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

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Project Objectives

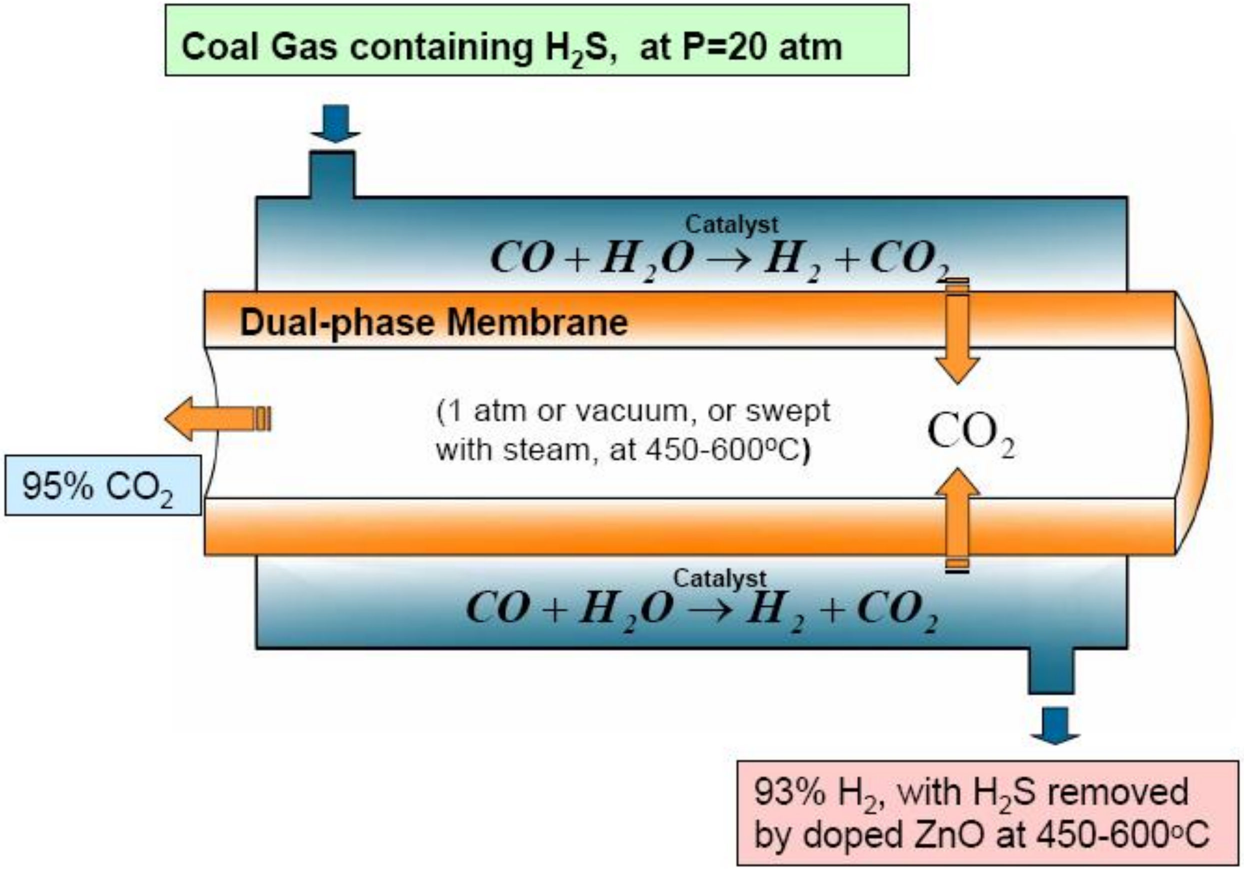
1. Synthesize chemically/thermally stable dual-phase ceramic-carbonate membranes with CO_2 permeance and CO_2 selectivity (with respect to H_2, CO or H_2O) larger than $5x10^{-7}$ mol/m^2.s.Pa and 500;

2. Fabricate tubular dual-phase membranes and membrane reactor modules suitable for WGS membrane reactor applications:

3. 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.

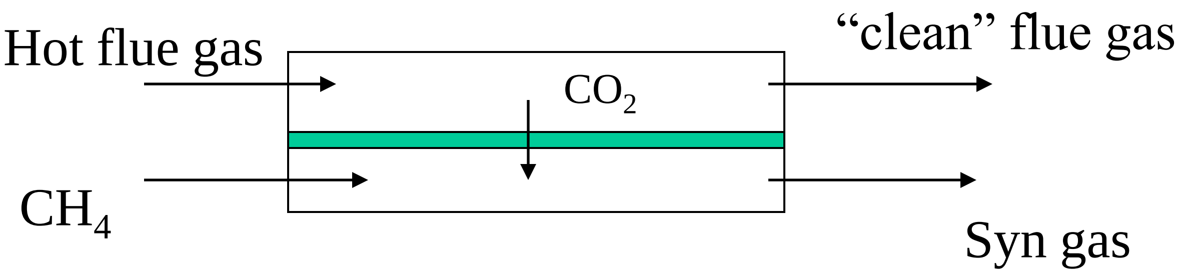
Technology Fundamentals/Background

Proposed Membrane Reactor for WGS Reaction



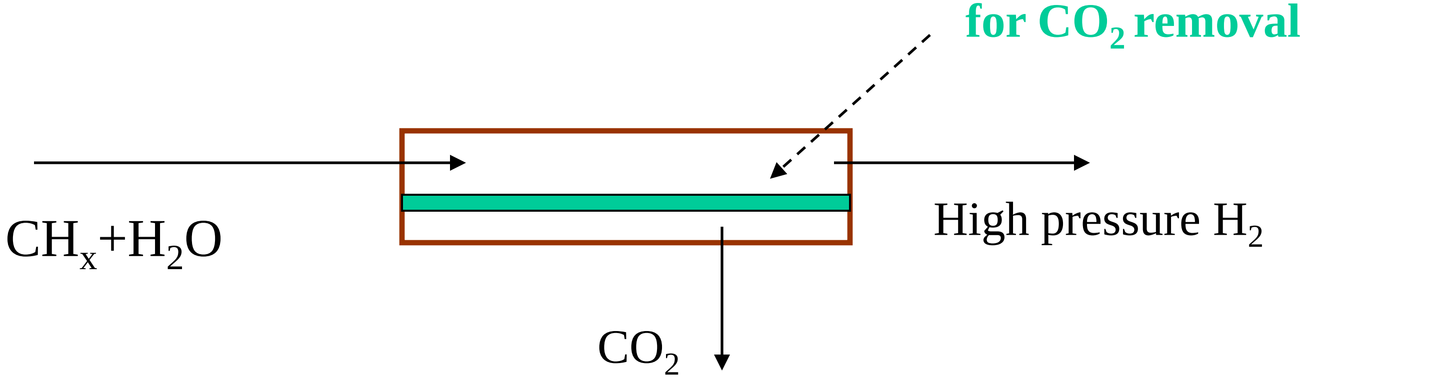
High Temperature CO_2 Selective Membranes

- Post-combustion CO_2 capture at higher temperatures

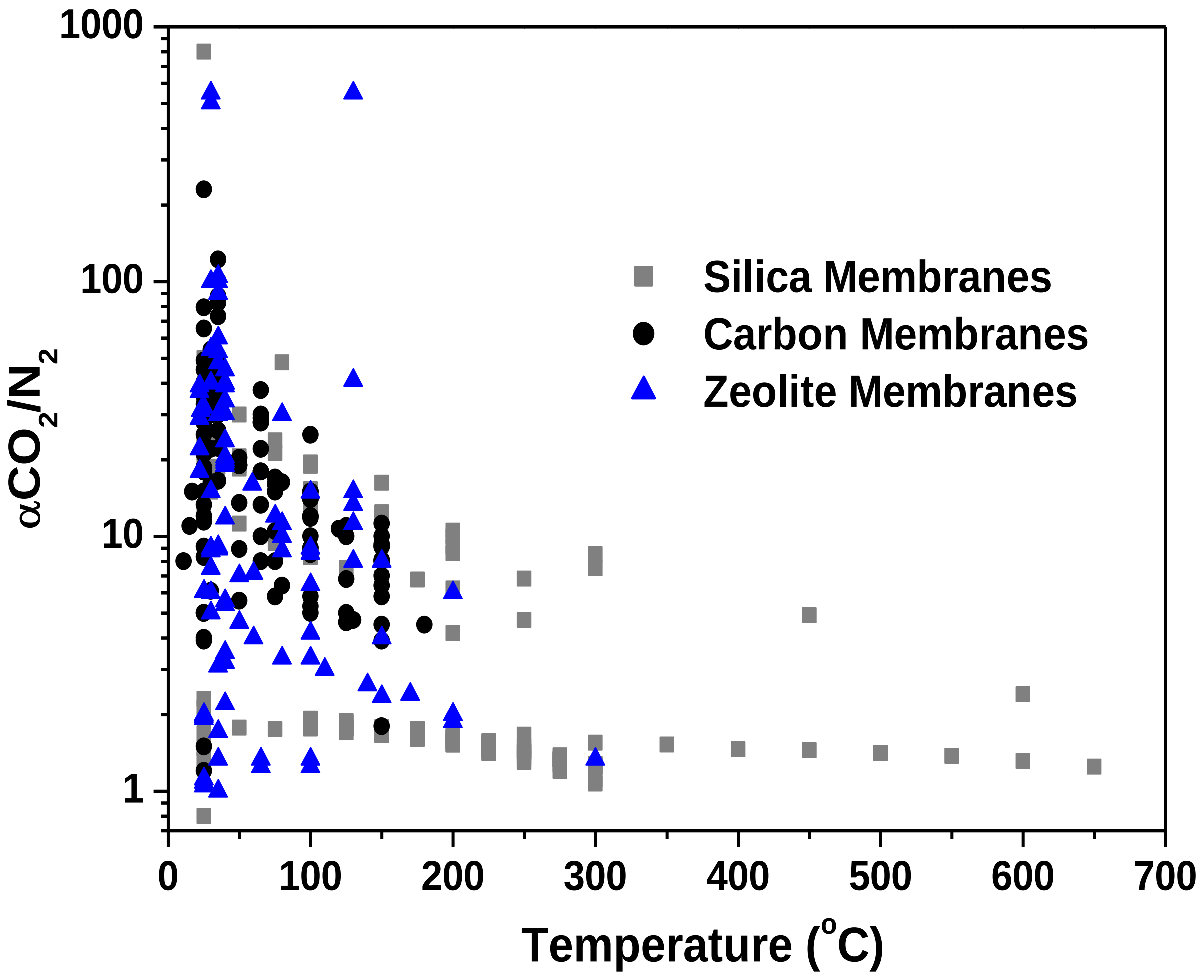


- Reforming reaction with CO_2 removal

$$CH_x + H_2O \Rightarrow H_2 + CO_2$$



CO_2 Perm-Selective Inorganic Membranes



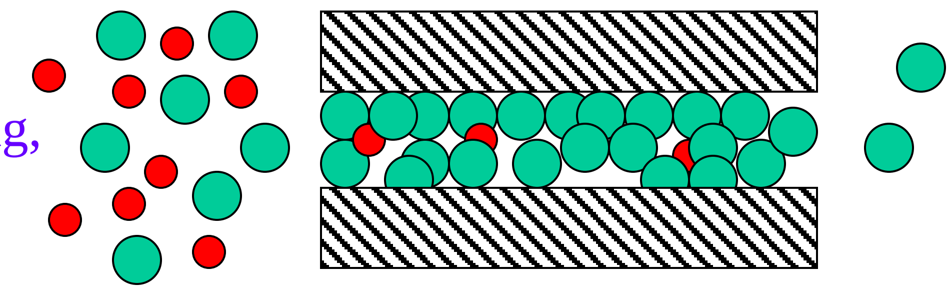
- Microporous membranes made from silicas, carbons and zeolites are capable of separating CO_2 from N_2 at low temperature
- Ultrathin, ion exchanged Y-type zeolites are best candidates for low temperature separation
- CO_2/N_2 selectivity decreases with increasing temperatures

Separation Mechanism - Adsorption & Diffusion

F = [Solubility][Diffusivity]

Adsorption Dominating

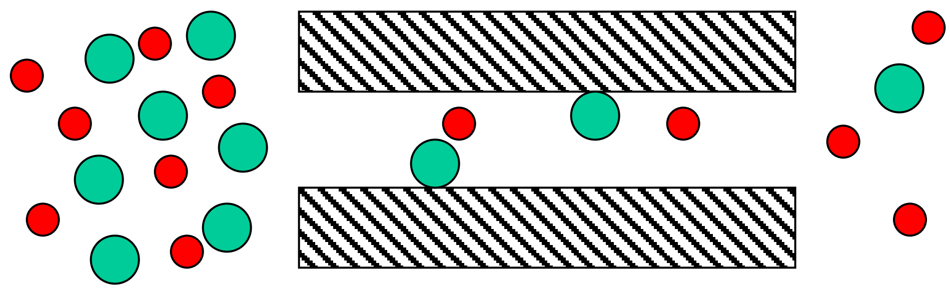
(strongly adsorbing, low temperature)



$$\alpha_{1/2} \propto \frac{S_1}{S_2}$$

Diffusion Dominating

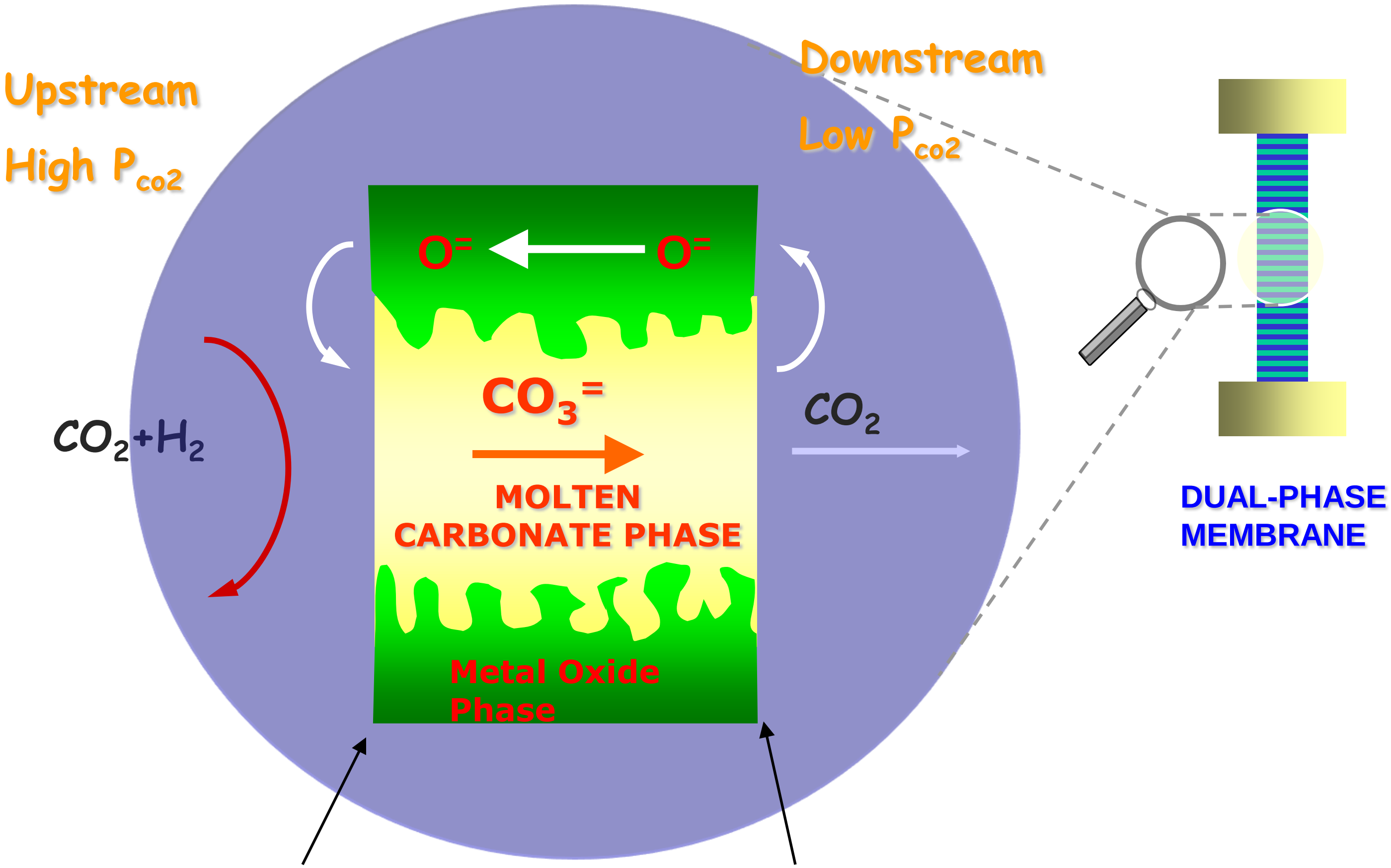
(non-adsorbing, or high temperature)



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

At high temperature diffusion controlled selectivity for or CO_2/H_2 is less than 1 for microporous membranes

Concept of Dual-Phase Membrane



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

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

Progress and
Current Status of Project

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 Economic Analysis

Oxygen Ionic Conducting Metal Oxide Supports

Material	Abbr-eviation	Structure	$O^{=}$ conduct-ivity σ_i (600°C) (S/cm)	Transference 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

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 (^oC)	397	488	501	710
$CO_3^=$ Conductivity (S/cm)	1.24	1.15	1.75	1.17

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Synthesis of Porous Ceramic Supports

Synthesis of ceramic powder by citrate or other method

↓

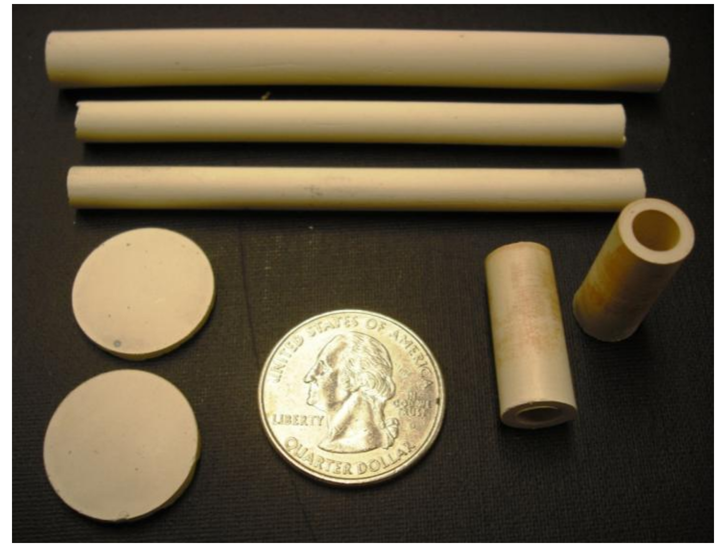
Calcination/heat-treatment to obtain desired phase

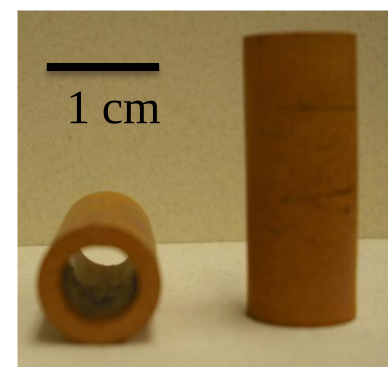
↓

Press or centrifugal casting to obtain disks, tubes or hollow fibers

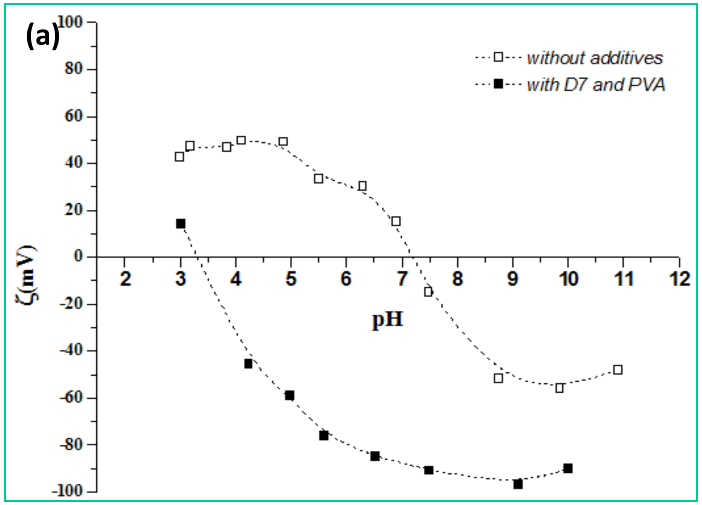
↓

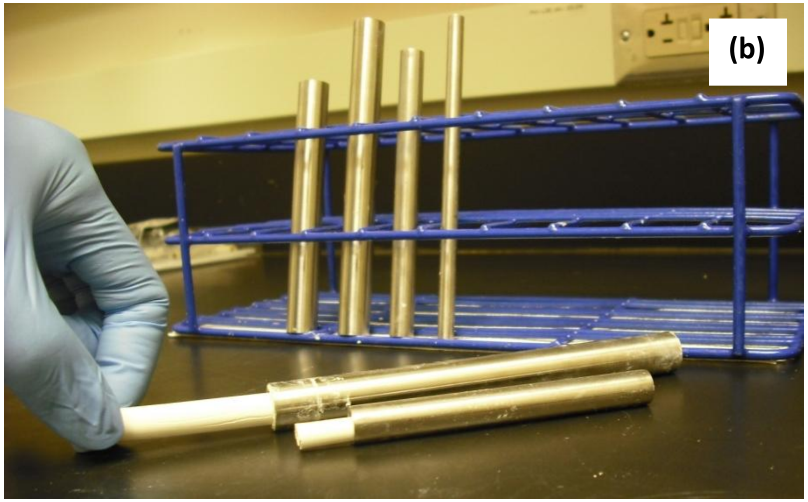
Sintering to strengthen structure and obtain desired porosity

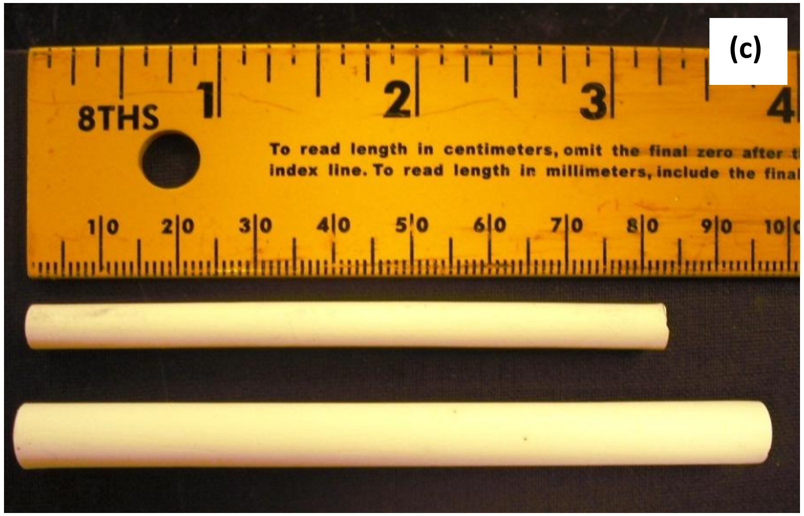




Porous Tubular Support via Centrifugal Casting



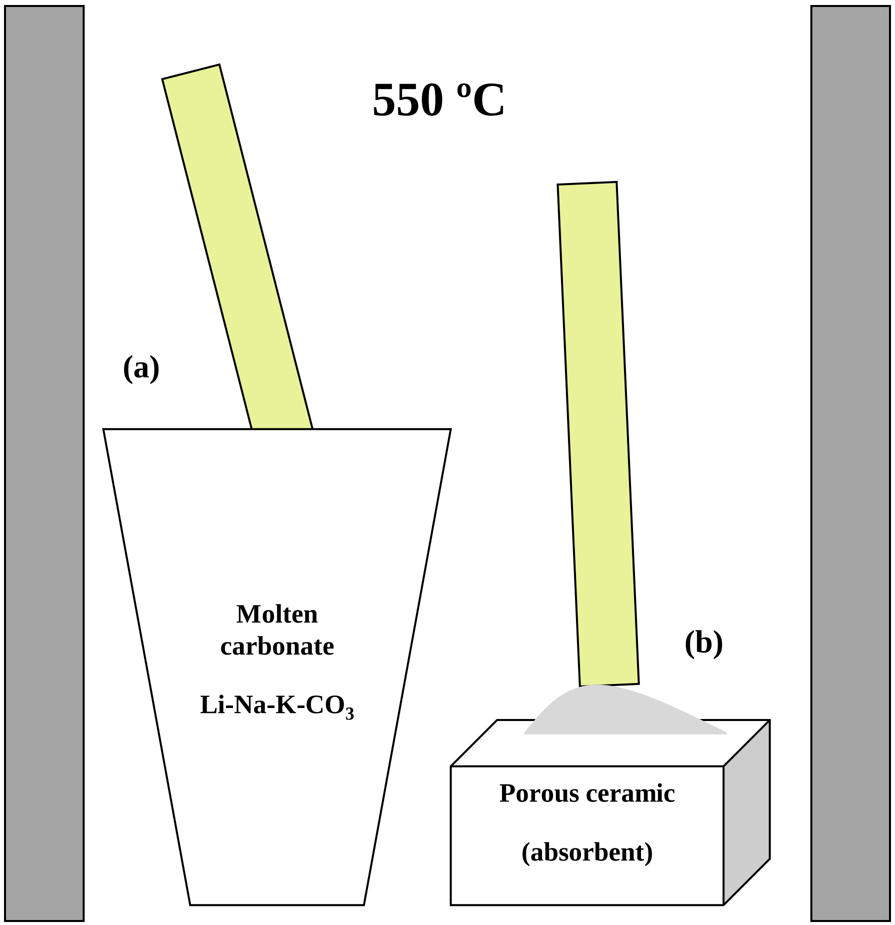




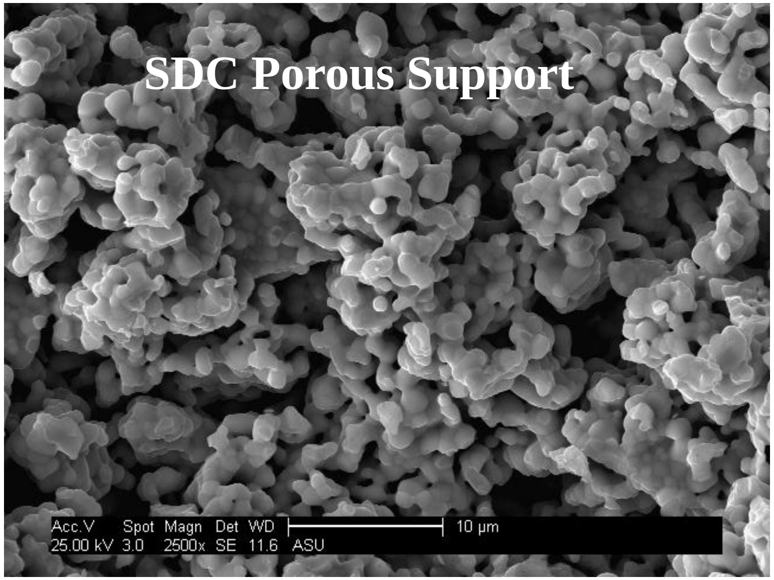
- Preparation of stable suspensions
- Centrifugal casting process
- Drying under controlled conditions
- Sintering

Synthesis of Tubular Dual-Phase Membrane

- The Li/Na/K molten carbonate mixture was heated to 550°C in a vertical tube furnace
- The tubular support is immersed into the molten carbonate and left for 30 minutes
- Infiltration occurs via capillary forces within the pores of the support
- The excess of carbonate remained in the bore of the tube is removed by using and absorbent material



Dual-Phase Membrane Characteristics



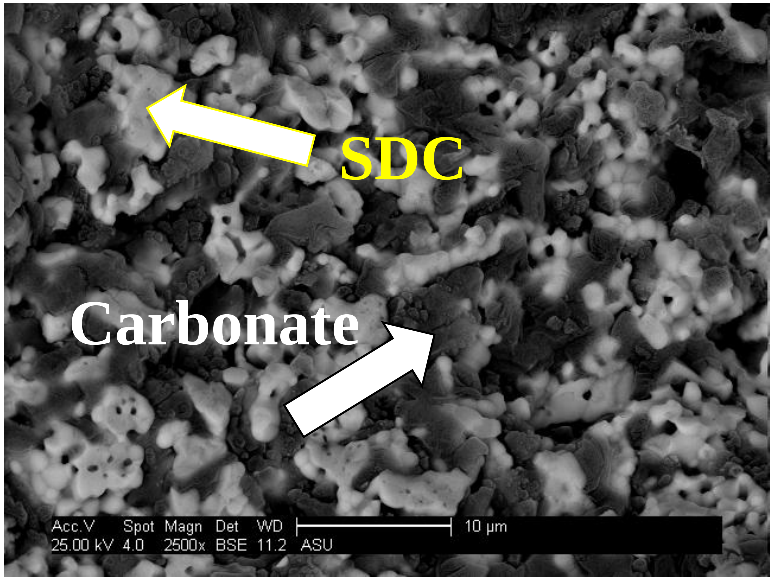
- **He permeance of support:**

  ~ 10^{-6} mol/m^2·s·Pa

- **After infiltration of carbonate:**

  - He permeance:

  <10^{-10} mol/m^2·s·Pa



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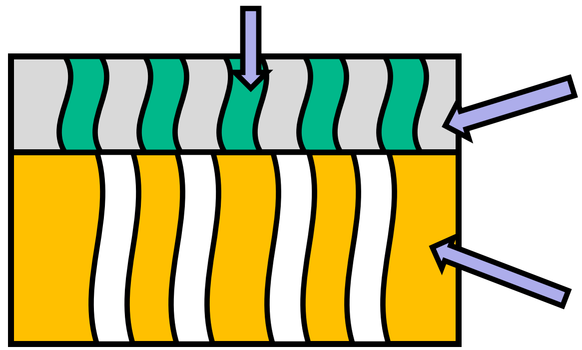
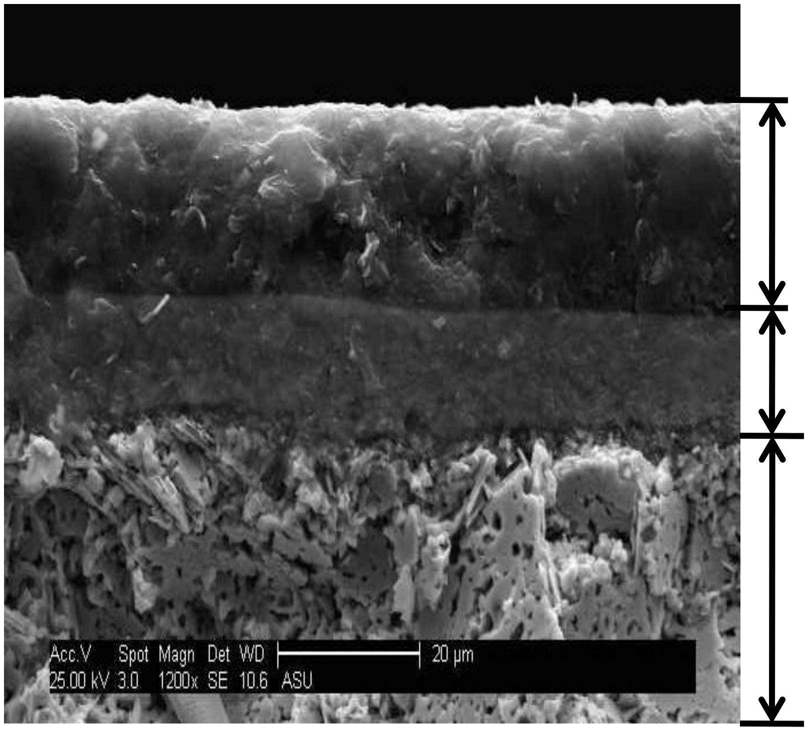
Synthesis of Thin Dual-Phase Membranes



- Macroporous top layer (YSZ, SDC, LSCF)
- Stable suspension prepared from ball-milling technique with optimum milling time, pH, and solution concentration
- Increase the CO_2 permeance to 10^{-7} mol /$m^2 \cdot s \cdot Pa$ and decrease separation temperature to 500-700°C

Characterization of Macroporous YSZ Layer

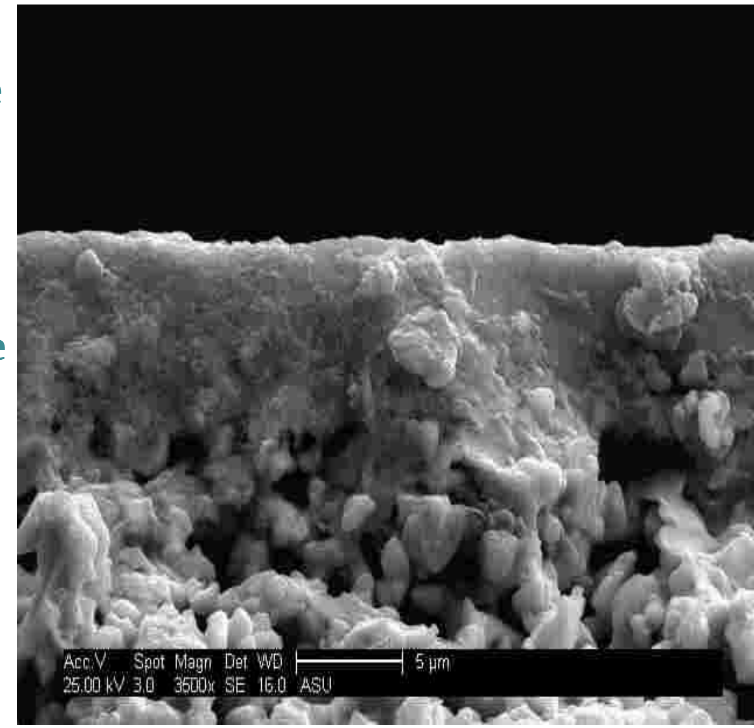


Carbonate residuals ~ 20 μm

Dual phase thin film ~ 10 μm

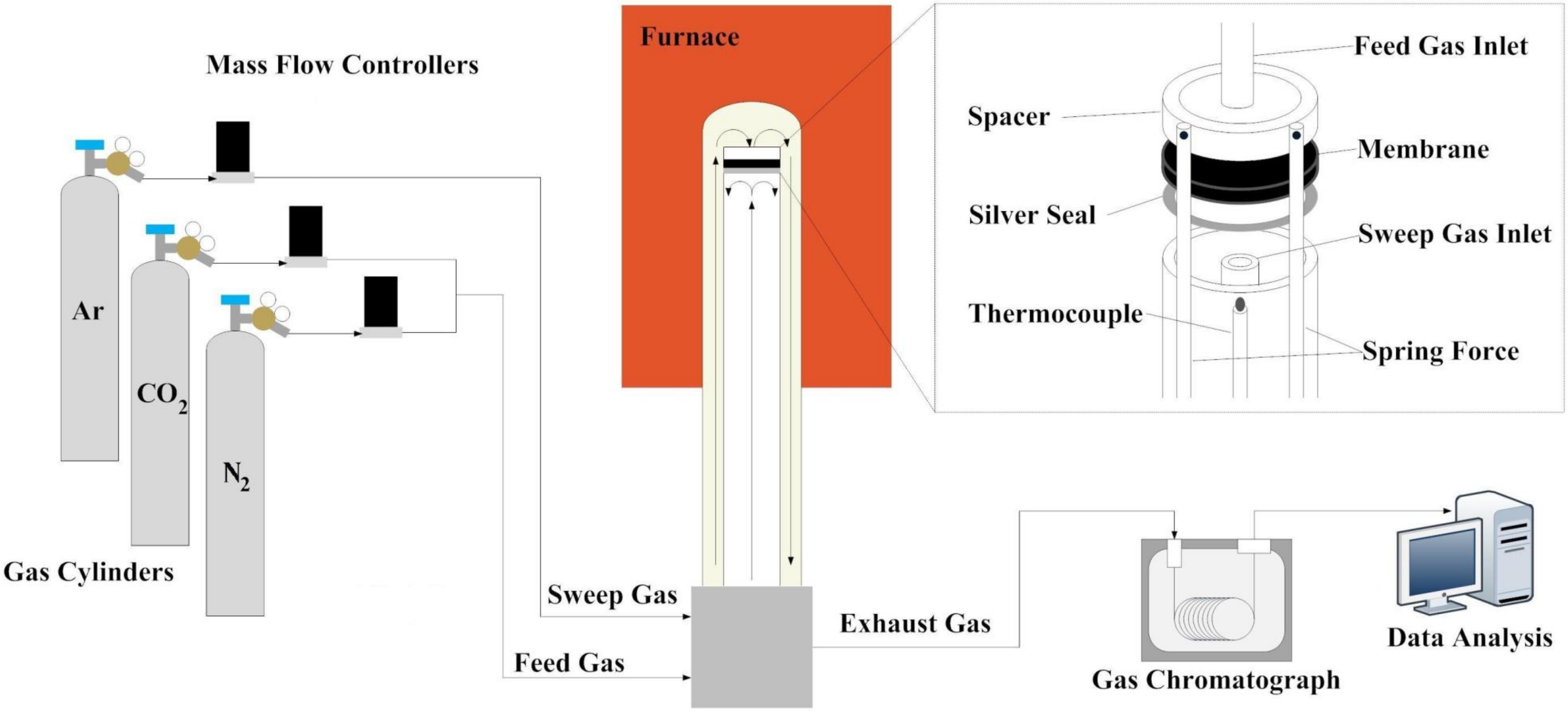
BYS Support

Cross section of YSZ-Carbonate thin film dual phase membrane

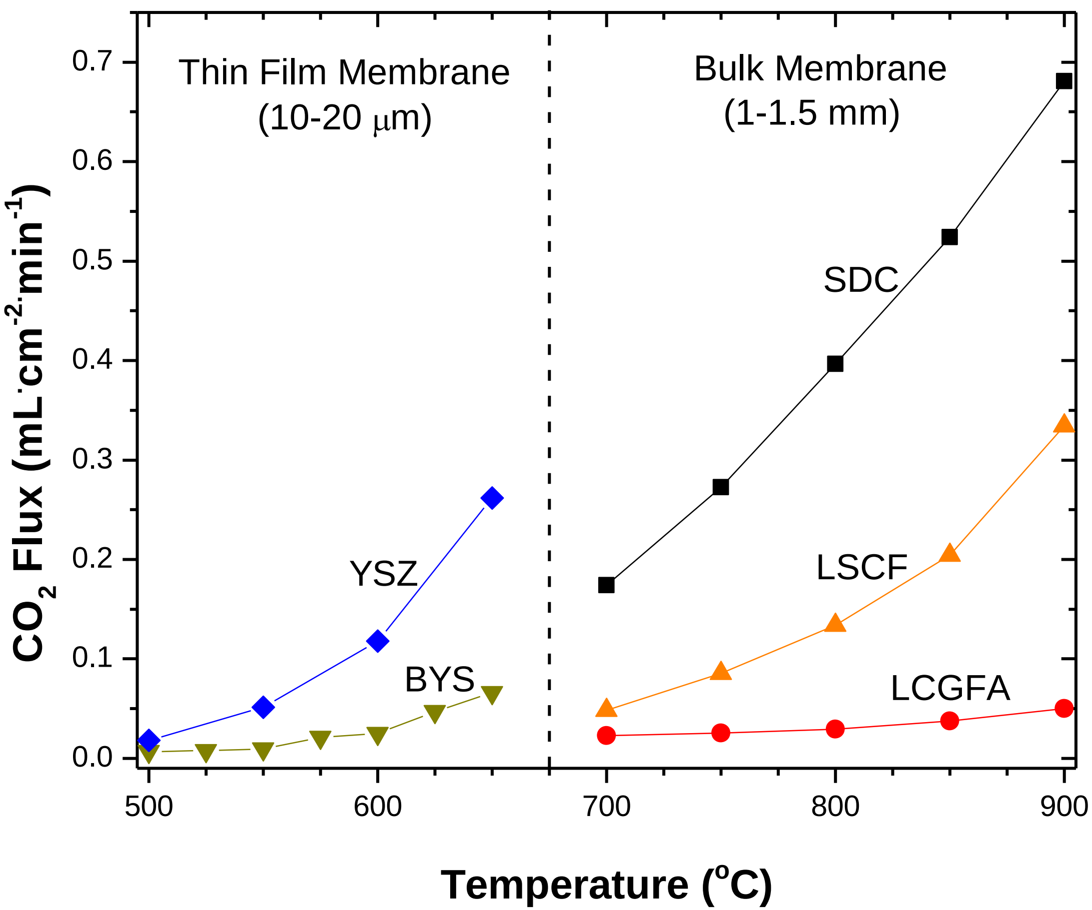


SEM image of thin dual-phase membrane after treatment

High Temperature Permeation Measurements



Carbon Dioxide Permeance



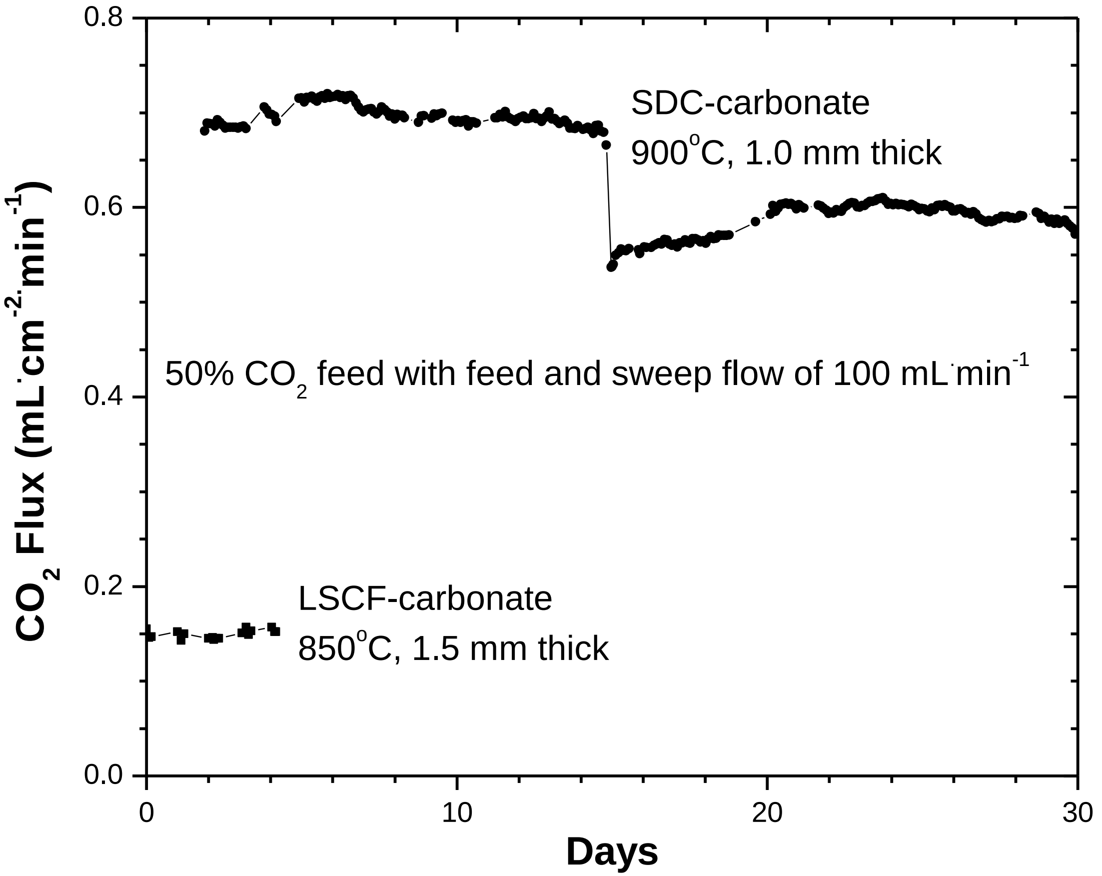
- **All ceramic supports infiltrated with Li/Na/K molten carbonate**
- **Feed CO_2 concentration of 50% (YSZ tested with 25%)**
- **Feed and sweep flow rates of 100 $mL \cdot min^{-1}$**

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} $mol/m^2.s.Pa$

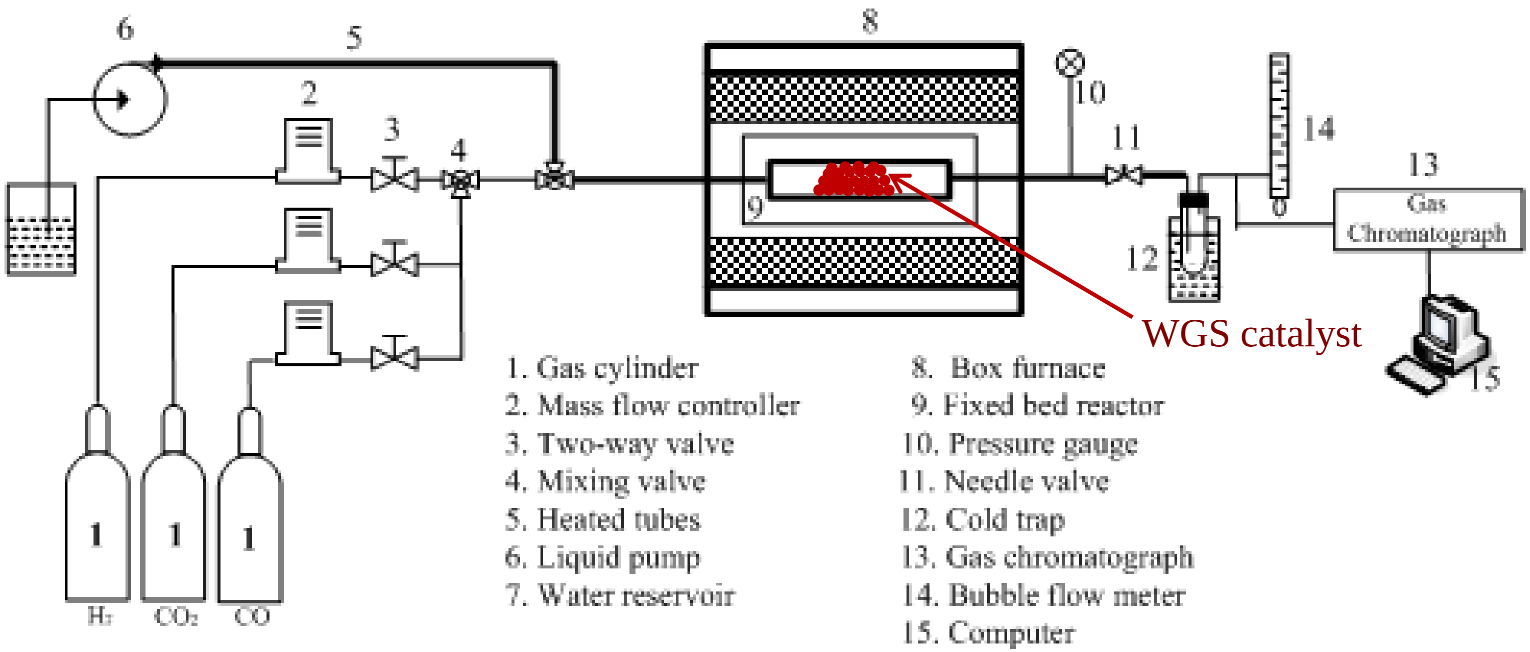
$\alpha_{CO2/N2}$ =500-3000

Membrane Permeation and Chemical Stability



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

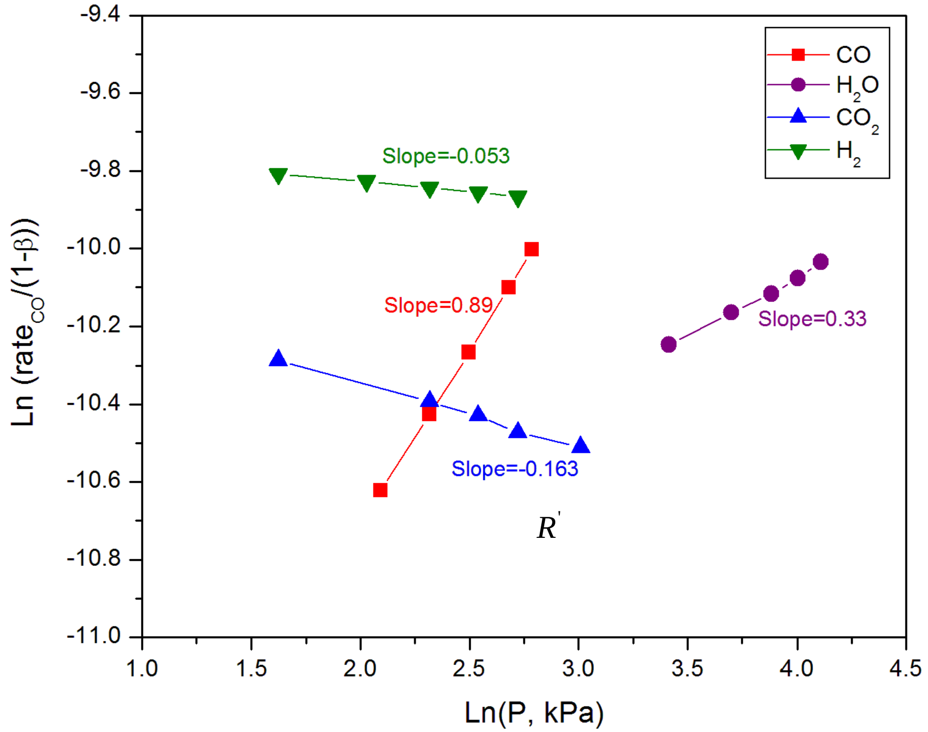
Kinetic Study of WGS Catalyst



Schematic of the setup used for kinetic study of WGS catalyst

- WGS catalyst: $Fe_{1.82}Ce_{0.18}O_3$ spinel oxide
- Testing temperature: 500°C
- Pressure in the fixed bed: 101 kPa
- Total gas flow rate: 80 cc/min

WGS Catalyst Kinetics



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

R': Gas constant

CO_2 Flux Equation and Membrane Reactor Model

- **CO_2 permeation equation:**

$$J_{CO_2} = \frac{\varepsilon_{MC}}{H\tau_{MC}} \frac{C_C D_C RT\sigma_{V^{\bullet\bullet}}}{\frac{\varepsilon_{MC}\tau_{SO}}{\tau_{MC}\varepsilon_{SO}} z_{V^{\bullet\bullet}} z_C C_C D_C F^2 - RT\sigma_{V^{\bullet\bullet}}} \ln \frac{P''_{CO_2}}{P'_{CO_2}}$$

- **Membrane reactor model:**

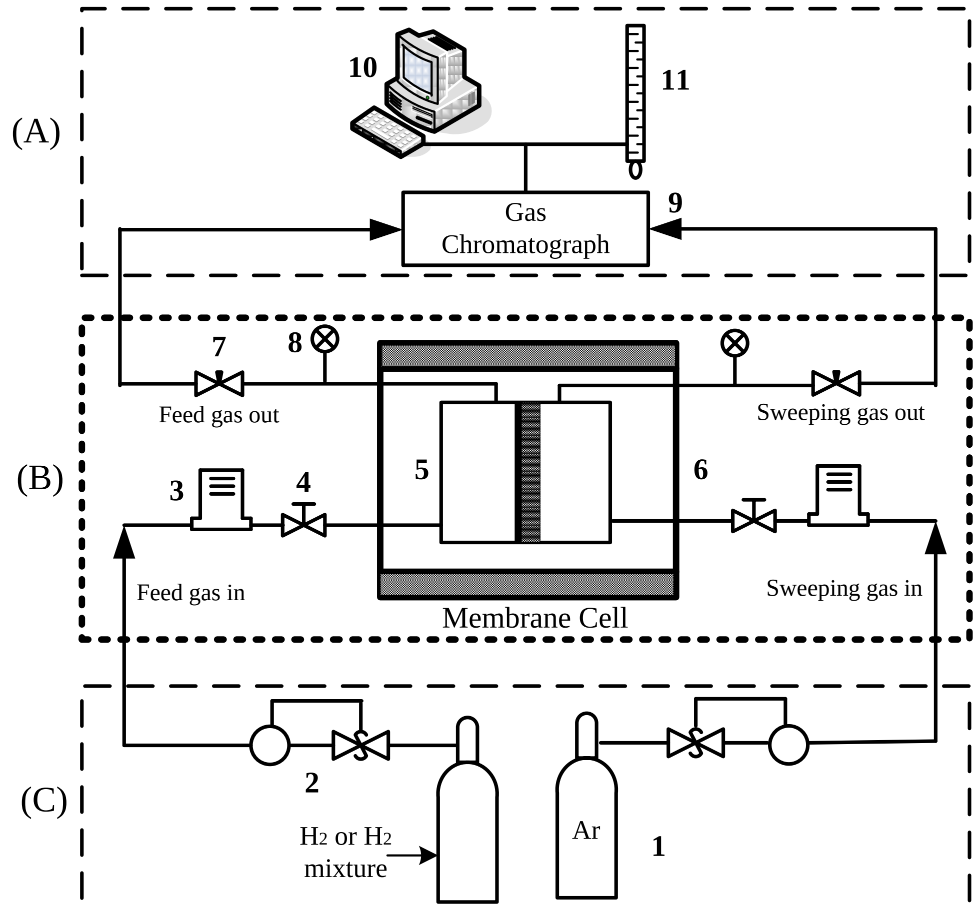
$$\frac{dQ_{CO_2}}{dl} = -\pi r_i^2 \rho_B R + 2\pi r_i J_{CO_2}\Big|_{r=r_i}$$

$$\frac{dQ_j}{dl} = -\pi r_i^2 \rho_B R$$

j=1, 2, ..
for all other species in WGS except for CO_2

where R is reaction rate given on previous slide

High Temperature/Pressure Reactor System



1. High pressure gas supply system
2. High pressure gas regulator
3. High pressure mass flow controller
4. Two-way valve
5. Gas permeation cell
6. Box furnace
7. Needle valve
8. Pressure gauge
9. Gas chromatograph
10. Computer
11. Bubble flow meter

A: Measurement & Analysis Module

B: Gas Permeation & Separation Module

C: High Pressure Gas Supply Module

- **Membrane reactor type:**
  Disk and tubular
- **Designed operation conditions:**
  Temperature: up to 700°C
  Pressure: up to 20 atm

Future Testing/Development Work

Project Schedule

Year/Quarter Task	Year 1				Year 2				Year 3				Year 4			
Task A Synthesis of Dual-Phase Membrane Disks	X	X	X	X												
Task B Studying Permeation and Separation Properties of Disk Membranes (Phase I)		X	X	X	X	X										
Task C Synthesis of Tubular Dual-Phase Membranes (Phase I)				X	X	X	X	X								
Task D Gas Separation and Stability Study on Tubular Membranes (Phase I)						X	X	X	X	X	X	X				
Task E Synthesis and WGS Reaction Kinetic Study of High Temperature Catalyst (Phase II)									X	X	X	X				
Task F Modeling and Analysis of Dual-Phase Membrane Reactor for WGS (Phase II)										X	X	X	X			
Task G Experimental Studies on WGS in Dual-Phase Membrane Reactors (Phase II)													X	X	X	X
Task H. Economic Analysis (Phase II)														X	X	X
Task I. Project Management	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

Summary

- Various ceramic-carbonate dual-phase (disk and tubular) membranes prepared.
- Prepared dual-phase membranes showed excellent CO_2 selectivity, good CO_2 permeance and performance.
- Progress made on synthesis and CO_2 permeation of thin dual-phase membranes .
- WGS reaction kinetics and flux equations obtained. Modeling on membrane reactor for WGS is on going.