Project Closeout Presentation

Pre-Combustion Carbon Dioxide Capture by a New Dual-Phase Ceramic-Carbonate Membrane Reactor

DoE Project: DE-FE0000470

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Project Background and Objectives

Project Overview

Funding:

DOE Fund: $656,316

- Personnel & etc: $586K
- Equipment: $70K

ASU Cost-Share: $164,088

- PI's summer salary: $129K
- Equipment: $35K

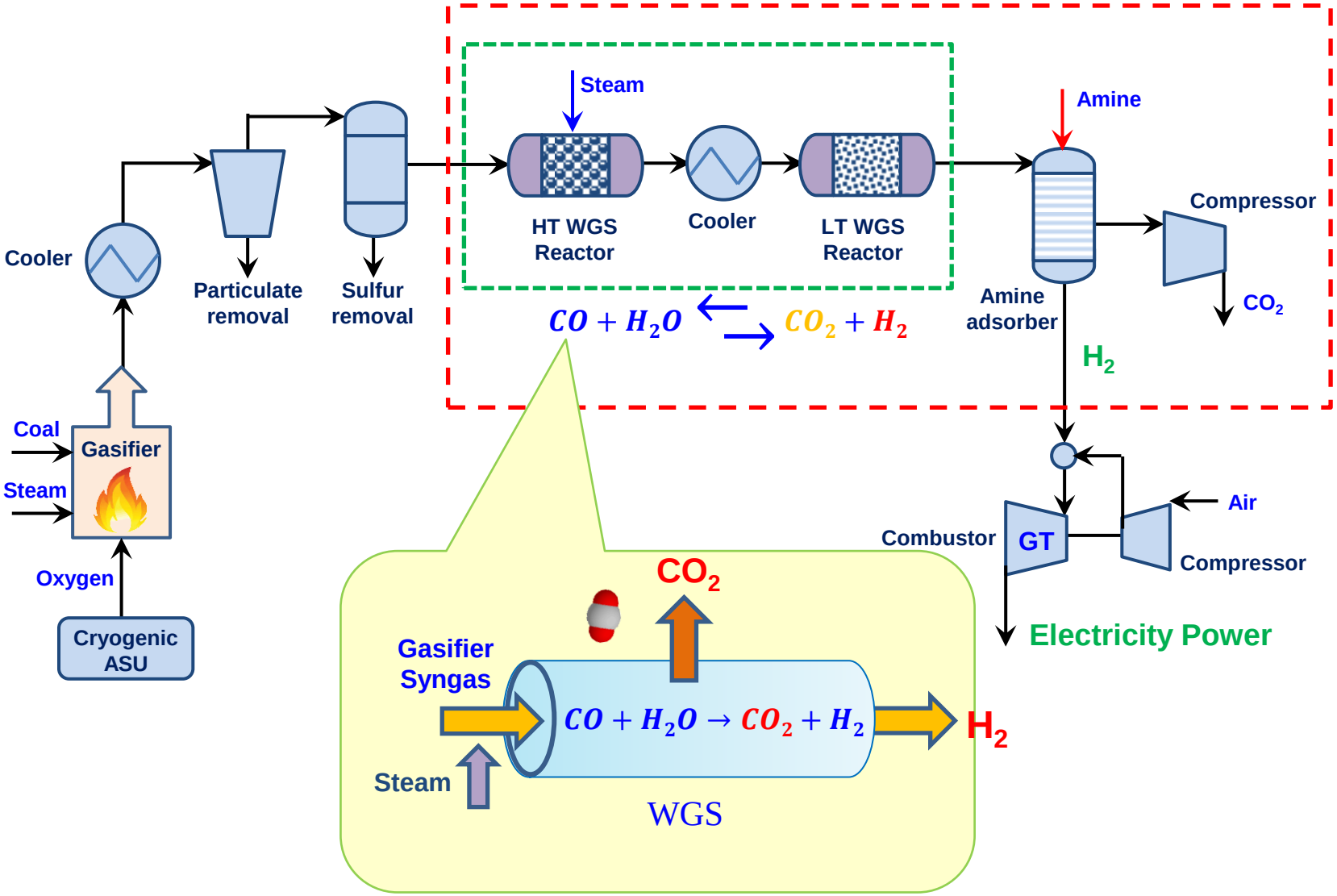
Project Performance Dates:

Oct.1, 2009-Sept.31, 2014

Project Participants:

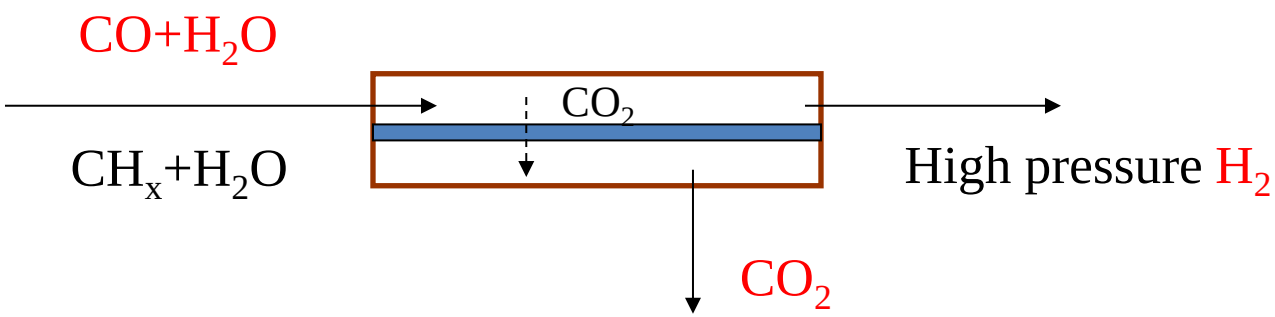
Arizona State University

CO_2-Permeable Membrane Reactor for IGCC with CO_2 Capture

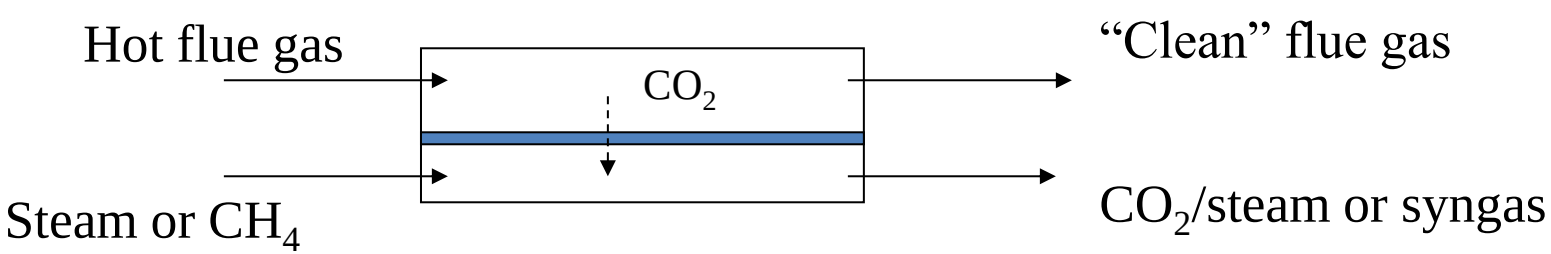


Applications of CO_2 Perm-Selective Membranes

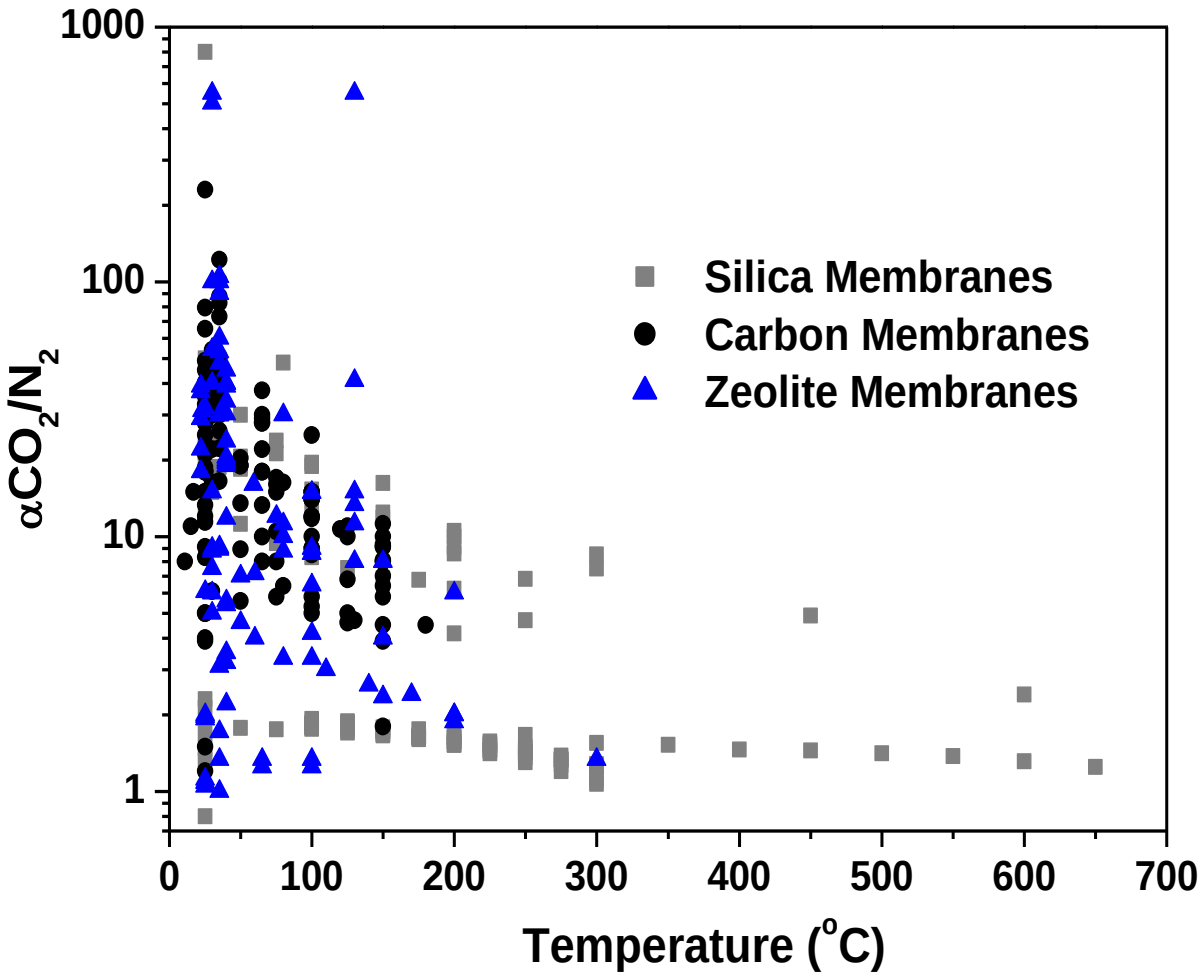
- **Water gas shift reaction**
- **Steam-reform of methane (SRM)**



- **Dry-reform of methane with CO_2 separation**



CO_2 Perm-Selective Inorganic Membranes



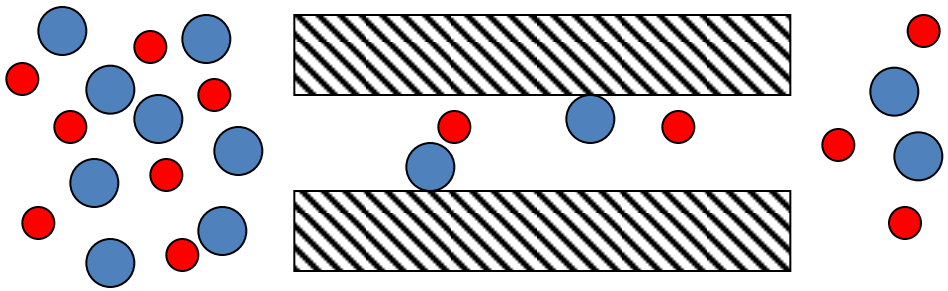
- Microporous membranes made from silicas, carbons and zeolites are capable of separating CO_2 from N_2 at low temperature
- Ultrathin, ion exchanged Y-type zeolites are best candidates for low temperature separation
- CO_2/N_2 selectivity decreases with increasing temperatures

Diffusion-Controlled Permeation

F = [Solubility][Diffusivity]

Diffusion Dominating

(non-adsorbing, or high temperature)



$$\alpha_{1/2} \propto \frac{D_1}{D_2}$$

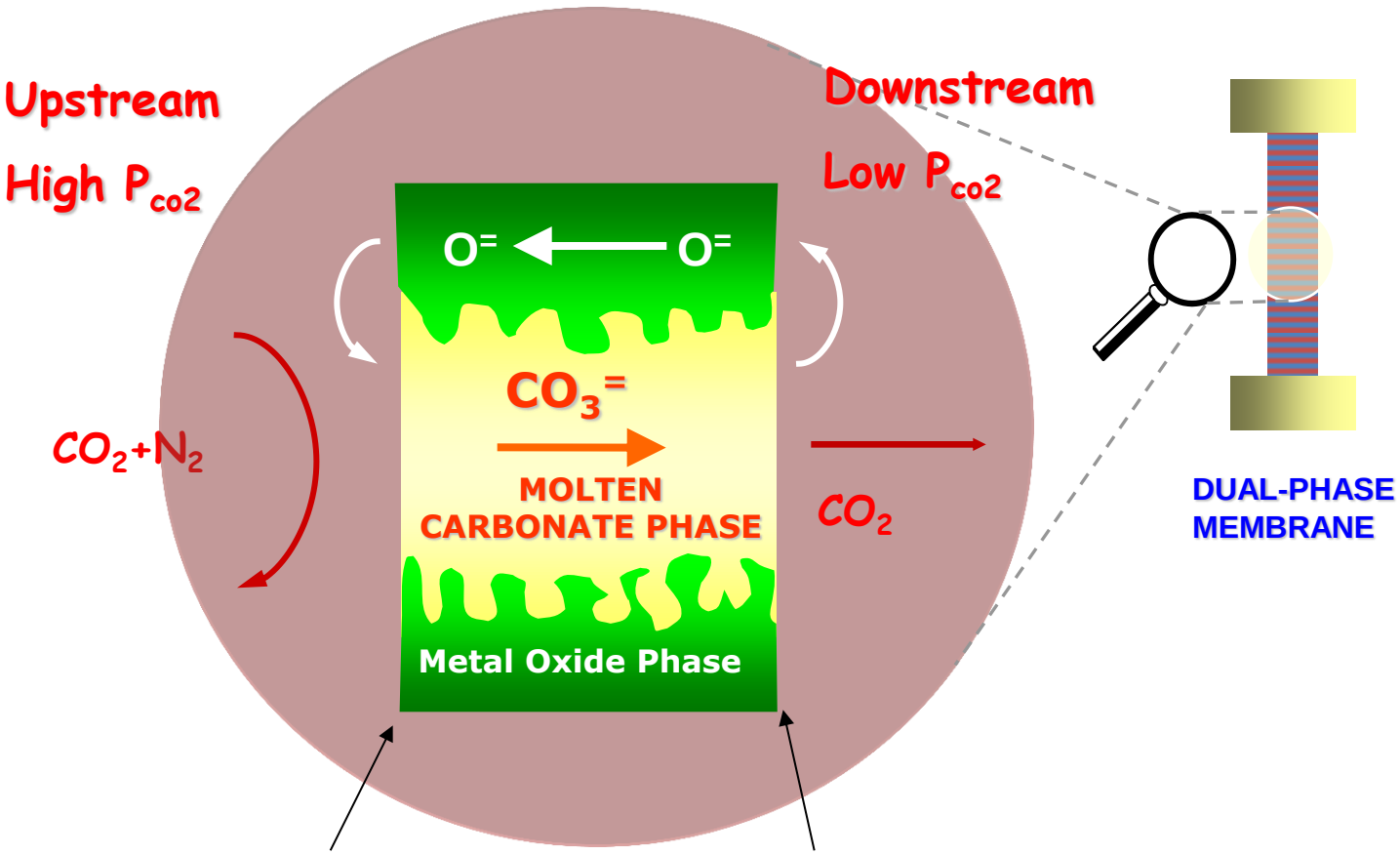
At high temperature (>300°C) solubility difference diminishes:

F = [1][Diffusivity]

$$\alpha_{CO2/N2} = \frac{F_{CO_2}}{F_{N2}} = \frac{D_{CO_2}}{D_{N_2}} \sim 1.1$$

M Kanezashi & YS Lin, *J. Chem. Phys. C*, 113, 3767(2009)

Concept of Ceramic-Carbonate Dual-Phase Membrane



$CO_2 + O^= \Rightarrow CO_3^=$

$CO_3^= \Rightarrow CO_2 + O^=$

M Anderson & YS Lin, Proc. *ICIM2006*, pp. 678-681 *(2006)*

Project Objectives

1. Synthesize chemically/thermally stable dual-phase ceramic-carbonate membranes with CO_2 permeance and CO_2 selectivity (with respect to H_2, CO or H_2O) larger than $5x10^{-7}$ mol/m^2.s.Pa and 500;

1. Fabricate tubular dual-phase membranes and membrane reactor modules suitable for WGS membrane reactor applications;

2. Identify experimental conditions for WGS in the dual-phase membrane reactor that will produce the hydrogen stream with at least 93% purity and CO_2 stream with at least 95% purity.

Technical Tasks

- Task A Synthesis of Dual-Phase Membrane Disks
- Task B Studying Permeation and Separation Properties of Disk Membranes
- Task C Synthesis of Tubular Dual-Phase Membranes
- Task D Gas Separation and Stability Study on Tubular Membranes
- Task E Synthesis and WGS Reaction Kinetic Study of High Temperature Catalyst
- Task F Modeling and Analysis of Dual-Phase Membrane Reactor for WGS
- Task G Experimental Studies on WGS in Dual-Phase Membrane Reactors
- Task H Integration to IGCC and Economic Analysis

Task A

Synthesis of Dual-Phase Membrane Disks

Molten Carbonates

	Li/Na/K Carbonate	Li/K Carbonate	Li/Na Carbonate	Na/K Carbonate
Composition (mol%)	43.5/31.5/25	62/38	52/48	56/44
Melting Point (°C)	397	488	501	710
$CO_3^=$ Conductivity (S/cm)	1.24	1.15	1.75	1.17

Oxygen Ionic Conducting Metal Oxide Supports

Desired characteristics

- High ionic conductivity
- Long-term chemical stability
- Compatible with molten carbonate
- Controllable pore size, porosity

Material	Abbreviation	Structure	$O^{=}$ conductivity σ_i (600°C) (S/cm)	Transfer-ence number t_i
$LaCeGaFeAlO_3$	LCGFA	Perovskite	~ 0.001	~ 0.02
$LaSrCoFeO_3$	LSCF	Perovskite	~ 0.003	~ 0.01
$YZrO_2$	YSZ	Fluorite	~ 0.004	~ 1.0
$CeSmO_2$	SDC	Fluorite	~ 0.005	~ 1.0
$BiYSmO_2$	BYS	Fluorite	~ 0.08	~ 0.9

$\sigma_{CO3=}$ ~ 1.2 S/cm for molten carbonate at 600°C

Synthesis of Porous Ceramic Disks

- Mix metal nitrate precursors in desired ratio in water
- Add excess citric acid and heat the covered solution
- Uncover solution and heat until a brick-red gel remains; dry remnants
- Self ignite remnants at 400°C in an oxygen-rich environment to remove the organics
- Grind the powder and pre-sinter it at 600°C

- Mix pre-sinterred metal oxide powder with PVA solution
- Place the metal-oxide and PVA mixture into a 30.0 mm stainless steel die-mold
- Press the powder at 30 MPa for 1 minute, and then 160 MPa for 4 minutes
- Remove the disk from the die and dried at 40°C and 40% RH for 1 day
- Sinter the support at about 900°C for 1 day

$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF)

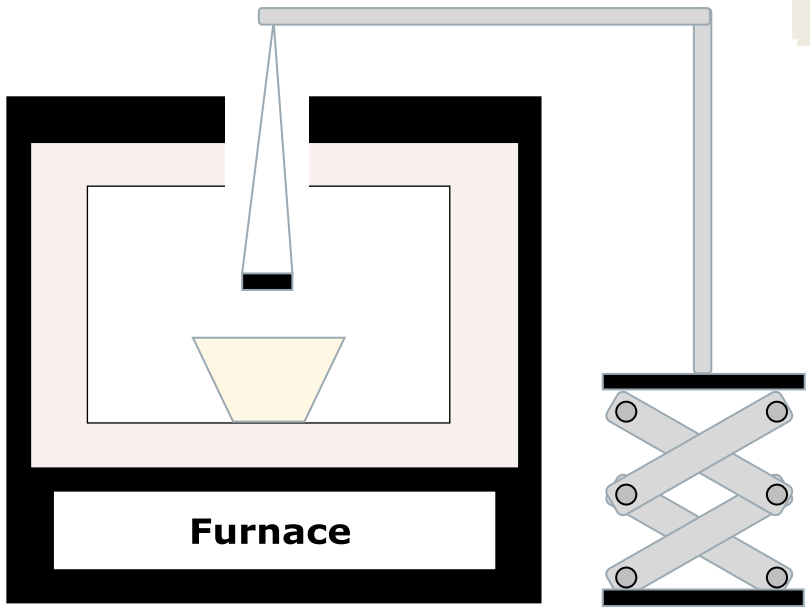
powder

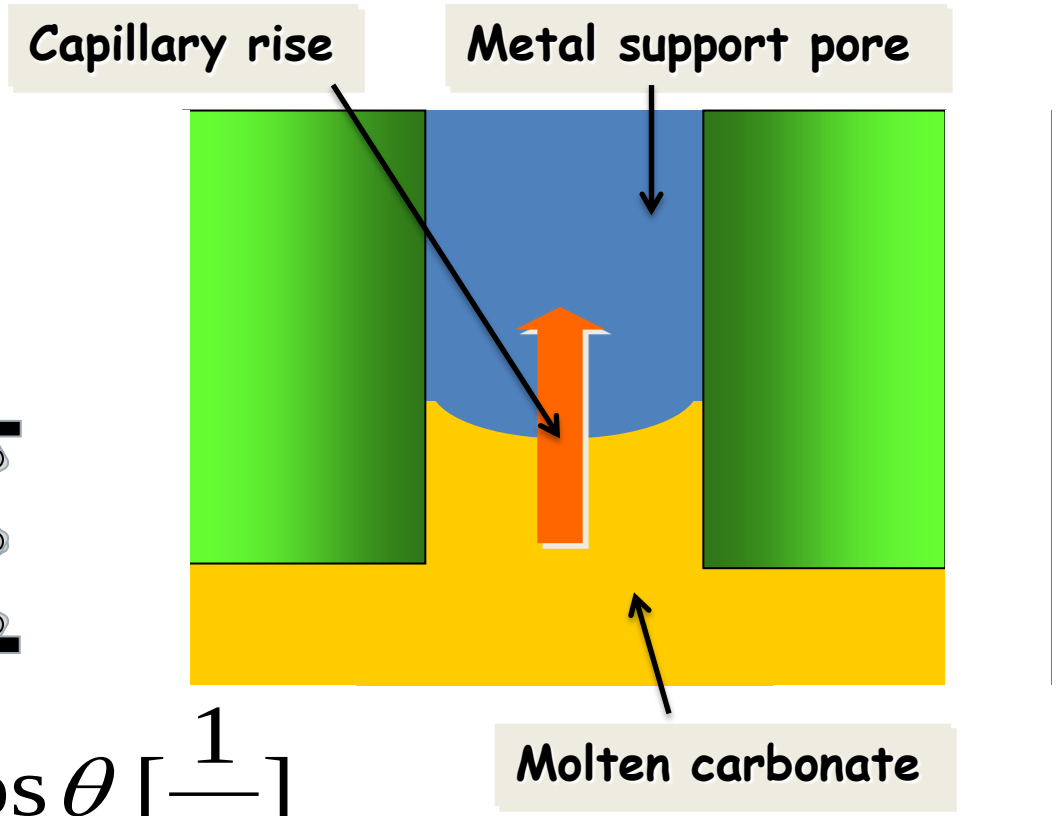
disk

$La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.6}Al_{0.1}O_{3-\delta}$ (LCGFA)

$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC)

Carbonate Infiltration Method





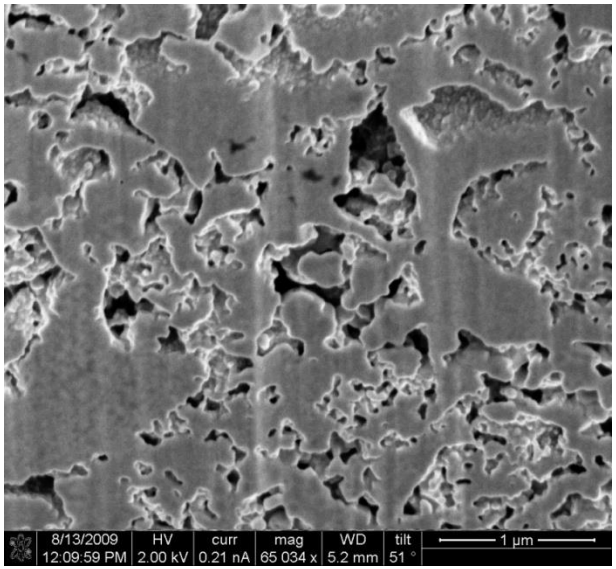
$$P_C = -\gamma_{lv} \cos\theta \left[\frac{1}{r_p}\right]$$

Capillary force drives carbonate to support during preparation or holds it in operation

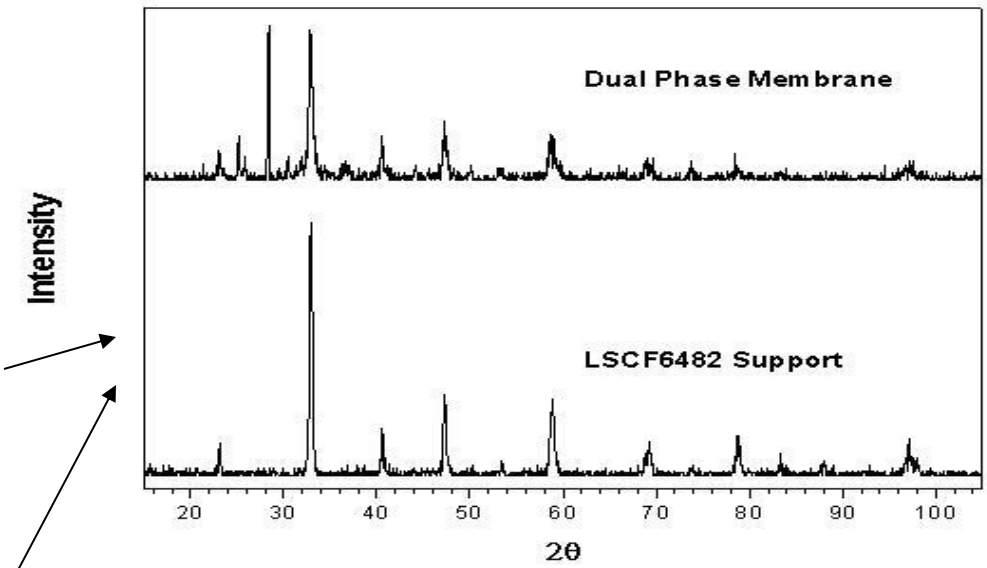
Carbonate wettability on support surface

Support pore size

Dual-Phase Membrane Characteristics

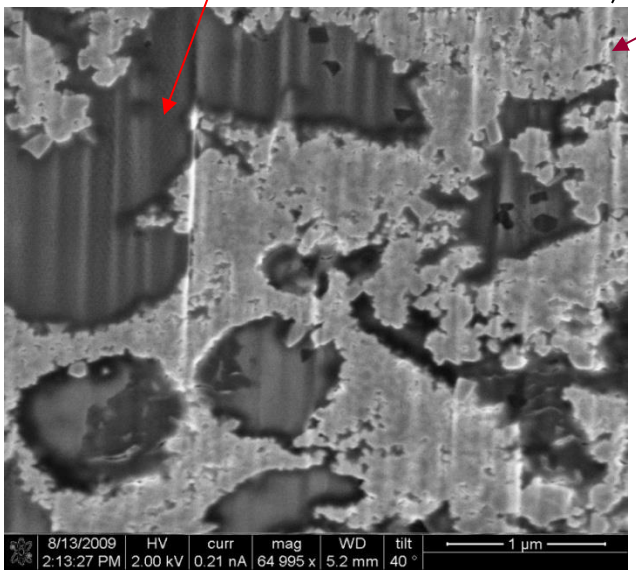


XRD



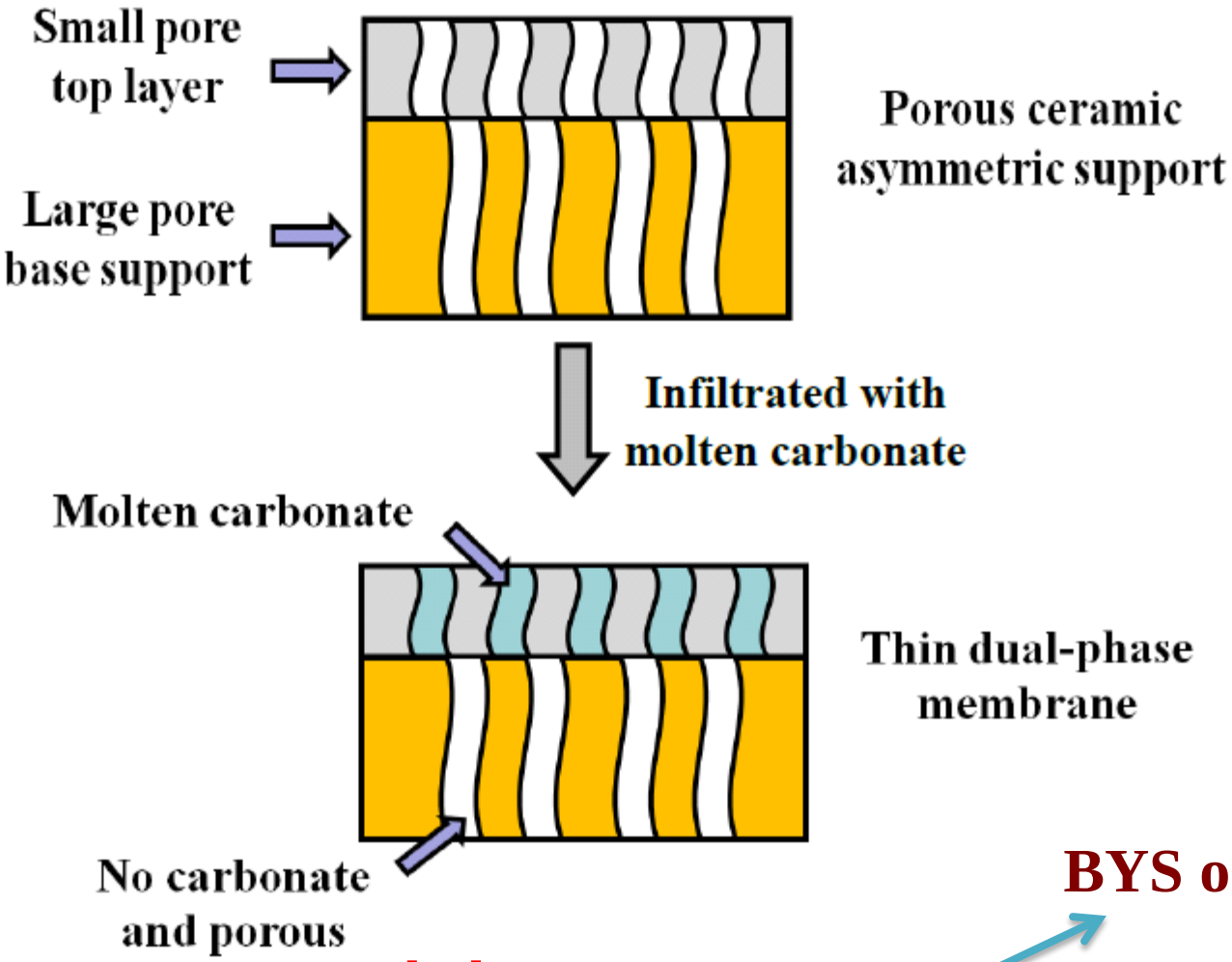
$(Li/Na/K)_2CO_3(43/32/25)$

LSCF- $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$



- **He permeance of support:**
  ~ 10^{-6} mol/m^2·s·Pa
- **After infiltration of carbonate:**
  - **25% weight increase**
  - **He permeance: <10^{-10} mol/m^2·s·Pa**

Thin Dual-Phase Membrane – the Concept

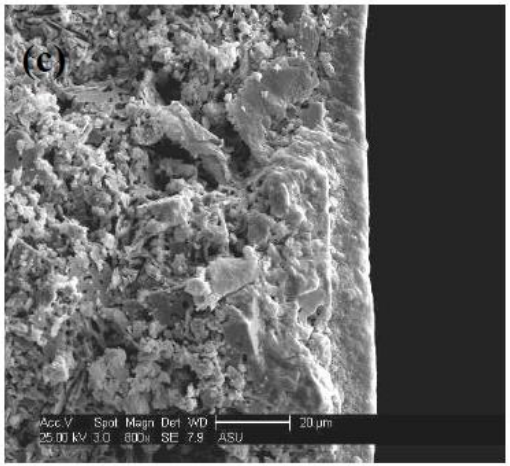


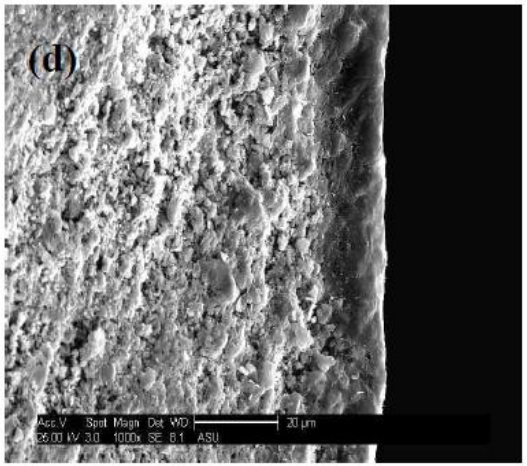
BYS or BYS-SDC

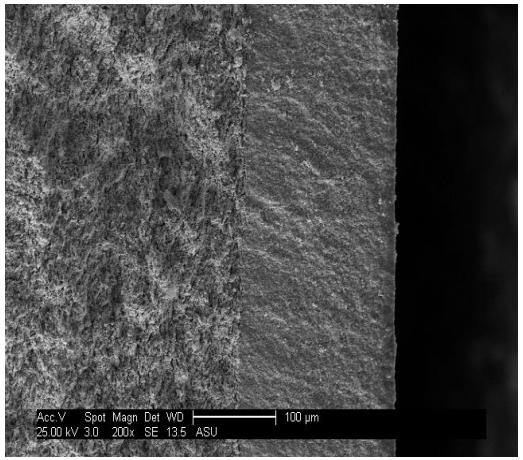
The base support

- **non-wettable to molten carbonate**
- **ionic-conducting**

Asymmetric Porous Membranes







BYS | YSZ BYS | LSCF BYS40SDC60 | SDC

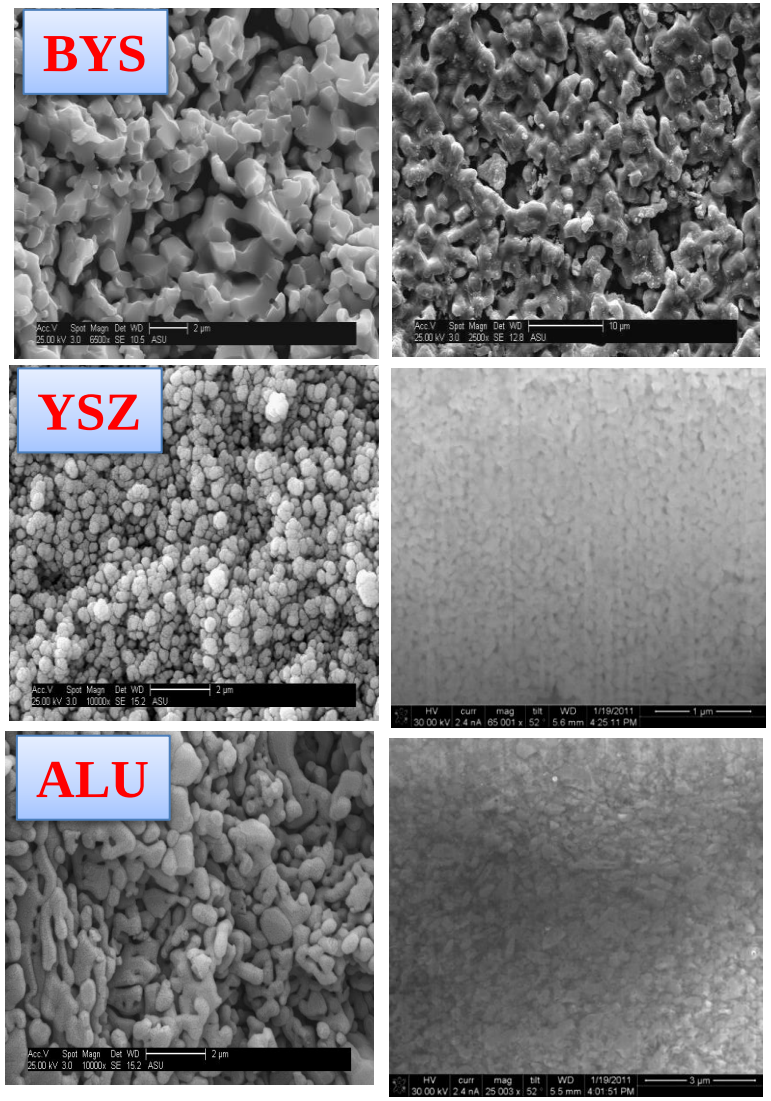
BYS = Bi-Y-Sm-O_2 SDC = Sm-Ce-O_2

YSZ = Y-Zr-O_2 LSCF = La-Sr-Ce-Fe-O_3

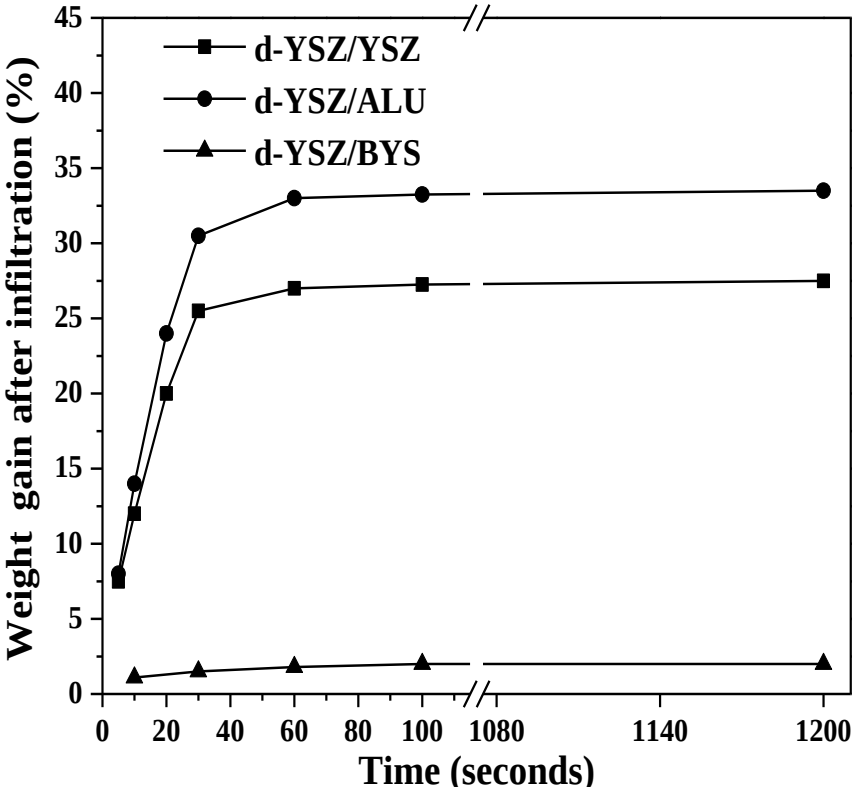
Carbonate Infiltration on Asymmetric Supports

Before Infiltration

After Infiltration



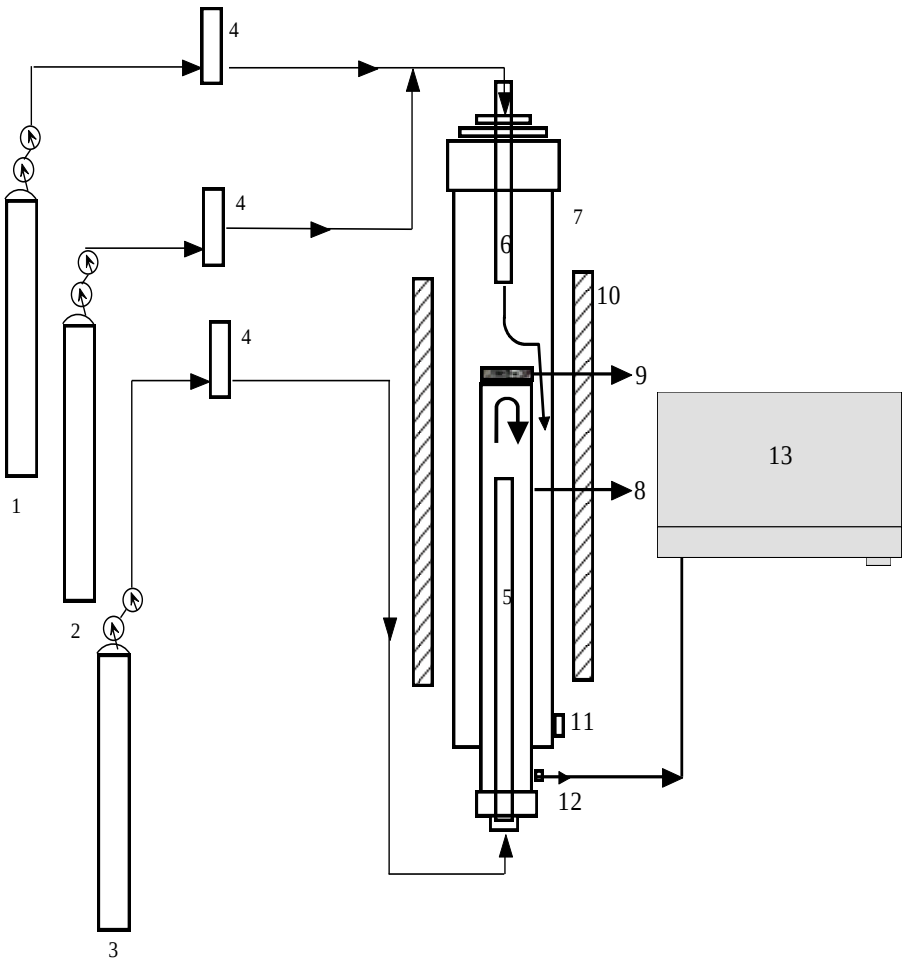
Weight gain infiltration contact time



- **LSCF top layer peeled after infiltration**
- **Carbonate penetrates to YSZ and ALU supports**
- **Only YSZ on BYS or SDC on BYS-SDC work**

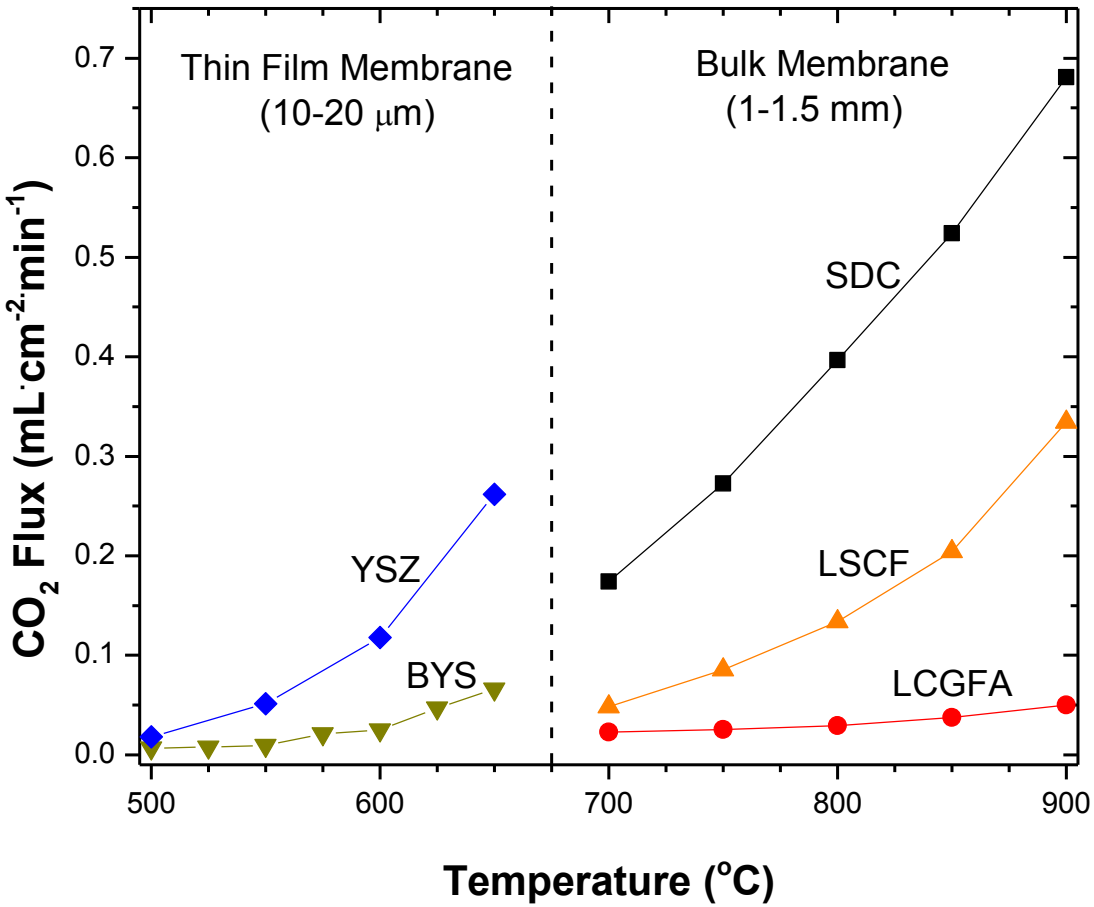
High Temperature Permeation Schematic

- Membrane is sealed to alumina tube
  - Pyrex™, LSCF6482, $Al_2O_3 \cdot Na_2O$
- System is heated to 900°C at 1°C/min
- Gases fed:
  - Feed: CO_2, Ar (50 mL/min each)
  - Sweep gas: Helium (100 mL/min)
- Measure the composition of the permeate using a GC (TCD)



High Temperature Permeation Apparatus

Carbon Dioxide Permeance



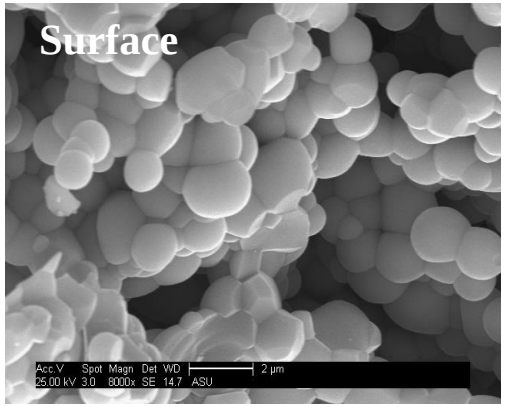
- **All ceramic supports infiltrated with Li/Na/K molten carbonate**
- **Feed CO_2 concentration of 50% (YSZ tested with 25%)**
- **Feed and sweep flow rates of 100 $mL \cdot min^{-1}$**

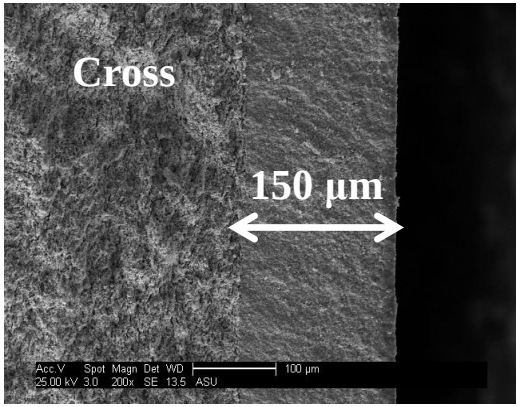
Name	Ceramic Phase
YSZ	$Zr_{0.92}Y_{0.08}O_2$
BYS	$Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$
SDC	$Ce_{0.8}Sm_{0.2}O_{1.9}$
LSCF	$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$
LCGFA	$La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.6}Al_{0.05}O_{3-\delta}$

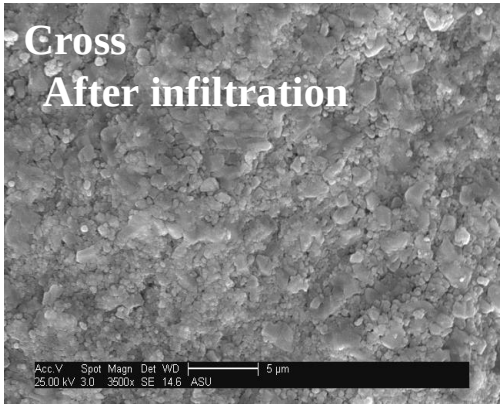
Measured CO_2 Permeance = 10^{-8}-10^{-7} mol/m^2.s.Pa

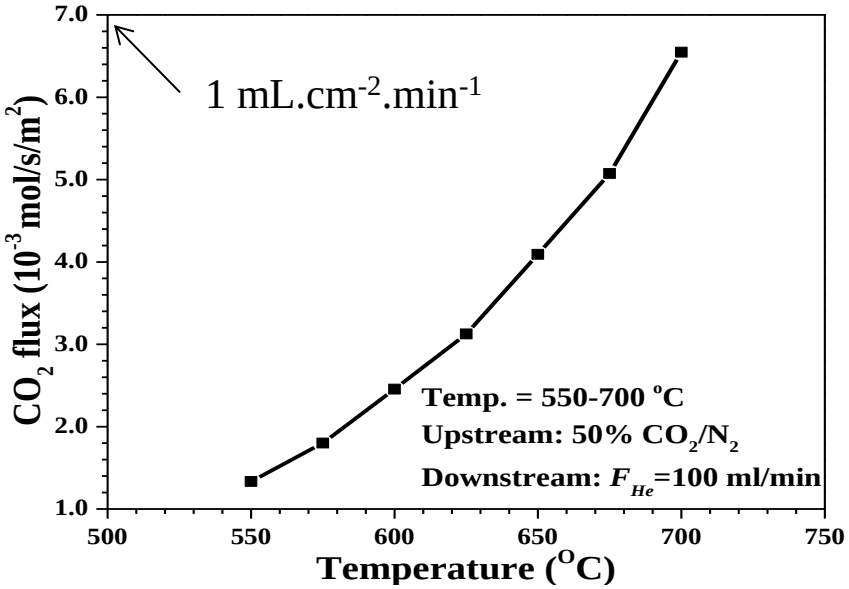
$\alpha_{CO2/N2}$ =500-3000

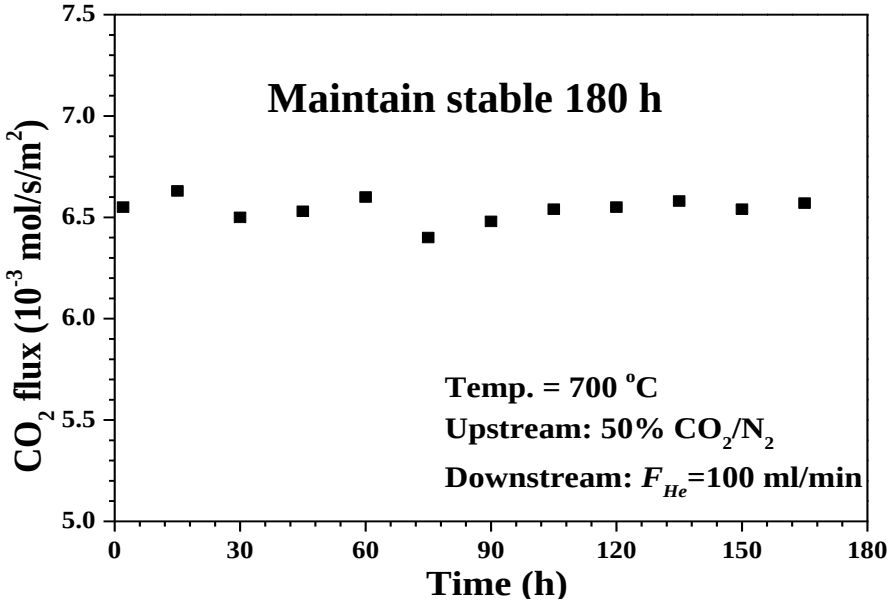
Thin SDC-Carbonate Dual-Phase Membrane



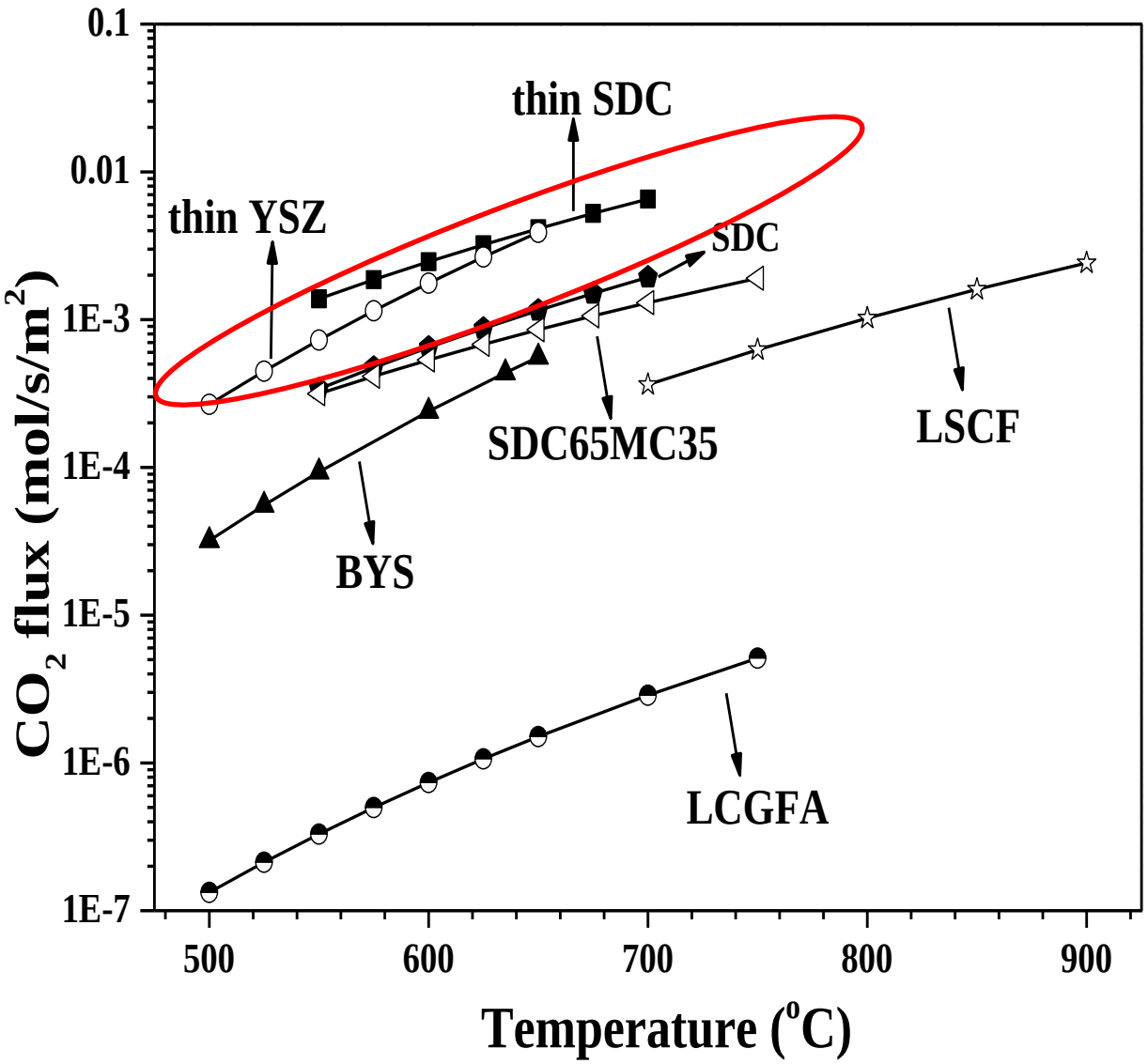








Carbon Dioxide Permeation Flux



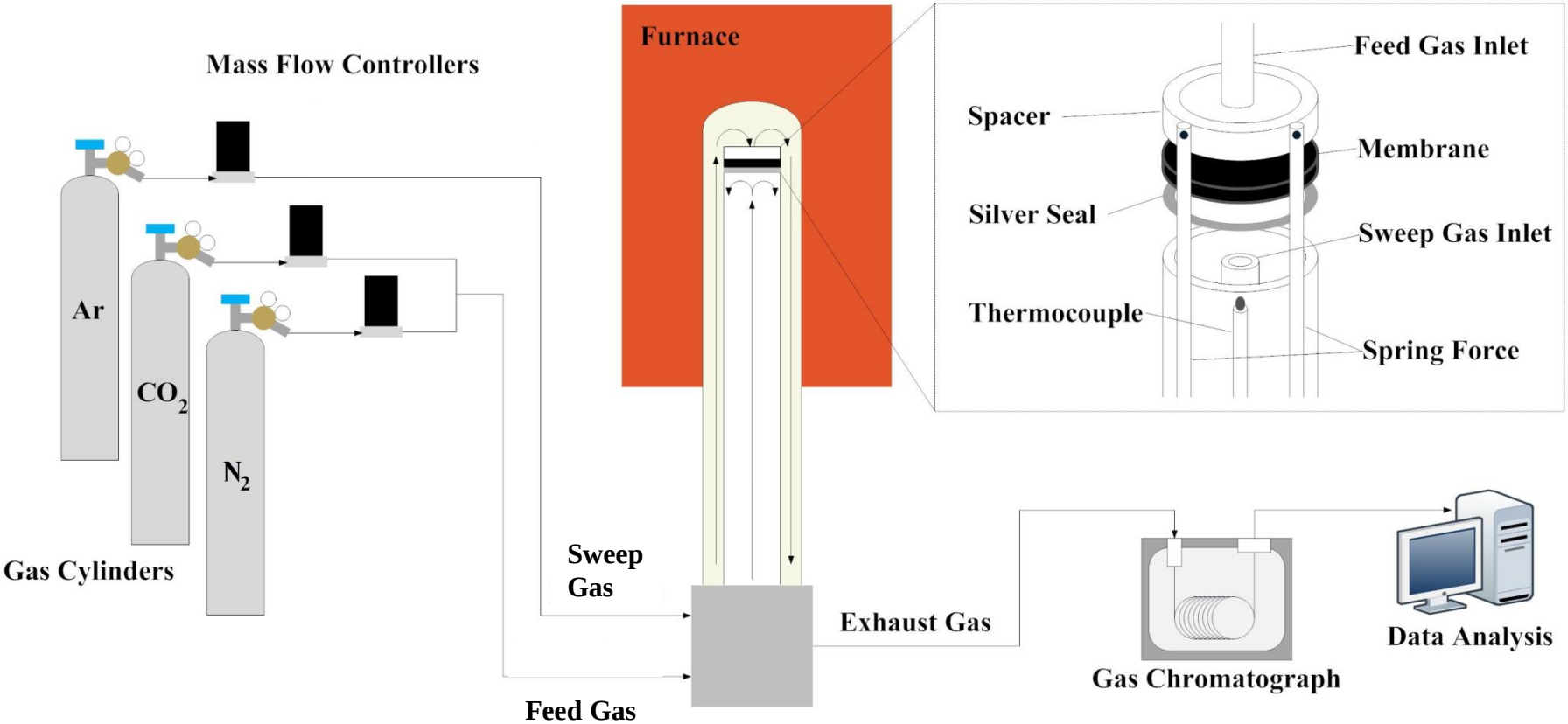
Task B

Studying Permeation and Separation Properties of Disk Membranes

High Temperature CO_2 Permeation Measurements

Atmospheric Feed

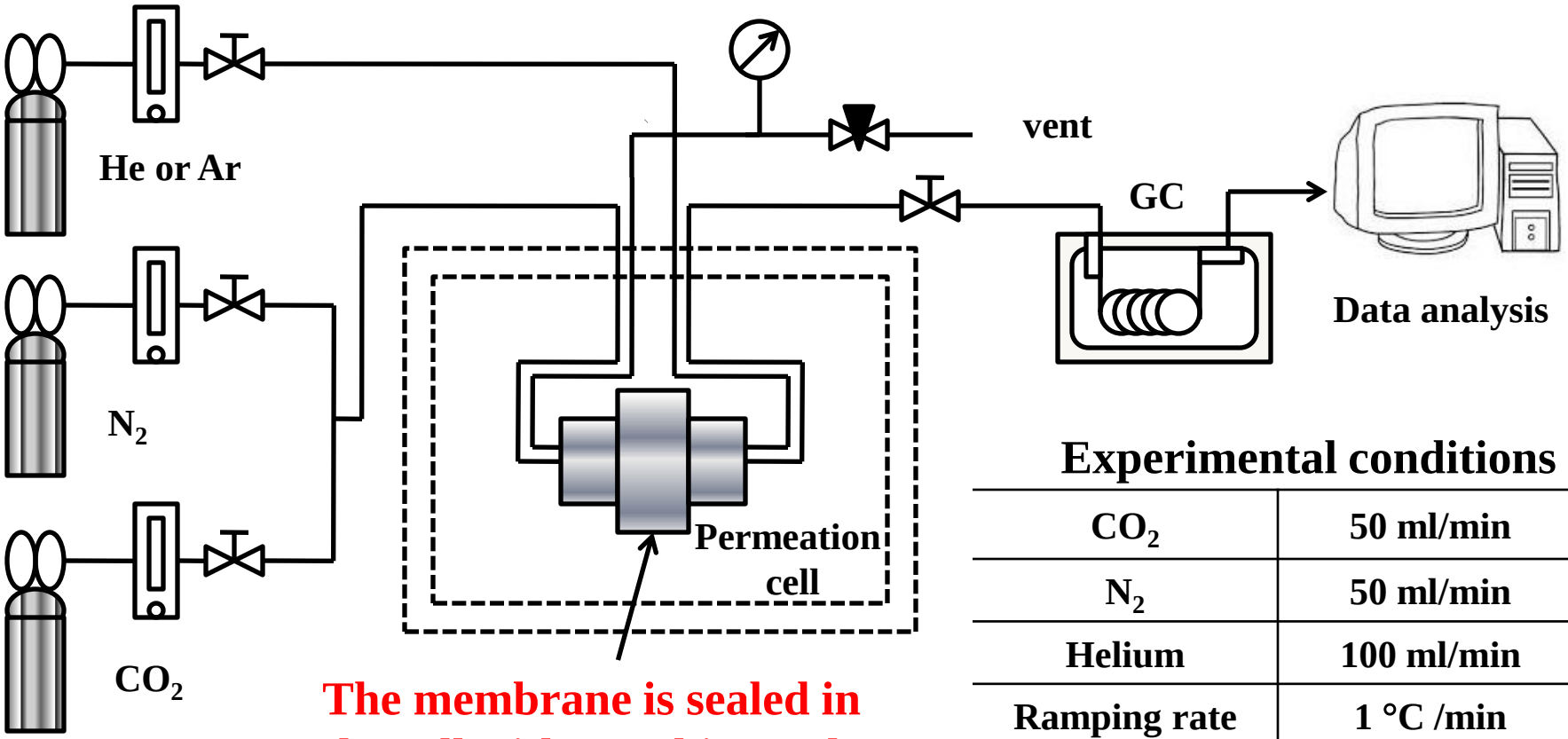
The membrane is sealed with silver rings or glass seal



Probostat module

High Temperature CO_2 Permeation Measurements

High Pressure Feed



The membrane is sealed in the cell with graphite gaskets

Experimental conditions

CO_2	50 ml/min
N_2	50 ml/min
Helium	100 ml/min
Ramping rate	1 °C /min
Testing Temp.	450 ～650 °C

Carbon Dioxide Permeation Flux - Theory

$$J_{CO_2} = \int_{P''_{CO_2}}^{P'_{CO_2}} \frac{\sigma_T RT}{4F^2 L} d\ln P_{CO2}$$

constant σ_T

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

Total conductance

Membrane thickness

Experimental conditions

Carbonate ion conductivity

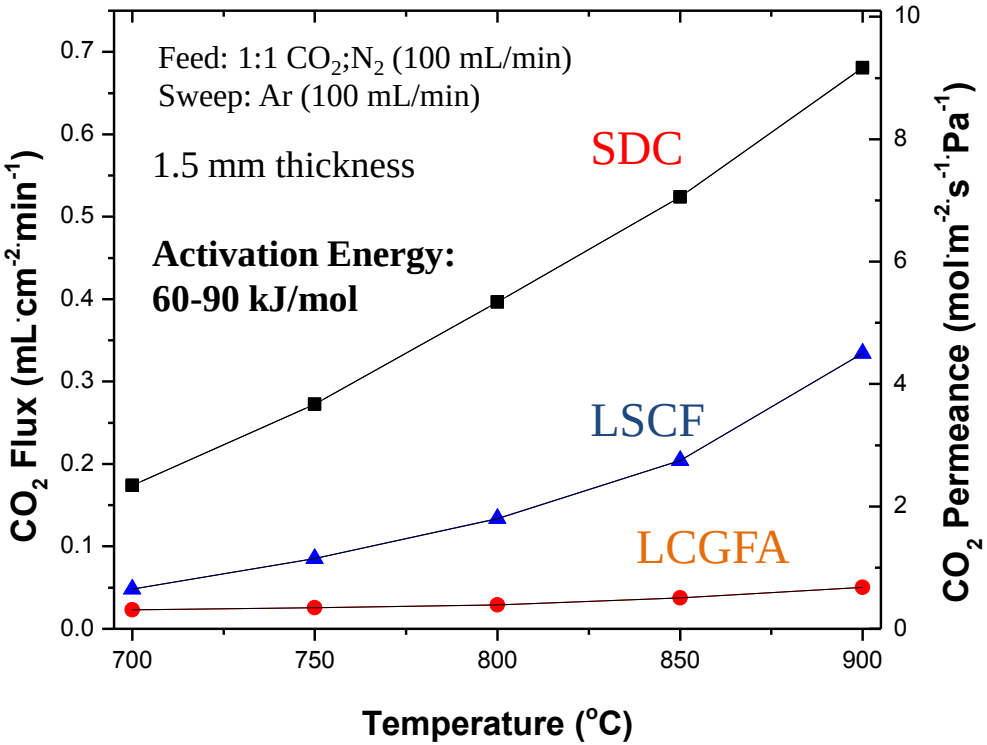
oxygen ionic conductivity

$$\sigma_T = \frac{[\gamma_p \sigma_C][\gamma_s \sigma_i]}{[\gamma_p \sigma_C] + [\gamma_s \sigma_i]}$$

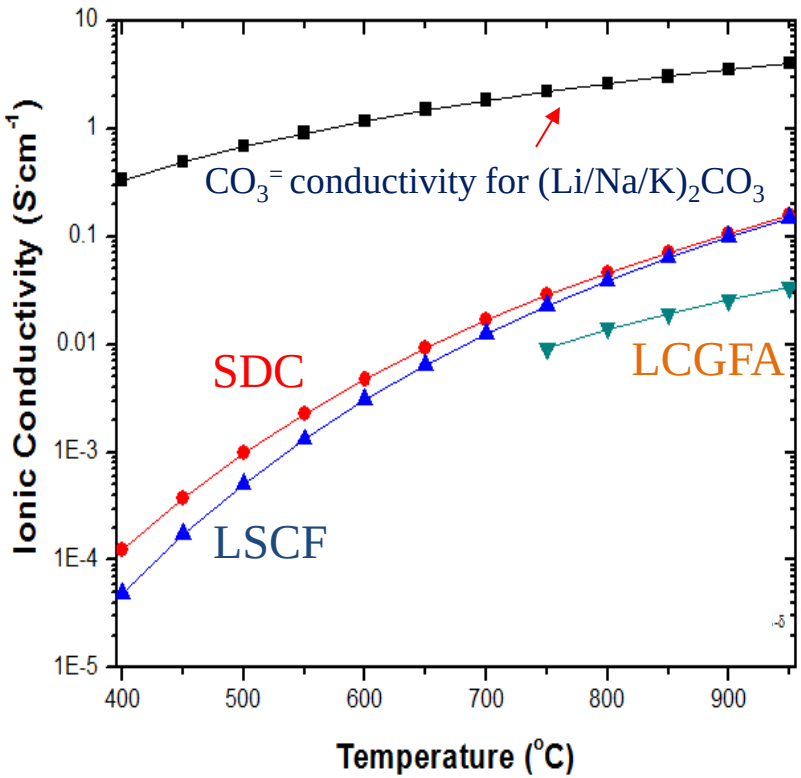
Pore or solid fraction to tortuosity ratio for carbonate and ceramic phase

Conductivity Dependence of CO_2 Permeation Flux

CO_2 Permeation Flux



Conductivity

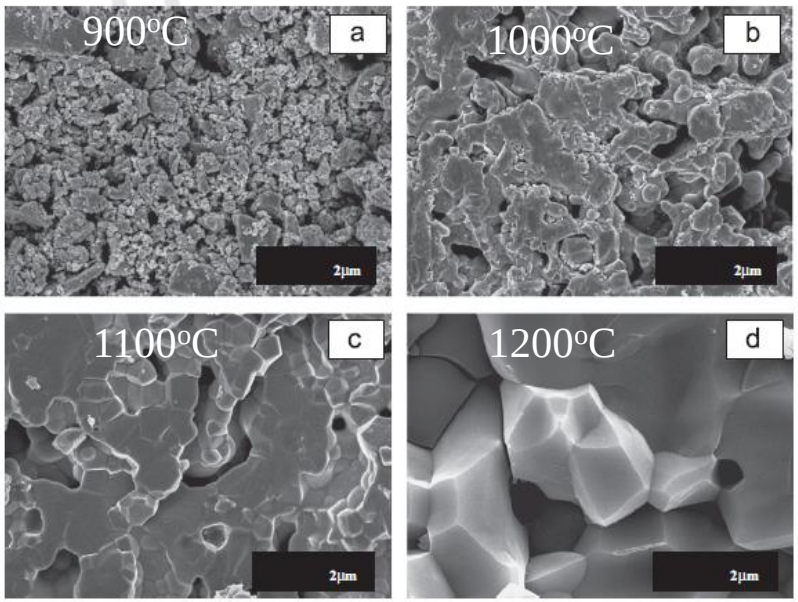


CO_2 permeation flux is mainly controlled by oxygen ionic conductivity of ceramic phase

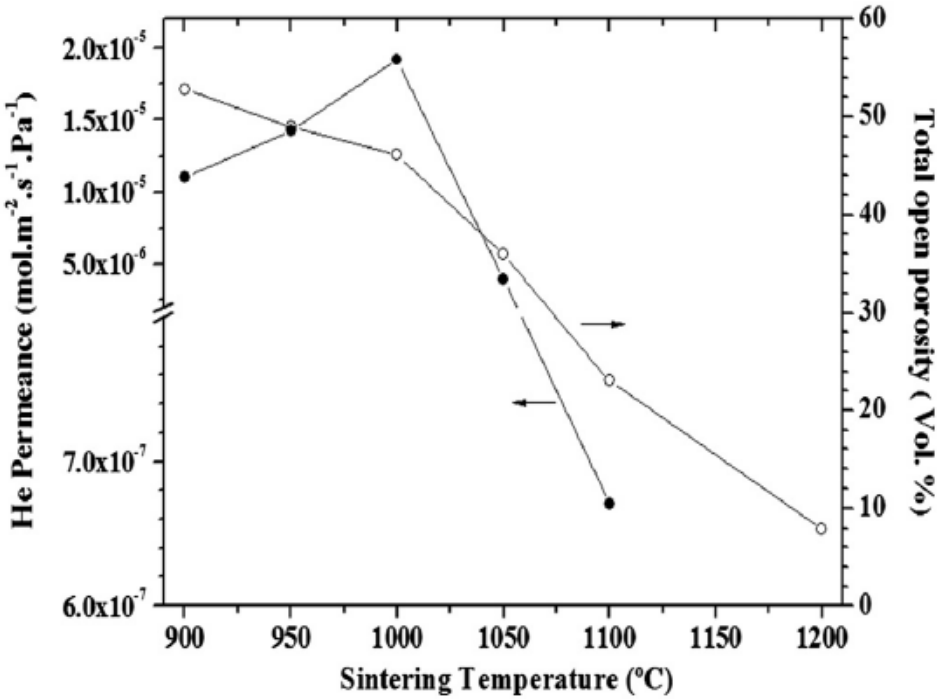
Ceramic Supports of Different Structure

$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF)

Morphology of the supports prepared at different sintering temperature



Porosity and He permeance of the supports prepared at different sintering temperature

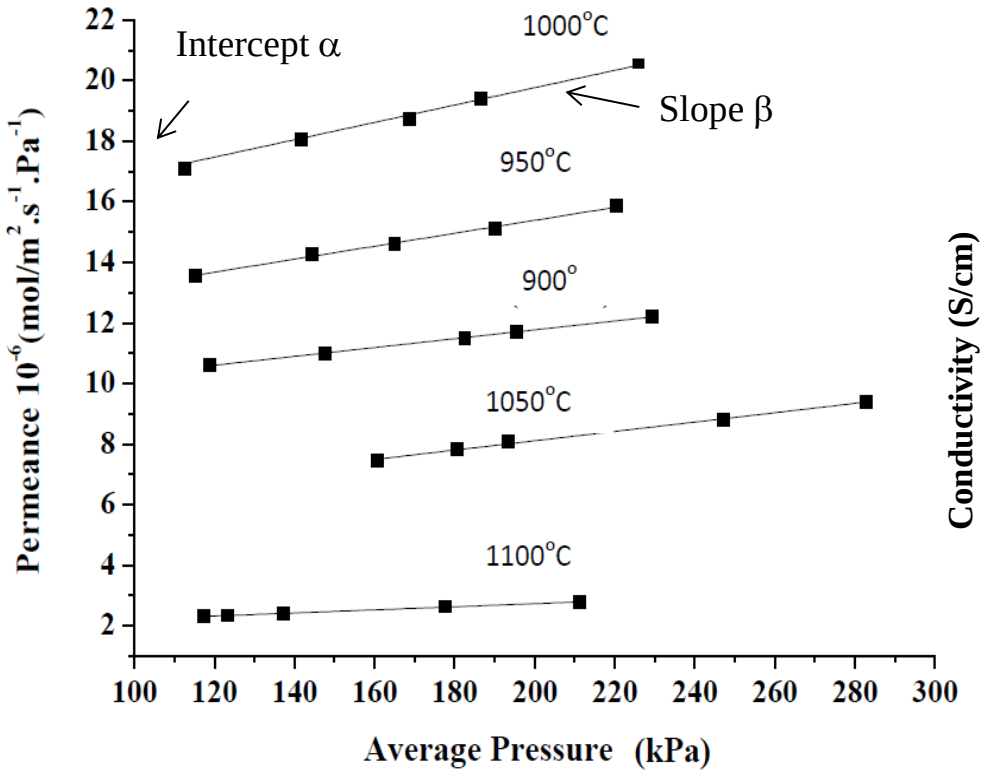


Pore and Solid Structure of Ceramic Support

Pore (carbonate) fraction to tortuosity ratio

$$\gamma_p = \left(\frac{\varepsilon}{\tau}\right)_{Pore} = \left(\frac{\alpha^2}{\beta}\right)\left(\frac{M_w L}{8.988\mu}\right)$$

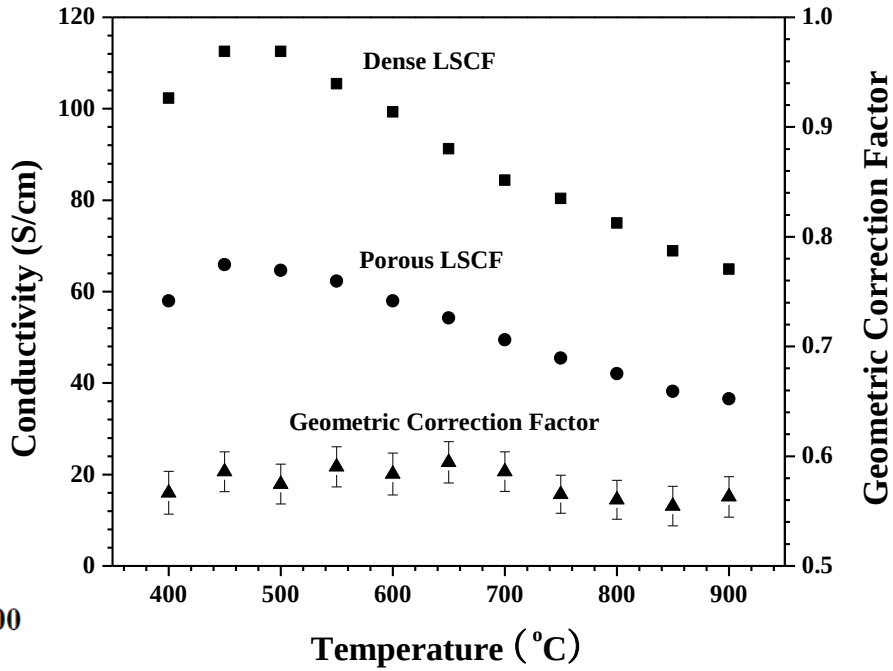
He permeation to measure pore structure



Solid fraction to tortuosity ratio

$$\gamma_S = \left(\frac{\phi}{\tau}\right)_{Solid} = \left(\frac{\sigma_s}{\sigma_i}\right)$$

Electrical conductivity of porous and dense LSCF ceramic for solid phase structure

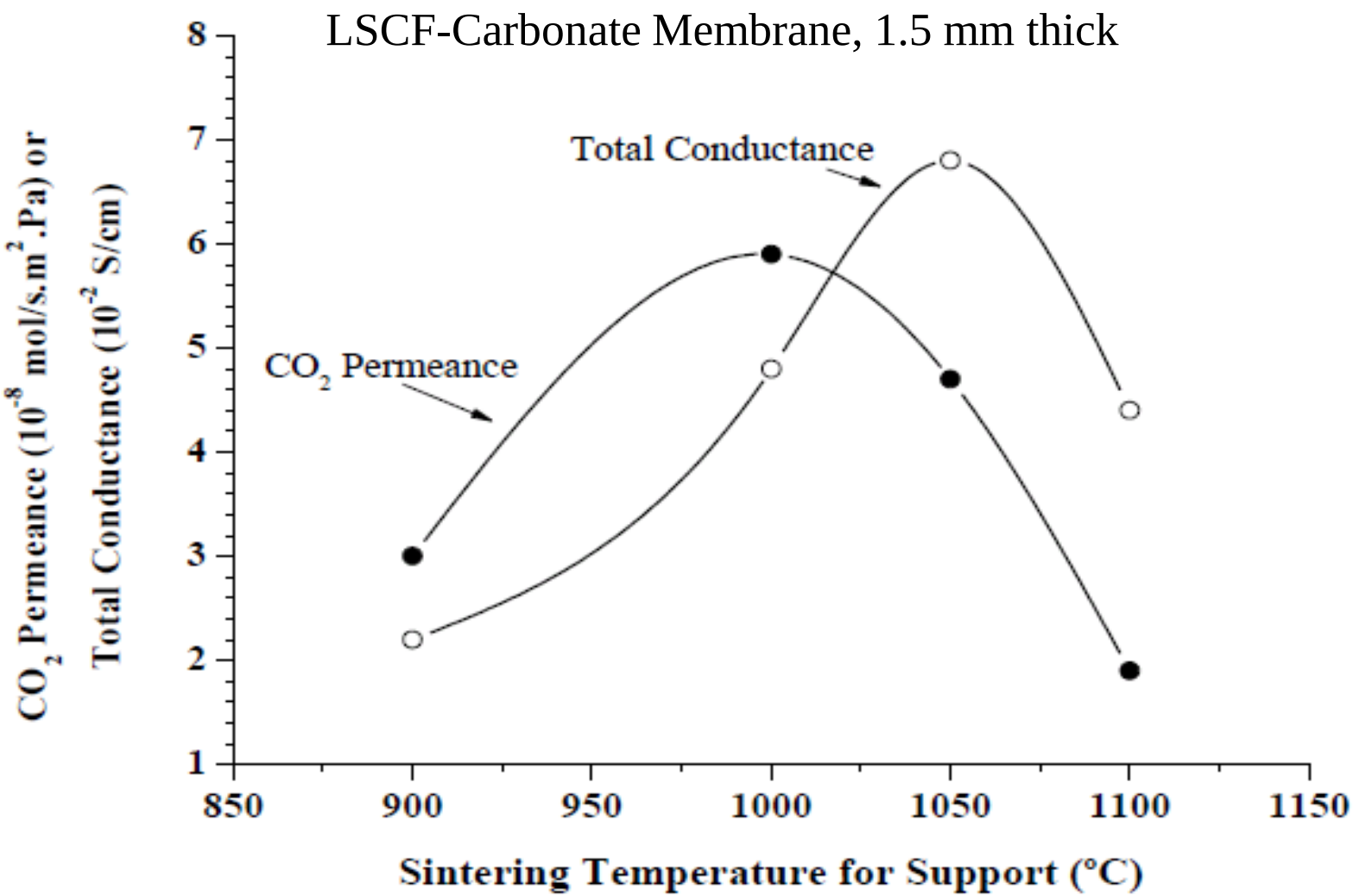


Characteristics of Pore (Carbonate) and Solid Structure

Support Sample Number	Sintering temp for preparing support (°C)	Solid (pore) fraction ϕ (ε)	Solid fraction to tortuosity ratio γ_s	Pore (carbonate) fraction to tortuosity ratio γ_p
LSCF-900	900	0.47 (0.53)	0.11	0.16
LSCF-1000	1000	0.54 (0.46)	0.26	0.18
LSCF-1050	1050	0.64 (0.36)	0.59	0.041
LSCF-1100	1100	0.77 (0.23)	0.82	0.013

Used to calculate the total conductance

Effect of Pore Structure on CO_2 Permeance



How CO_2 Flux Depends on Pressures?

General Flux Equation:

$$J_{CO_2} = \int_{P''_{CO_2}}^{P'_{CO_2}} \frac{\sigma_T RT}{4F^2L} d\ln P_{CO2} \xrightarrow{\text{constant } \sigma_T} J_{CO_2} = \frac{\sigma_T RT}{4F^2L} \ln\left(\frac{P'_{CO_2}}{P''_{CO_2}}\right)$$

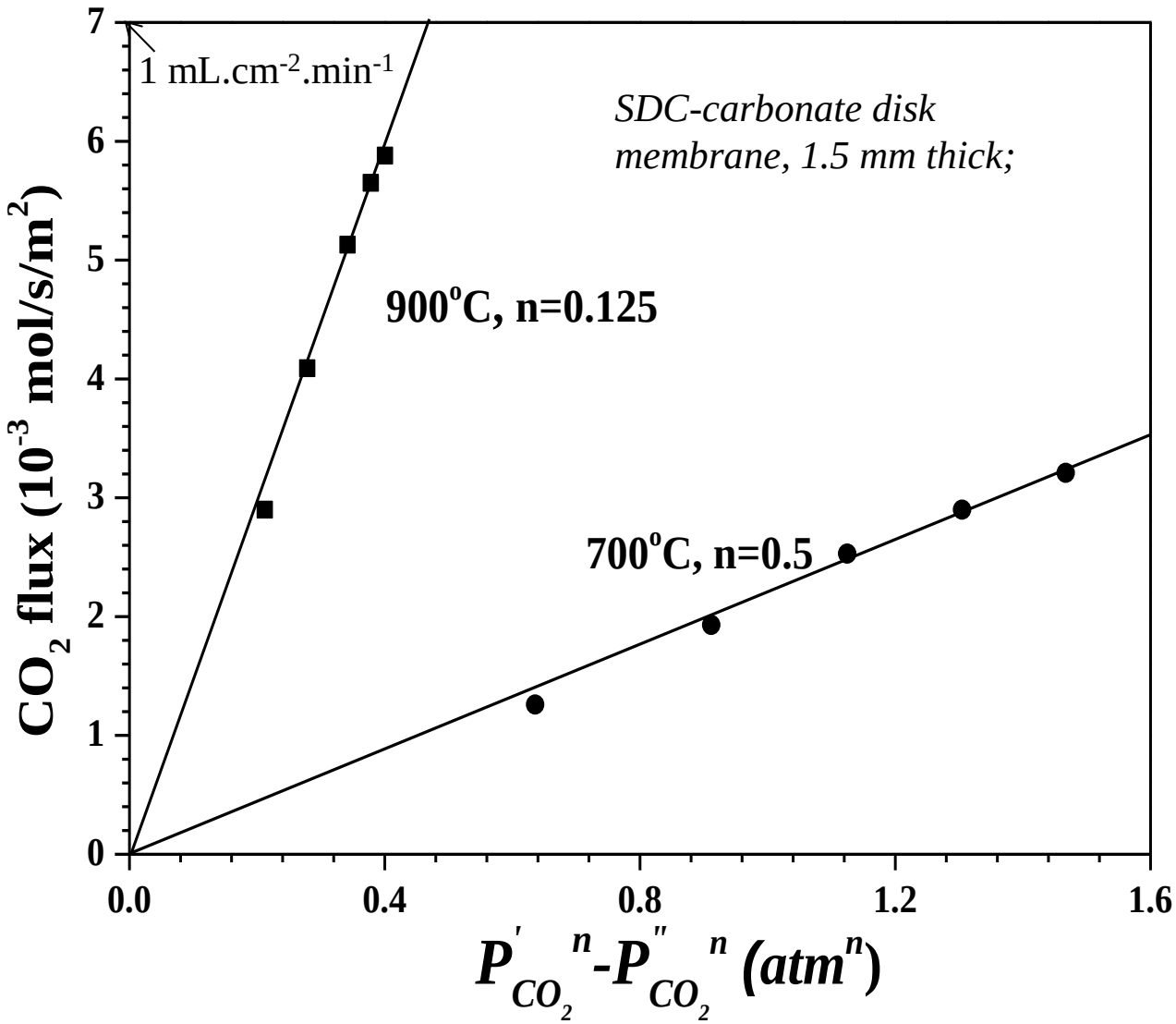
$\sigma_T \sim \sigma_i = k^o P_{O2}{}^m$ *Depends on defect reaction equilibrium between gas phase and ceramic phase*

$P_{O2} = \phi P_{CO2}{}^q$ *Depends on gas phase reaction equilibrium or mass balance*

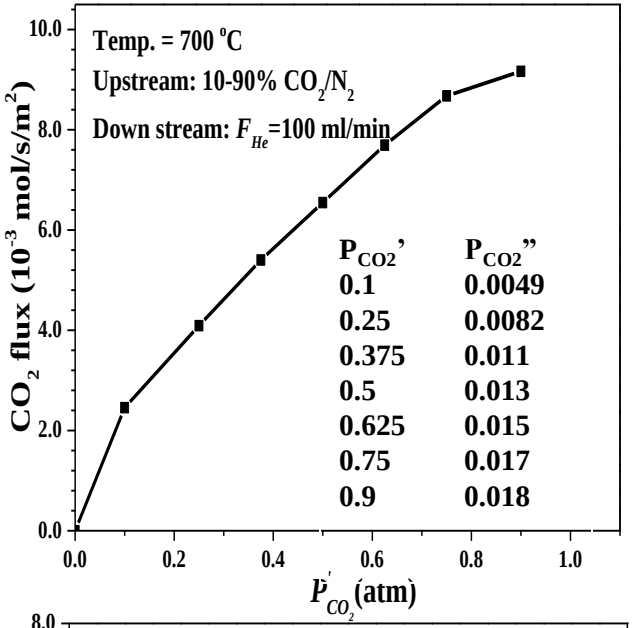
$$\boxed{J_{CO_2} = \left[\frac{k'RT}{4F^2L}\right]\left[(P'_{CO2})^n - (P''_{CO2})^n\right]}$$

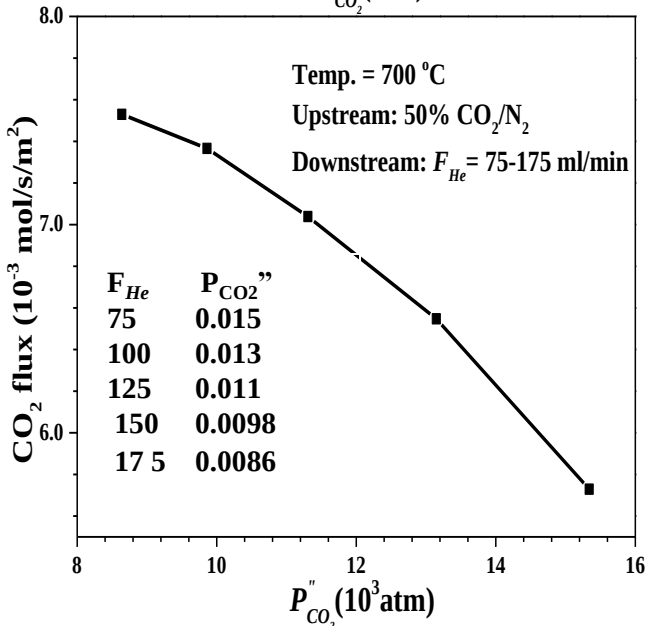
with $k' = \frac{k^o \phi^m}{mq}$

CO_2 Permeation of Thick SDC-Carbonate Membrane

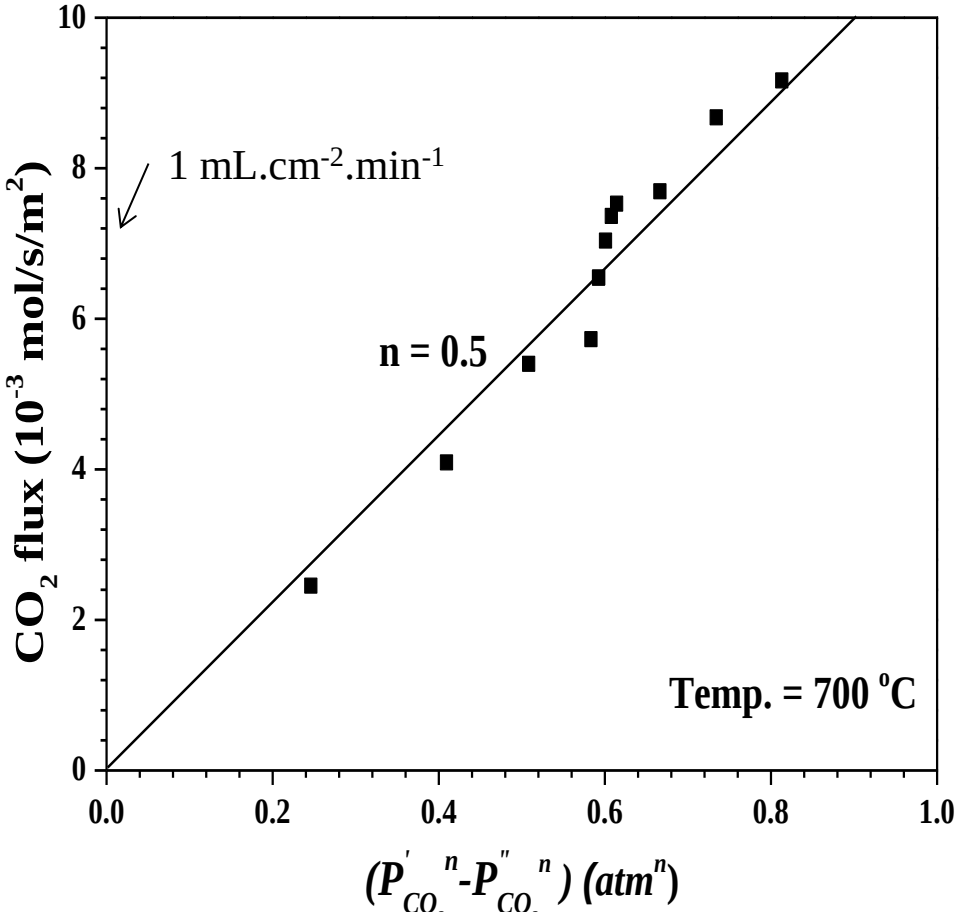


CO_2 Permeation of Thin SDC-Carbonate Membrane





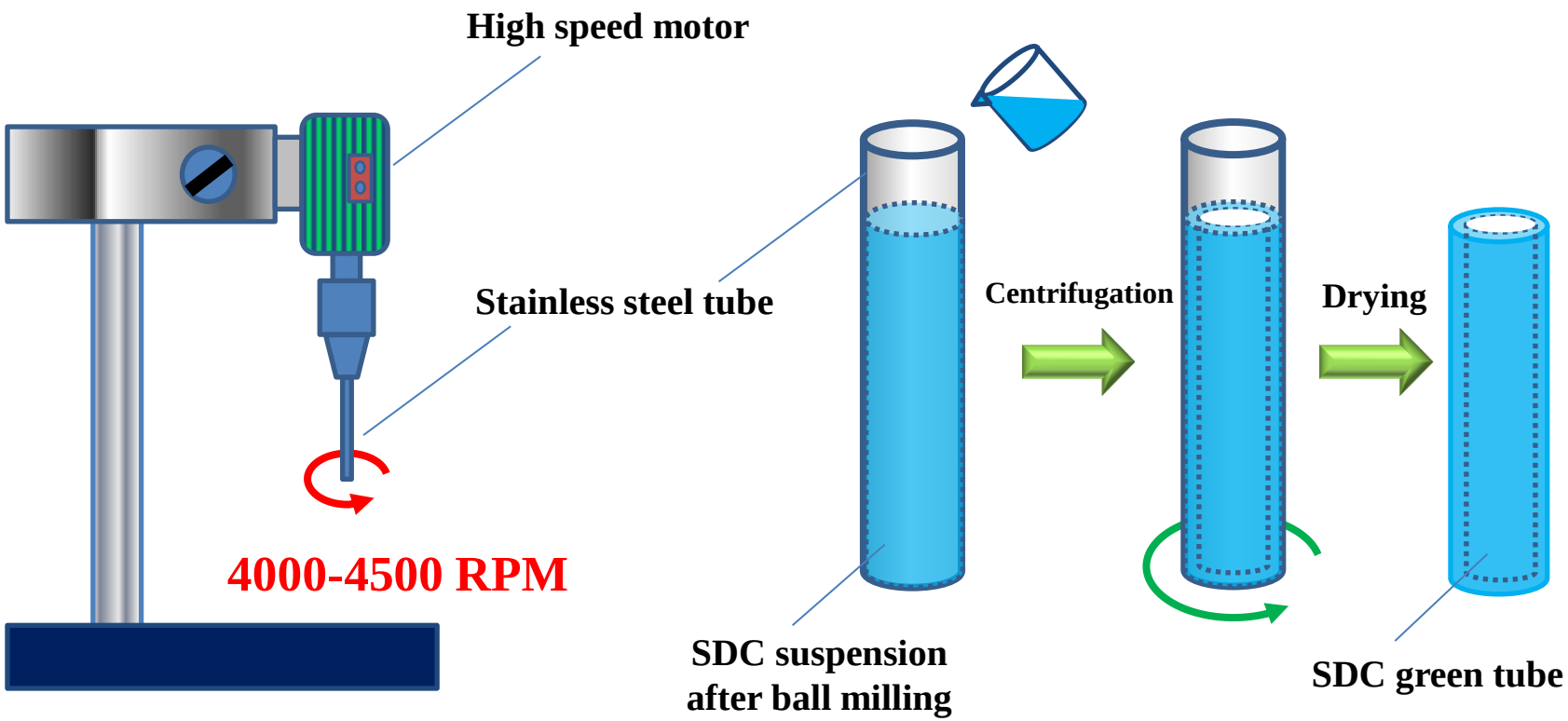
Thin 150 μm SDC-carbonate Membrane



Task C
Synthesis of Tubular Dual-Phase Membranes

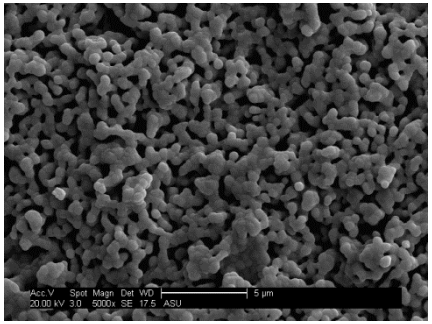
Preparation of Tubular SDC-Carbonate Dual Phase Membranes

◆Centrifugal casting method

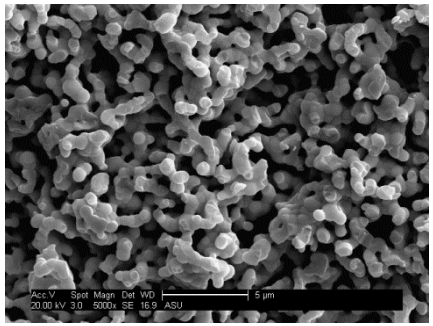


Porous SDC Tubes

Porosity: 30-45%

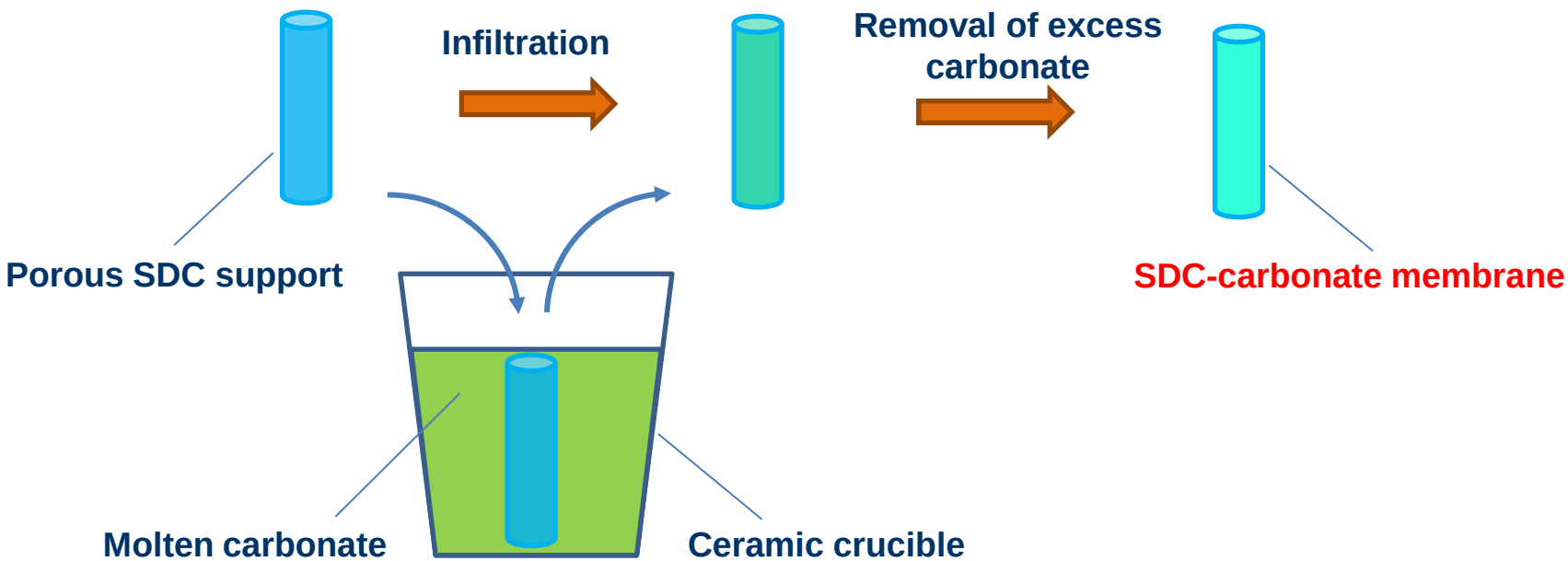


Inner surface



Cross section

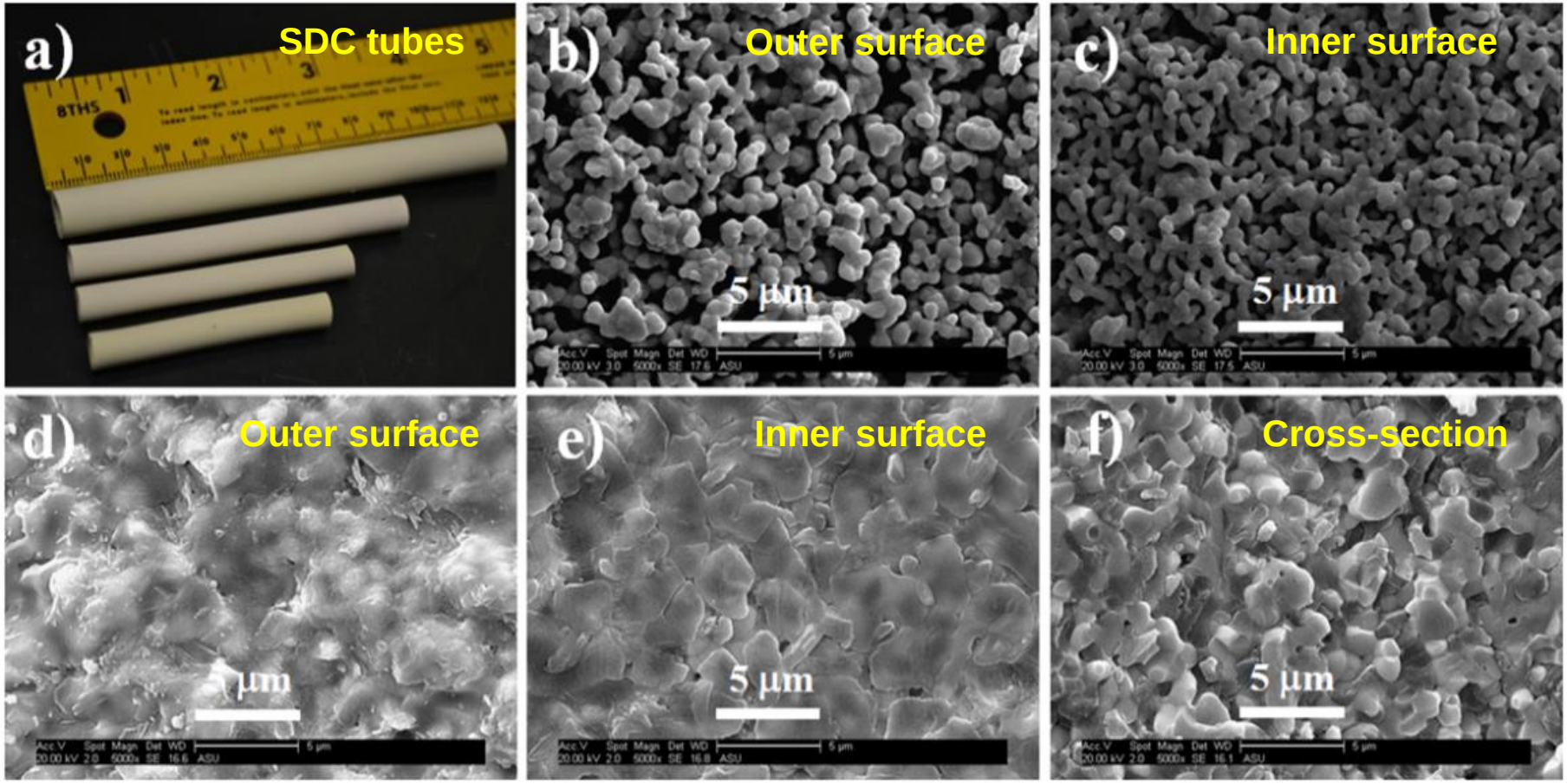
Carbonate Infiltration of Tubular SDC Supports



This process was operated at 550-600 ^{o}C

Morphology of tubular dual-phase membrane

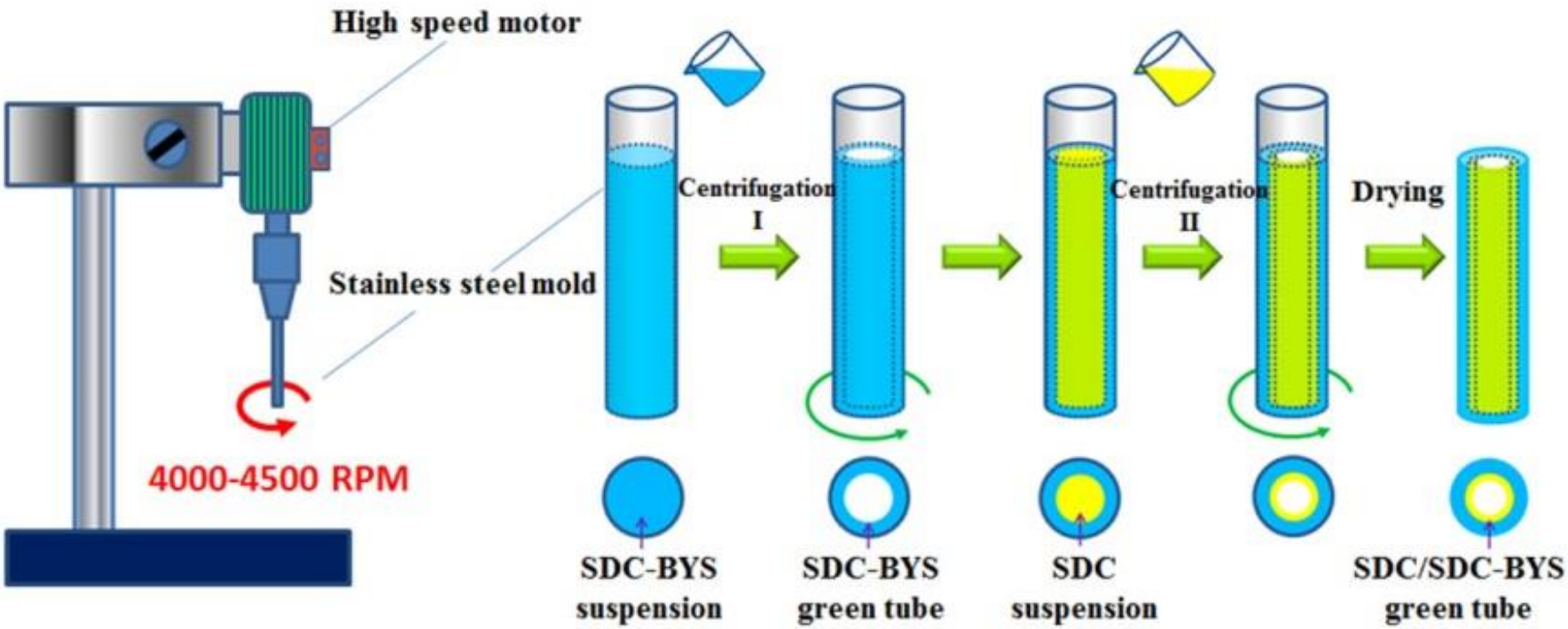
Porosity: 30-45%



a-c: porous supports; d-f: dual phase membrane

Preparation of Tubular Dual-Phase Membranes wih Thin SDC-Carbonate Layer

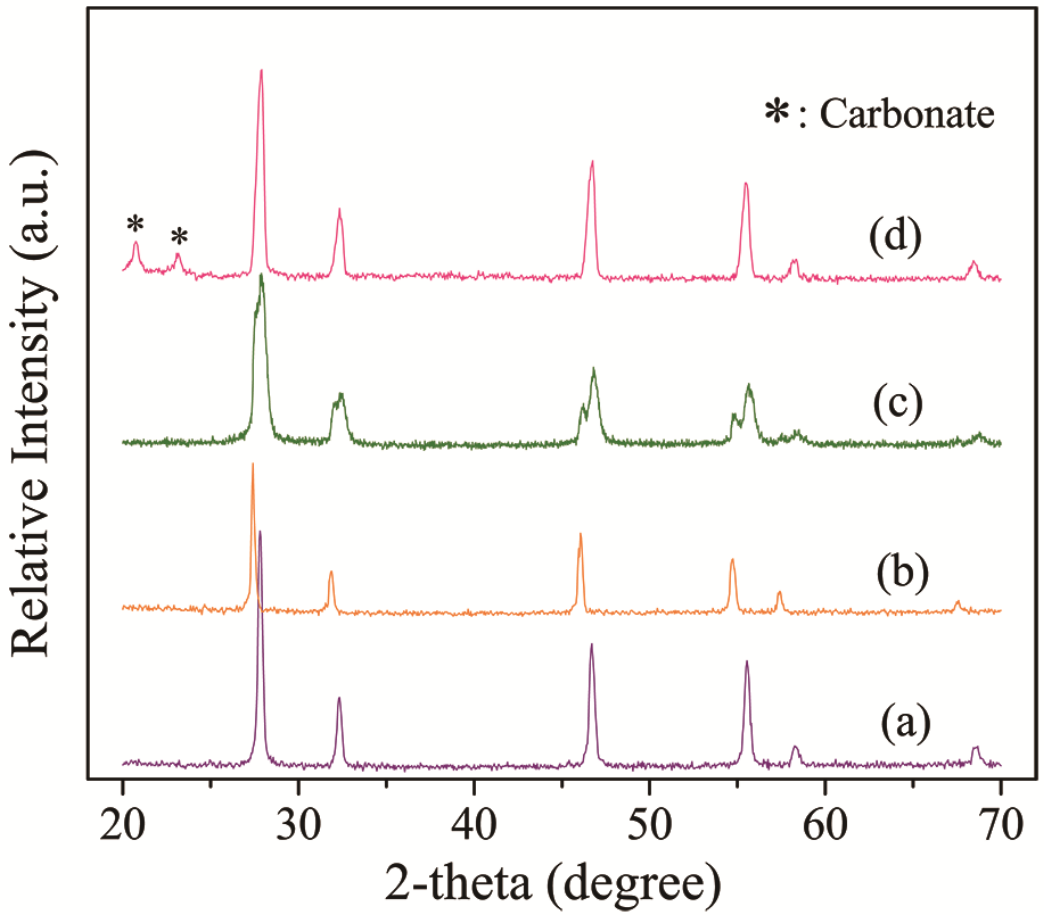
Preparing thin SDC layer on the inner surface of carbonate-non-wettable porous SDC-BYS tubes



Membrane tube with a dense inner SDC-carbonate layer

Carbonate infiltration

XRD Patterns of Tubular SDC-Carbonate in Various Stages



SDC-carbonate dual phase membrane

SDC-BYS porous support sintered at 1120 ^{o}C

BYS powders calcined at 900°C

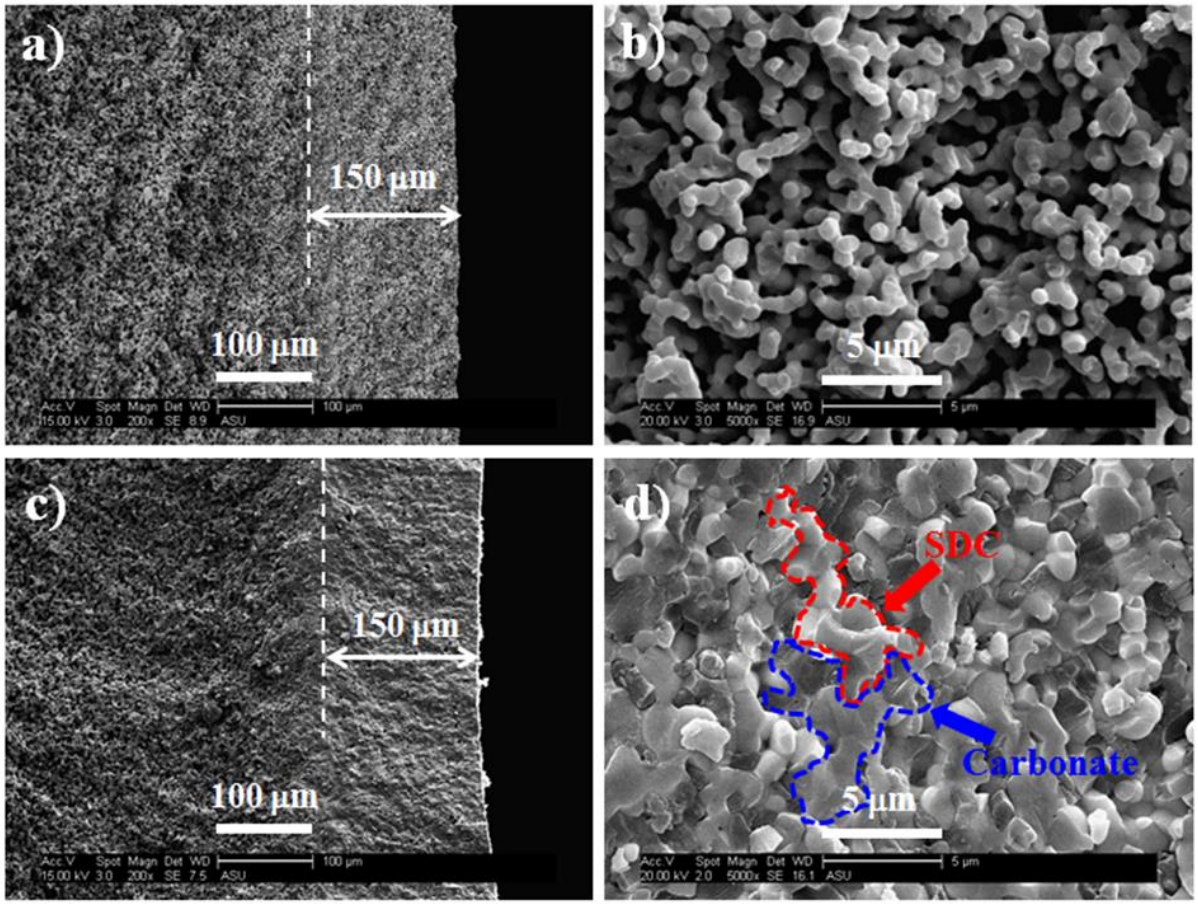
SDC powders calcined at 900 ^{o}C

Structure of Tubular SDC-carbonate Membrane

Ccross-section **Surface**

Before carbonate infiltration

After carbonate infiltration



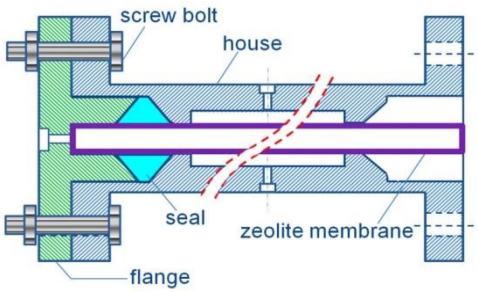
Porous SDC-BYS base

Porous SDC inner surface layer

Task D

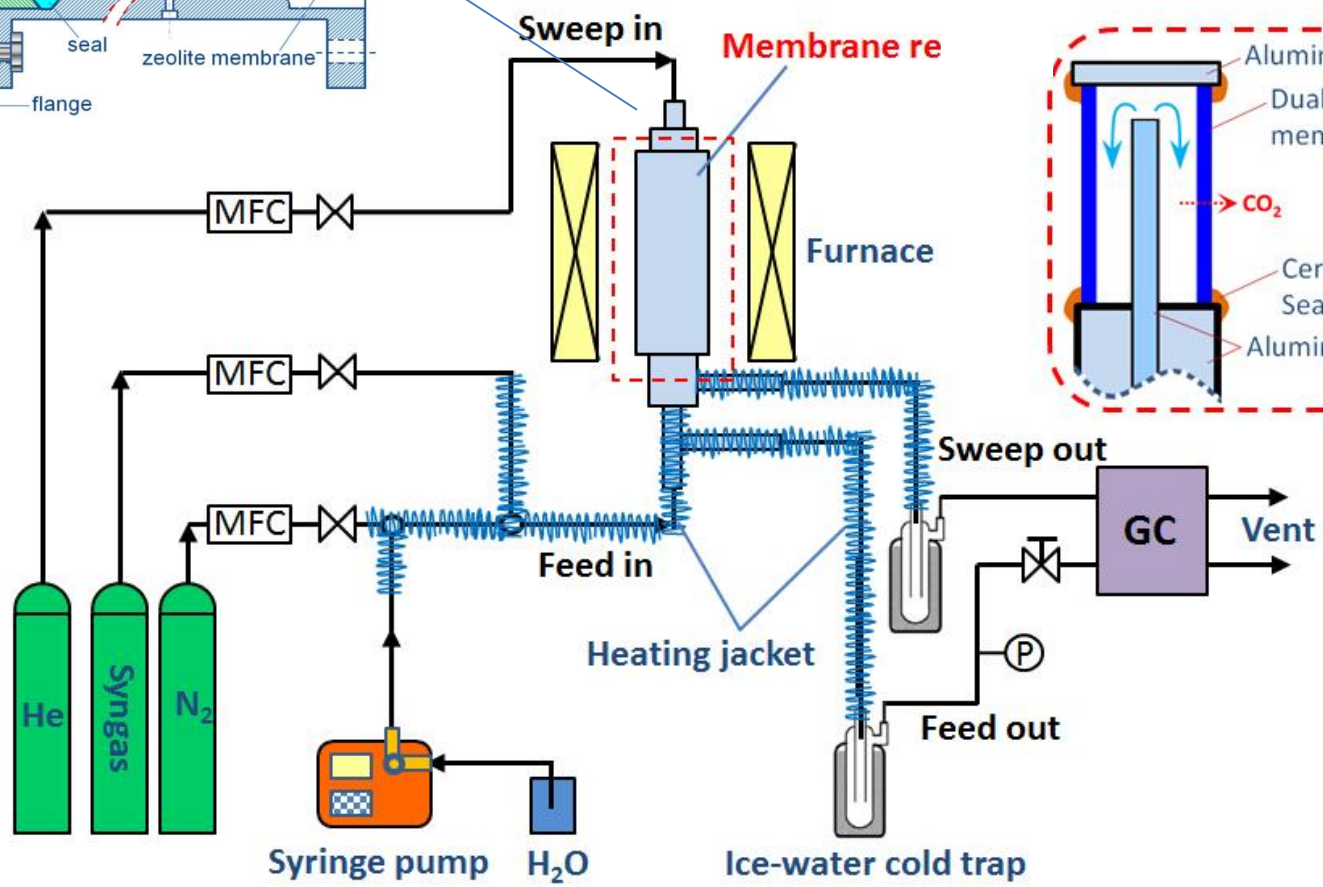
Gas Separation and Stability Study on Tubular and Disk Membranes

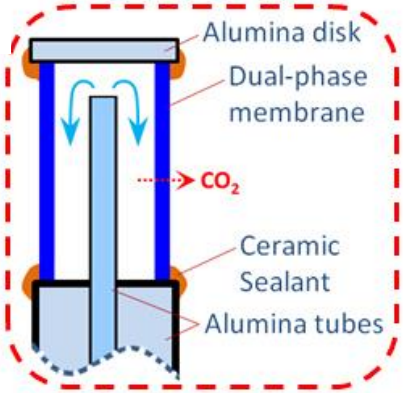
Experimental Setup for Tubular SDC-carbonate Membrane



Membrane module

Or membrane module for reaction



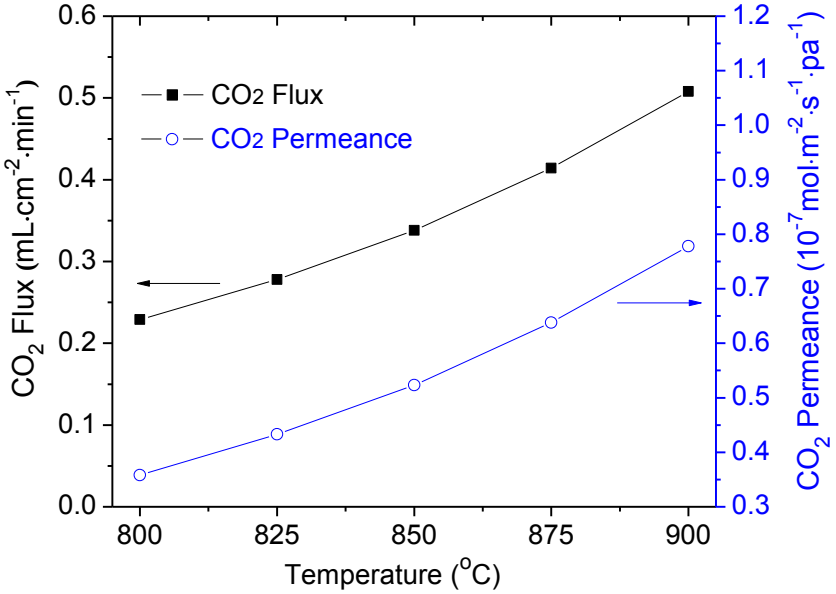


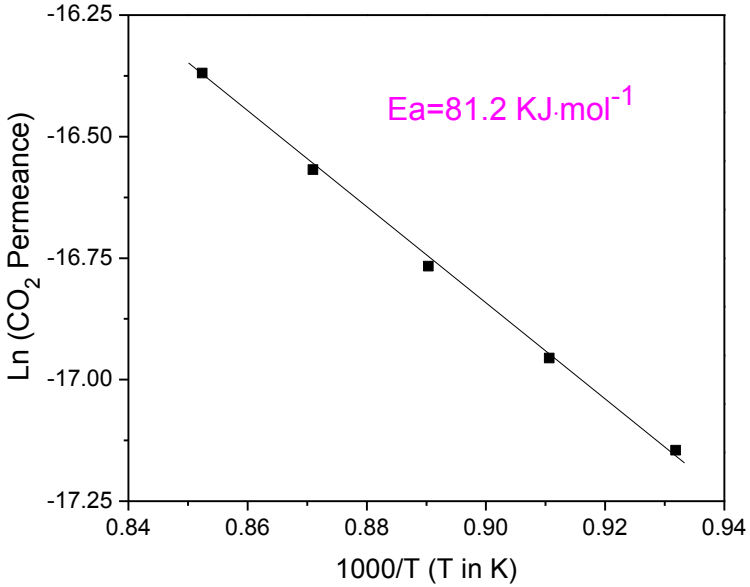
or CO_2

CO_2 Permeation and Separation Performance

◆ CO_2/N_2 separation

SDC tubular dual-phase membrane: membrane thickness 1.5 mm





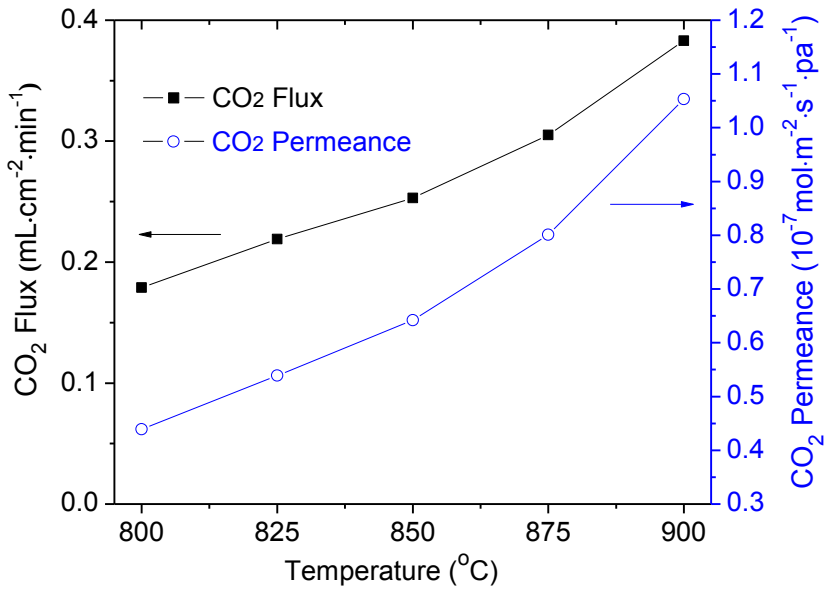
CO_2/N_2 selectivity > 200

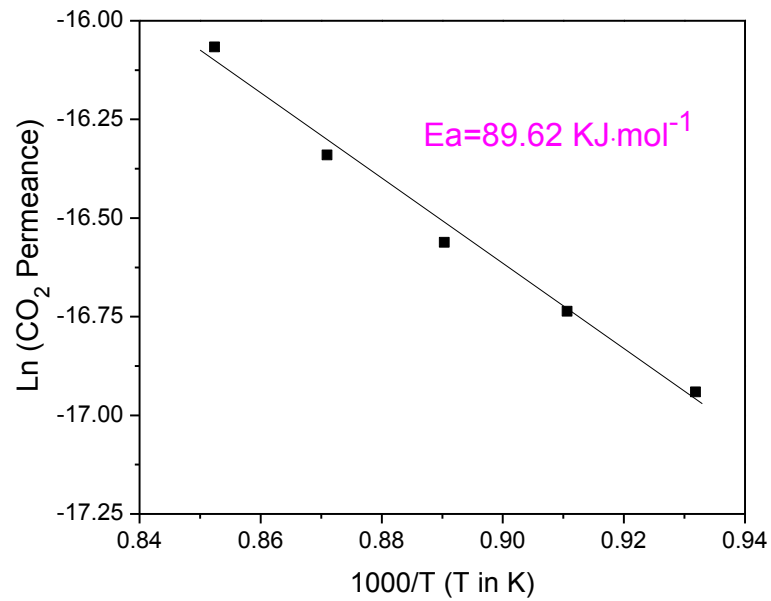
Feed side: CO_2 flow rate 25 ml·min^{-1}, N_2 flow rate 25 ml·min^{-1};
Sweep side: He flow rate 50 ml·min^{-1}

CO_2 Permeation and Separation Performance

CO_2 separation from simulated syngas

Feed side: simulated syngas (49.5% CO, 36% CO_2, 10% H_2 and 4.5% N_2)
Thickness of the membrane is about 1.5 mm.



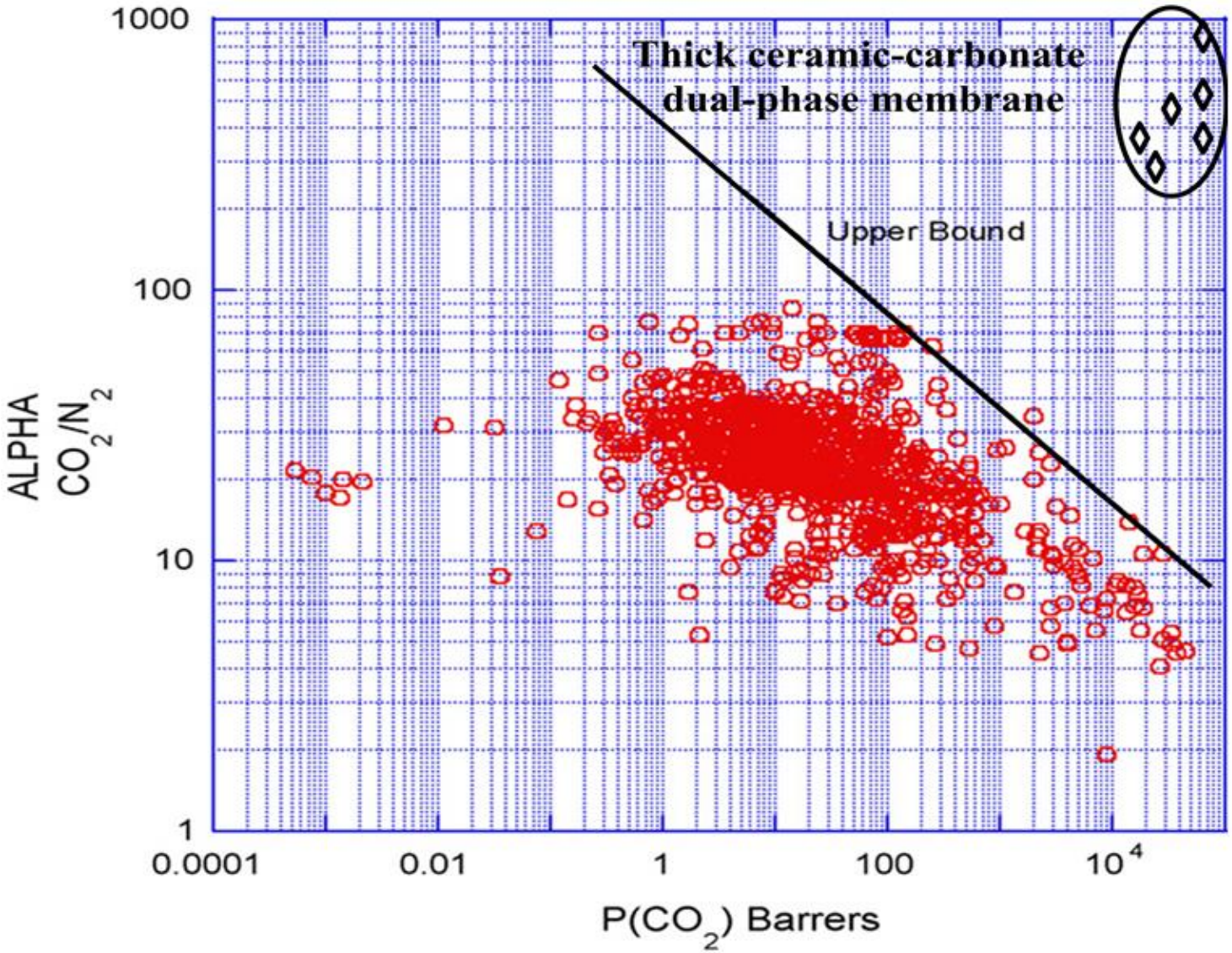


CO_2 permeation flux similar to CO_2/N_2 feed

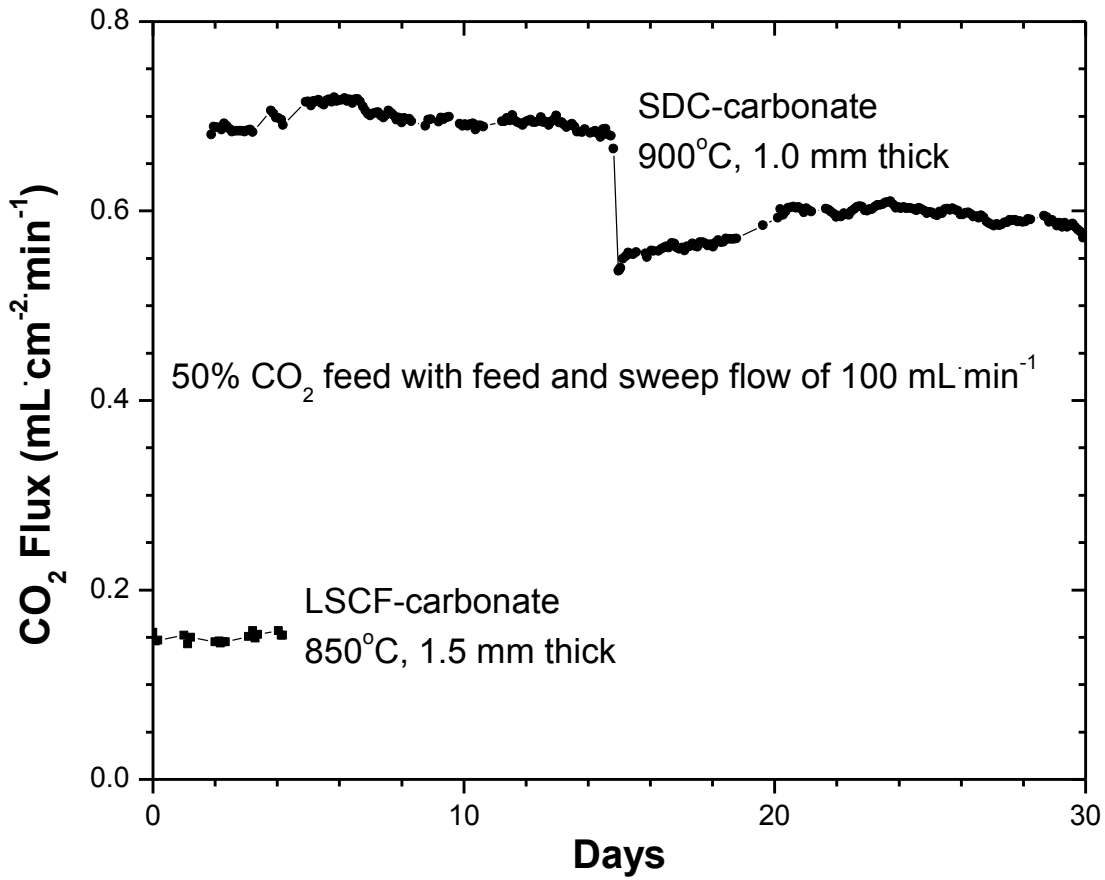
CO_2/N_2 and CO_2/H_2 selectivity is about 2200 and 65

Feed side: flow rate 50 ml·min^{-1}
Sweep side: He flow rate 50 ml·min^{-1}.

Measured CO_2/N_2 Selectivity for Dual-Phase Membranes

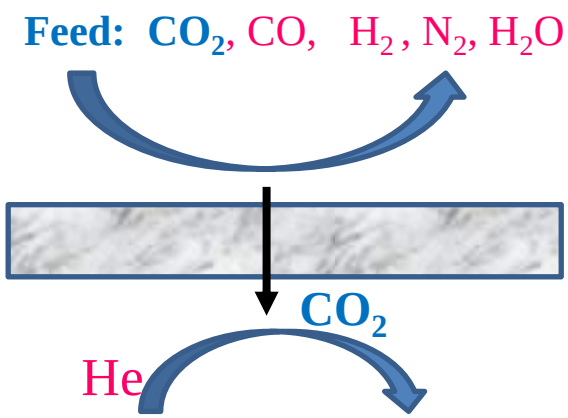


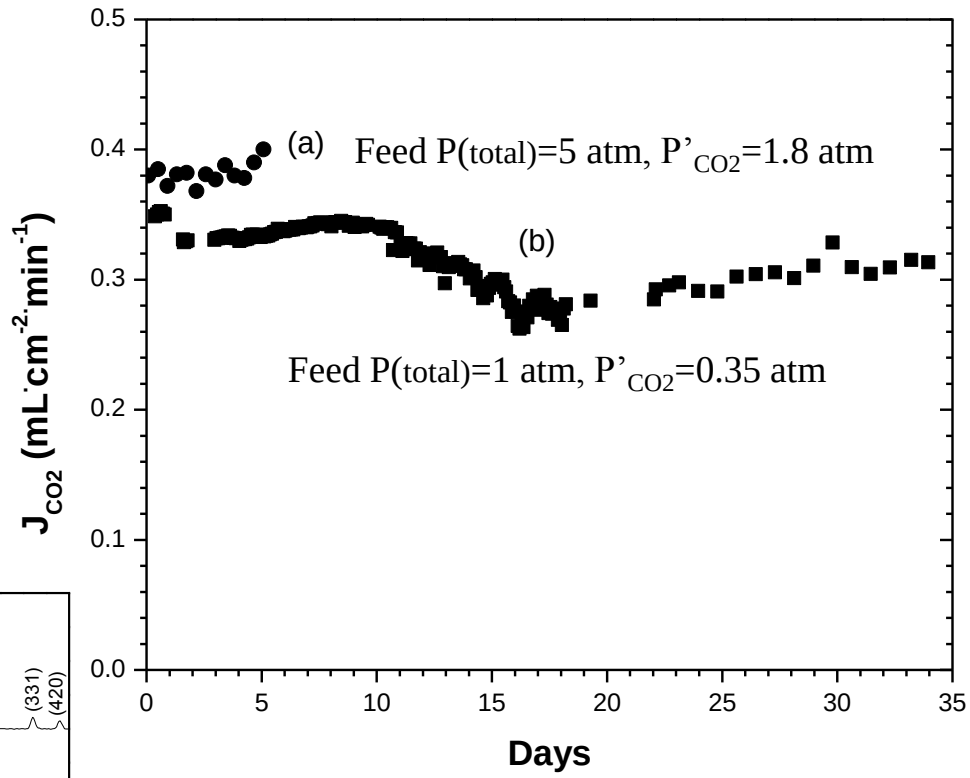
Membrane Permeation and Chemical Stability



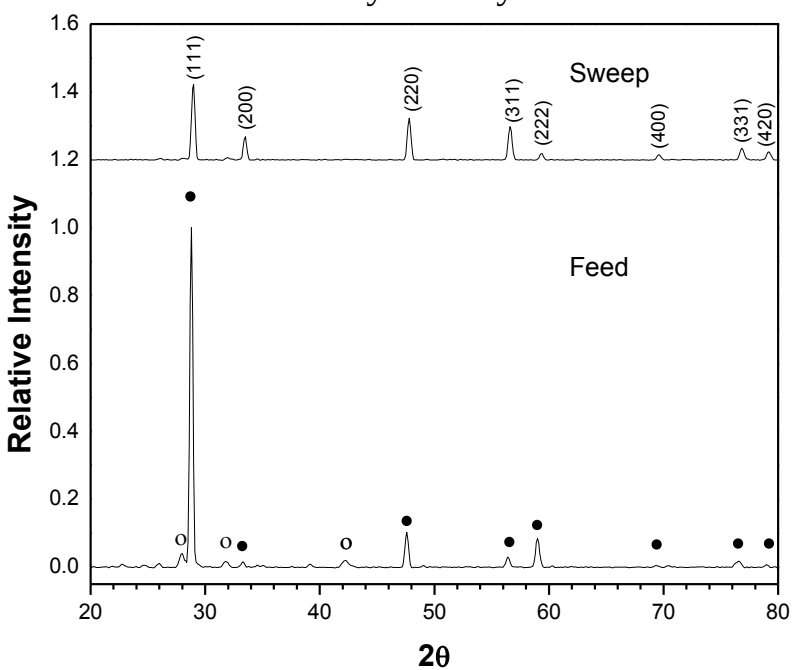
- **LSCF-carbonate membrane was tested for 4 days**
- **SDC-carbonate was tested for one month at 900°C**

Membrane Stability – Permeation Flux





XRD after 35 day stability test



- **SDC-carbonate membrane, 1.5 mm**
- **Feed and sweep flow rates: 50 mL·min^{-1}**
- **Separation temperature: 700°C**

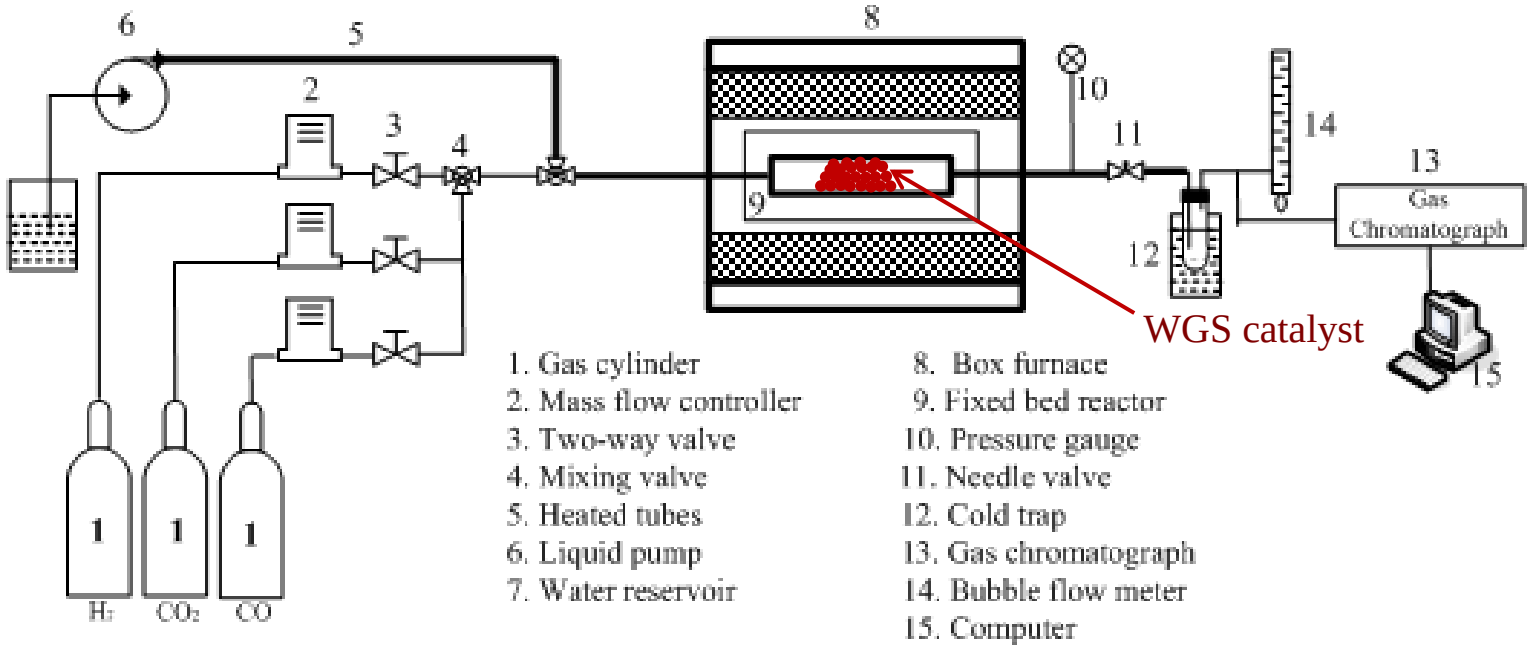
Task E

Synthesis and WGS Reaction Kinetic Study of High Temperature Catalyst

WGS Catalyst and Kinetic Study

Catalyst: Fe-Cr-Cu spinel oxide catalyst (atomic ratio of 10:1:0.25) was prepared following the published procedures*

Differential Fixed-Bed Reactor for Kinetic Study :

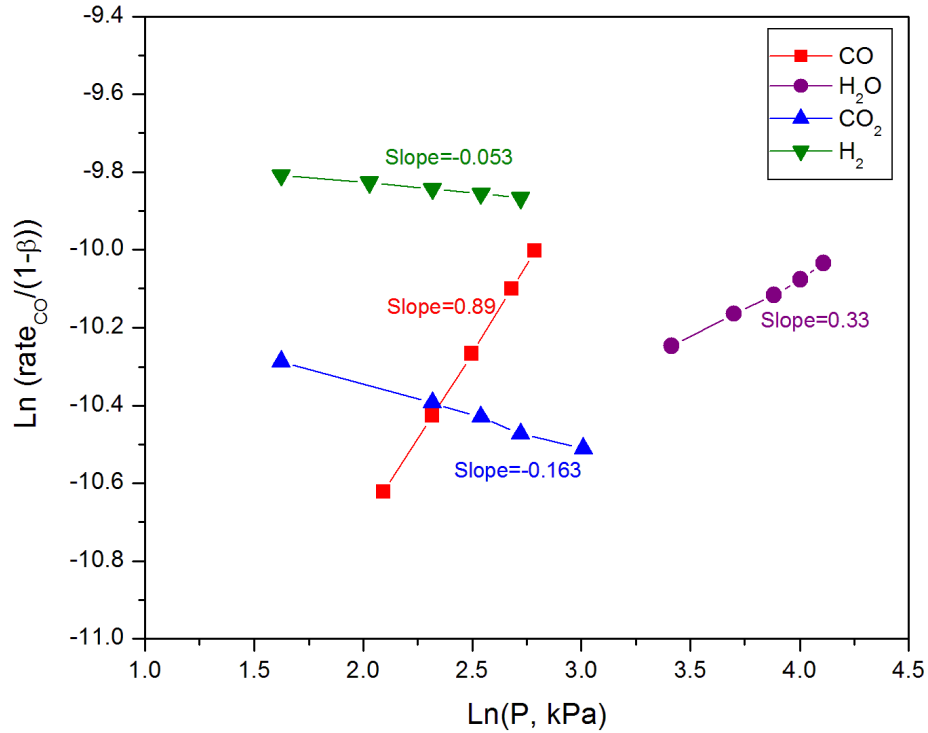


- Testing temperature: 500°C
- Total gas flow rate: 80 cc/min
- Pressure in the fixed bed: 101 kPa

* Reddy GK, Gunasekera K, Boolchand P, Dong J, Smirniotis PG. J Phys Chem C 115 (2011)7586–95.

WGS Catalyst Kinetics

WGS reaction rate on catalyst was obtained at different partial pressure of reacting or product gases



Regressed Reaction rate (mol g^{-1} s^{-1}):

$$R = K\exp\left(\frac{-88 \pm 2.18}{R'T}\right) P_{CO}^{0.89} P_{H2O}^{0.33} P_{CO2}^{-0.163} P_{H2}^{-0.053} \left(1 - \frac{1}{K_e}\frac{P_{H_2}\cdot P_{CO_2}}{P_{CO}\cdot P_{H_2O}}\right)$$

$$(1-\beta) = \left(1 - \frac{1}{K_e}\frac{P_{H_2}\cdot P_{CO_2}}{P_{CO}\cdot P_{H_2O}}\right)$$

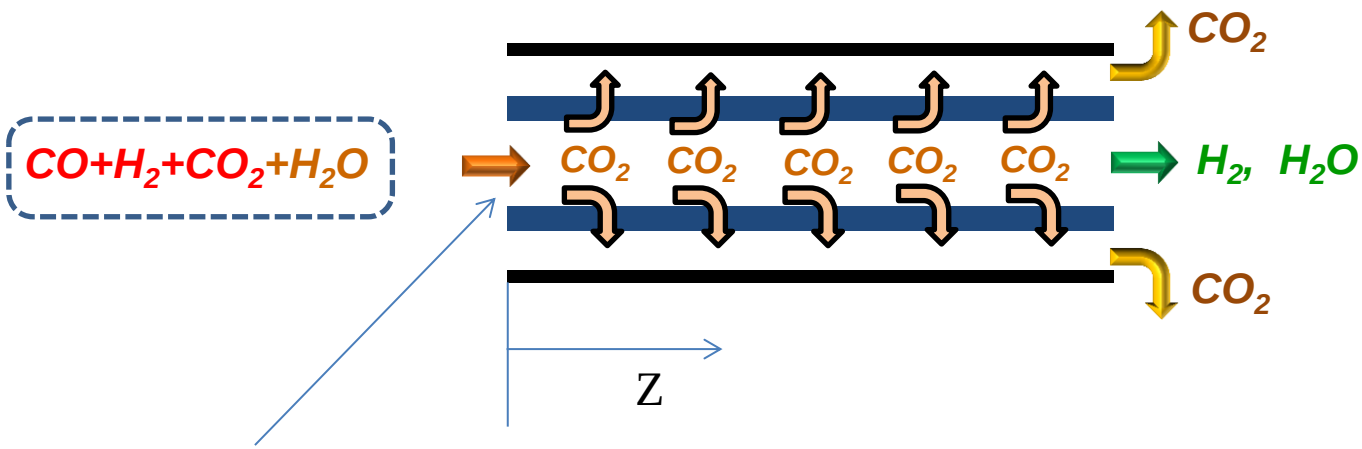
K_e: Equilibrium constant of WGS reaction

$$K_e = \exp\left(\frac{4577.8}{T} - 4.33\right)$$

Task F

Modeling and Analysis of Dual-Phase Membrane Reactor for WGS

Modeling Dual-phase WGS Membrane Reactor



- Packed with WGS catalyst, has to be operated at lower temperature (<500°C); Low CO_2 permeance for the membrane

- Catalyst-free, operated at high temperatures (>800°C); High CO_2 permeance for membrane #

Model to find C_i=f(z) and then at reactor exit

Homogeneous high temperature WGS: F. Bustamante, R.M. Enick, R.P. Killmeyer, B.H. Howard, K.S. Rothenberger, and A.V. Cugini, B. D. Morreale M.V. Ciocco, Uncatalyzed and wall-catalyzed forward water–gas shift reaction kinetics, *AIChE J.*, 51 (2005) 1440.

Mathematical Model

Mass balance on the reaction (tube) side:

$$\frac{dq_i}{dz} = \pi R^2 \rho_B \nu_i \gamma - 2\pi R F_i \Delta P_i$$

q_i (i= CO, H_2O, CO_2, H_2, N_2) = molar flow rate in the tube side,
v_i = stoichiometry of species i in WGS reaction, v_{N2} = 0,
F_i = permeance for species i
ΔP_i = transmembrane partial pressure difference of species i
γ = reaction rate for WGS.

Mass balance on sweep (shell) side

$$\frac{dQ_i}{dz} = 2\pi R F_i \Delta P_i$$

Q_i = molar flow rate in the shell side.

Gas permeance or flux through the membrane:

For CO_2

$$F_{CO_2} = \frac{1}{P'_{CO2} - P''_{CO2}} \int_{P''_{CO_2}}^{P'_{CO_2}} \frac{\sigma_T RT}{4F^2 L} dlnP_{CO2}$$

$$J_{CO_2} = k' \cdot \frac{RT}{4F^2 L} \cdot (P'^{\,n}_{CO_2} - P''^{\,n}_{CO_2})$$

For other gases

F_i=0

Mathematical Model

WGS Reaction Kinetic Equation:

- On catalyst (heterogeneous WGS) (slide 53)
- Catalyst-free WGS (homogeneous WGS)*

$$\gamma = Fk_f[CO]^{0.5}[H_2O](1 - \frac{[CO_2][H_2]}{K_{eq}[CO][H_2O]})$$

Model equation solved by Matlab to Find

CO conversion

Membrane reactor (MR)

$$X_{CO}(\%) = \frac{q_{CO}^0 - q_{CO} - Q_{CO}}{q_{CO}^0} \times 100(\%)$$

Traditional reactor (TR)

$$X_{CO}(\%) = \frac{q_{CO}^0 - q_{CO}}{q_{CO}^0} \times 100(\%)$$

CO_2 recovery or capture

$$Y_{CO_2}(\%) = \frac{Q_{CO_2}}{q_{CO_2} + Q_{CO_2}} \times 100(\%)$$

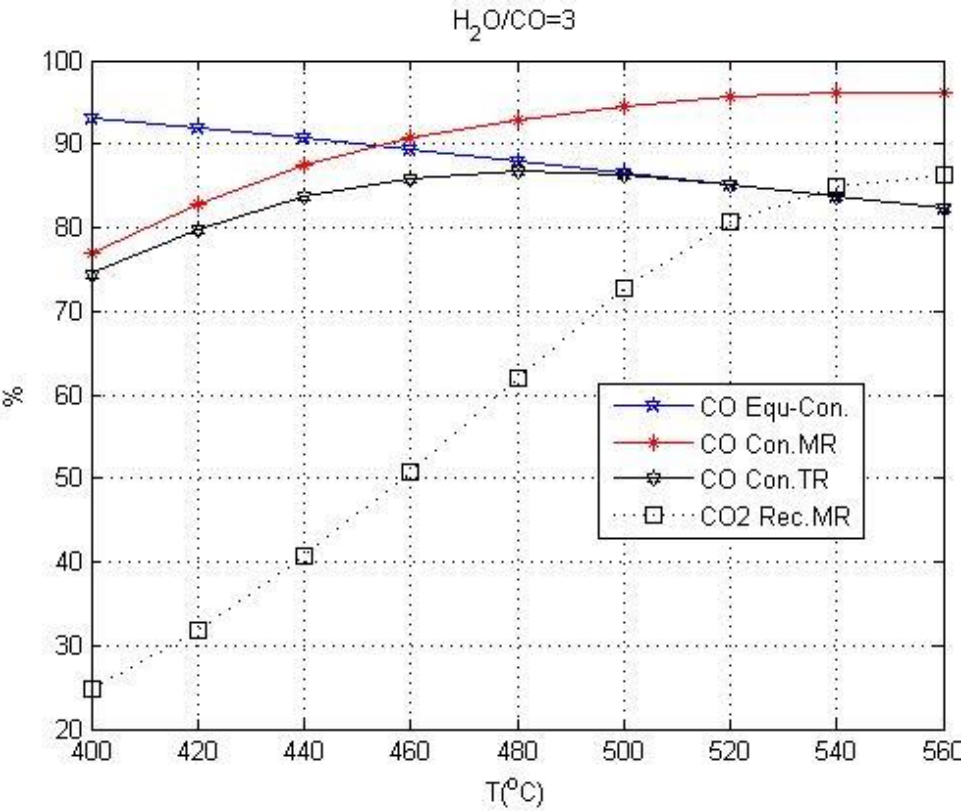
* Modified from F. Bustamante et al., *AIChE J.*, 51 (2005) 1440

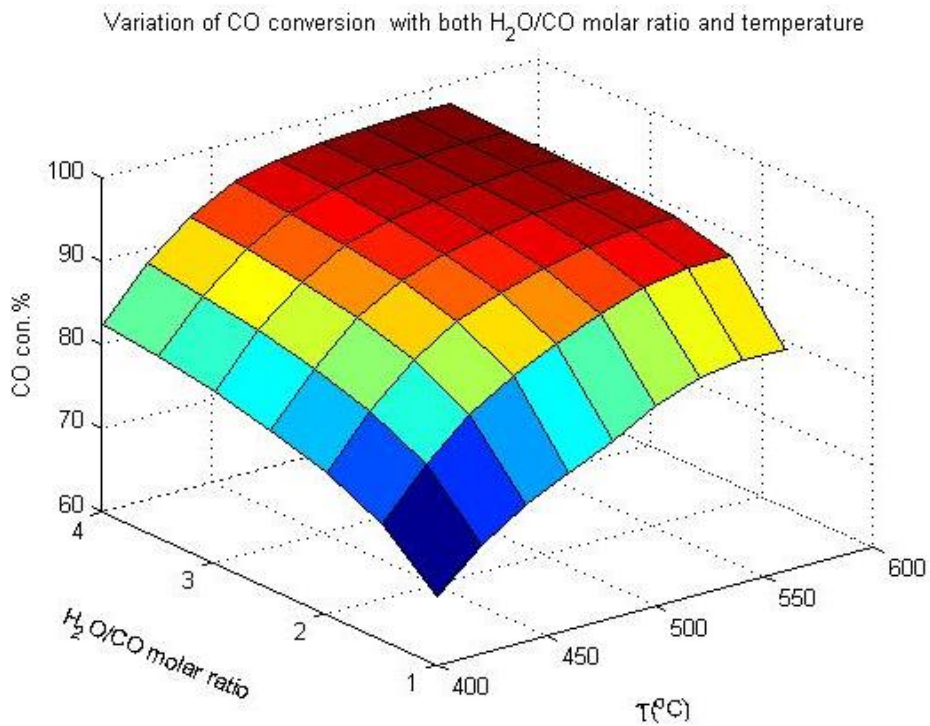
Heterogeneous WGS in Dual-Phase Membrane Reactor – Effect of Temperature and H_2O/CO ratio

Reactor length: 1.0 cm
H_2O/CO ratio is 3.0

Weight of catalyst is 0.4 g
Sweep gas flow rate: 30 ml·min^{-1}

CO flow rate: 15 ml·min^{-1}
Feed pressure is 5 atm.



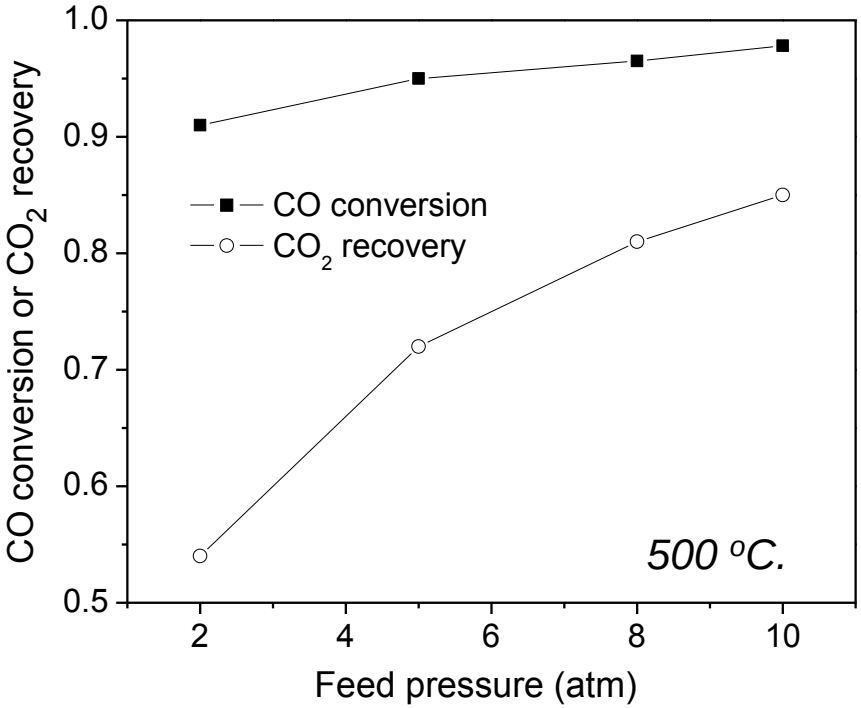


Simulations were performed with **CO_2 permeance = 30 x Measured**

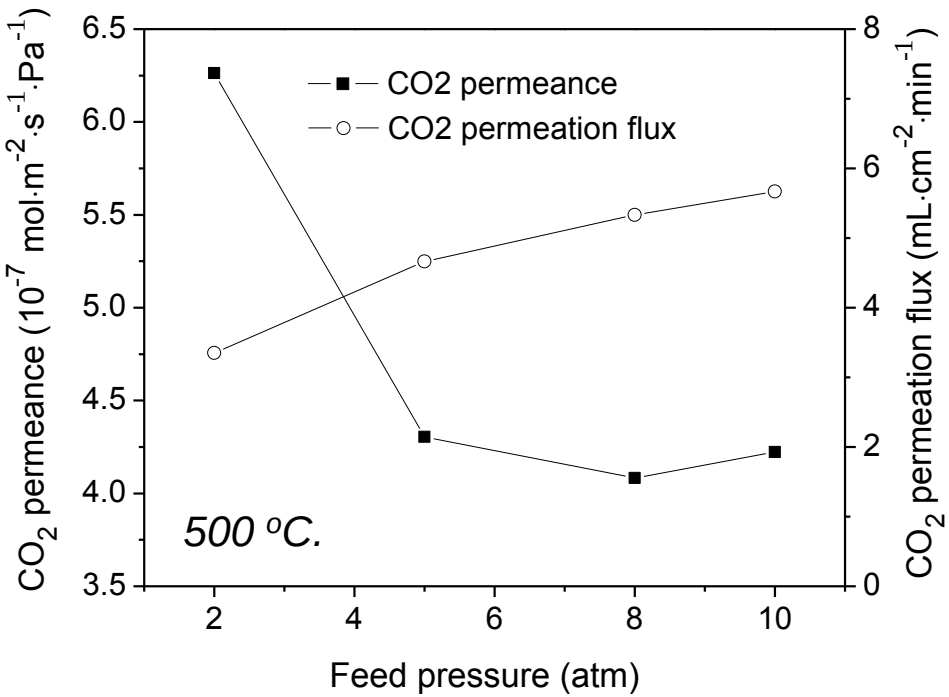
Otherwise the results of MR are same as TR

Heterogeneous WGS in Dual-Phase Membrane Reactor – Effect of Feed Pressure

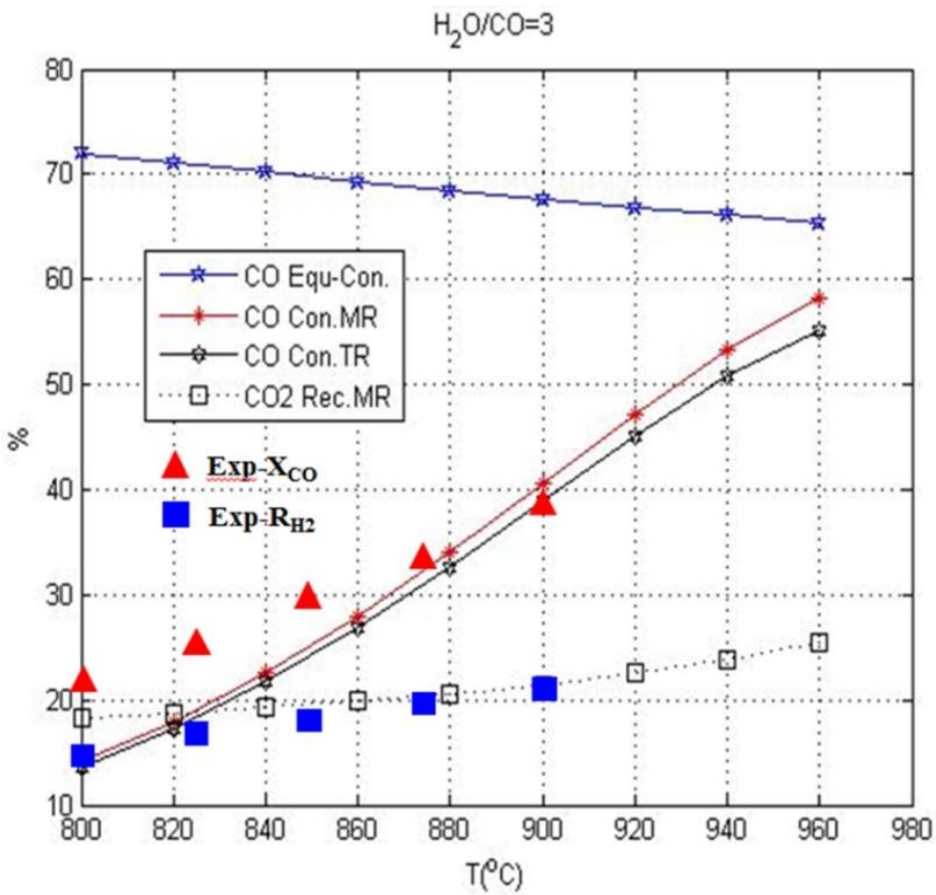
CO conversion and CO_2 recovery as a function of feed pressure

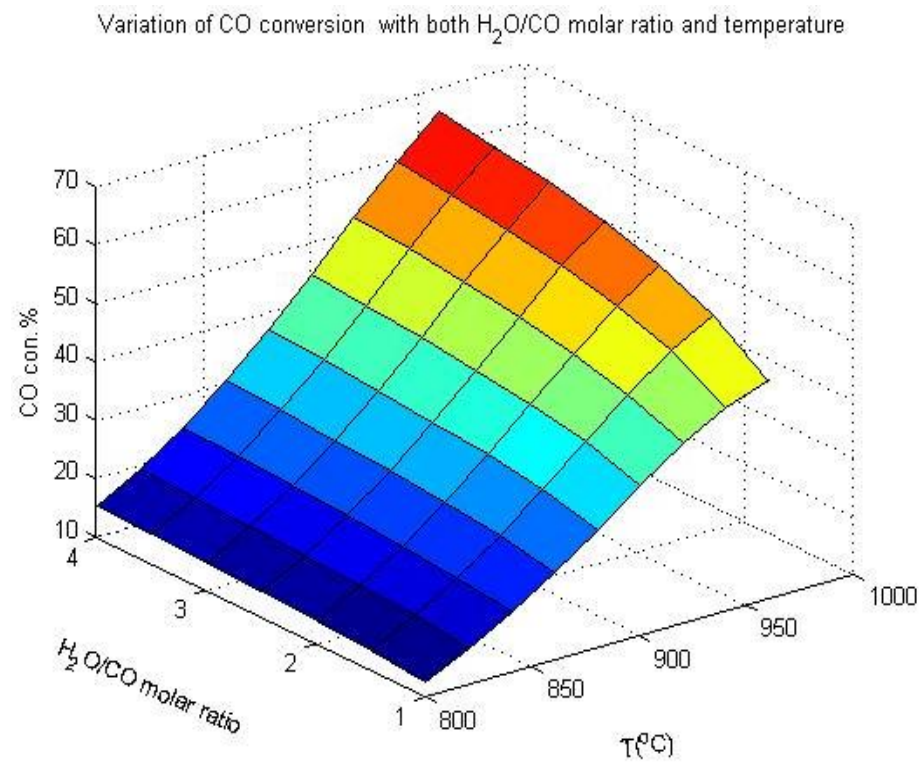


CO_2 permeation flux and permeance as a function of feed pressure



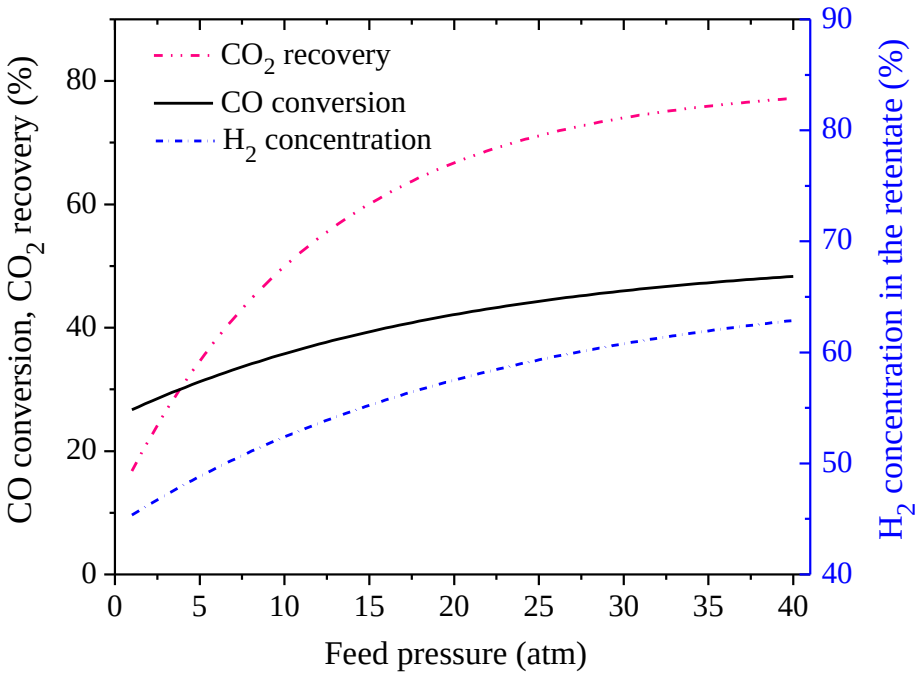
Homogeneous Catalyst-Free WGS in Dual-Phase Membrane Reactor – Effect of Temperature



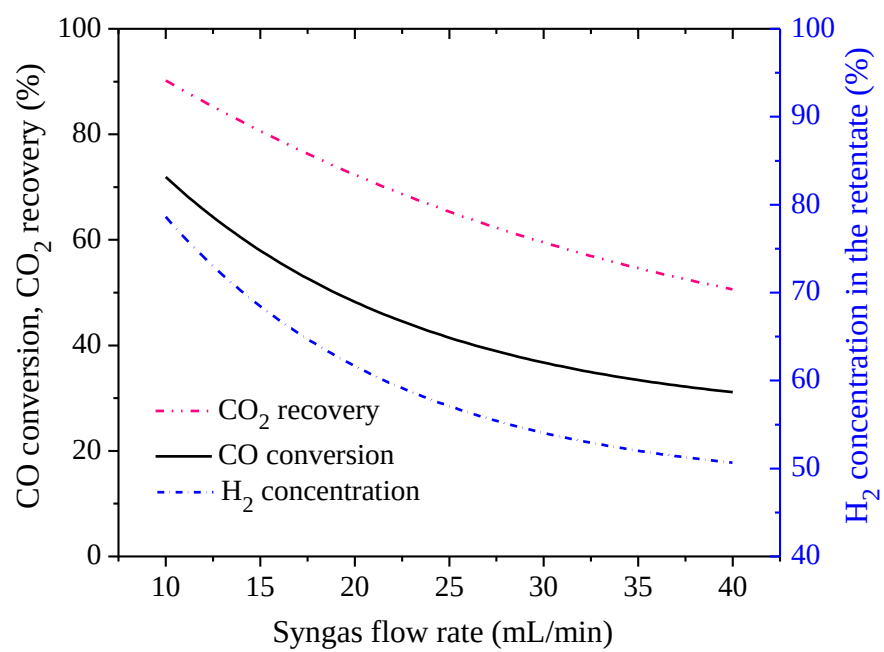


The feed pressure is 1 atm, H_2O/CO ratio is 3.0

Homogeneous Catalyst-Free WGS in Dual-Phase Membrane Reactor – Effect of Pressure and Flow Rate



Steam to CO ratio is 3.0; syngas flow rate 25 mL·min^{-1}; syngas space velocity 19.89 min^{-1}; reaction temperature is 900 ^{o}C.

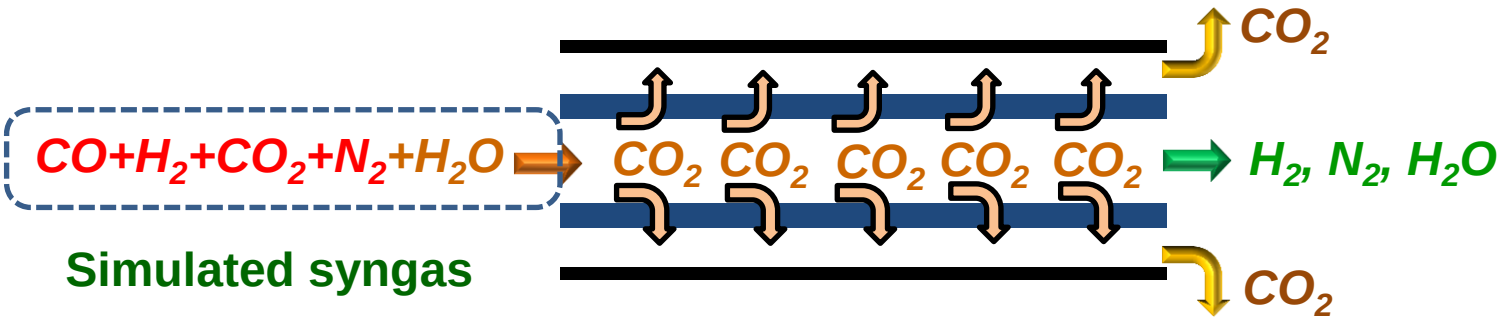


Syngas space velocity 7.96-31.83 min^{-1}; Steam to CO ratio is 3.0; reaction temperature is 900 ^{o}C; feed pressure is 20 atm.

Task G

Experimental Studies on WGS in Dual-Phase Membrane Reactors

Experiments on High Temperature WGS Reaction



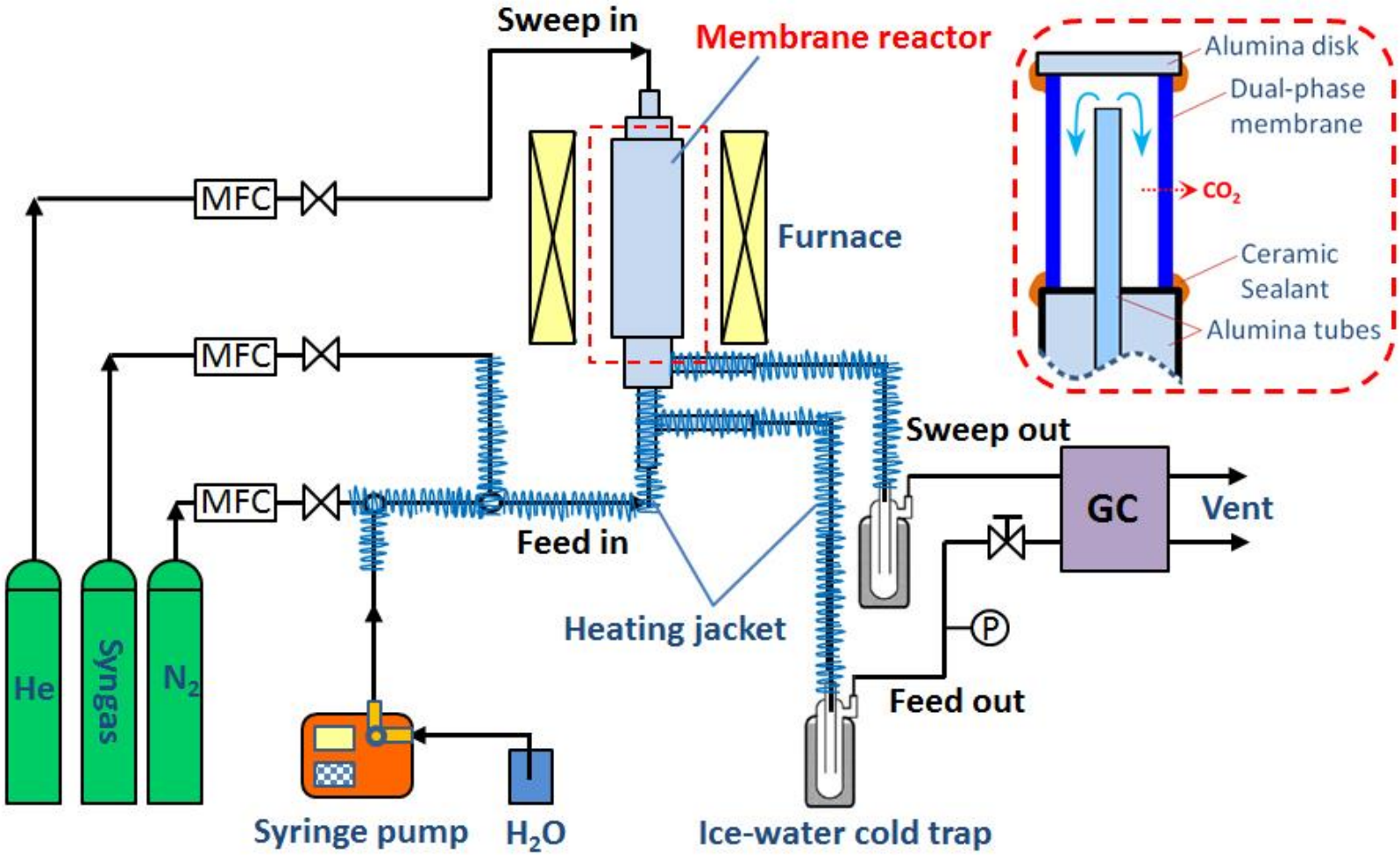
◆ Membrane

Ceramic: SDC; **Carbonate:** $Li_2CO_3/Na_2CO_3/K_2CO_3$
OD: 1.1cm; **ID:** 0.8cm; **Thickness:** 1.5 mm; **Effective length:** 2.5cm.

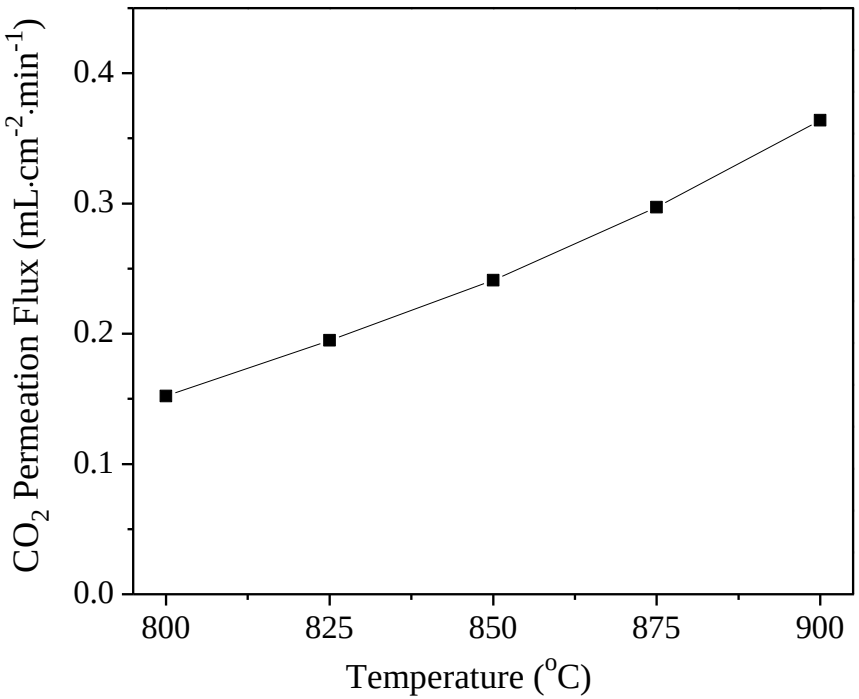
◆ Reaction conditions

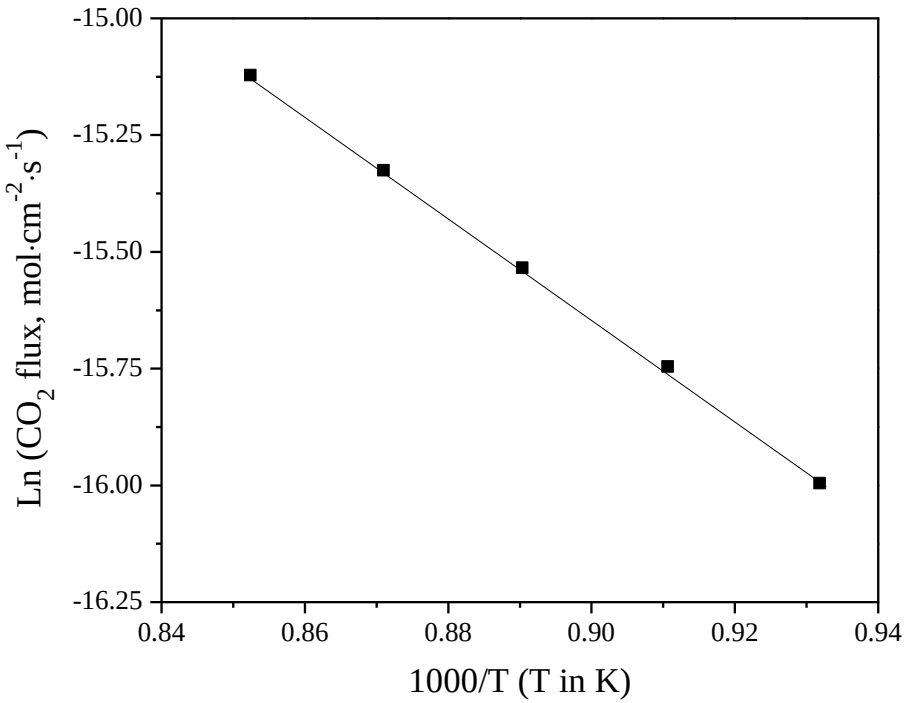
Temperature: 800-900 ^oC;
Feed, Sweep side pressure: 1 atm;
Catalyst: No;
Simulated syngas: 49.5% CO, 36% CO_2, 10% H_2 and 4.5% N_2;
Feed side: Syngas flow rate 10-30 $mL\cdot min^{-1}$, N_2 flow rate 10 $mL\cdot min^{-1}$,
steam to CO molar ratio 1.0-3.0;
Sweep side: He flow rate 60 $mL\cdot min^{-1}$.

High Temperature WGS Reaction Setup



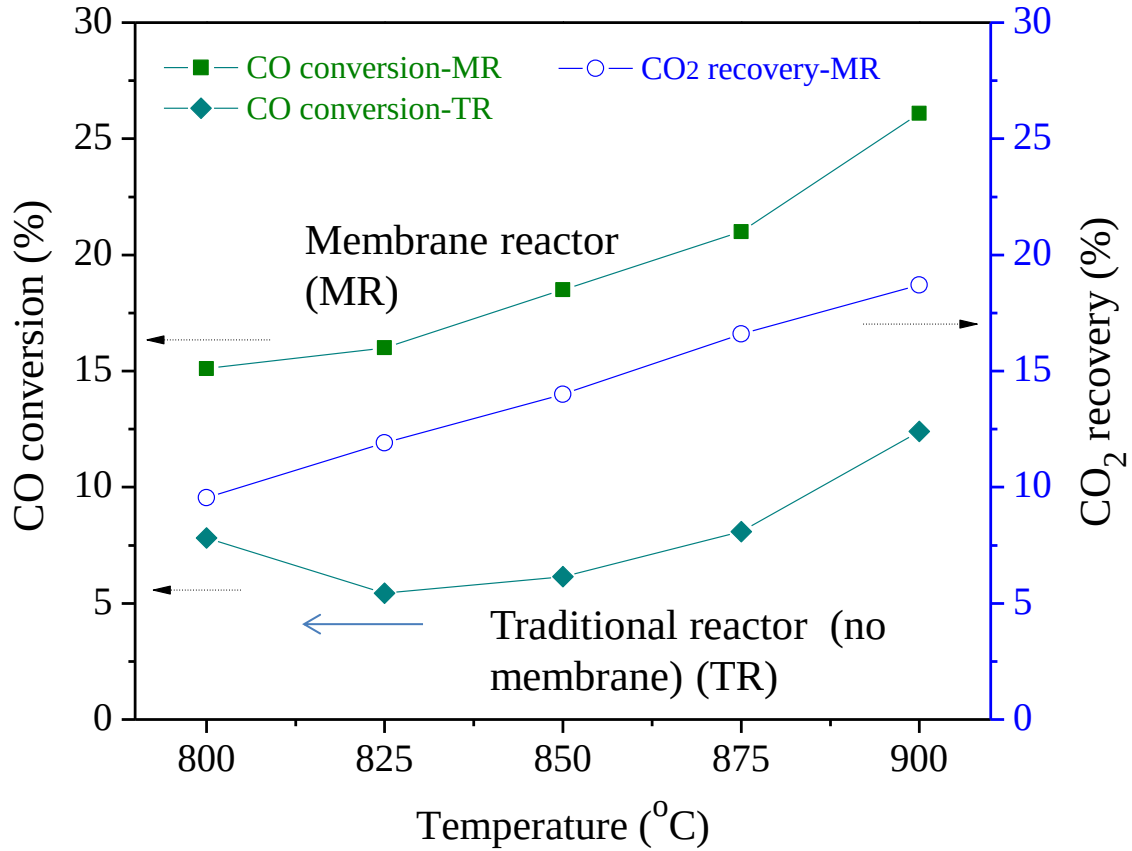
CO_2 Permeation Flux during WGS Reaction





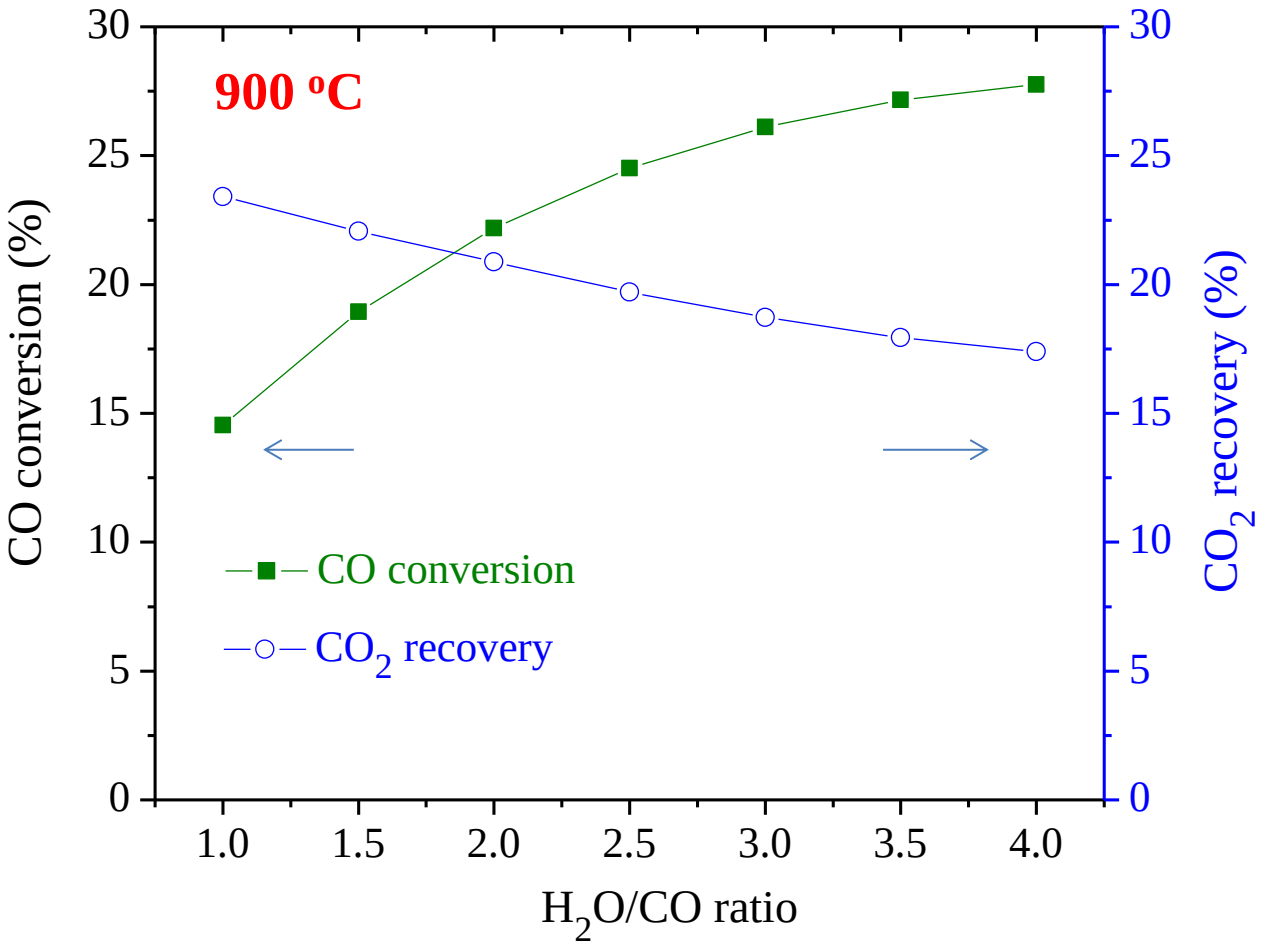
- **900 ^oC, CO_2 permeation flux 0.36 $ml \cdot cm^{-2} \cdot min^{-1}$;**
- **CO_2 permeation activation energy is 90.8$kJ \cdot mol^{-1}$.**

WGS Performance – Effect of Temperature



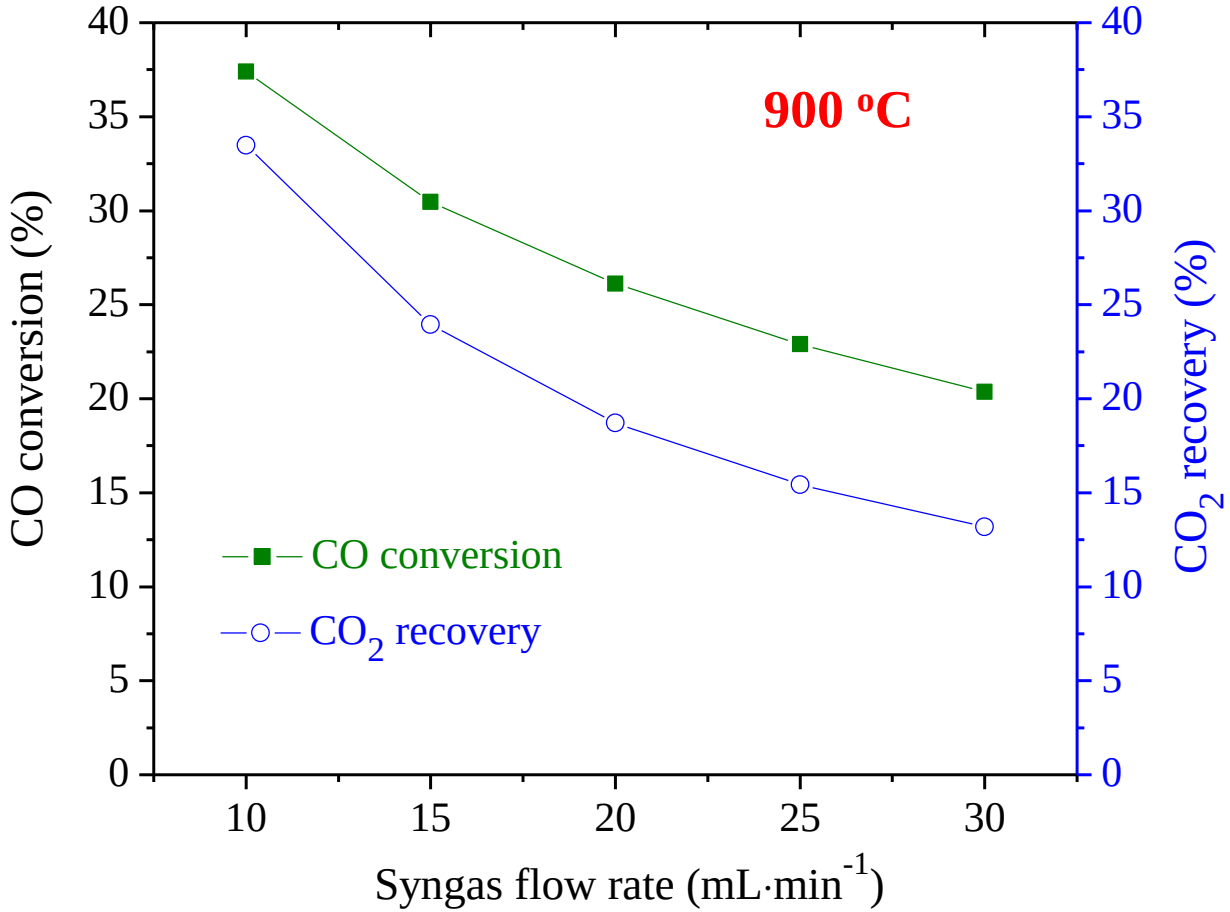
- **900 °C, CO conversion and CO_2 recovery are 26.1% and 18.7%, respectively, in membrane reactor (MR); CO conversion of traditional reactor (TR) is much lower.**

WGS Performance – Effect of H2O/CO Ratio



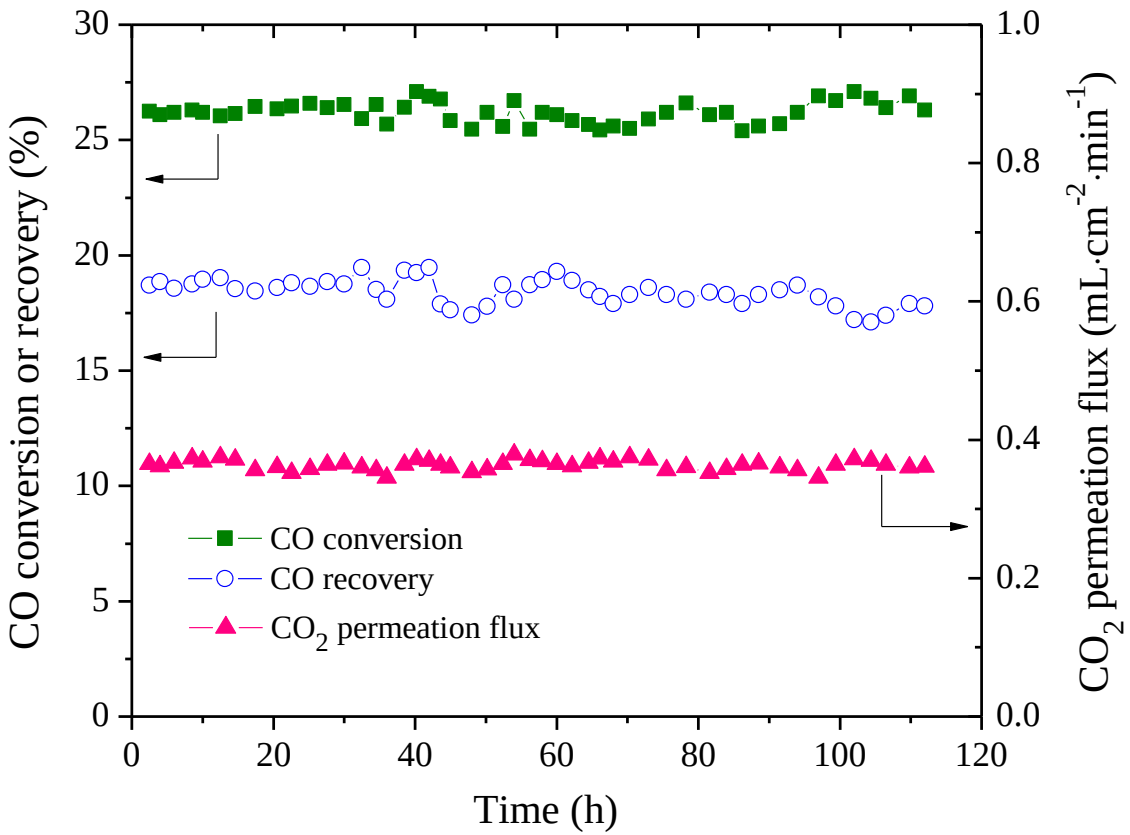
- **CO conversion increases with steam/CO ratio, CO_2 recovery decreases.**

WGS Performance – Effect of Syngas Flow Rate



- **Both CO conversion and CO_2 recovery decrease with increasing syngas flow rate.**

High Temperature WGS Reaction in Membrane Reactor - Stability



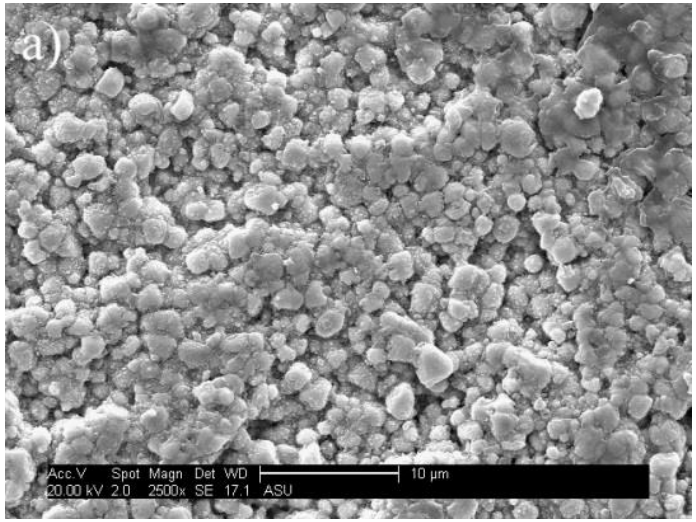
Cycle	Time
1	0-30 h
2	30-58 h
3	58-84 h
4	84-112 h

Between cycles:
900°C => RT => 900°C

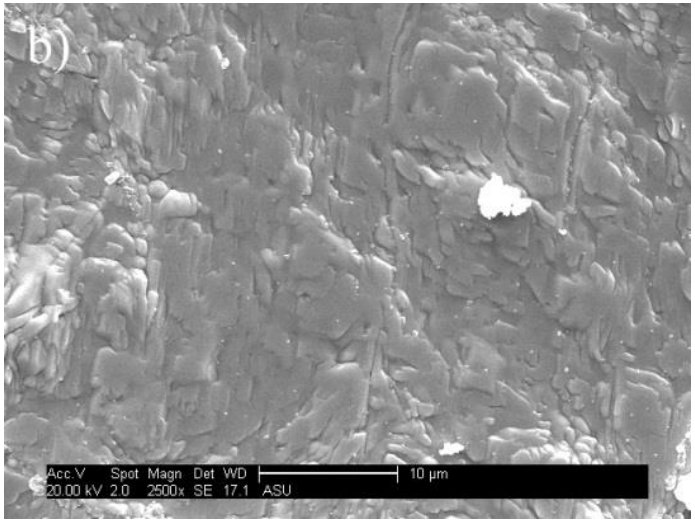
- **900 °C, CO conversion and CO_2 recovery and CO_2 flux maintain at around 26.2%, 18.4% and 0.36 $mL \cdot cm^{-2} \cdot min^{-1}$, respectively, for more than 110h.**

Characteristics of Membrane after WGS Reaction

After 120 hr WGS Operation



(a) Outer surface (sweep side)

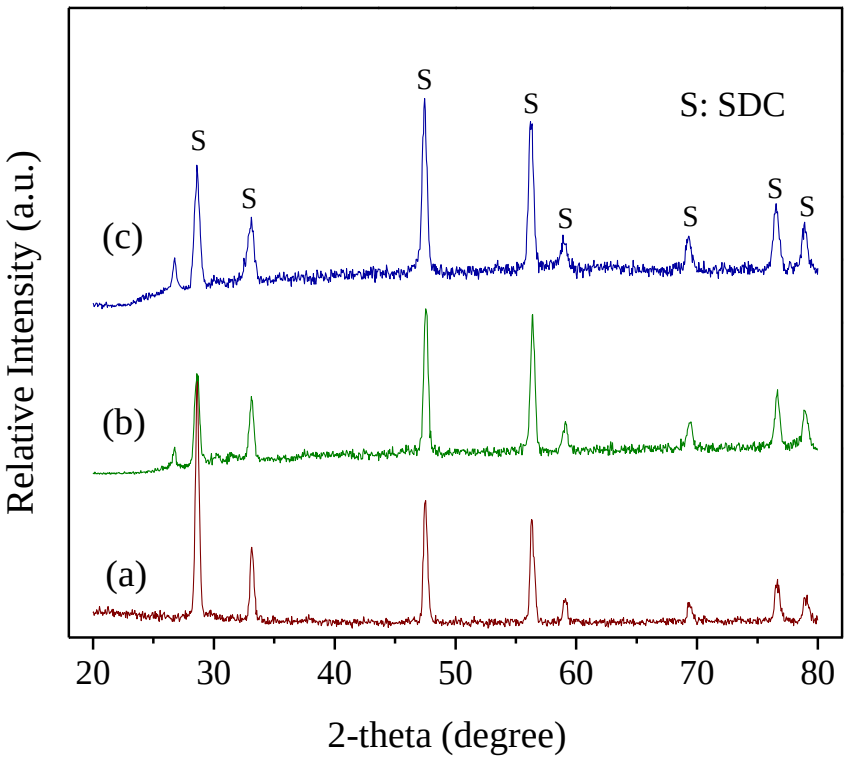


(b) Inner surface (reaction side)

- The surface of sweep side is slightly eroded, 1-2 µm;
- The surface of reaction side is dense and the corrosion is not obvious.

Characteristics of Membrane after WGS Reaction

❖ **XRD pattern of membrane after long-term operation**



(c) Reaction side

(b) Sweep side

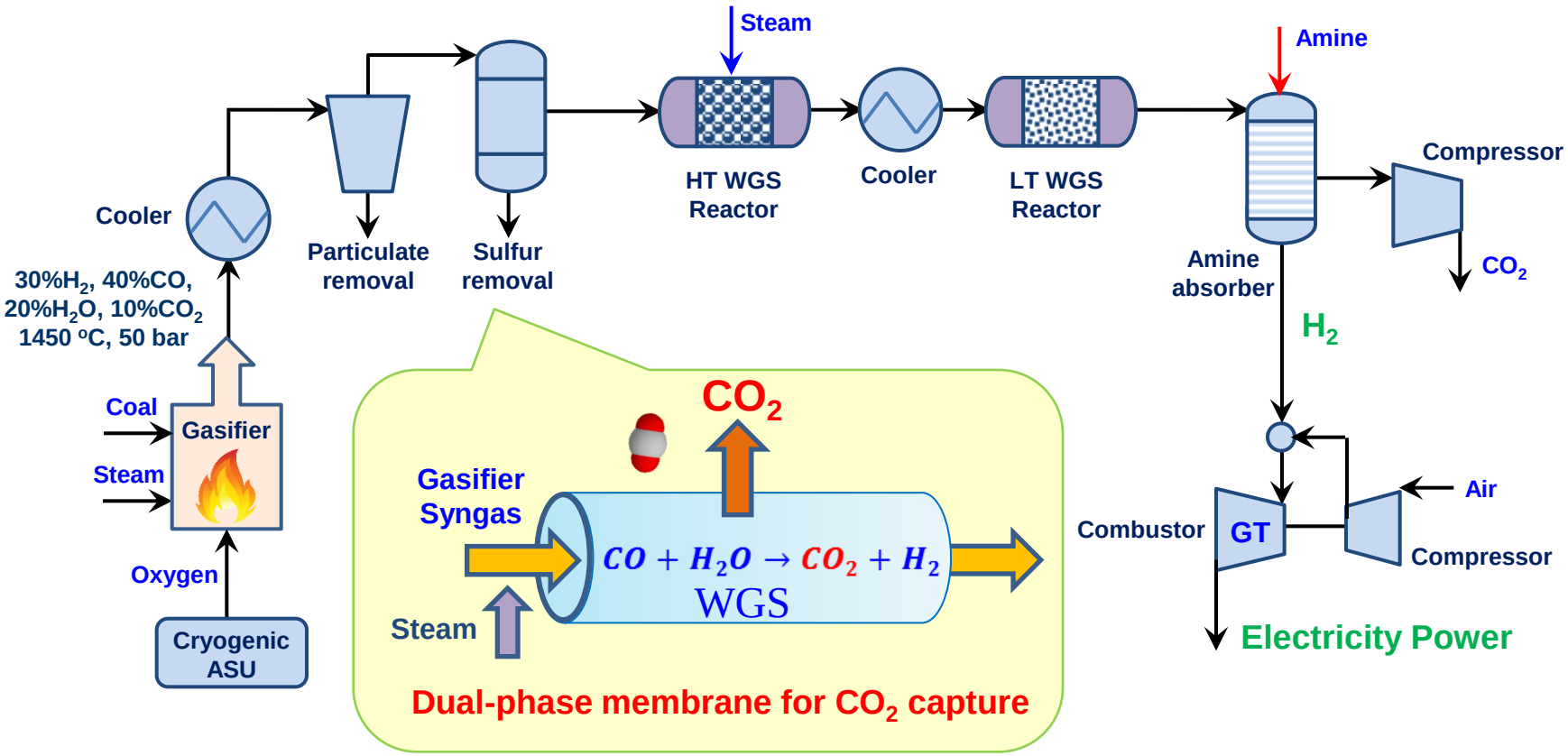
(a) Fresh membrane

- **Both reaction side and sweep side maintain full fluorite structure**

Task H

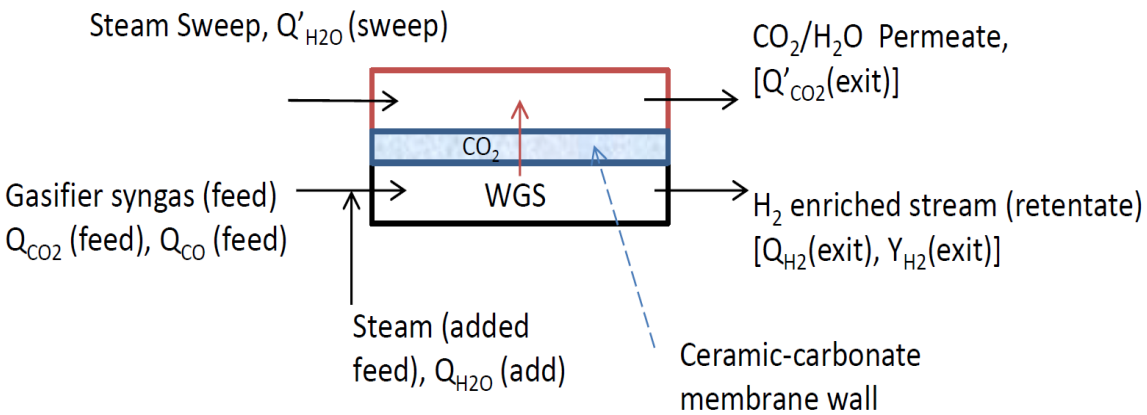
Integration to IGCC and Economic Analysis

Use of Dual-Phase Membrane Reactor for High Temperature WGS in IGCC



For best heat integration, the membrane reactor might have be put closer to the gasifier

Optimizing WGS Membrane Reactor with CO_2 Capture

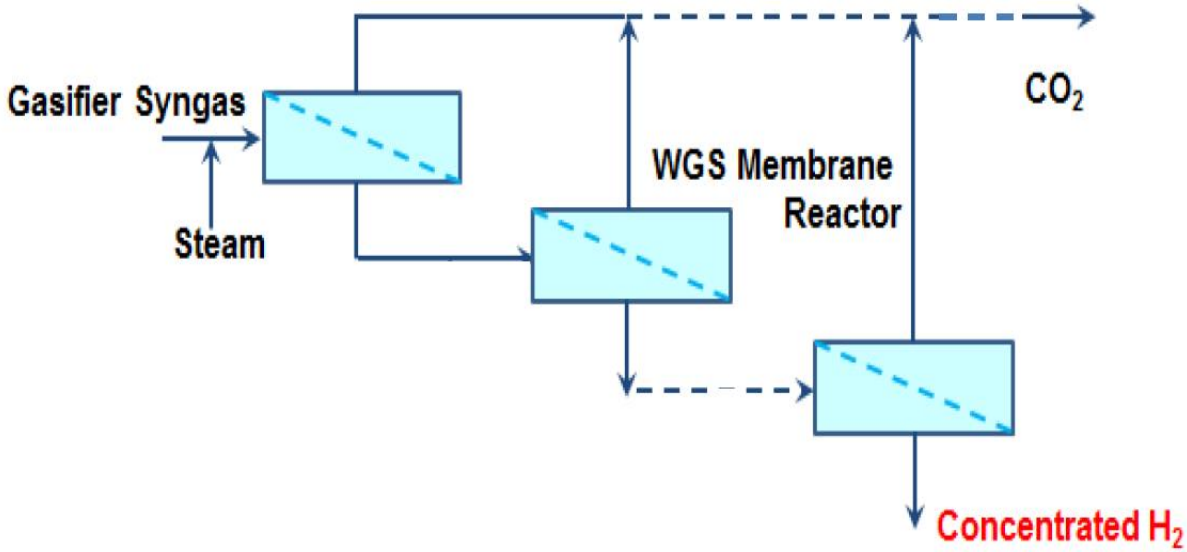


Membrane Dimension and WGS/CO2 Separation Operation Conditions for a Single Tube Membrane Reactor

Parameter		Range	Values used in the calculations
Inner diameter of membrane (cm)		0.5-0.1.5	0.8
Membrane length (cm)		50-200	100
Temperature (°C)		700-900	850
Feed coal syngas flow rate ($mL \cdot min^{-1}$)		10-1000	50-730
Feed dry composition (mol%)#	H_2	10-40	29.8
	CO	20-60	41.0
	H_2O	10-30	16.8
	CO_2	5-20	10.2
Feed steam to CO molar ratio (after added steam)		2-4	3
Feed pressure (atm)		10-40	10-40
Sweep flow rate ($mL \cdot min^{-1}$)		50-500	200
Sweep side pressure (atm)		1	1

 # Composition of coal syngas from Texaco coal gasifier, with 0.3% CH_4, 1.1% H_2S, 0.8%N_2

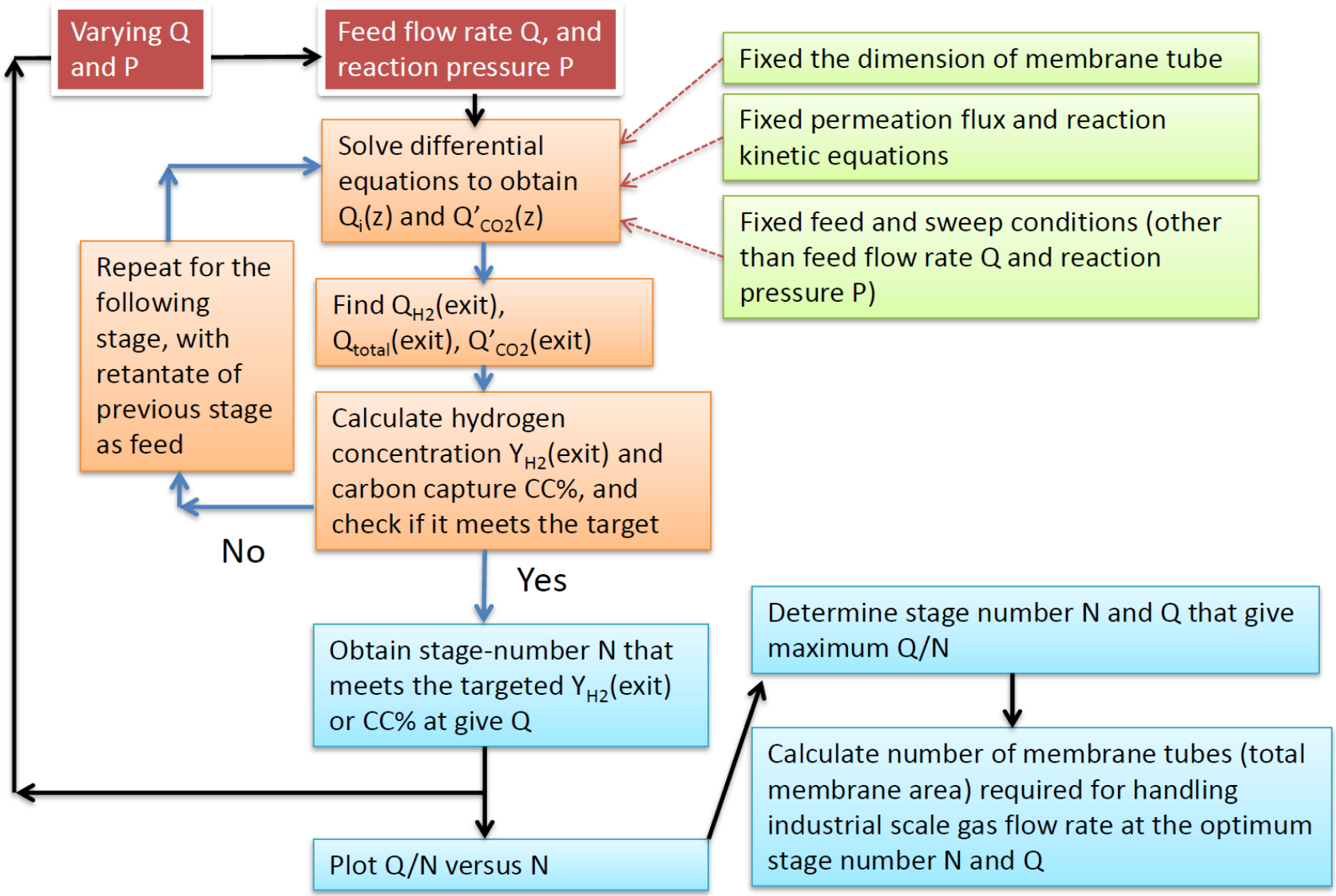
Multiple-Stage Membrane Reactor with CO_2 Capture



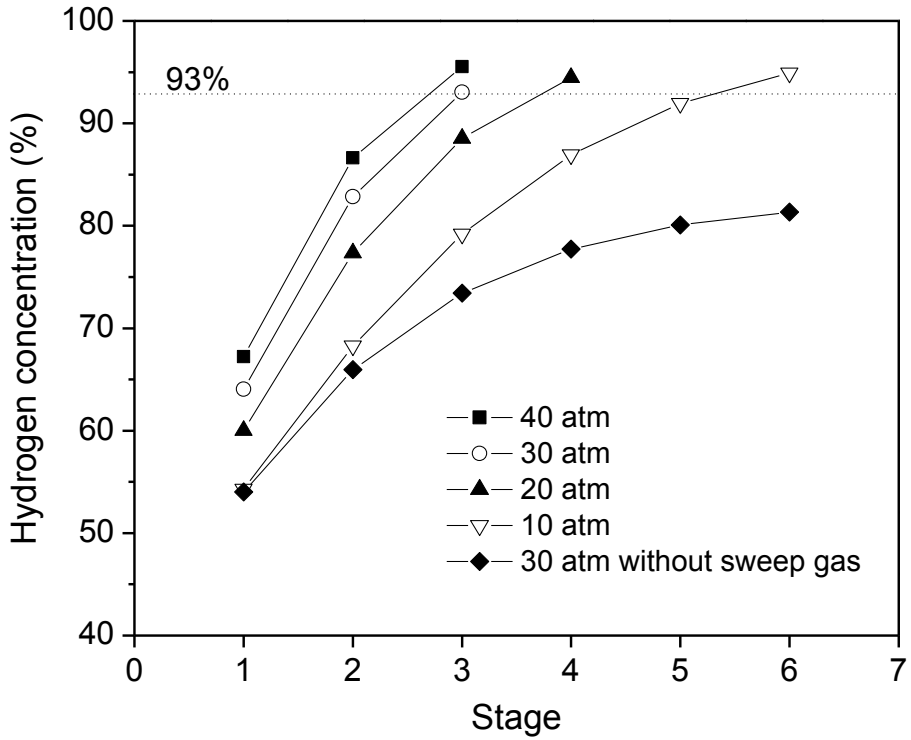
$$\text{Hydrogen Concentration, } (y_{H2(exit)}) = \frac{\text{Flow rate of } H_2 \text{ in retentate, } Q_{H2}(\text{exit})}{\text{Total dry-based flow rate of the retentate, } Q_{total(d)}\ (\text{exit})}$$

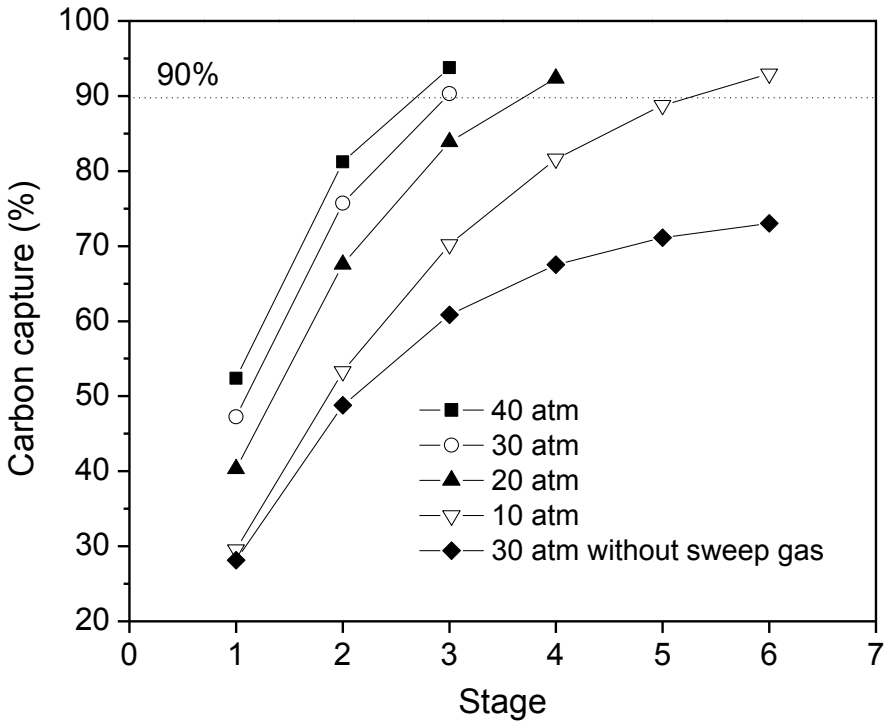
$$\text{Carbon Capture, CC\%} = \frac{\text{Flow rate of } CO_2 \text{ in the permeate, } Q'_{CO2}(\text{exit})}{\text{Total carbon species flow rate in the feed, } Q_{CO}(\text{feed})+Q_{CO2}(\text{feed})}$$

Methodology for Design of Membrane Reactor and Calculation of Membrane Area



Calculation Results



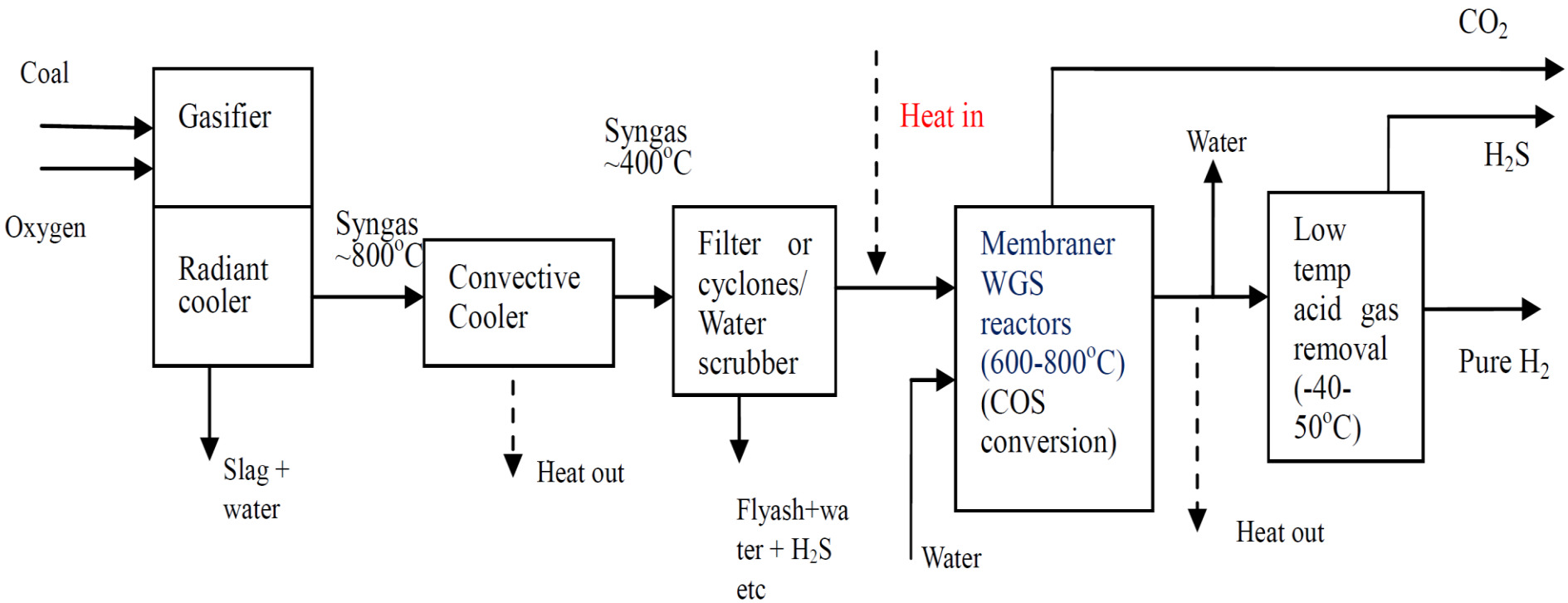


Concentration of hydrogen (dry-based) in retentate from the final stage of the multi-stage WGS membrane reactor and carbon capture operated under various feed pressures at Q_{syngas}=300 mL/min

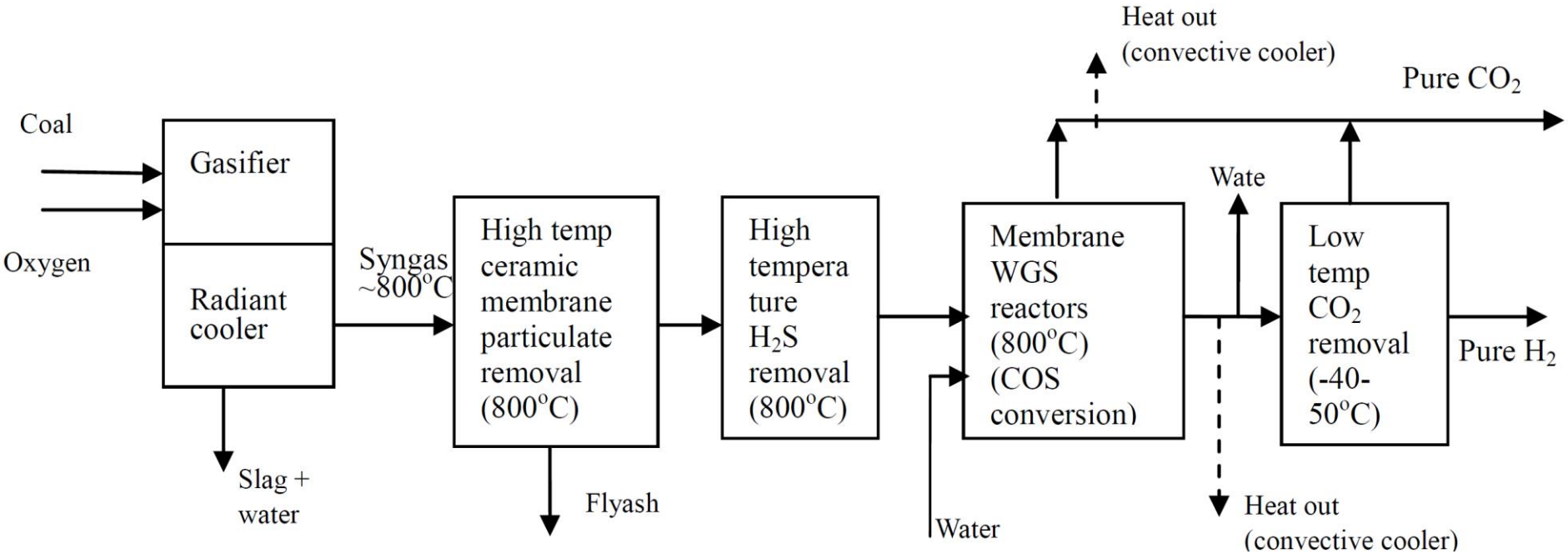
Optimized Results

Parameter		Value
Membrane		
Inner diameter of membrane (cm)		0.8
Membrane length (cm)		100
Number of stages		2
Membrane area (based on average radius/inner radius) (cm^2)		592/502
Operation Conditions		
Operation Temperature (°C)		850
Feed syngas flow rate ($mL \cdot min^{-1}$)		205
Feed syngas composition (mol%)	H_2	29.8
	CO	41.0
	H_2O	16.8
	CO_2	10.2
Flow rate of total added steam to the feed ($mL.\ min^{-1}$)		218
Feed pressure (atm)		30
Sweep steam flow rate (each stage) ($mL \cdot min^{-1}$)		200
Sweep side pressure (atm)		1
Reaction and Separation Performance		
CO conversion %		90.0
Permeate total flow rate ($mL \cdot min^{-1}$)		495
CO_2 concentration in the permeate (dry-based) (mol%)		100
Permeate composition (wet-based) (mol%)	CO_2	19.1
	H_2O	80.9
Carbon capture %		90.2
Retentate (product) total flow rate ($mL \cdot min^{-1}$)		323
H_2 concentration in retentate (product) (dry-based) (mol %)		93
Retentate composition (wet-based) (mol%)	H_2	42.23
	CO	2.6
	H_2O	54.6
	CO_2	0.5
Averaged CO_2 permeation flux ($mL.cm^{-2}.min^{-1}$)		0.16

Integration with IGCC-Process I



Integration with IGCC-Process II



Cost Estimate for Membrane Reactor

Electric Powder Production Capacity	800	MW
Efficiency of IGCC	0.4	
Higher Heating Value of Coal	12,774	Btu/lb
	23,769.84	kJ/kg
Coal Consumption Rate (mass)	67.28	kg/s
Carbon content	60	%
Percentage of Carbon converted to CO_2	85	%
Rate of CO_2 produced	2,859.40	mol/s
CO_2 Permeation Rate (90% Capture)	2,573.46	mol/s
Areas of Membranes (2 tube in series)	600	cm^2
Membrane cost	500	$\$/m^2$
CO_2 flux under optimum conditons for current membrane	0.2	cc (STP)/cm^2.min
Estimate number of 2-tube-sieries	28,822,752	
Total membrane area required	1,729,365	m^2
Estimate membrane costs	864,682,560	$

Summary and Conclusions

- CO_2 perm-selective disk and tubular ceramic-carbonate membranes were fabricated:
  - Perm-selective to CO_2 (measured selectivity up to 3000)
  - Chemically/thermally stable
  - CO_2 permeance in $0.5\text{-}5\times10^{-7}$ mol/m^2.s.Pa at 500-900°C
- CO_2 permeation mechanism and factors affecting CO_2 permeation of the dual-phase membranes have been identified.
- WGS reaction in the dual-phase membrane reactor was studied by modeling and experiments. Conditions to produce hydrogen of 93% purity and CO_2 stream of > 95% purity, with 90% CO_2 capture have been identified
- Dual-phase membrane reactor can improve IGCC process efficiency but the membrane reactor is too expensive with membranes having current CO_2 permeance.

Other Accomplishments

- Refereed Journals: 12 SCI Papers Published
- Presentations: 15
  - Including ICIM2014 Plenary Lecture
- Patents: 1 US Patent Application Filed
- Ph.D. Students Trained: 3
  - Matt Anderson
  - Norton Tyler
  - Bu Lu
- Post-Dr. Trained: 3
  - Xueliang Dong
  - Jose Ortis-Lenderos
  - Zebao Rui

THANK YOU
Palm
Walk