperature >700 °C
  - ✓ High-pressure > 20 atm
  - ✓ WGS membrane reactor applications.
- To identify experimental conditions for WGS.
  - ✓ 99% purity of CO_2 stream
  - ✓ 90% purity of H_2 stream

Budget Period 2
April 2020 – September 2021
Progress and Accomplishments

Task 1.0 Project Management and Planning

- The ASU and USC completed contract negotiation.
- Both ASU and USC teams recruited post-doctoral fellows for working on the project.
- ASU and USC teams held one monthly teleconference to review the progress of the research.
- Eleven quarterly reports were submitted on time between October 2019 and June 2021.
- We accomplished four of the five milestones of the project.
- We attended the conference "Addressing the Nation's Energy Needs Through Technology Innovation - 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting" from August 26 – August 30, 2019
- We presented the Budget Period 1: Progress and Accomplishments, on March 18, 2020.
- Publications and Presentations:

  # Three scientific papers were published in peer reviewed journals.

  S. Sun, K. Huang, Efficient and Selective Ethane-to Ethylene conversion assisted by a mixed electron and proton conducting membrane, J. Membr. Sci., 599 (2020), 117840

  S. Sun, Y. Wen, K. Huang. A New Ceramic–Carbonate Dual-Phase Membrane for High-Flux CO2 Capture. ACS Sustainable Chemistry & Engineering, 2021, 9, 5454-5460.

  L. Meng, O. Ovalle-Encinia, and J.Y.S. Lin. Catalyst-Free Ceramic-Carbonate Dual-Phase Membrane Reactors for High Temperature Water Gas Shift: A Simulation Study. Ind. Eng. Chem. Res. 2021, 60, 3581-3588.

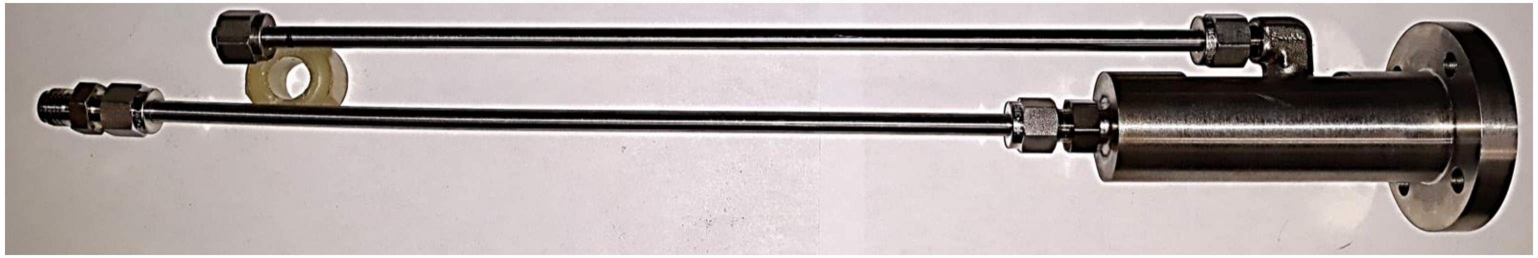
  # One poster was presented on NAMS 2020 Online Conference, on May 18, 2020.

  # Two presentations were given at the MST2020 virtual conference on November 2, 2020.

Task 3.0 – High Temperature, High Pressure, CO_2 Permeation Studies

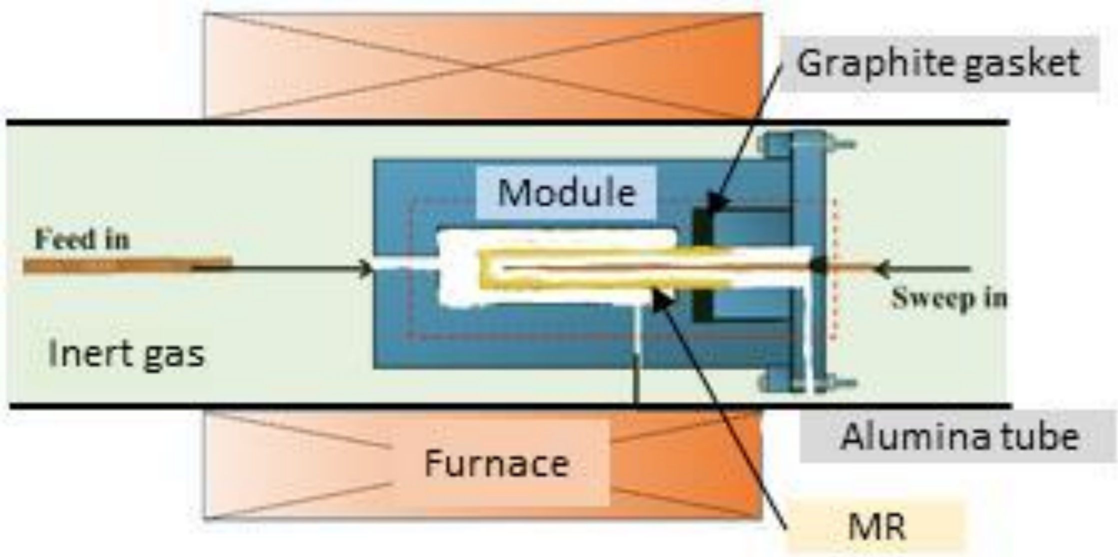
- *Subtask 3.1 – Construction of high-temperature and high-pressure CO_2 permeation/separation setup*

Membrane housing



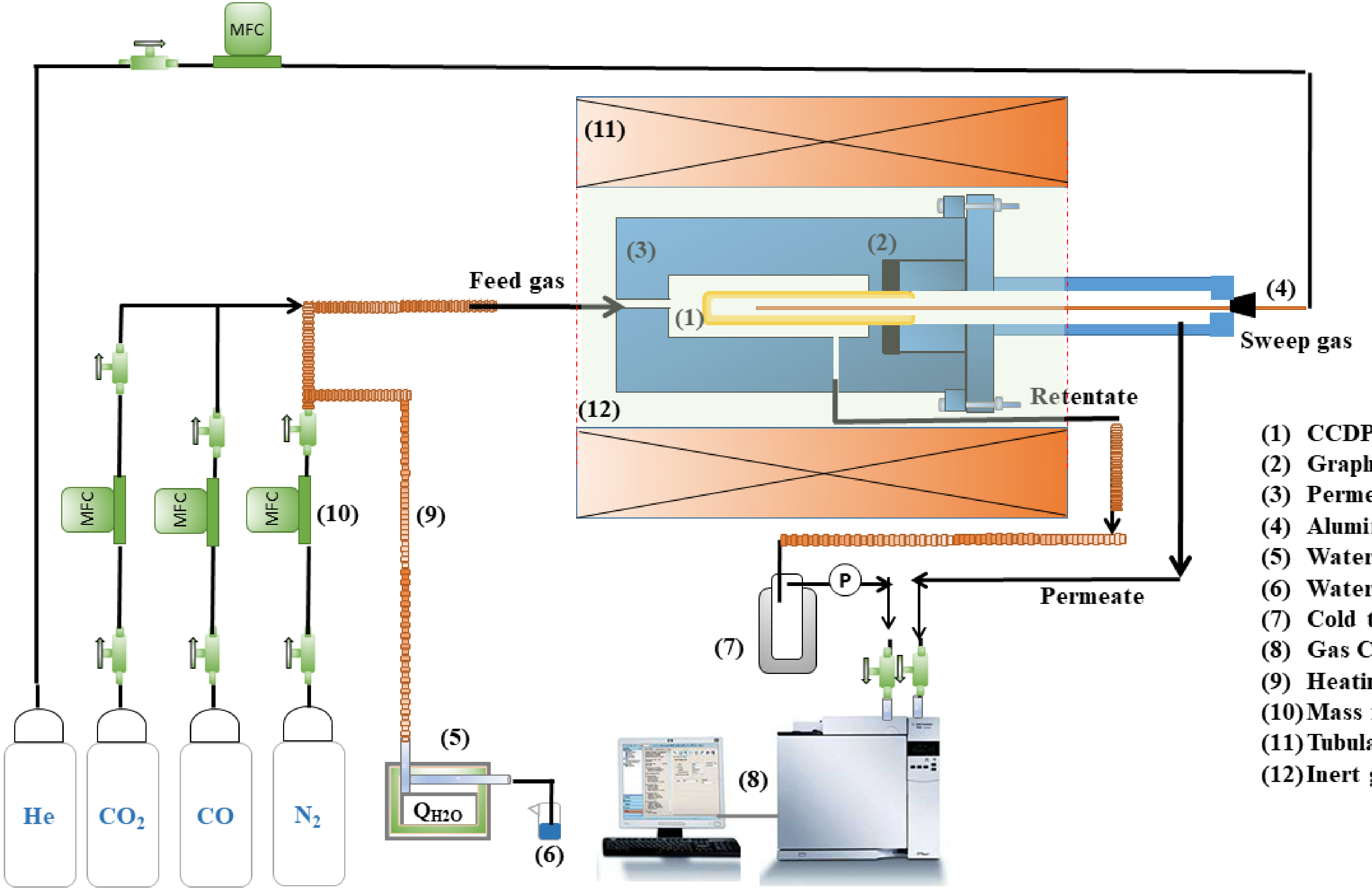
Module head (Sweep gas inlet)

Set-up for HT and HP WGS MR tests



Milestone B accomplished

Schematic representation of the setup for high-temperature and high-pressure CO_2 separation and water gas-shift (WGS) reaction tests



(1) CCDP membrane
(2) Graphite gasket
(3) Permeation cell
(4) Alumina tube for sweep gas
(5) Water pump
(6) Water supply
(7) Cold trap
(8) Gas Chromatograph
(9) Heating tapes
(10) Mass flow controllers
(11) Tubular furnace
(12) Inert gas

Task 3.0 – High Temperature, High Pressure, CO_2 Permeation Studies

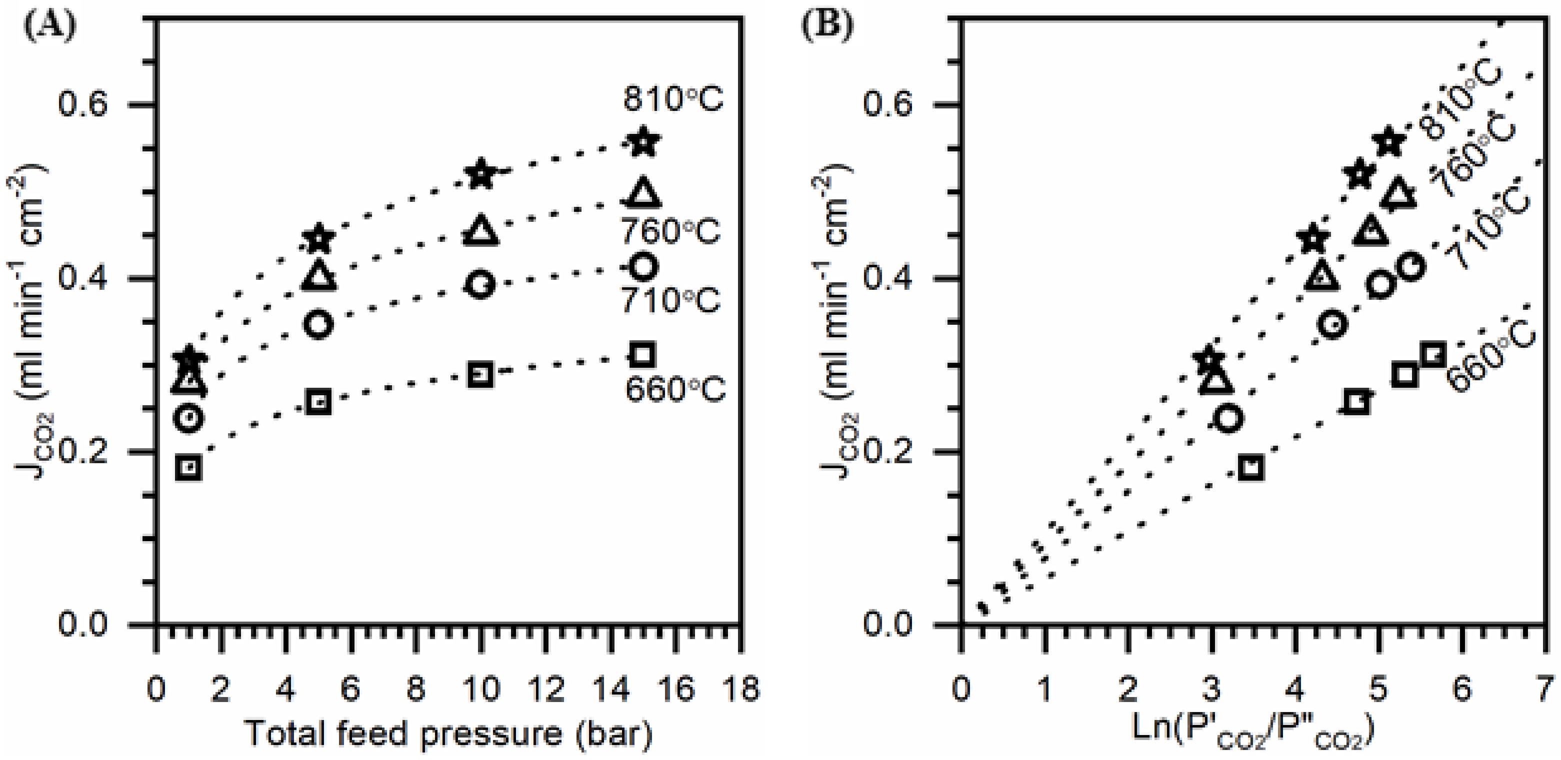
- *Subtask 3.1 – High-Pressure CO2 Permeation and Separation Study*

$Ce_{0.8}Sm_{0.2}O_{2-\delta}$(**SDC**)- (52/48 Li/Na/)$_2CO_3$ (**MC**)

Feed gas: CO_2/N_2 (25/25 ml·min^{-1})
Sweep gas: helium (50 ml·min^{-1})

$$J_{CO_2} = \frac{kRT}{4F^2L}\ln\left(\frac{P'_{CO_2}}{P''_{CO_2}}\right)$$

Carbonate conducting rate-limiting for this CCDP membrane



Task 3.0 – High Temperature, High Pressure, CO_2 Permeation Studies

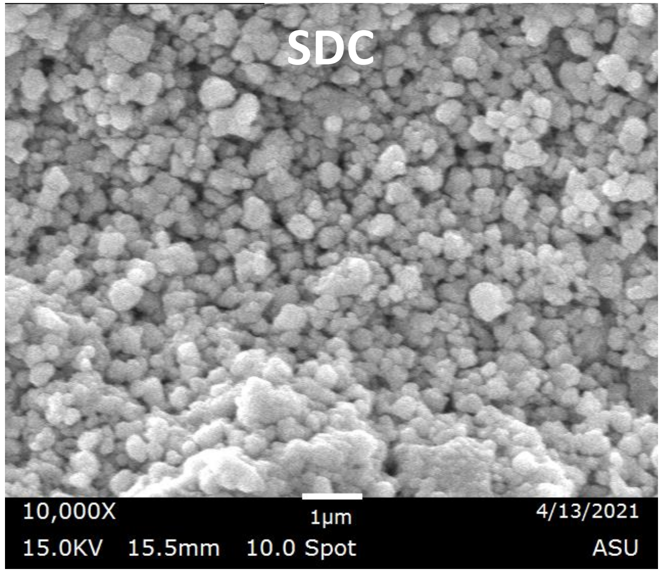
❑ *Subtask 3.1 – High-Pressure CO_2 Permeation and Separation Study*

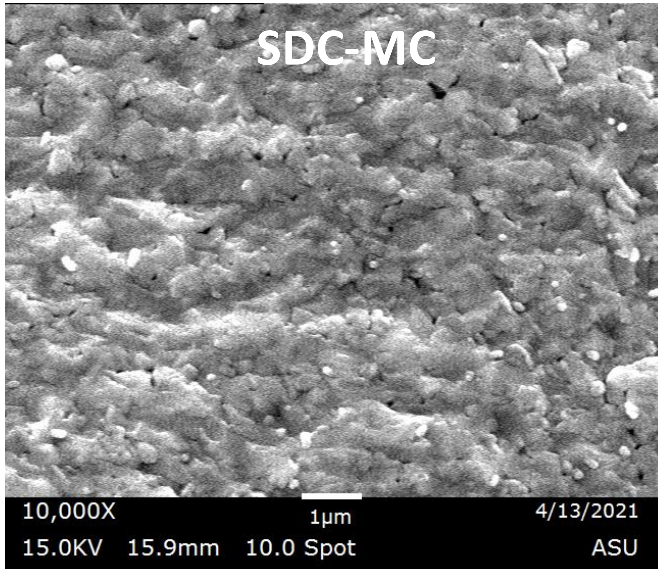
Helium permeance for dense SDC-MC membranes after CO_2 separation test under different operating conditions

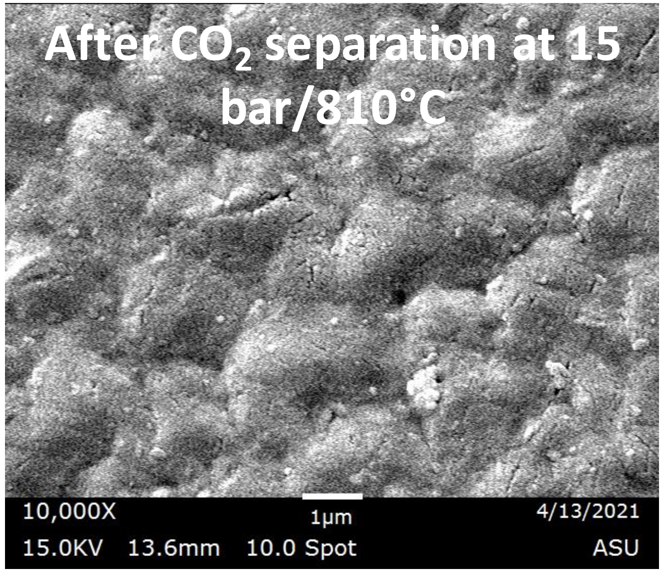
Membr.	Experimental Conditions			Helium Permeance ($mol \cdot s^{-1} \cdot m^{-2} \cdot Pa^{-1}$)	
	Feed gas	Max. Temp. (°C)	Max. P (bar)#	Before test	After test
1	CO_2/N_2	810	15	$\sim 10^{-10}$	8.1×10^{-10}
2	CO_2/N_2	810	8	$\sim 10^{-10}$	1.9×10^{-10}
3	$CO/H_2O/CO_2/N_2$	810	10	$\sim 10^{-10}$	3.7×10^{-10}
4	$CO/H_2O/CO_2/N_2$	810	7	$\sim 10^{-10}$	1.6×10^{-10}

- Maximum feed total pressure during experiments. Sweep total pressure is 1 bar.

Surfaces Views of the High-Pressure Side





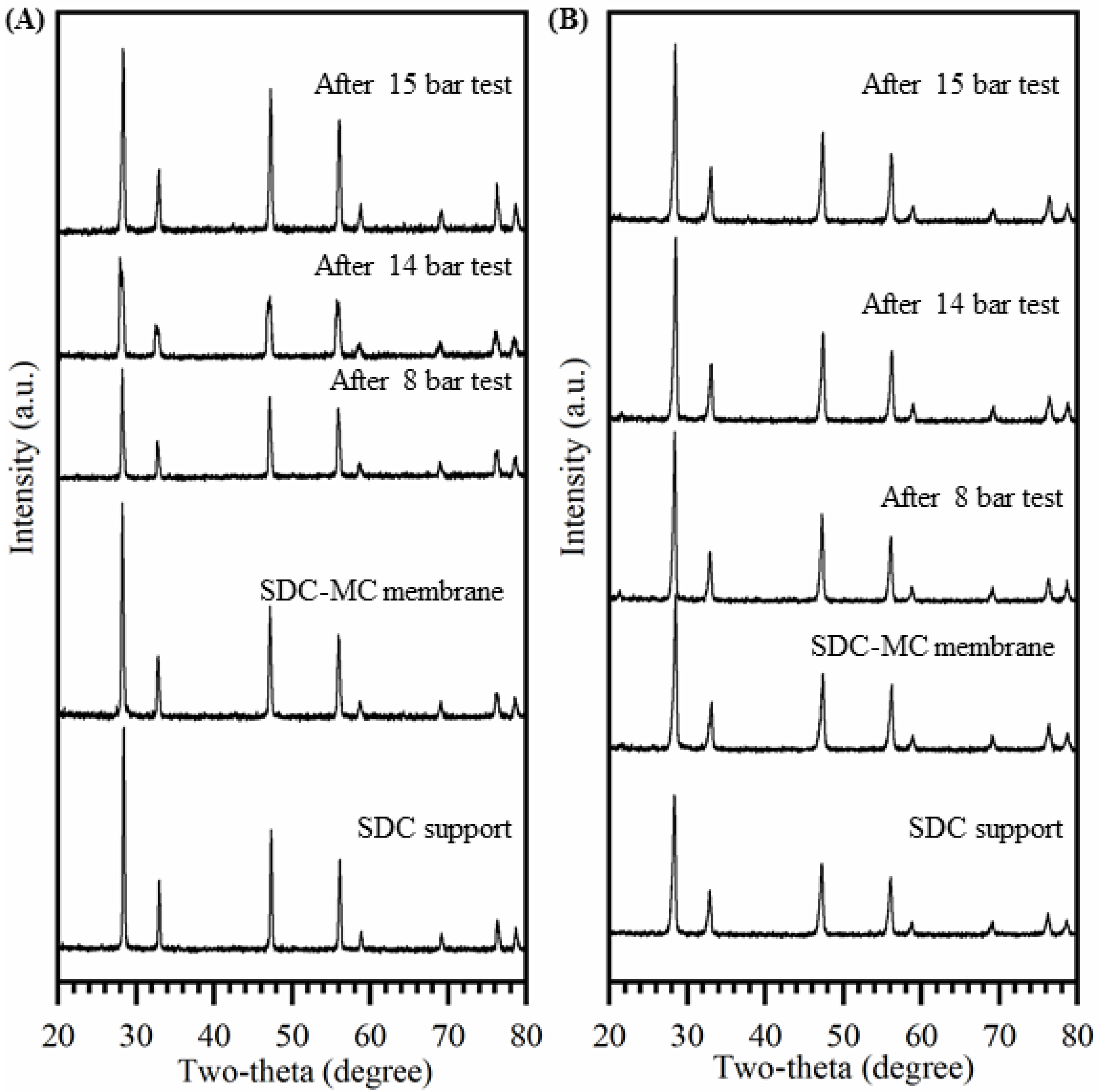


Task 3.0 – High Temperature, High Pressure, CO_2 Permeation Studies

- *Subtask 3.1 – High-Pressure CO_2 Permeation and Separation Study*

(A) High -pressure membrane side (feed side)

SDC crystal structure remains stable

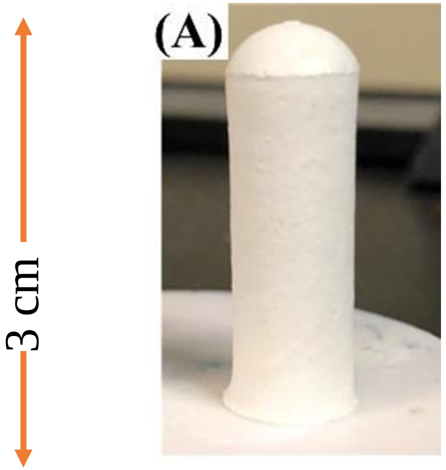


(B) Low-pressure membrane side (permeate side)

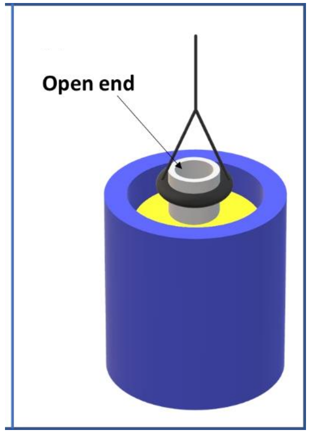
Task 6.0 – Fabrication and Characterization of ScSZ-MC Tubular Membrane

Sc-doped ZrO_2 (**ScSZ**) - (52/48 Li/Na)$_2CO_3$ (**MC**)

Dead-end tubes made by CIP method

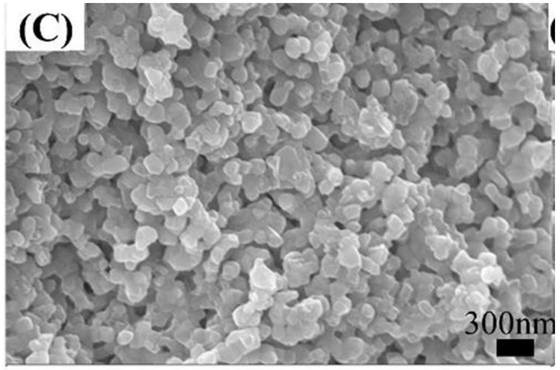


ScSZ

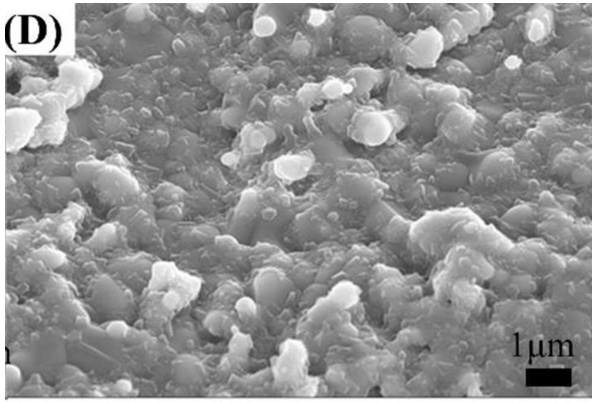


Direct infiltration of molten carbonates at 600°C

ScSZ-MC



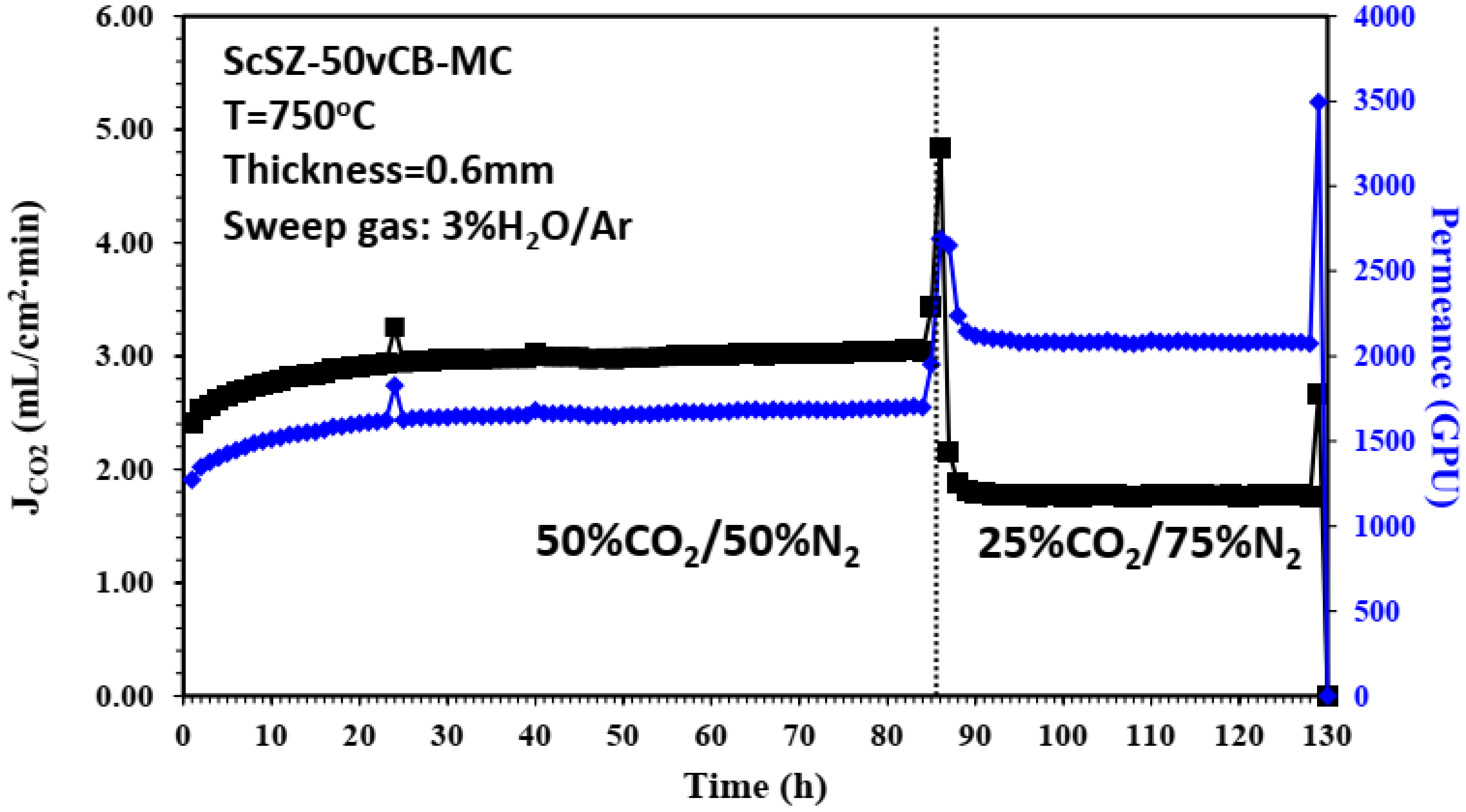
Cross-section of the ScSZ dead-end tubular support sintered at 1000°C



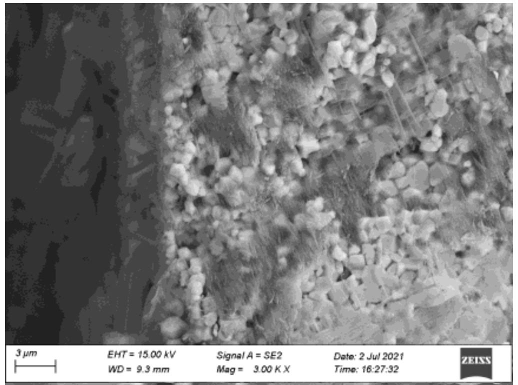
Cross-section of the ScSZ-MC membrane

Task 6.0 – Fabrication and Characterization of ScSZ-MC Tubular Membrane

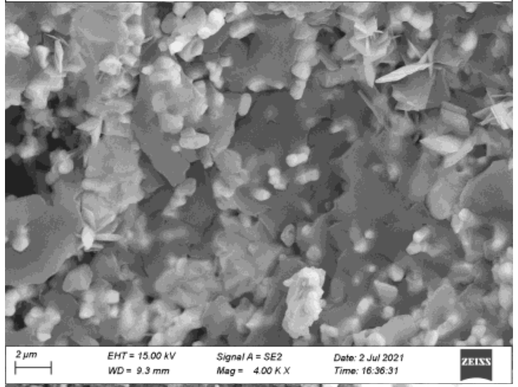
CO_2 permeation flux of ScSZ tubular membrane with 50vol% carbon black as pore-former



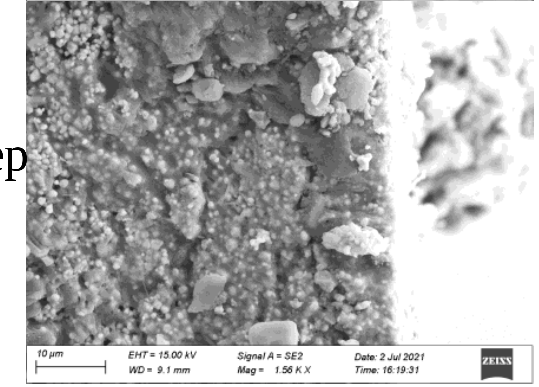
Cross-section near to the feed side.
After test



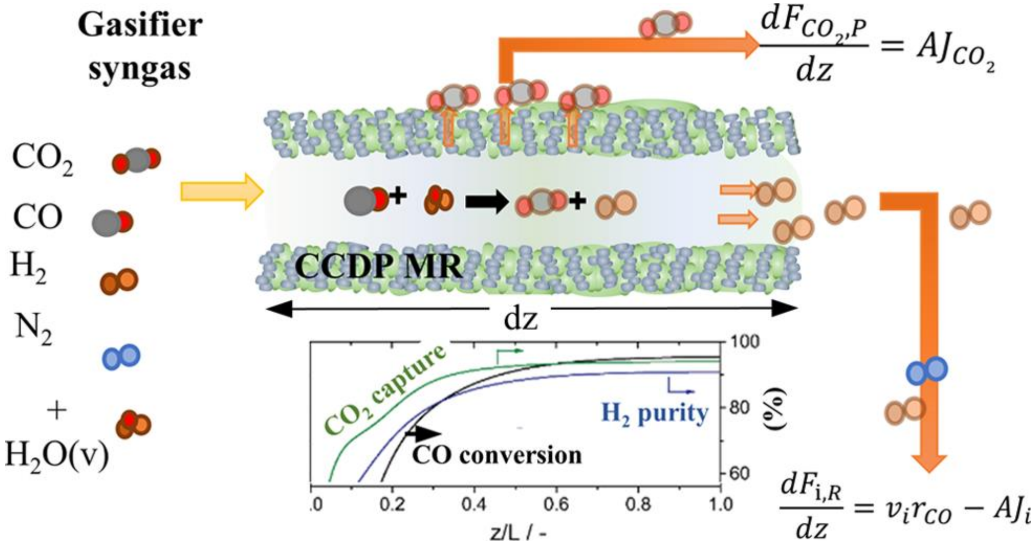
Cross-section bulk.
After test



Cross-section near to the sweep side.
After test



Task 7.0 – Modeling and analysis of CCDP membrane reactor for WGS

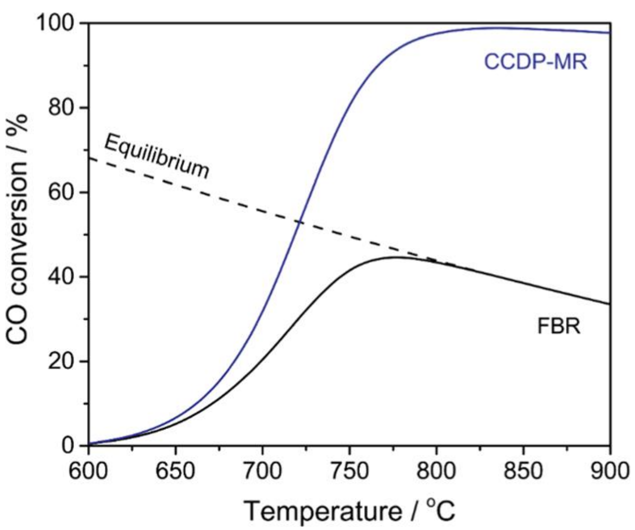


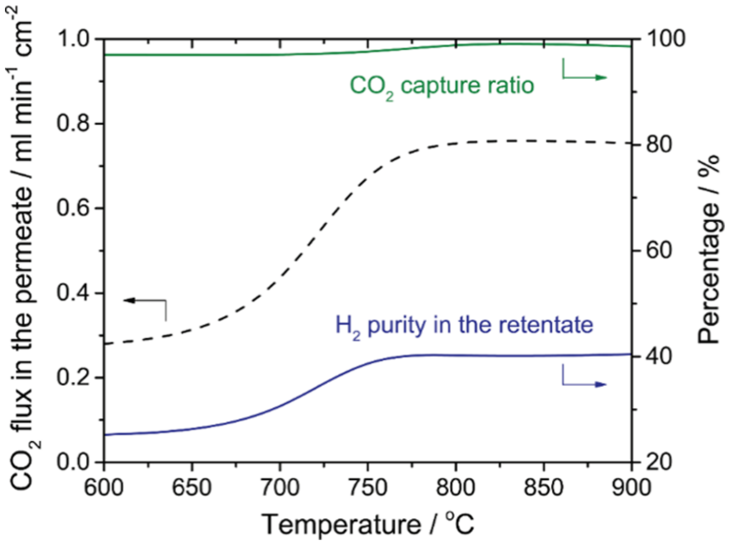
Reaction rate of CO

$$r_{CO} = k_f p_{CO,R}^{0.5} p_{H_2O,R} \left(1 - \frac{1}{K_{eq}} \frac{p_{CO_2,R} p_{H_2,R}}{p_{CO,R} p_{H_2O,R}} \right)$$

CO_2 permeation flux equation for CCDP membrane

$$J_{CO_2} = \frac{\alpha RT}{4nF^2L} \left(p_{CO_2,R}^n - p_{CO_2,P}^n \right)$$





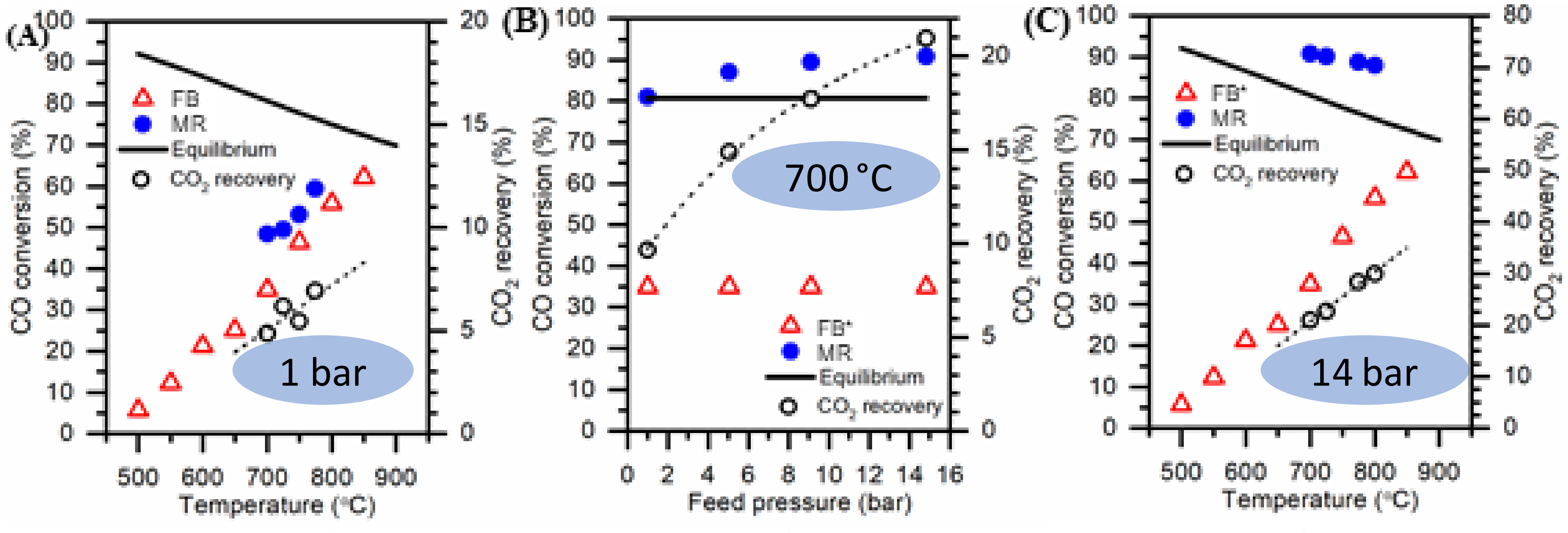
Modeling parameters

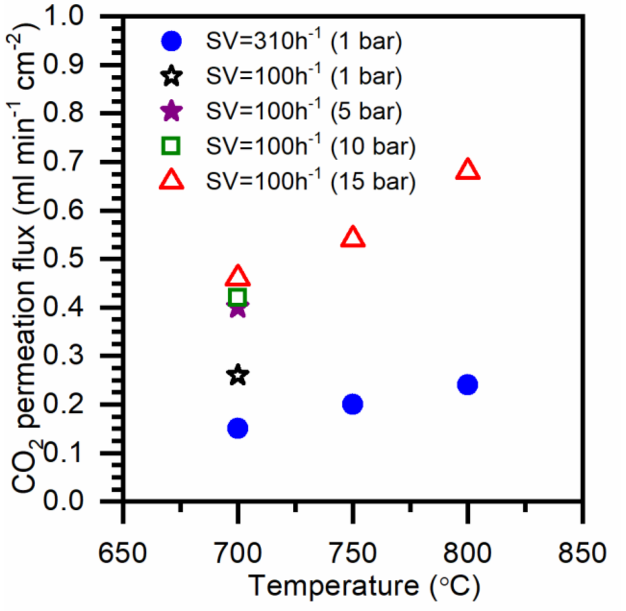
- Feed gas (air-blown gasifier)
  - ➢ 23% H_2
  - ➢ 16% CO
  - ➢ 9% CO_2
  - ➢ 52% N_2
  - ➢ steam/CO = 4.0
- Feed pressure 30 bar
- Sweep pressure 1 bar
- GHSV 25344 h^{-1}

Task 8.0 – Experimental studies on WGS in dual-phase membrane reactors

Effect of ***high temperatures***, ***feed pressures***, *and steam to carbon* ***(S/C)*** *ratio on WGS reaction in the membrane reactor*

Membrane reactor: SDC-MC ***without*** *catalyst*





CO	13%
CO_2	6%
H_2O	52%
N_2	29%

CO	5.5%
CO_2	3.0%
H_2O	79.0%
N_2	12.5%

*Effect of **high temperatures**, **feed pressures**, and **S/C** ratio on WGS reaction in the membrane reactor*

*Membrane reactor: SDC-MC **without** catalyst*

Feed gas composition

CO 4.9 ml·min^{-1}

CO_2 1.4 ml·min^{-1}

N_2 10 ml·min^{-1}

Feed gas	Samples A-B (ml/min)	Sample C (ml/min)	Sample D (ml/min)
H_2O(v)	34.2	51.3	98.7
Total flow rate	50.5	67.6	115
SV (h^{-1})	168	225	383

Low SV improves the WGS reaction kinetic

Experiment C‡
Carbon balance: 85%
Space velocity (SV): 225 h^{-1}

Membrane	Feed Pressure (bar)	Temp. (°C)	S/C	MR CO Con.	Eq. Con.	FB	CO_2 Recov.	Perm. flux (ml/min cm^2)		Mem. Area (cm^2)
								CO_2	N_2 leak	
B	1	800	4	65	76	56	9	0.12	0	2.6
	3			80			17	0.25	0	
	5			84			17	0.26	0.03	
A	1	850	4	69	73	62	19	0.32	0.02	2.6
	7	850	4	92			29	0.53	0.1	
C‡	**7**	**850**	**7**	**95**	**82**	**62**	**30.1**	**0.56**	**0.04**	**2.6**
D	7	850	14	97	91	62	30	0.55	0.04	2.6
D After 0.5h	7			94		62	53	1.0	1.5	
E	7	850	14	96	91	62	15	0.37	0	1.8
	10			95		62	17	0.44	0	
	13			97		62	42	1.09	1	

Water gas-shift (WGS) reaction in membrane reactor with side reactions

WGS

$CO + H_2O \leftrightarrow CO_2 + H_2$, ΔH_{298K} = -41.2 kJ·mol^{-1}

WGS reaction favored at the following operating conditions in the MR:

- *High temperature (>800 °C)*
- *High feed pressure (>5bar)*
- *Low SV (100-400 h^{-1})*
- *High CO_2 permeation flux*

Boudouard reaction (coking formation)

$2CO \leftrightarrow C + CO_2$, ΔH_{298K} = -172 kJ·mol^{-1}

Coke formation favored at the following operating conditions in the MR:

- *Low temperature (<850 °C)*
- *High feed pressure (>5bar)*
- *Low SV (100-400 h^{-1})*
- *High CO_2 permeation flux*

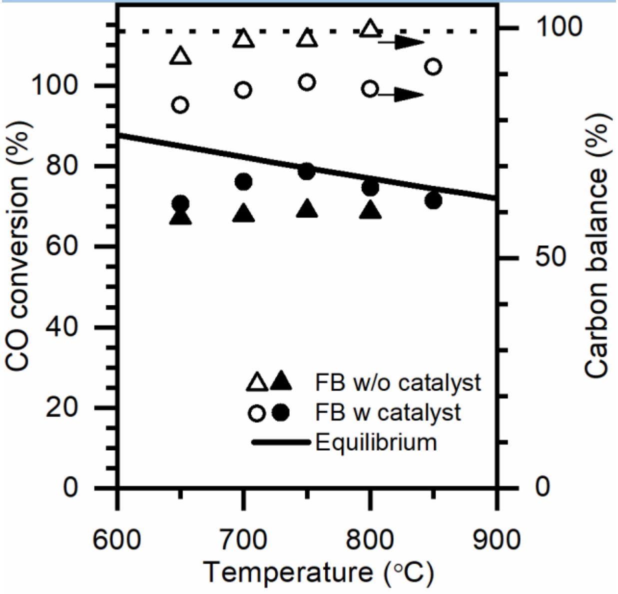
Operating conditions for WGS optimization with coking formation minimization

- *HT catalyst with high SV (> 1000 h^{-1})*
- *High temperatures (850-950 °C)*
- *Intermediate feed pressure (~7 bar)*
- *High CO_2 permeation flux*

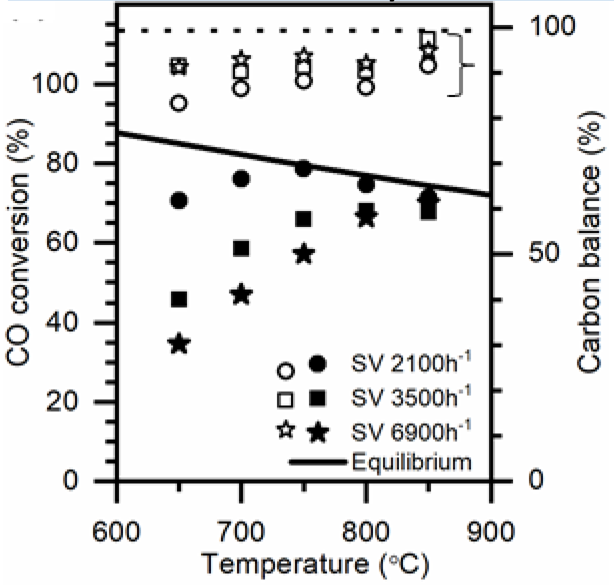
*Water gas-shift (WGS) reaction in **fixed-bed reactor** with catalyst [a $Co\text{-}Mo\text{-}Mg(AlO_2)_2$ based catalyst]*

Effects of operating conditions of temperature, total feed pressure and SV for WGS with HT catalyst and coking formation minimization

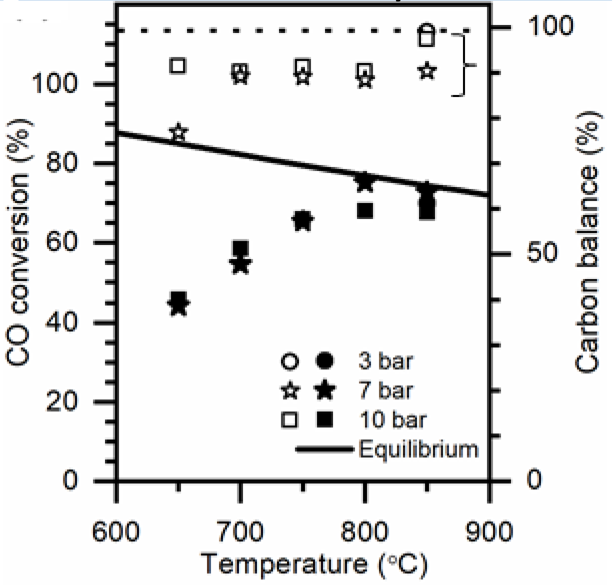
Feed pressure = 10 bar
SV = 2100 h^{-1}



Feed pressure = 10 bar
With catalyst



SV = 3500 h^{-1}
With catalyst

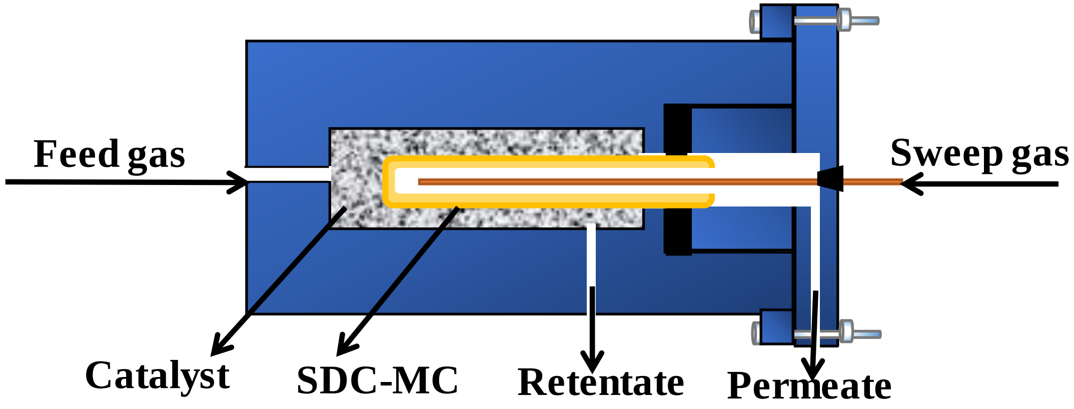


Feed molar concentration
CO/13%
CO_2/6%
N_2/29%
H_2O/52%
S/C = 4

Optimal conditions for WGS reaction with catalyst

- *SV ~ 2100 h^{-1})*
- *High temperature (> 850 °C)*
- *Intermediate feed pressure (3-7 bar)*

*Water gas-shift (WGS) reaction in **membrane reactor SDC-MC** with catalyst [a Co-Mo-Mg$(AlO_2)_2$ based catalyst]*



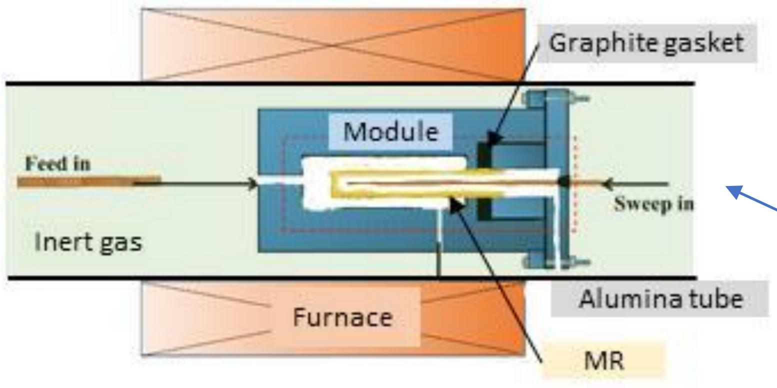
	Membr. area (cm^2)	SV (h^{-1})	TOT Feed P (bar)	Temp. (°C)	CO Conversion (%)		Carbon Balance (%)	CO_2 Recovery (%)
					Exp.	Eq.		
1	4.5	1020	7	850	82	73	93	39
2	4.5	**1140**	**10**	**850**	**78**	73	**97**	**36**
3	1.7	**1995**	7	850	73	73	95	9
			7	**900**	**74**	71	**99**	12
4	2.6	2850	10	850	73	73	95	11

Effects of operating conditions for WGS reaction with HT catalyst and coking formation minimization in MR

- *Carbon Balance > 95% at*
  - ✓ *temperature > 850 °C*
  - ✓ *feed pressure between 7-10 bar*
  - ✓ *SV > 1140 h^{-1}*
- *CO conversion > Equilibrium at*
  - ✓ *temperatures > 850 °C*
  - ✓ *feed pressure between 7-10 bar*
  - ✓ *SV between 1140-1995 h^{-1}*
  - ✓ *CO_2 recovery ~ 36%*

*Water gas-shift (WGS) reaction in **membrane reactor SDC-MC** with catalyst [a Co-Mo-Mg$(AlO_2)_2$ based catalyst] at temperatures between 800-950 °C*

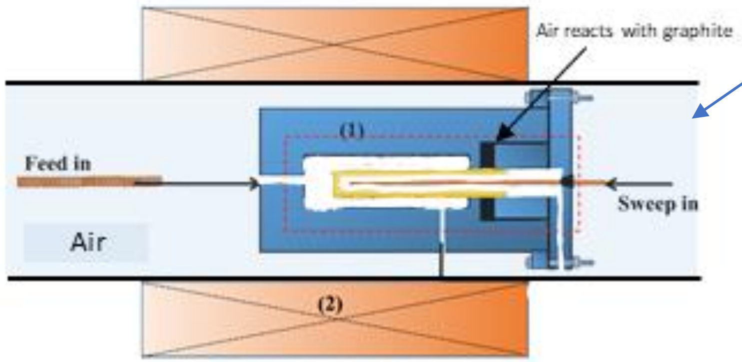
Permeation cell enclosed with inert gas



- ✓ *Temperature: 950 °C*
- ✓ *Time: at least 24 h*
- ✓ *Pressure: 15 bar*

After tests

Permeation cell in air



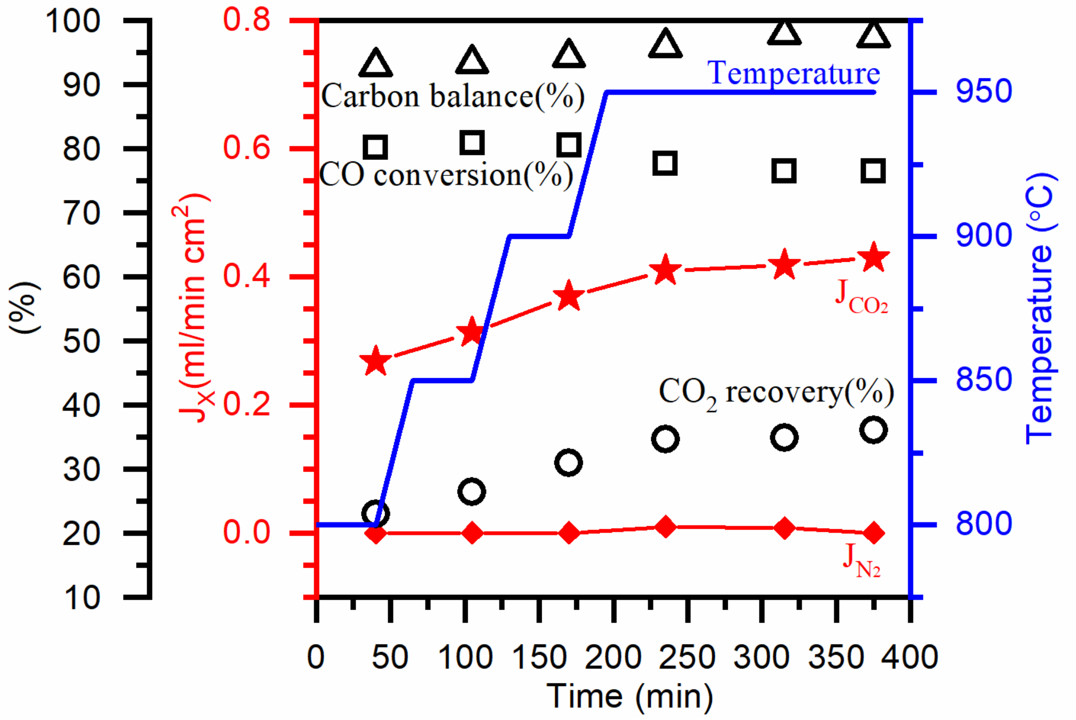
- ✓ *Temperature: 850 °C*
- ✓ *Time: 1.5 h*
- ✓ *Pressure: 15 bar*

Results performed in the setup with inert gas

CO conversion and CO_2 recovery stability at 950 °C for 3 h

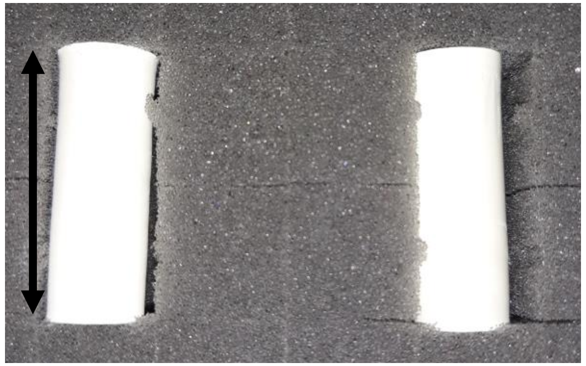
Carbon balance ~ 100%

N_2 leakage negligible



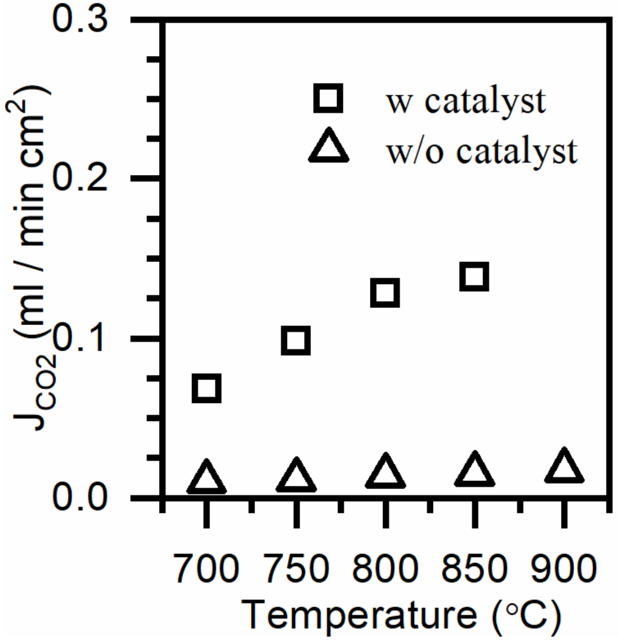
*Water gas-shift (WGS) reaction in **membrane reactor ScSZ-MC** without and with catalyst [a Co-Mo-Mg$(AlO_2)_2$ based catalyst]*

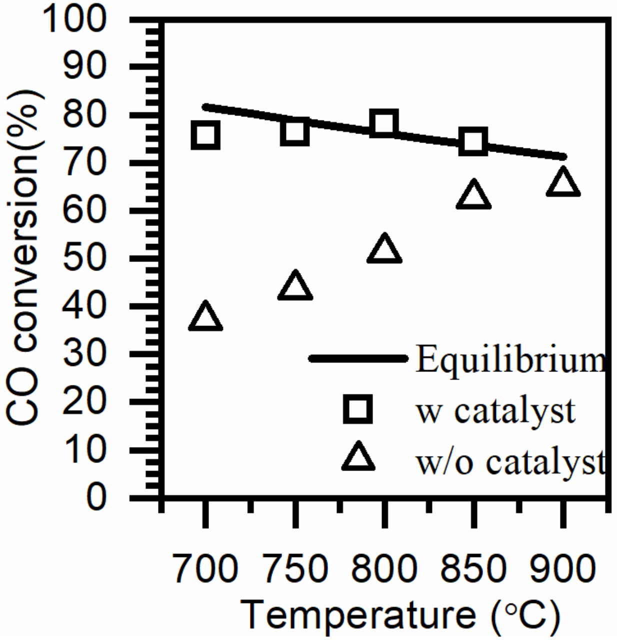
3 cm



ScSZ-MC dead-end tubular membrane fabricated at USC

- ✓ *Univ of South Caroline (USC) team sent ScSZ-MC dead-end tubular membranes to Arizona State University (ASU) team.*
- ✓ *The ScSZ-MC membranes were mounted in the HT and HP setup and permeation cell for WGS reaction at ASU.*
- ✓ *WGS reaction with catalyst was performed in membrane reactor ScSZ-MC.*





Total pressure (bar)	
Feed side	1
Sweep side	1
Feed gas flow rate (ml/min)	
CO	4.8
CO_2	1.3
N_2	3.9
H_2O	25.8
Space velocity (h^{-1})	645
Sweep gas flow rate (ml/min)	
He	100
Feed gas molar composition (mol%)	
CO	16.2
CO_2	4.6
N_2	14.6
H_2O	64.4

Milestone Status Report

ID	Task	Description	Planned Completion	Actual Completion	Verification Method
A	1	Update Project Management Plan	11/30/2018	11/30/2018	Project Management Plan submitted to DOE
B	3	Establish high temperature and high-pressure membrane permeation and reactor system (including modules)	3/31/2019	3/31/2019	Report to DOE
C	8.1	Complete WGS reaction in CCDP membrane reactor with contaminant-free syngas, with CO conversion of 95%	3/31/2020	12/31/2020	Report to DOE
D	6	Fabricate CCDP membrane tubes with CO_2 permeance 2000 GPU and stability under 30 atm transmembrane pressure drop	12/31/2020	6/30/2021	Report to DOE
E	8.3	Complete WGS reaction in H_2S resistant CCDP membrane reactor with simulated coal-gasified gas with H_2S with CO conversion of 99%	9/31/2021		Report to DOE

Plan for the final stage of the project

Task				BP 1						BP 2					
	Start date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 6.0 - Fabrication and Characterization of Sc-ZrO_2 Tubular Membranes (USC)	4/1/20	3/31/21													
Task 8.0 Experimental Studies on WGS in Dual-Phase Membrane Reactors (ASU)	10/1/20	9/31/21													
Subask 8.2 Modeling WGS reaction ScSZ-MC membrane reactor	1/1/21	6/31/21													
Subtask 8.3 Experiments on WGS reaction on ScSZ-MC membrane reactor	4/1/21	9/31/21													
Task 9.0 Process Design and Techno-Economic Analysis (ASU)	4/1/21	9/31/21													

Tasks for the remaining quarters 12 and achieving the last milestone:

1. *Further optimizing WGS in SDC-MC membrane reactor to achieve target conversion, recovery and steam purity*
2. *WGS reaction in ScSZ-MC membrane reactor modeling*
3. *Experiments on WGS reaction on ScSZ-MC membrane reactor including stability study*
4. *Process Design and Techno-Economic Analysis*

Thank You!

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