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

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&

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Project Overview

Funding:

DOE Fund: $656,316

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

ASU Cost-Share: $164,088

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

Overall Project Performance Dates:

Oct.1, 2009 - Sept.31, 2013

Project Participants:

Arizona State University

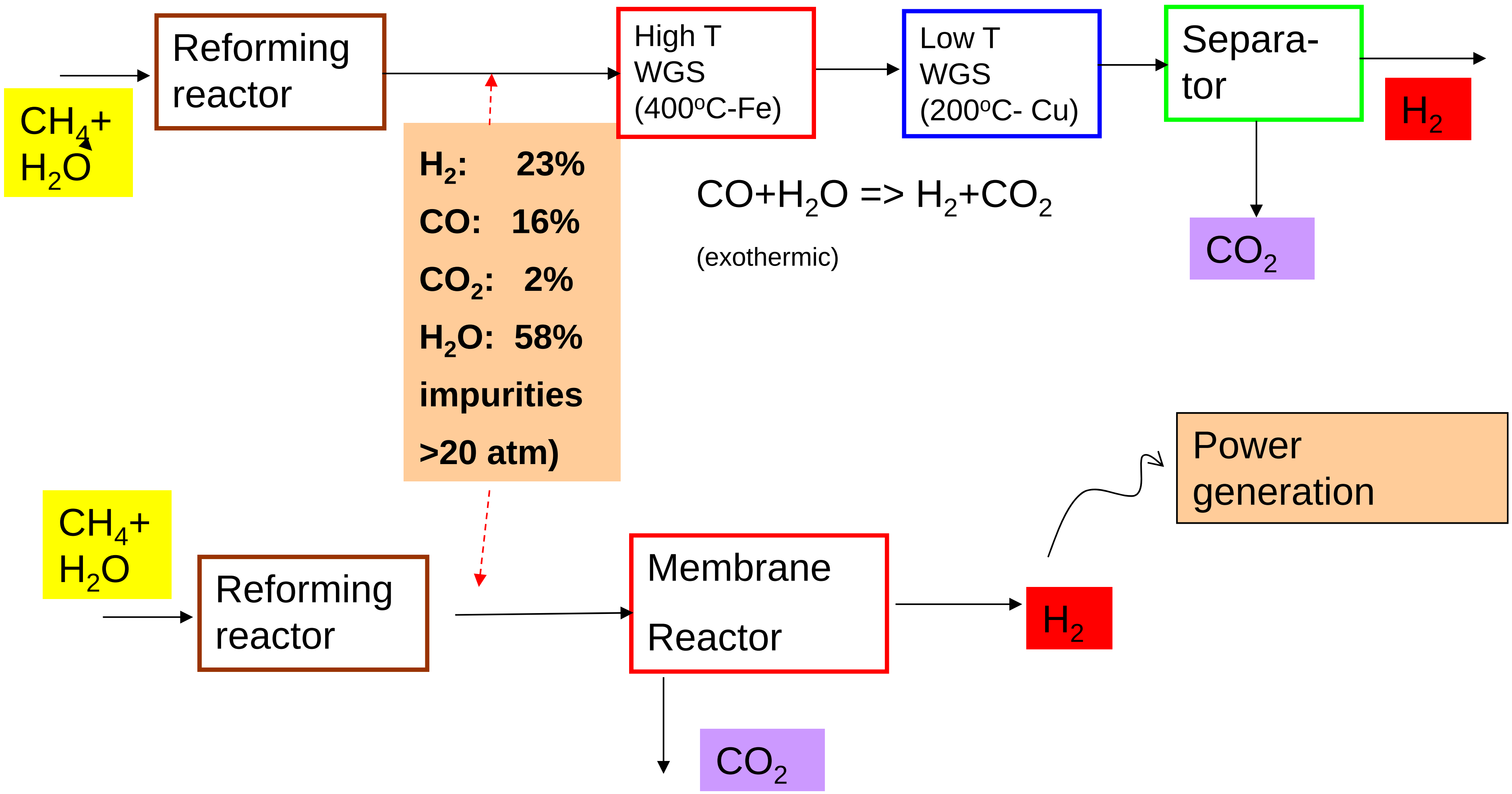
ASU

Project Objectives

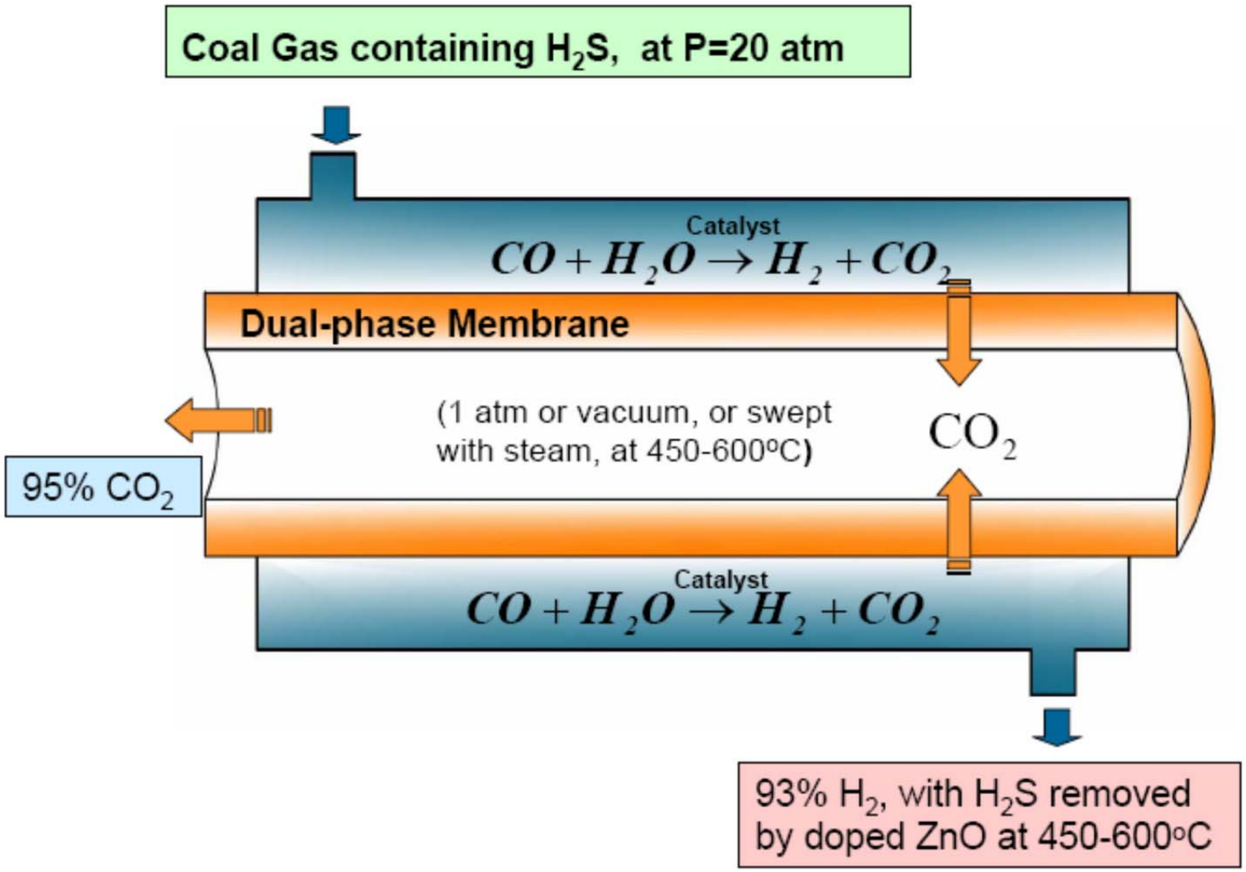
1. Synthesize chemically/thermally stable dual-phase ceramic-carbonate membranes with CO_2 permeance and CO_2 selectivity (with respect to H_2, CO or H_2O) larger than $5x10^{-7}$ mol/m^2.s.Pa and 500;
2. Fabricate tubular dual-phase membranes and membrane reactor modules suitable for WGS membrane reactor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

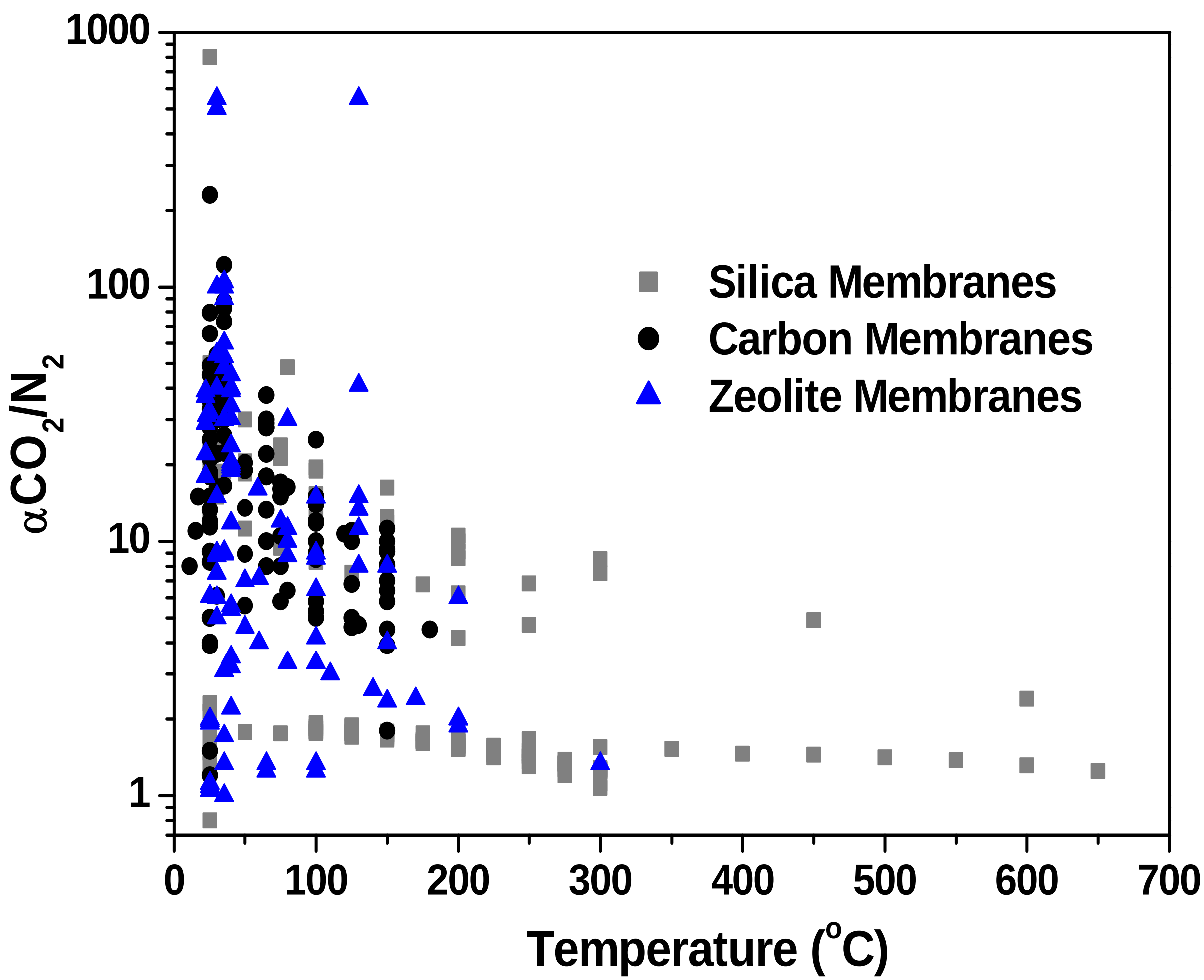
Water-Gas-Shift Reaction and Membrane Reactor



Proposed Membrane Reactor for WGS Reaction



CO_2 Perm-Selective Inorganic Membranes



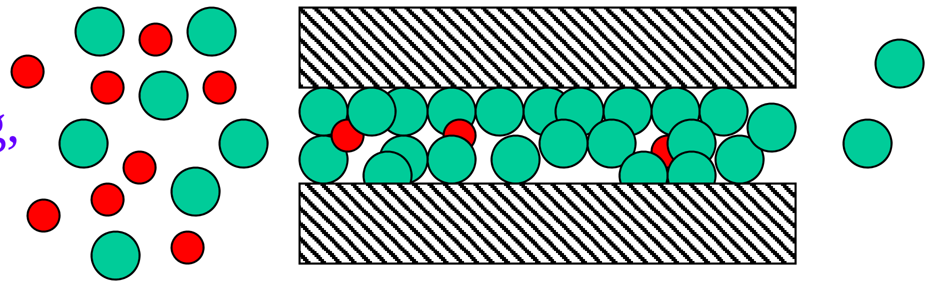
- **Microporous membranes made from silicas, carbons and zeolites are capable of separating CO_2 from N_2 at low temperature**
- **Ultrathin, ion exchanged Y-type zeolites are best candidates for low temperature separation**
- **CO_2/N_2 selectivity decreases with increasing temperatures**

Separation Mechanism - Adsorption & Diffusion

F = [Solubility][Diffusivity]

Adsorption Dominating

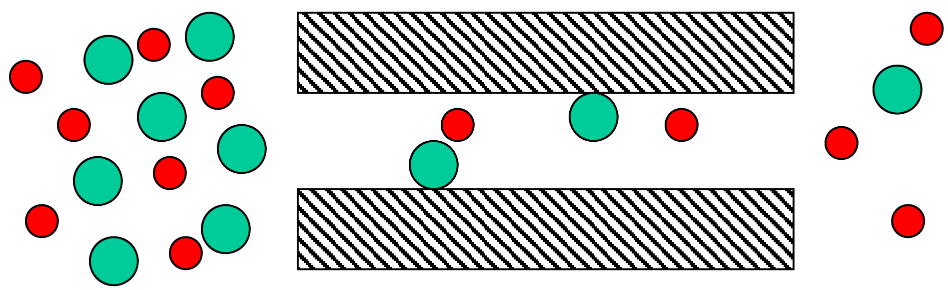
(strongly adsorbing, low temperature)



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

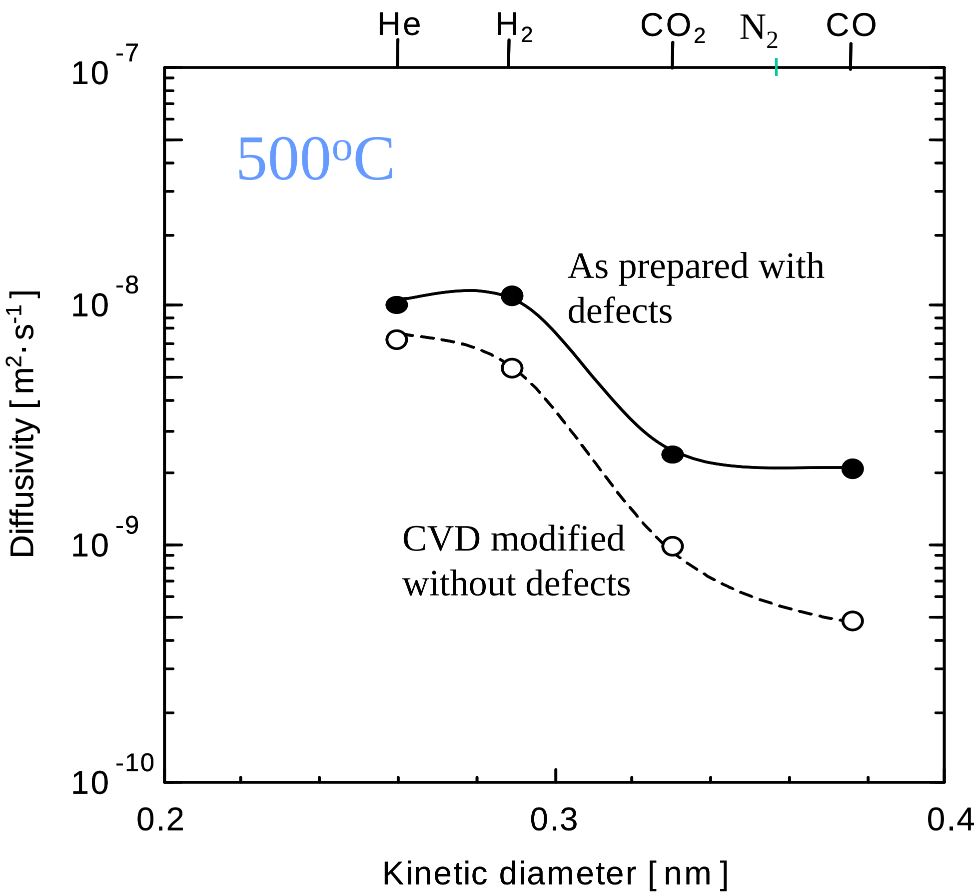
Diffusion Dominating

(non-adsorbing, or high temperature)



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

Gas Diffusivity through Microporous Material at High Temperatures



Measured on DDR zeolite membranes with d_{pore}=0.35-0.44 nm

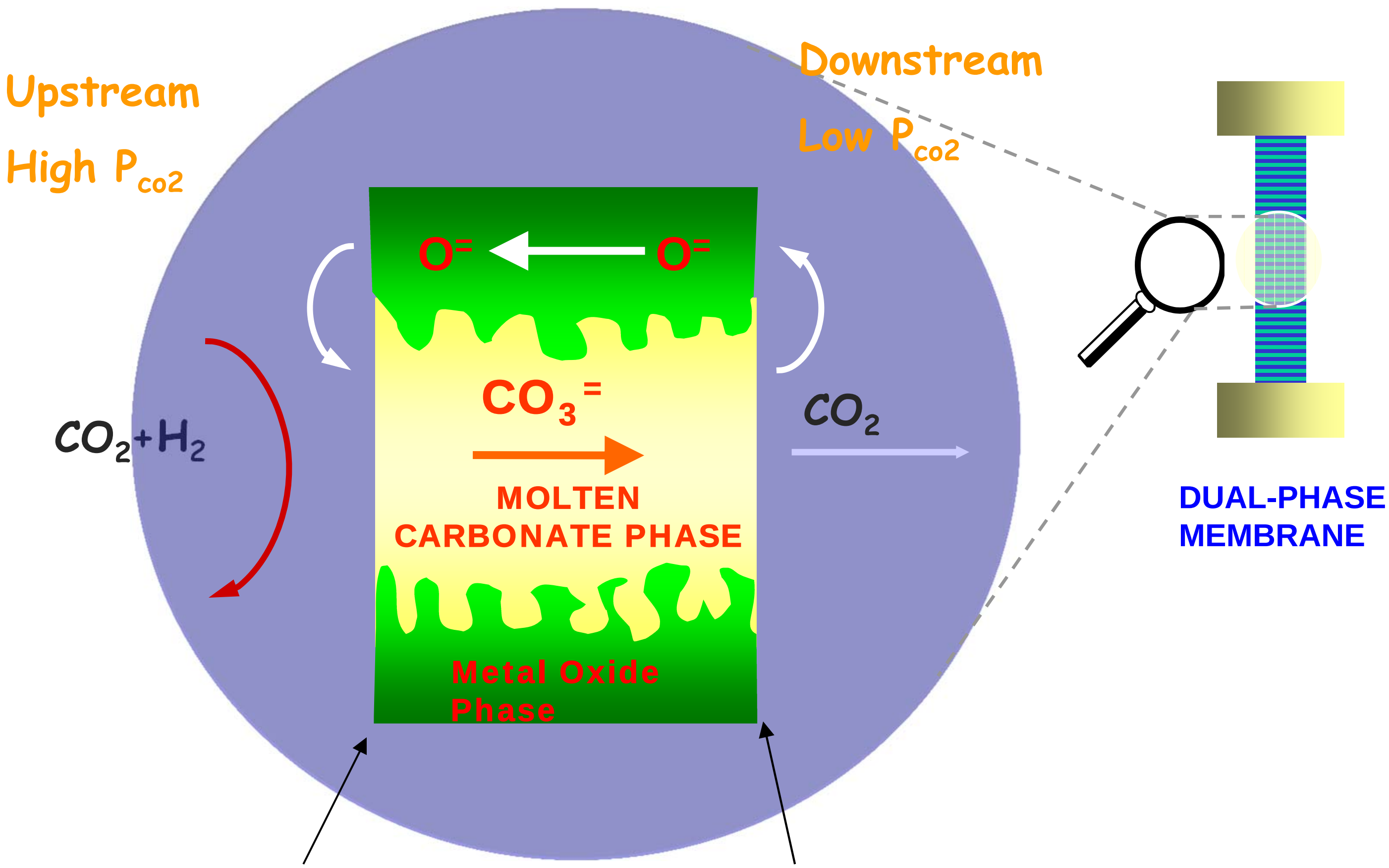
Diffusion controlled selectivity for CO_2/N_2 is less than 2

Kanezashi, Lin et al, AIChE J (2008)

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

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	Abbre-viation	Structure	$O^{=}$ conduct-ivity σ_i (600°C) (S/cm)	Transference number t_i
$LaSrCoFeO_3$	LSCF	Perovskite	~0.02	~ 0.01
$LaCoGaFeAlO_3$	LCGFA	Perovskite	~0.01	~ 0.02
$BiYSmO_2$	BYS	Fluorite	~0.08	~ 0.9
$YZrO_2$	YSZ	Fluorite	~0.004	~ 1.0

$\sigma_{CO3=}$ ~ 1 S/cm for molten carbonate at 600°C

Synthesis of Porous Ceramic Supports

Synthesis of ceramic powder by citrate or other method

↓

Calcination/heat-treatment to obtain desired phase

↓

Press or extrusion to obtain disks, tubes or hollow fibers

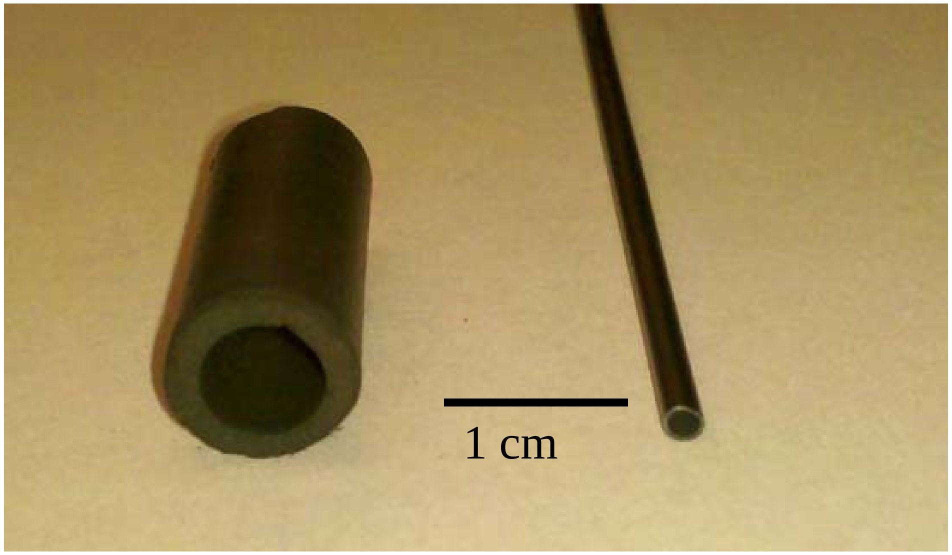
↓

Sintering to strengthen structure and obtain desired porosity

LSCF Powder

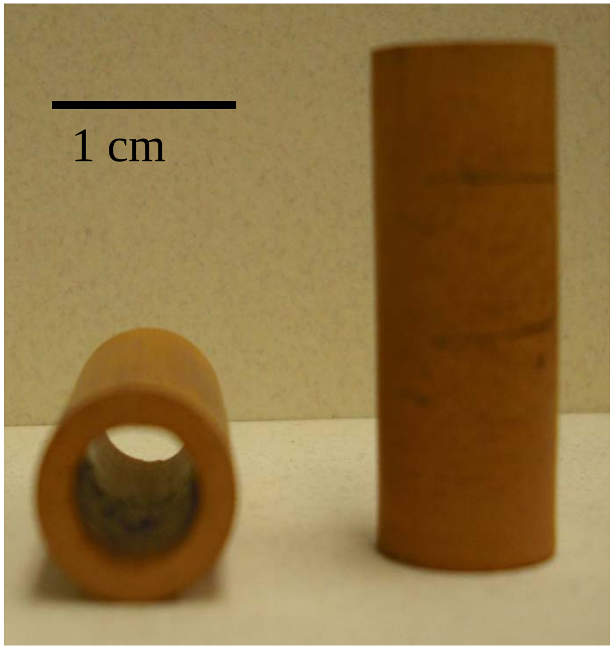
LSCF disk for lab tests

Synthesis of Porous Tubular Supports



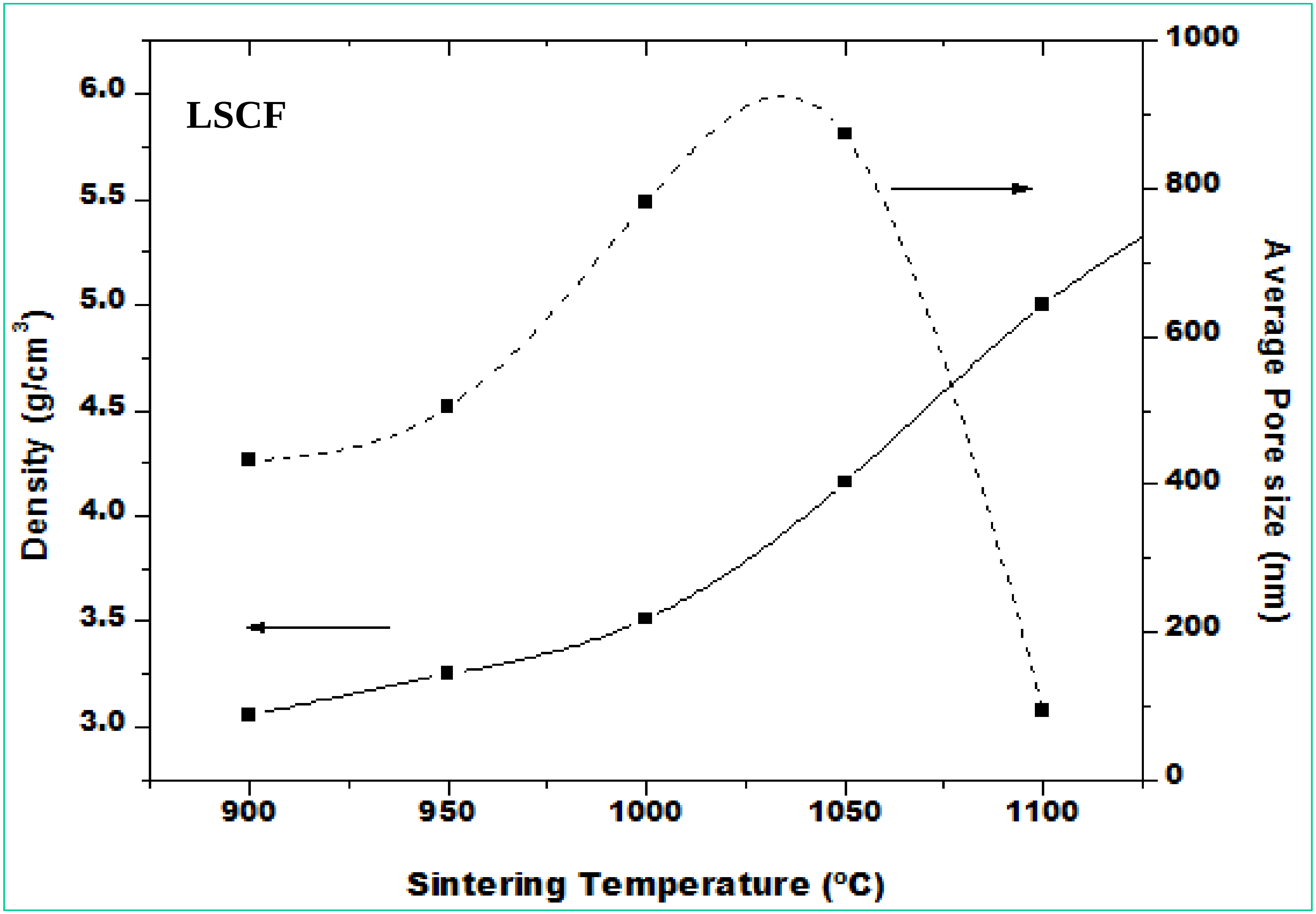
LSCF tubes or hollow fibers*

LCGFA tubes

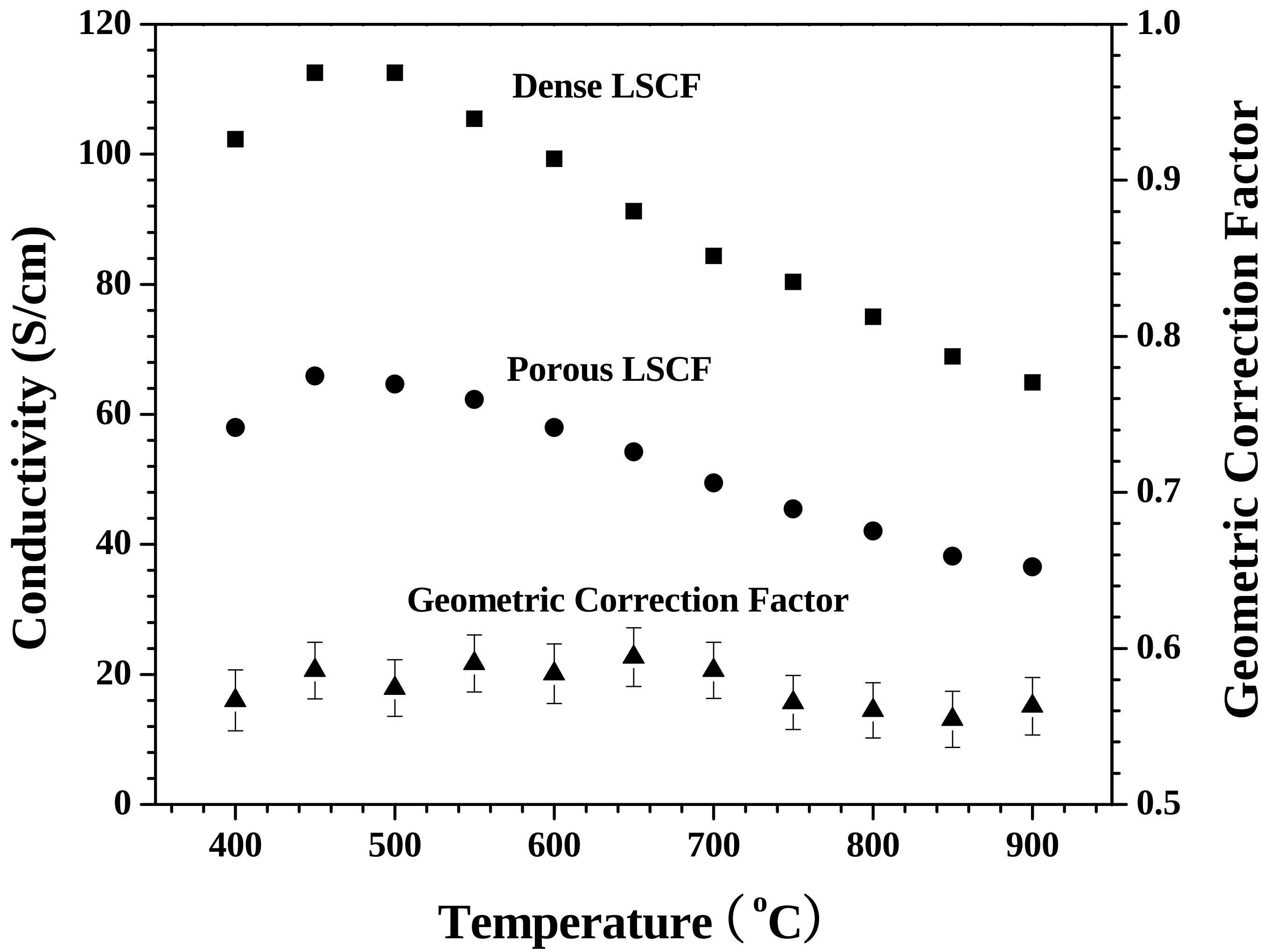


* Prepared by S. Liu, Curtin Univ of Tech

Control of Pore Structure of Ceramic Support



Total Conductivity for Dense and Porous Ceramic Supports



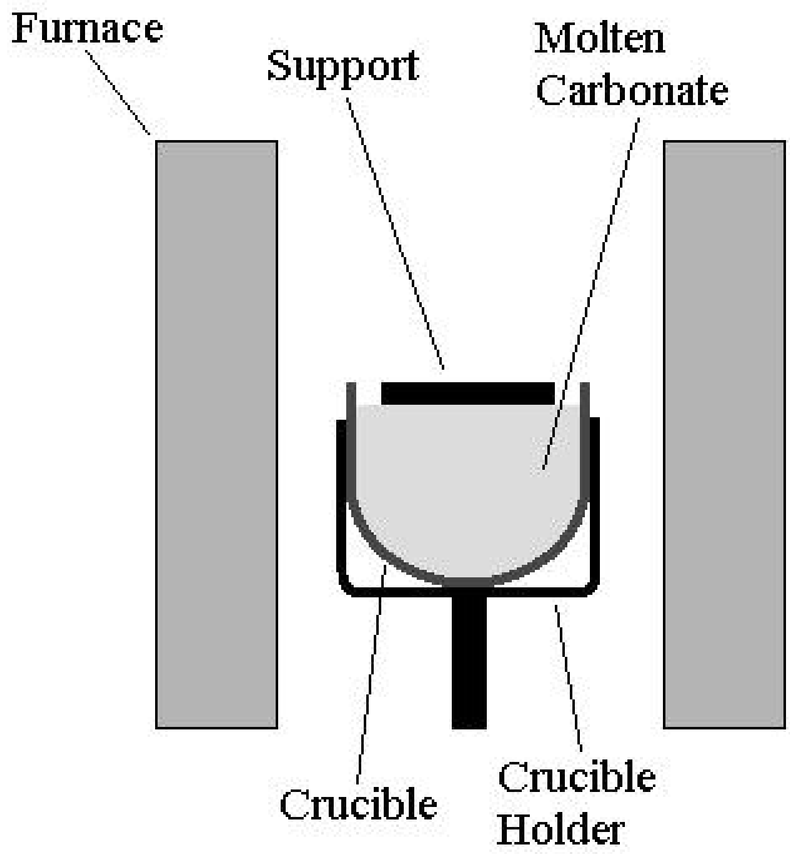
Synthesis of the Dual-Phase Membrane

- The Li/Na/K molten carbonate mixture was heated to 520° C in a vertical tube furnace

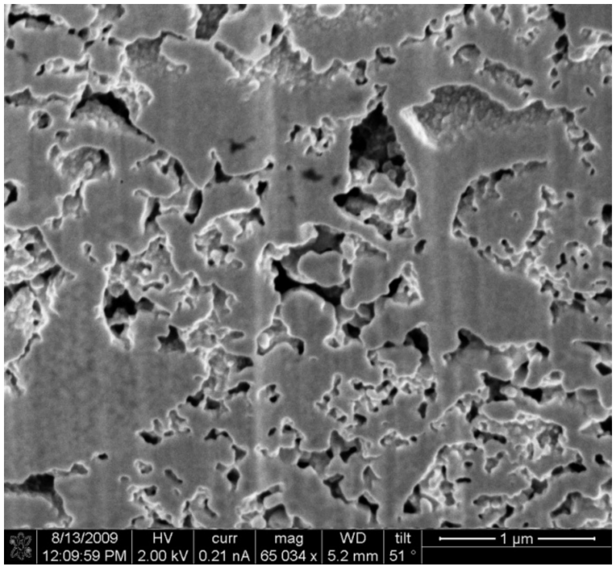
- The LSCF support should be preheated for 10 minutes prior to infiltration to prevent "frosting" or thermal shock

- The molten carbonate is raised until it touches the bottom of the support and left for 10-15 minutes

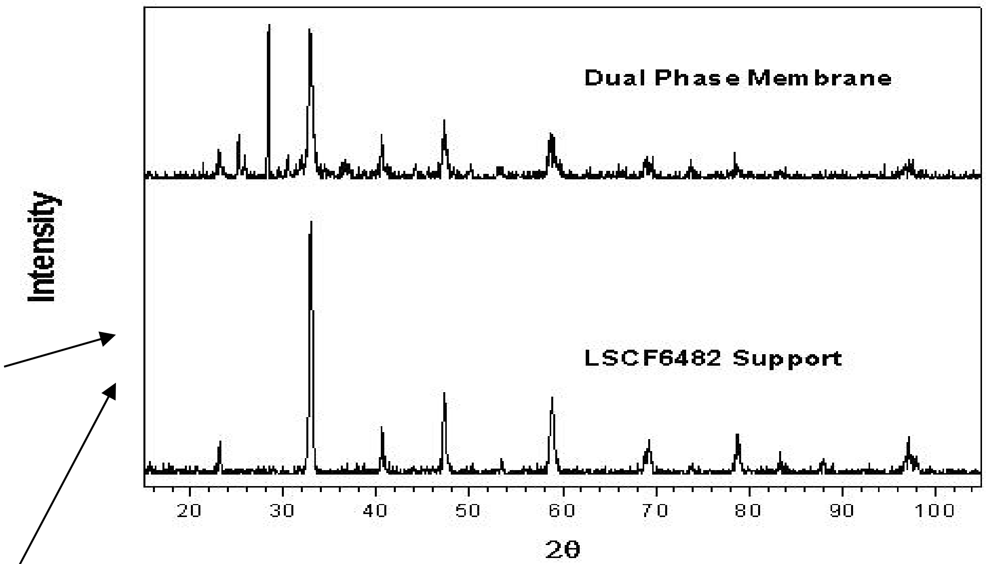
- Infiltration occurs via capillary forces within the pores of the support



Dual-Phase Membrane Characteristics

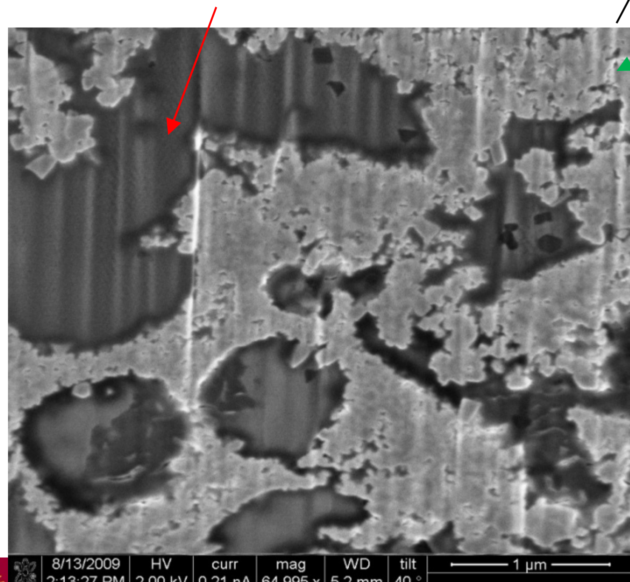


XRD



$(Li/Na/K)_2CO_3$(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

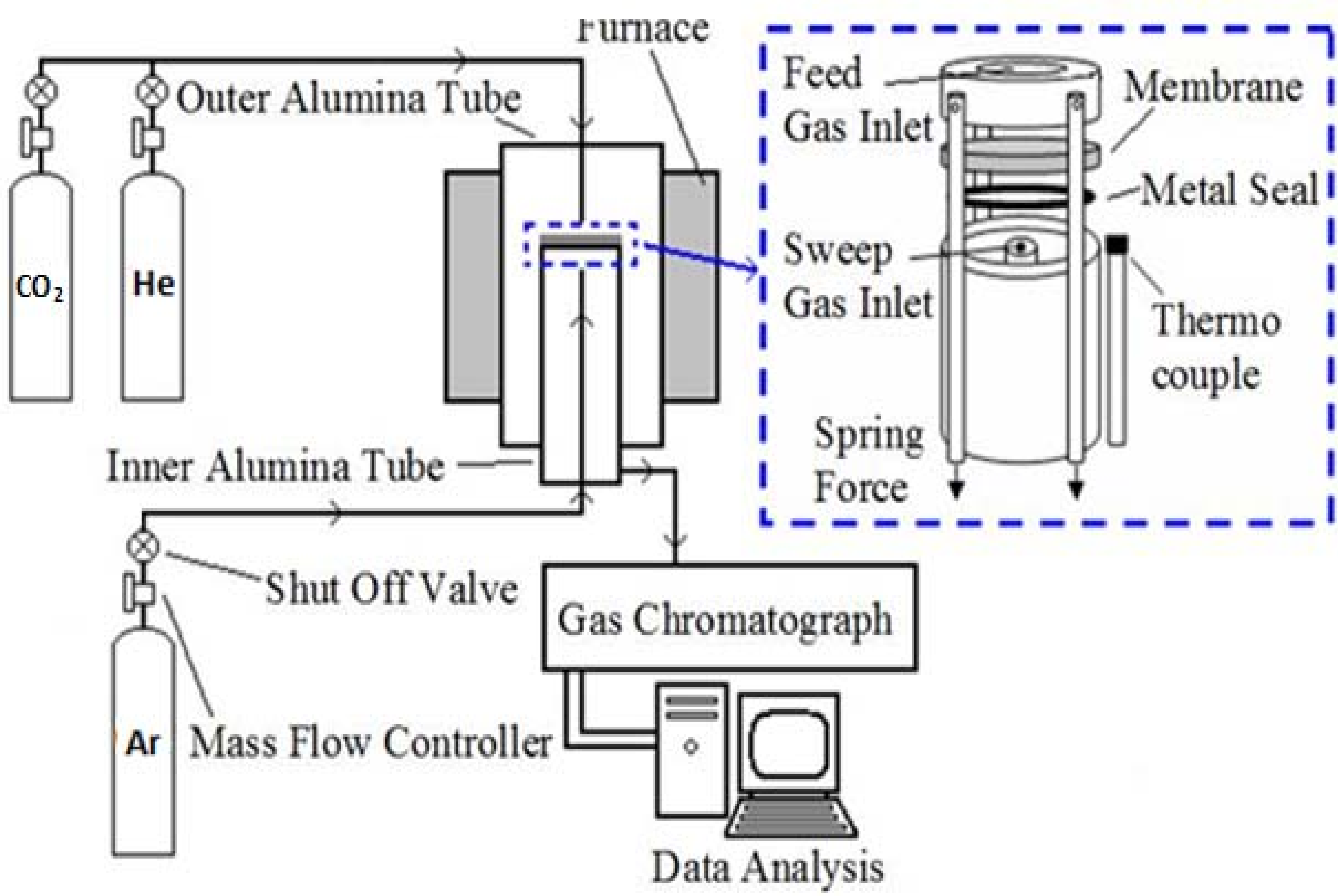
- **After infiltration of carbonate:**

  - 25% weight increase

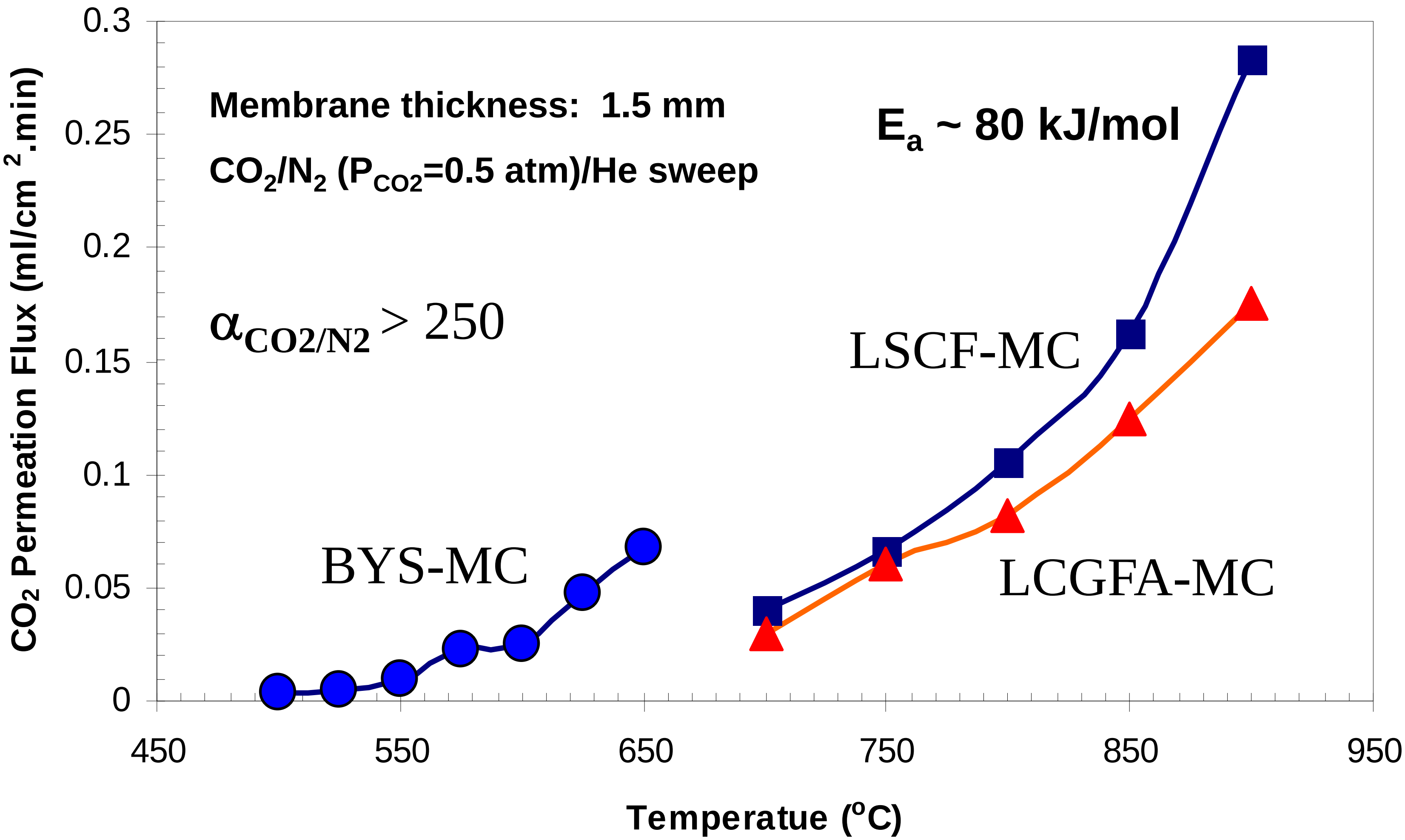
  - He permeance:

  <10^{-10} mol/m^2·s·Pa

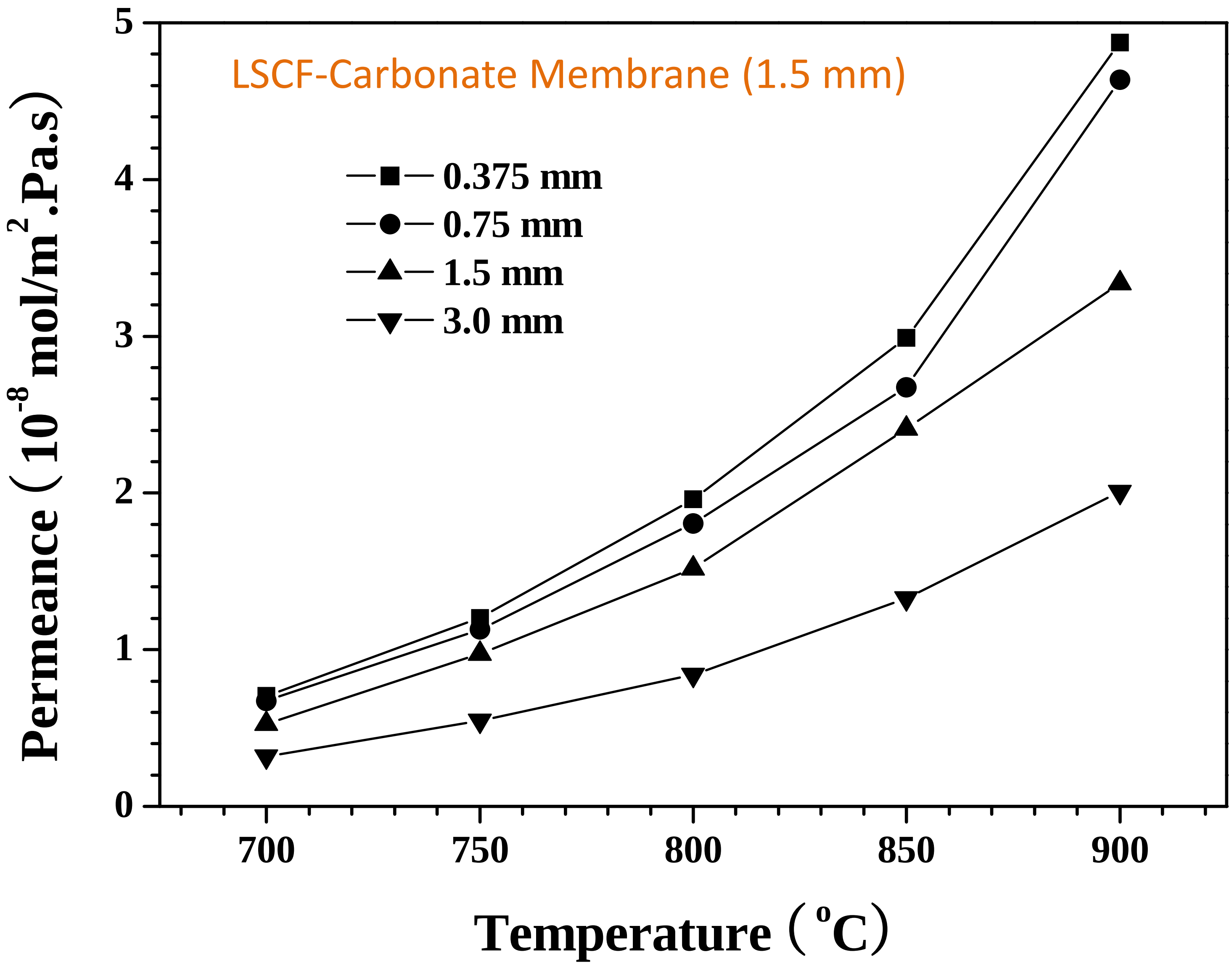
High Temperature Permeation Measurements



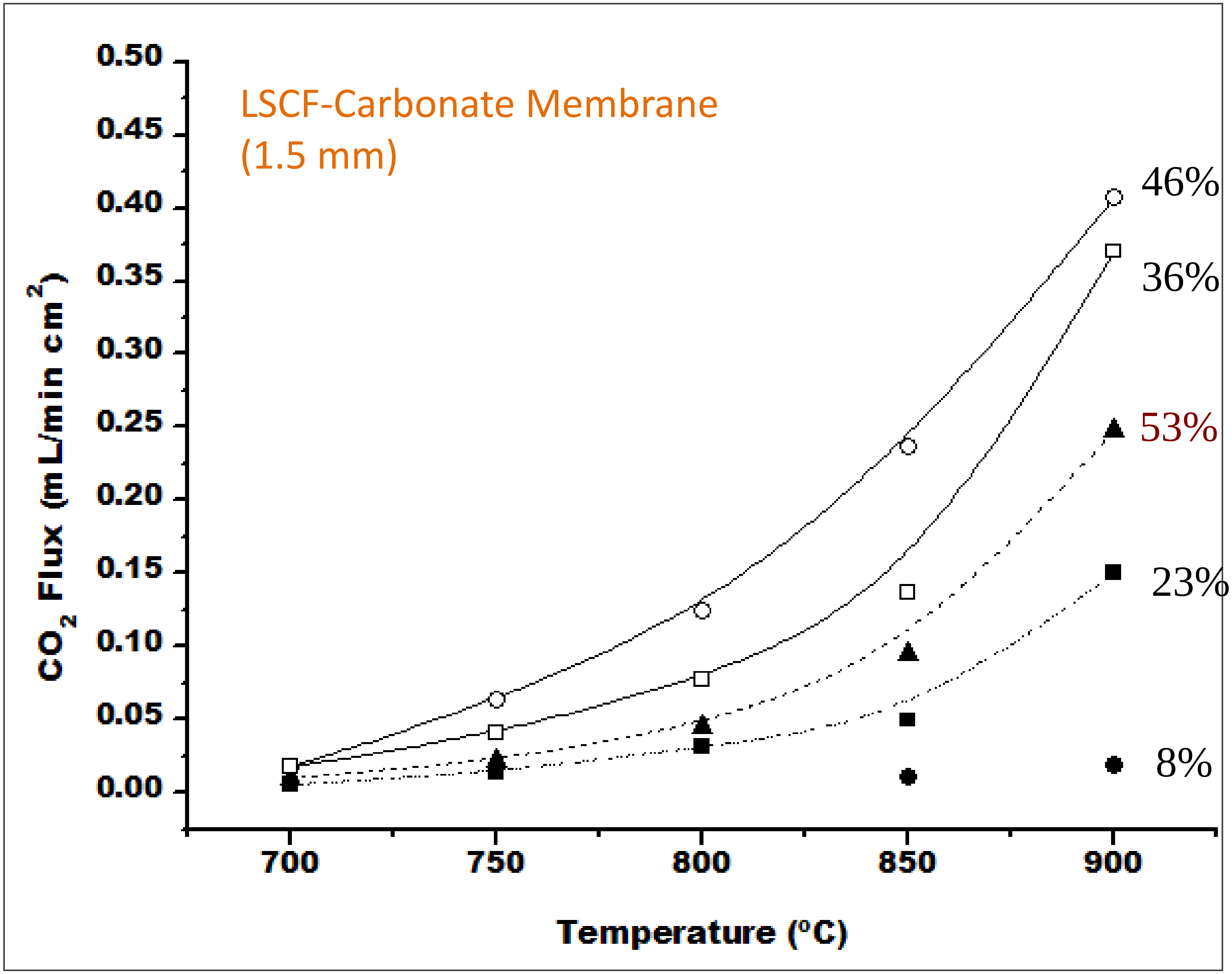
Carbon Dioxide Permeance



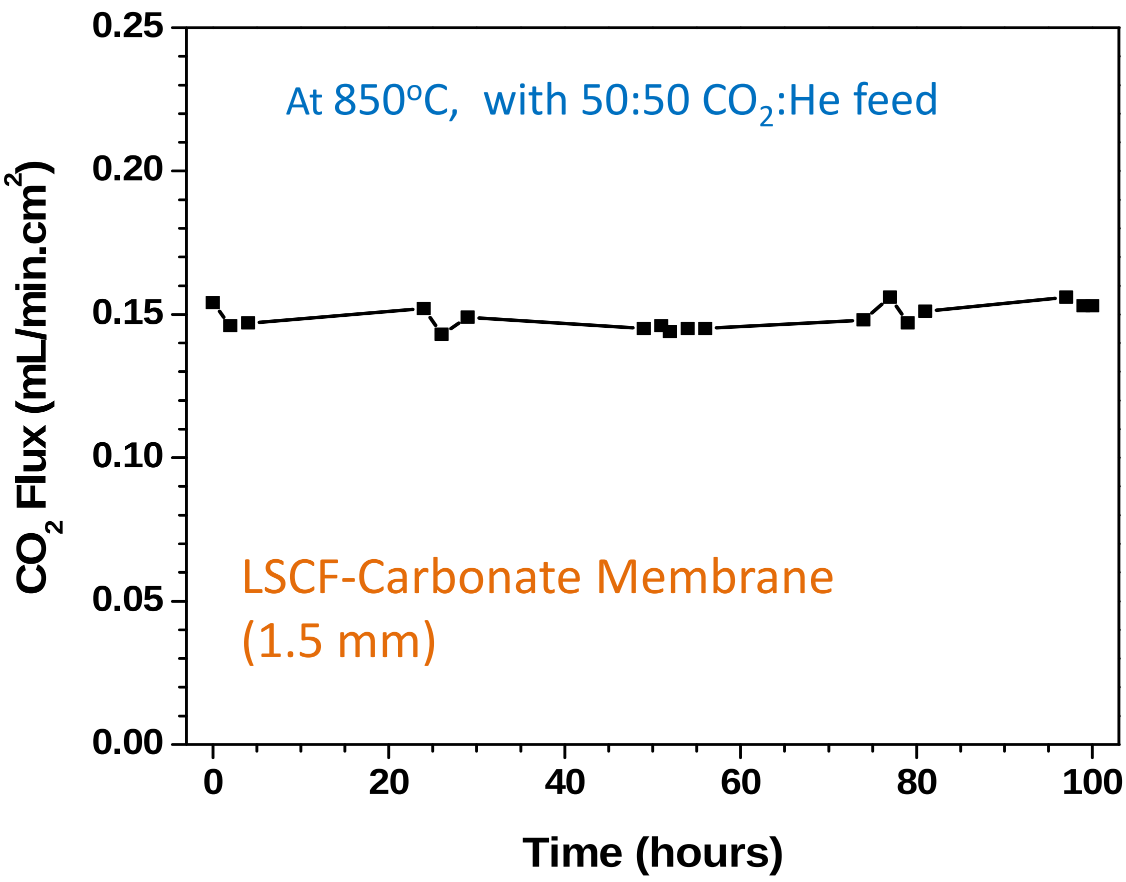
Effect of Membrane Thickness on CO_2 Permeance



Effects of Support Porosity



Membrane Permeation and Chemical Stability

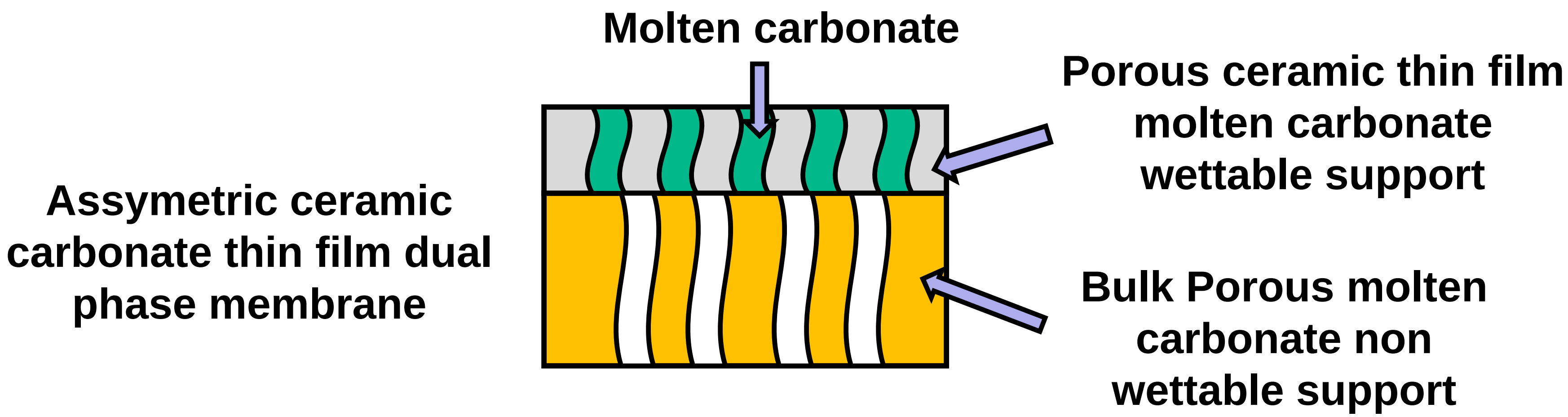


With feed of Simulated Coal Gas: $H_2/CO_2/CO/H_2O/H_2S$ (48:24:24:4:10ppm)

T (°C)	$\alpha_{CO2/H2}$	J_{CO2} %
700	500	40%
750	650	20%
800	920	-10%

$$J_{CO2}\% = \frac{J_{CO2(SCG)} - J_{CO2(REF)}}{J_{CO2(REF)}}$$

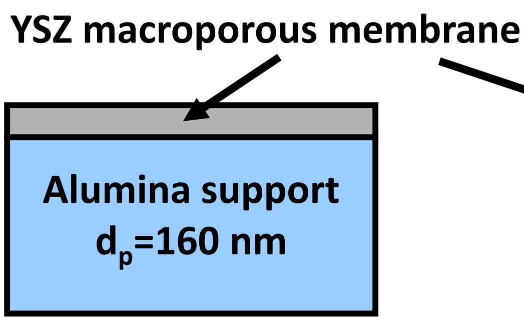
Synthesis of Thin Dual-Phase Membranes



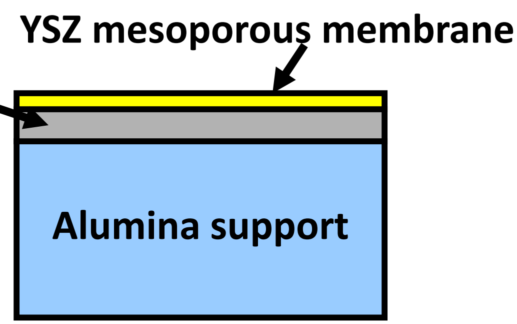
- **Making thin film ceramic-carbonate dual-phase membrane**
- **Increase the CO_2 permeance to 10^{-7} mol /m^2·s·Pa and decrease separation temperature to 500-700°C**

Synthesis of Thin Dual-Phase Membranes

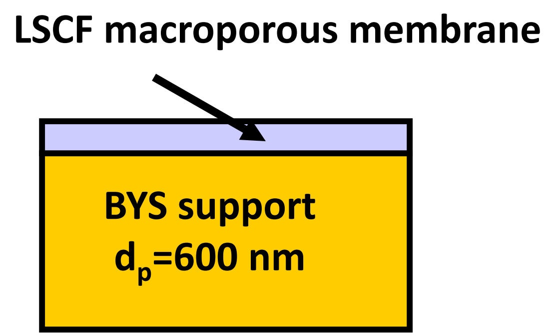
Multi-Layer Porous Supports



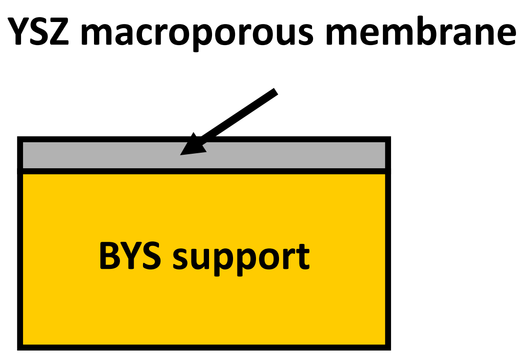
YSZ/AL



YSZ/YSZ/Al



LSCF/BYS



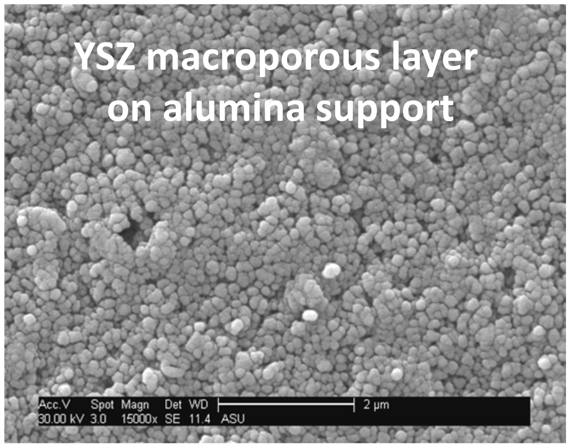
YSZ/BYS

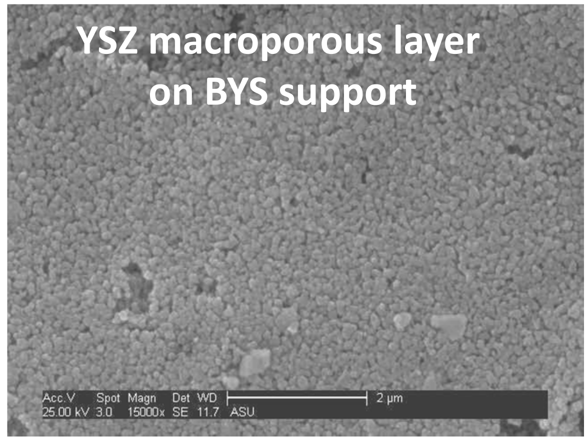
Membranes of other structures prepared:

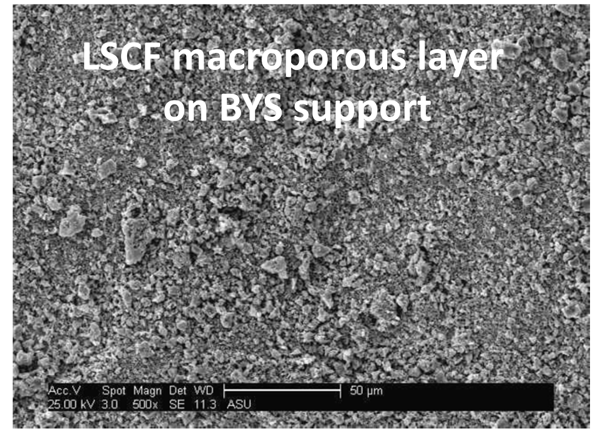
YSZ/BYS BYS/AL

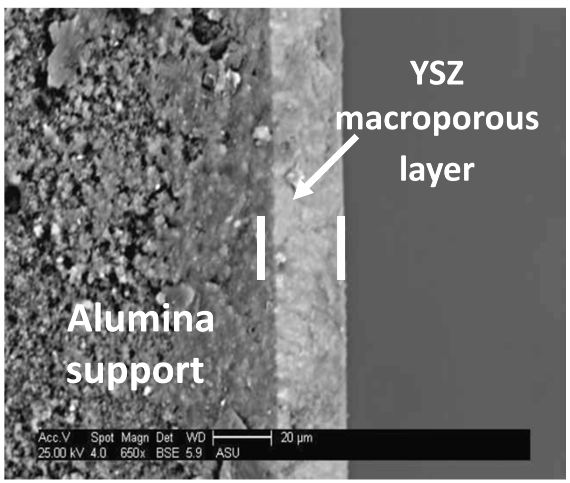
LCGFA/BYS YSZ/BYS/YSZ/AL

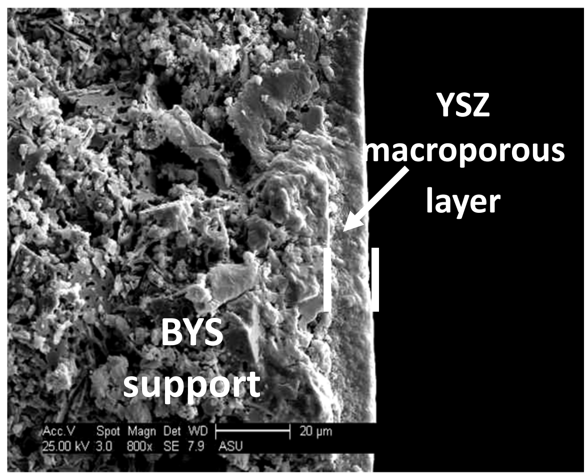
SEM Images of Selected Multi-Layer Supports

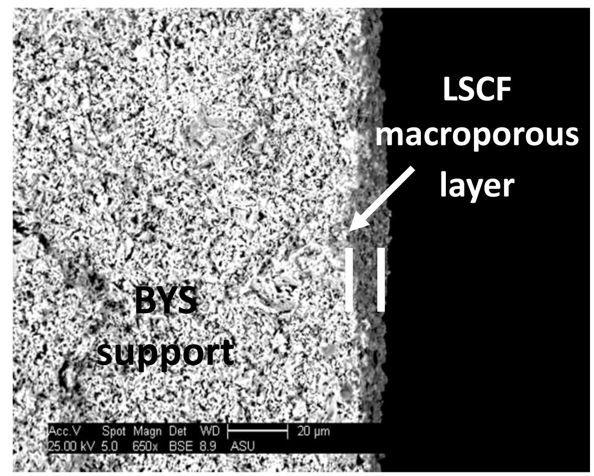








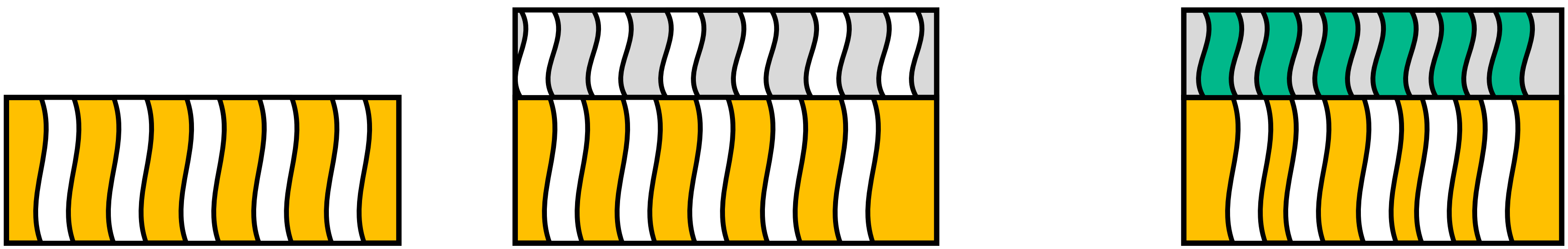




Synthesis of Thin Film Dual-Phase Membrane

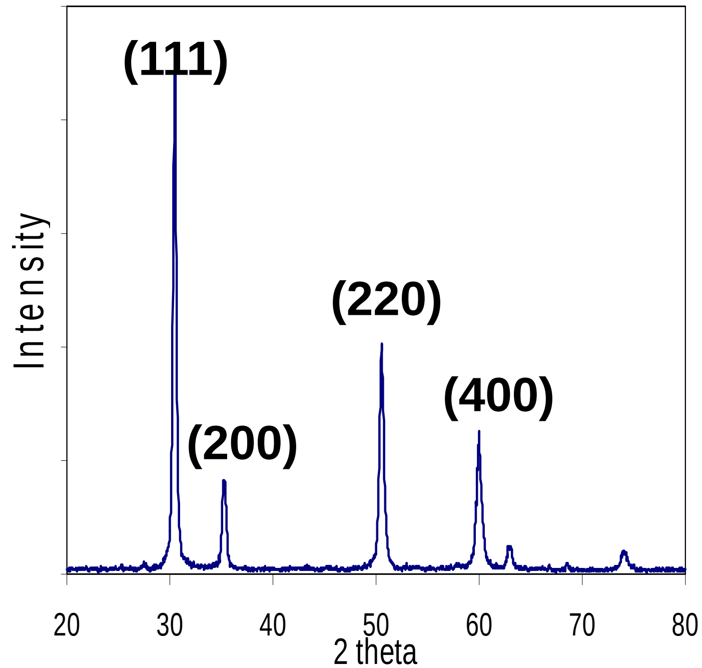
- **Yttria-stabilized-zirconia (YSZ)**
  High ionic conductivity and chemical and mechanical stability

- **BYS for porous support**
  Ionic conductive and non wettability to molten carbonate



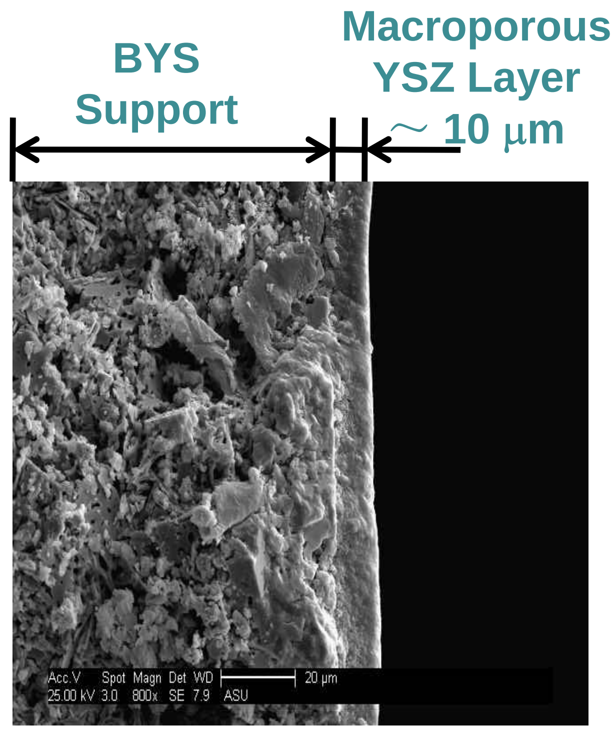
Bulk BYS Porous Support → **Dip-coated with YSZ suspension forming macroporous YSZ layer on top** → **Infiltrated with molten carbonate into top macroporous YSZ membrane**

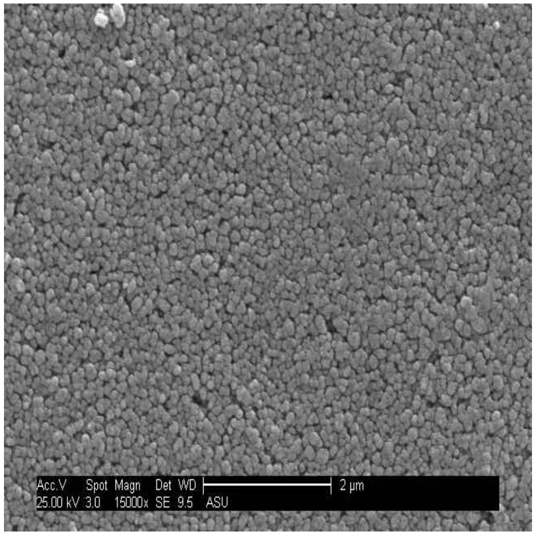
Characterization of Macroporous YSZ Layer



Index number of the peaks showed cubic structure of YSZ

Cross section of Macroporous YSZ Layer



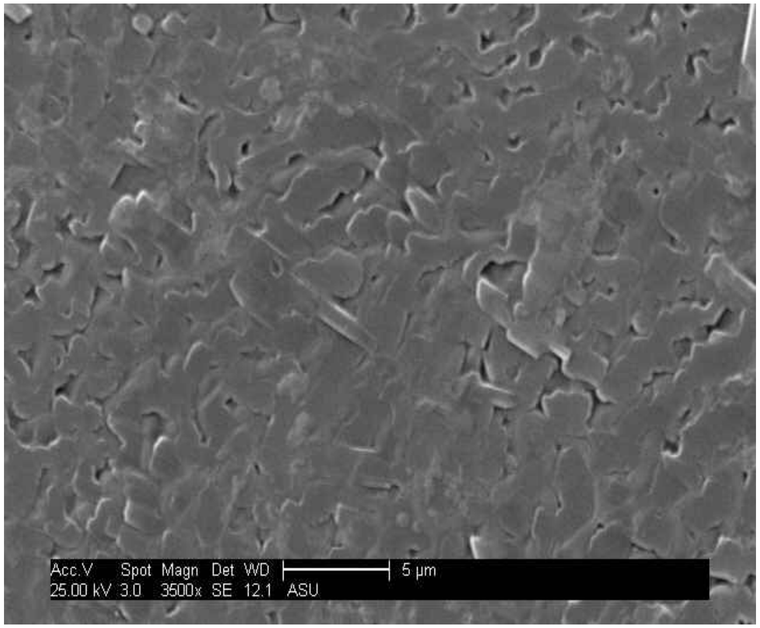


Surface image of Macroporous YSZ membrane

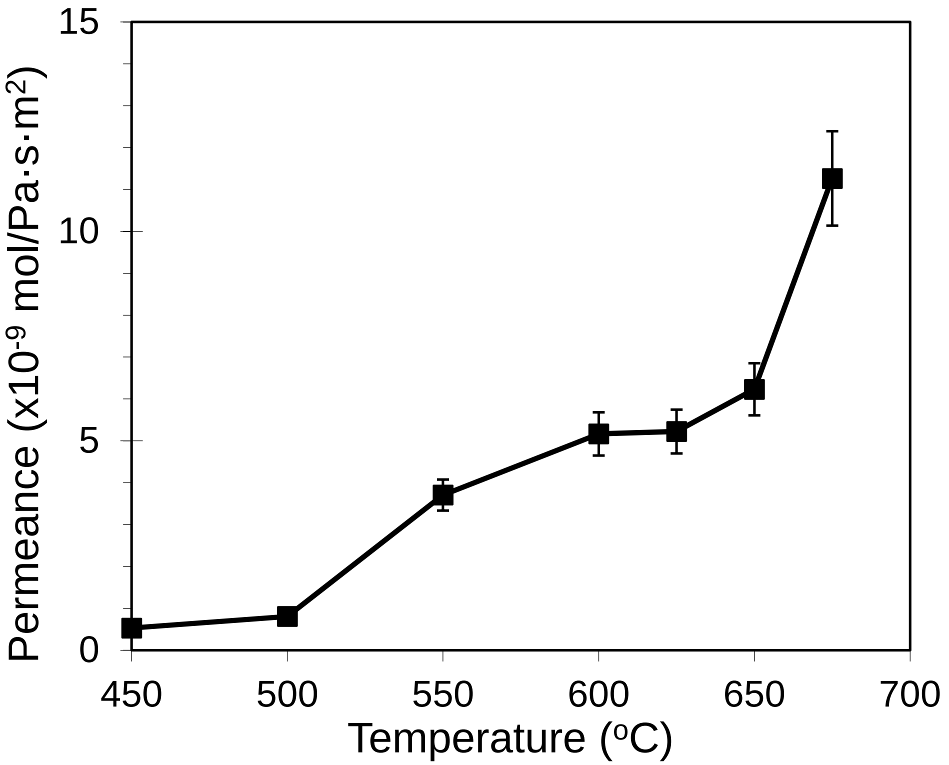
Results of Molten Carbonate Infiltration

Properties \ Support	Macroporous YSZ on alumina	Mesoporous YSZ on alumina	Macroporous YSZ on BYS	Macroporous LSCF on BYS
Weight increase after infiltrationg	0.2-0.4	0.2-0.3	0.1-0.2	0.1-0.2
He permeance before infiltration $mol/m^2 \cdot Pa \cdot s$	$1.3 \cdot 10^{-6}$	$5.8 \cdot 10^{-7}$	$5.5 \cdot 10^{-6}$	$6.1 \cdot 10^{-6}$
He permeance after infiltration $mol/m^2 \cdot Pa \cdot s$	$6.7 \cdot 10^{-9}$	$8.9 \cdot 10^{-10}$	$8.3 \cdot 10^{-9}$	$2.3 \cdot 10^{-9}$
CO_2 permeance $mol/m^2 \cdot Pa \cdot s$	$<10^{-9}$	$<10^{-9}$	10^{-9}-10^{-7}	10^{-9}-10^{-7}

CO2 Permeation through Thin Membranes

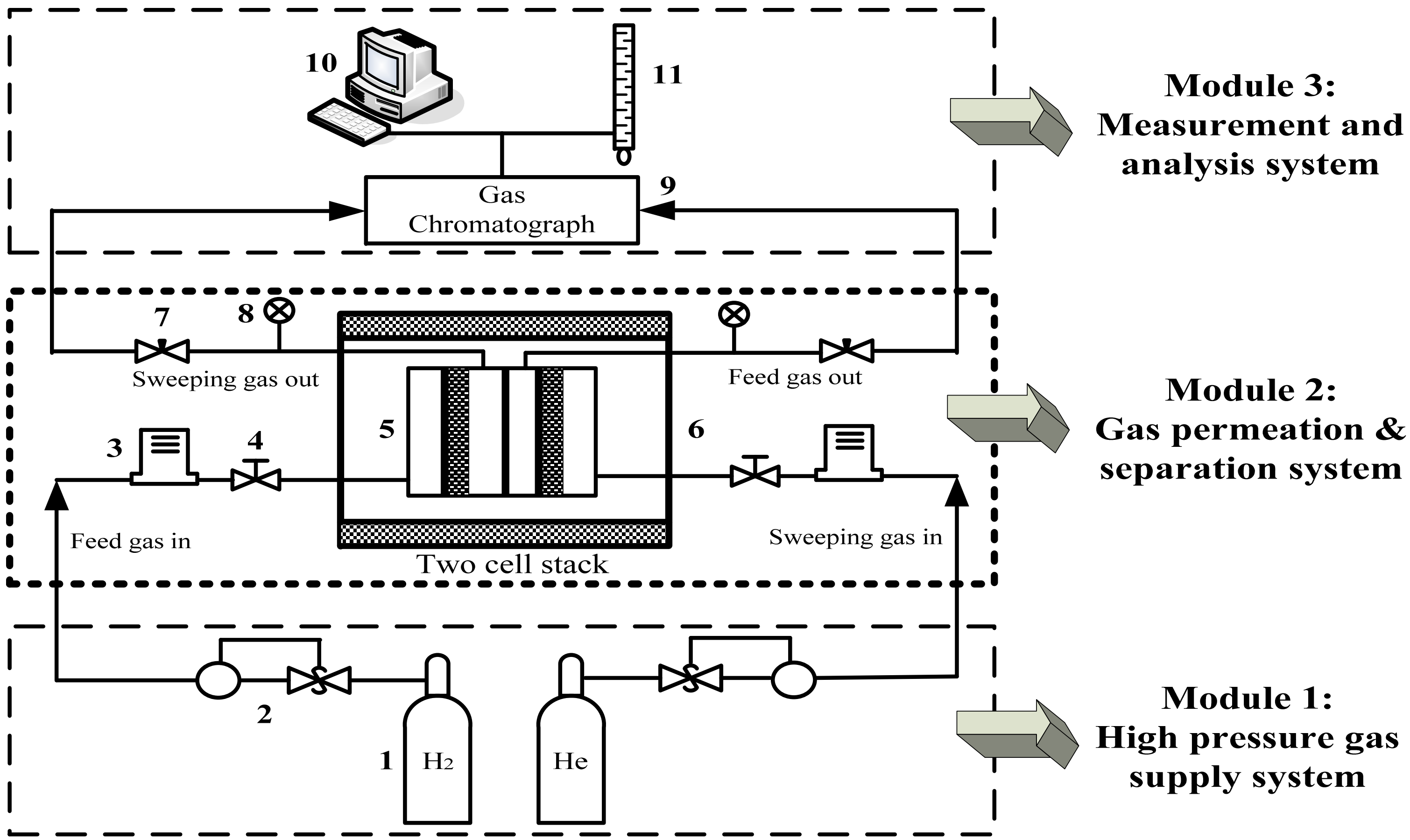


20 µm YSZ-MC/BYS membranes



- CO_2 permeance increases with rising temperature
- CO_2permeace is 1.2x10^{-8}mol/Pa·s·m^2 at 675^{o}C
- Activation energy for permeation is about 76 kJ/mol

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

Future Testing/Development Work

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

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 stability
- Multiple-layer ionic conducting porous supports prepared, and coating thin dual-phase membrane showed promising results
- Years 1 and 2 milestones met