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

Jerry Y.S. Lin

&

Matt Anderson, Bo Lu, Peter Rui, Tyler Norton

Chemical Engineering
School for Engineering of Matter, Transport and Energy

Arizona State University
Tempe, AZ 85287

Jerry.lin@asu.edu

Company Background – Arizona State University

- Largest university in the U.S. (70,440 students)
- 2009 Research Expenditure: $307M
- Ranked 81st among research universities in the world (objective based ranking)
- One of largest engineering colleges in the country (220 faculty)
- Energy research is a focus area – including membrane technology for energy applications

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:

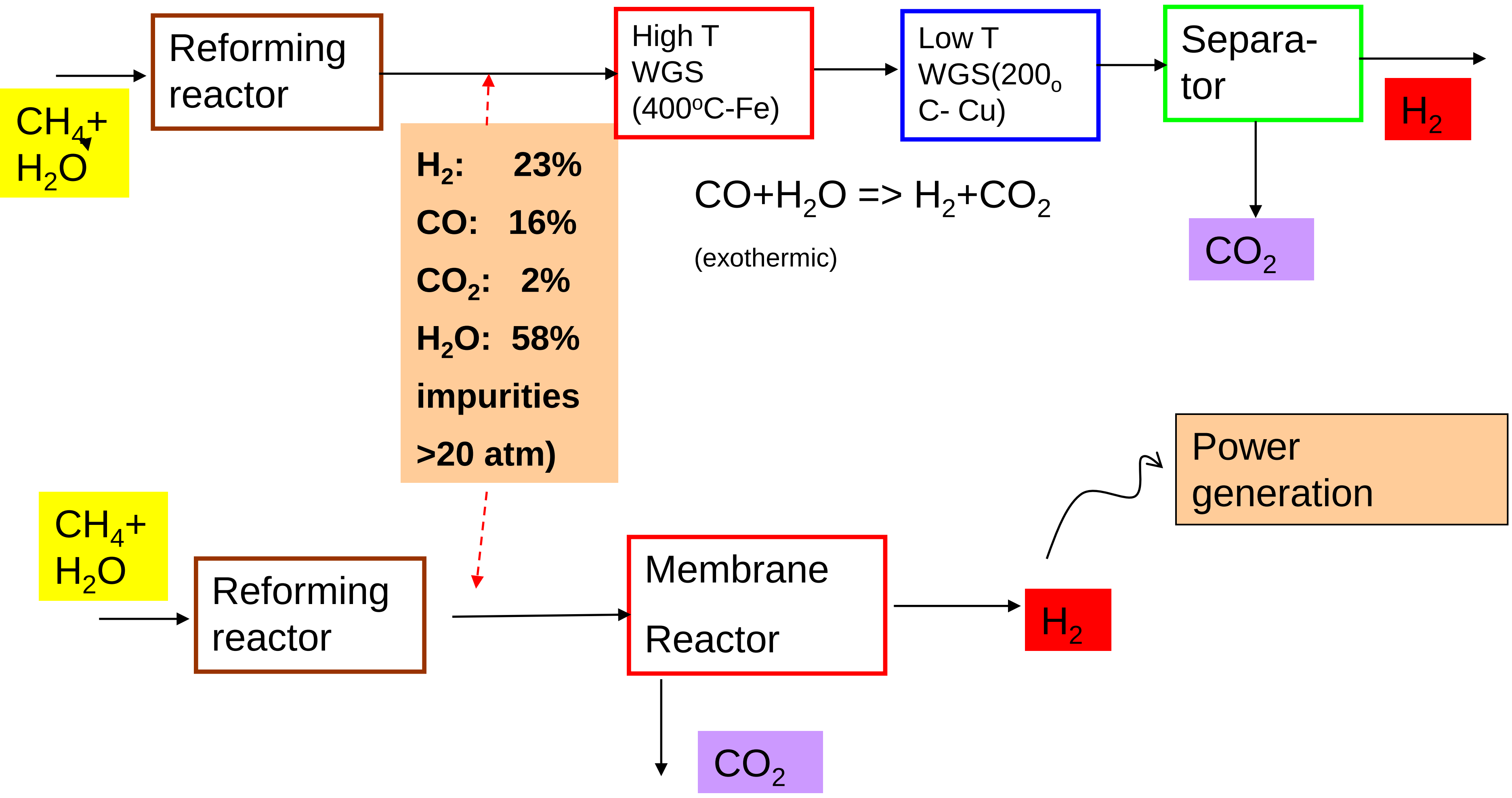
Arizona State University

Project Objectives

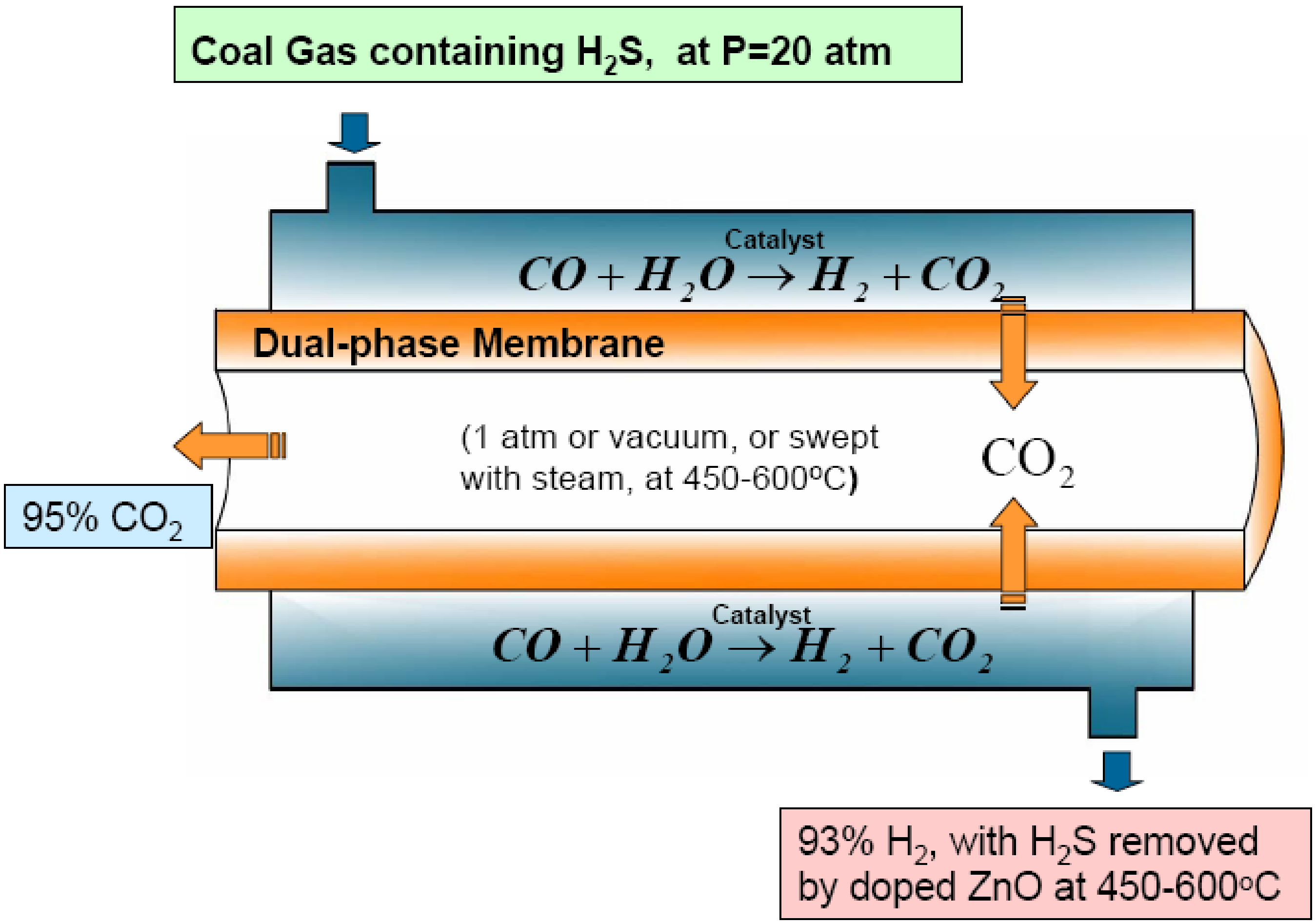
1. Synthesize chemically/thermally stable dual-phase ceramic-carbonate membranes with CO_2 permeance and CO_2 selectivity (with respect to H_2, CO or H_2O) larger than $5x10^{-7}$ mol/m^2.s.Pa and 500;
2. Fabricate tubular dual-phase membranes and membrane reactor modules suitable for WGS membrane reactor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



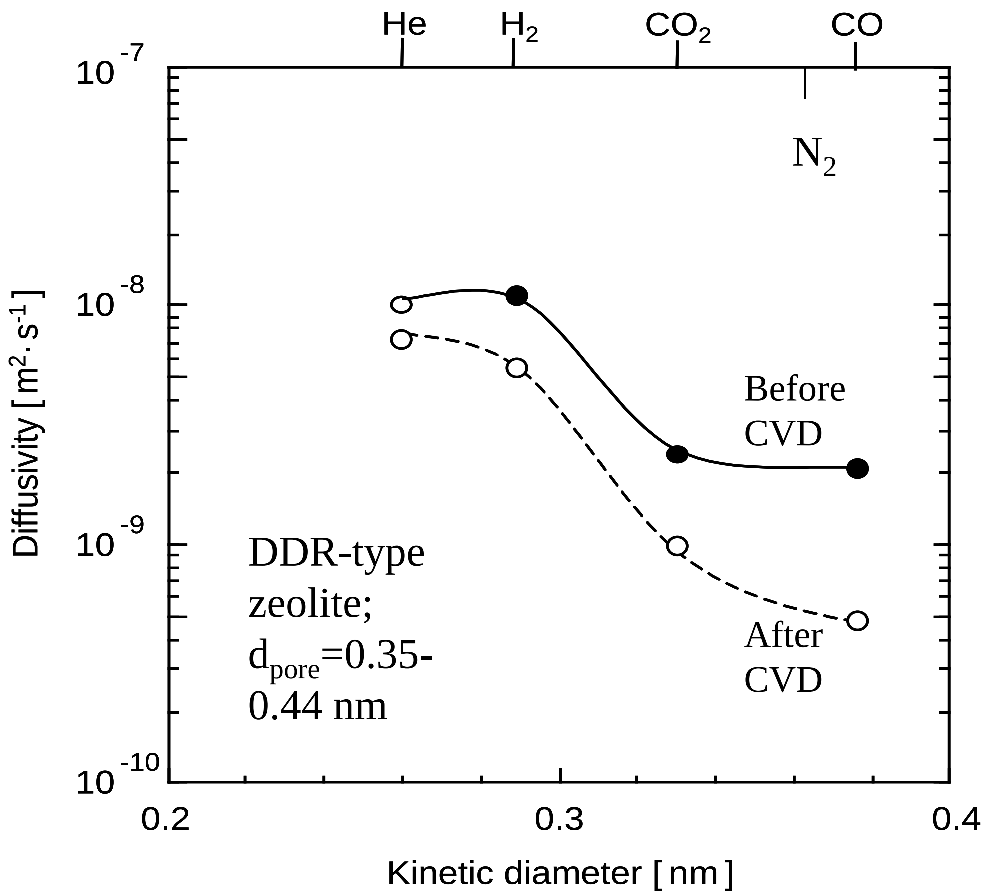
Proposed Membrane Reactor for WGS Reaction



Porous Inorganic Membranes for CO_2 Separation

- Microporous (silica, carbon and zeolite) membranes
- CO_2/N_2 or CO_2/H_2 selectivity up to 100, with CO_2 permeance up to $2x10^{-6}$ mol/m^2/s/Pa at room temperature
- The selectivity drops to about the unity at high temperatures (>300^{o}C)

Kinetic diameter dependency of measured diffusivity for DDR-type zeolite membrane at 500^{o}C

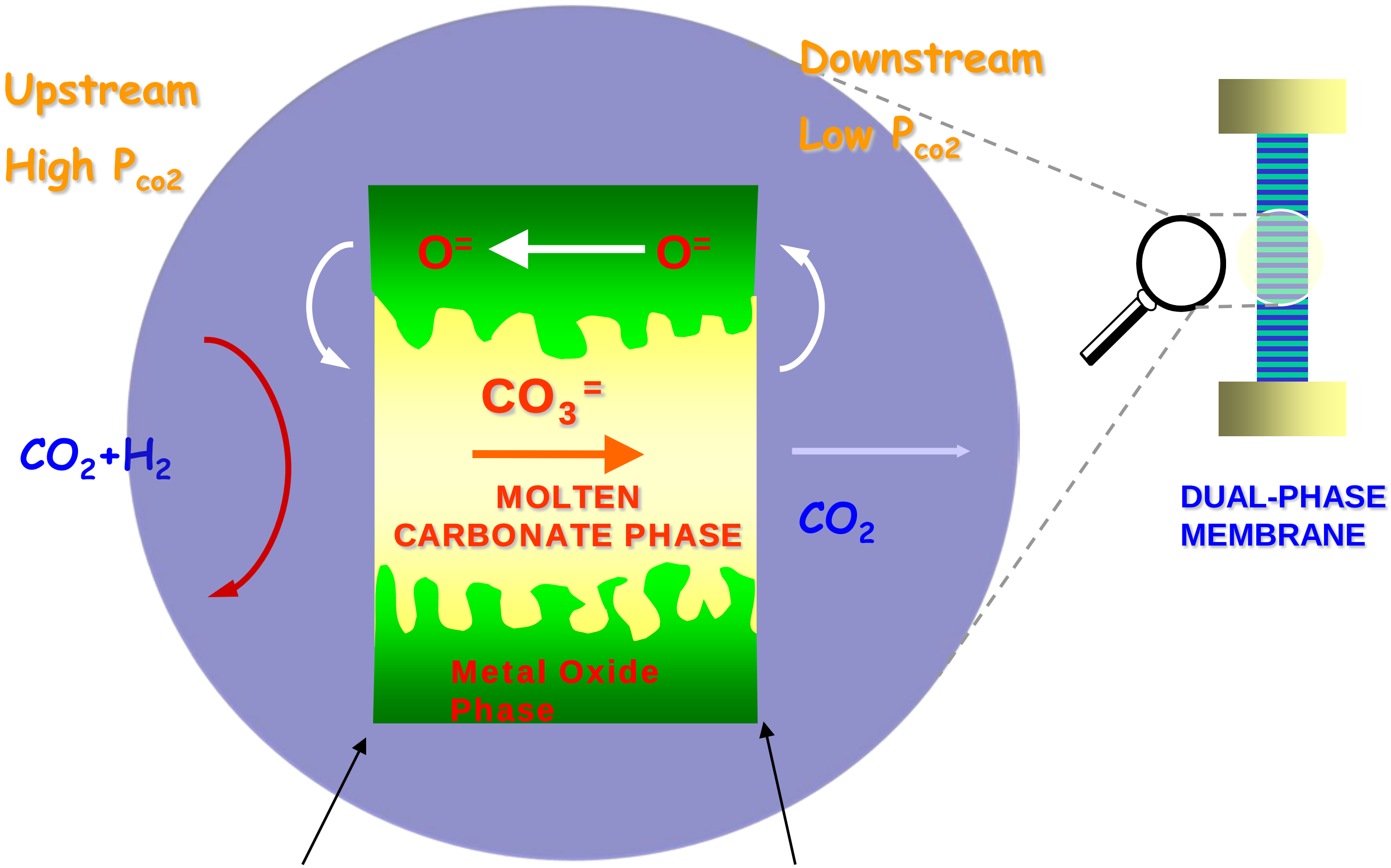


From Lin and coworkers, *AIChE J.* (2008)

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



$CO_2 + O^{=} => CO_3^{=}$

$CO_3^{=} => CO_2 + O^{=}$

Oxygen Ionic Conducting Metal Oxide Supports

Material	Abbre-viation	Structure	$O^=$ conduct-ivity σ_i (600°C) (S/cm)	Transference number t_i
$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$	LSCF	Perovskite	0.02	~ 0.01
$SrFeCoO_x$	SFC	Intergrown perovskite-rocksalt	0.1	~ 0.02
$Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$	BYS	Fluorite	0.06	~ 0.9
8% Y_2O_3-ZrO_2	YSZ	Fluorite	0.03	~ 1.0

High Temperature CO_2 Permselectivity - Comparison with Other Membranes

Membrane	Temperature (°C)	CO_2 Permeance ($mol/m^2 \cdot s \cdot Pa$)	CO_2/N_2
Li_4SiO_4[a]	525	1.0×10^{-8}	4-6
SiO_2[b] (Vycor)	600	3.0×10^{-10}	36
Metal Dual-Phase[c]	650	2.5×10^{-8}	16
Ceramic Dual-Phase	650	1.7×10^{-8}	> 360

a. T. Yamaguchi, et al., *J. Membr. Sci.*, 294 (2007) 16.
b. L. Cuffe, et al., *J. Membr. Sci.*, 272 (2006) 6.
c. S. Chung, et al., *Ind. Eng. Chem. Res*, 44, (2005) 7999.

Progress and
Current Status of Project

Milestone-Year 1

- Synthesize multiple-layer nanoporous YSZ, BYS and LSCF disk supports with desired pore structure
- Synthesize gas-tight dual-phase carbonate-ceramic membranes on disk-supports with CO_2 permeance $1x10^{-7}$ mol/m^2.s.Pa

ASU

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

Synthesis of Porous $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF6482) Support

Metal Nitrate precursors of La, Sr, Co and Fe are weighed out in a 6:4:2:8 molar ratio (LSCF6482)

Add excess citric acid and 1000 mL and heat the covered solution at 105°C for 4 hours

Uncover solution and heat until a brick-red gel remains; dry remnants for 24 hours at 120° C

Self ignite remnants at 400°C in an oxygen-rich environment to ensure removal of the organics

The powder is finely ground and placed in a crucible and heated to 600°C

LSCF6482 Powder

3.60 g of presintered LSCF powder is ground and mixed with 0.40 g of PVA solution

The LSCF and PVA mixture is evenly placed into a 30.0 mm stainless steel die-mold

The powder is pressed in the mold at 30 MPa for 1 minute, and then 160 MPa for 4 minutes

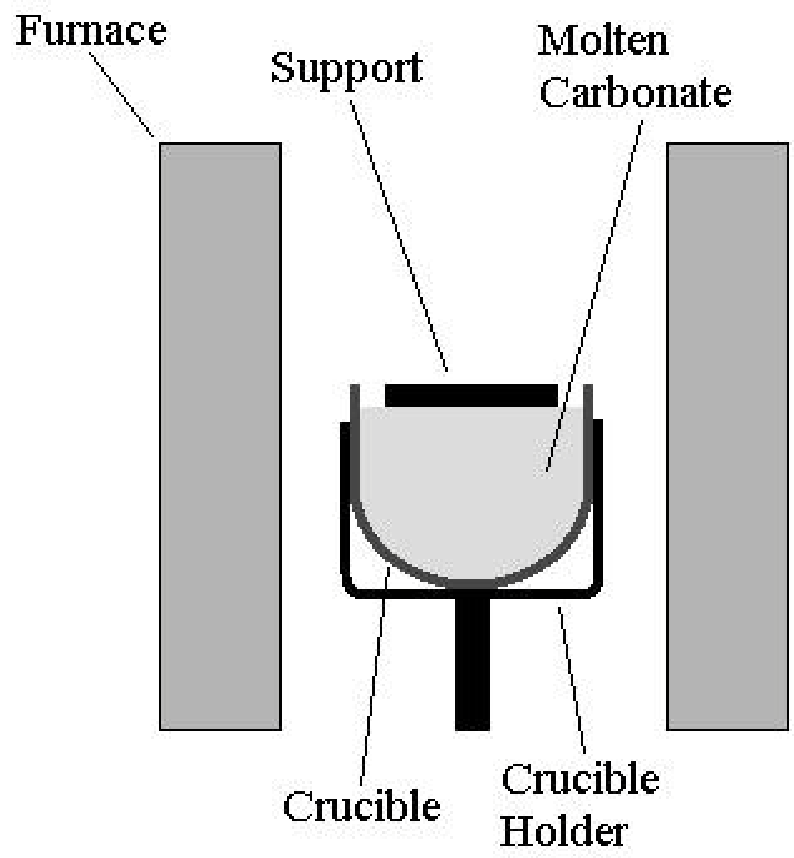
The support is carefully removed from the die and dried at 40°C and 40% RH for 1 day

Finally, the support is sintered for 24 hours at 900°C with ramping rates of 2°C/min

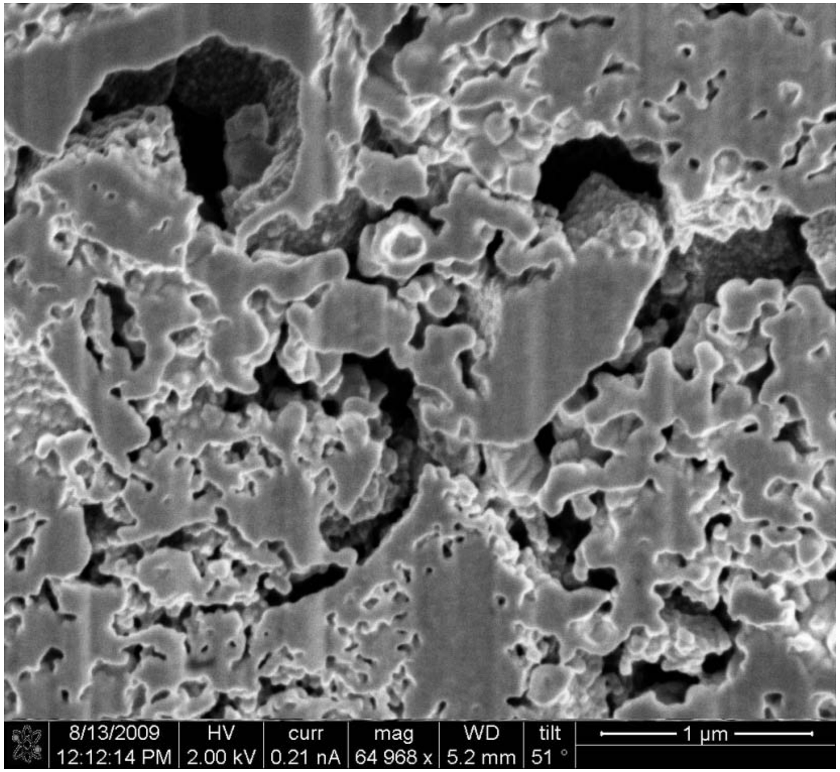
LSCF6482 Support

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



SEM Images

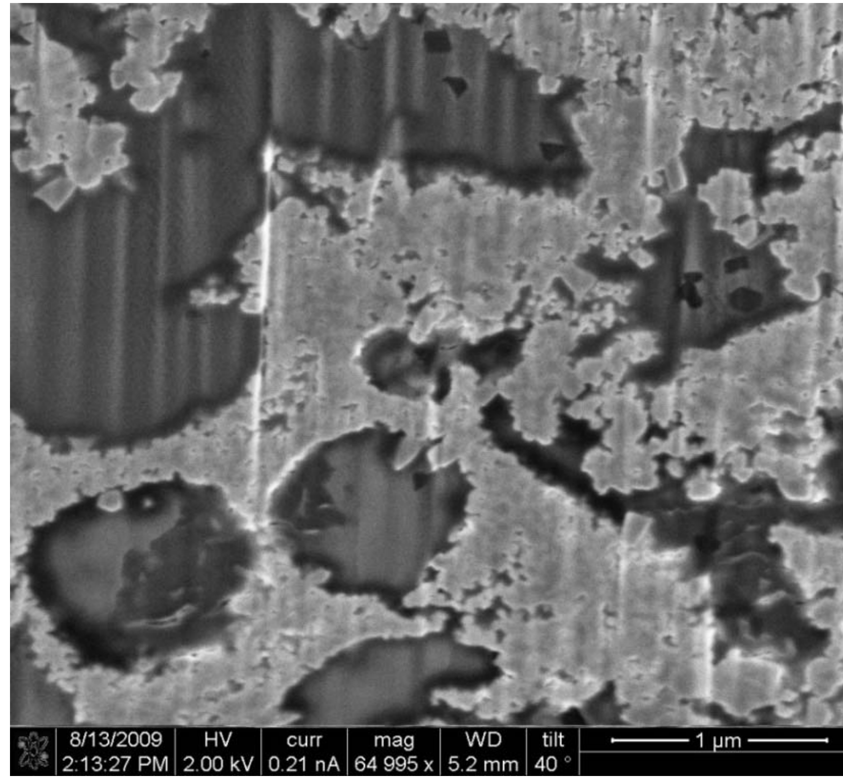


Before infiltration

Helium permeance: 10^{-6} mol/m^2·s·Pa

Average pore diameter: 355 nm

Porosity: ~40%



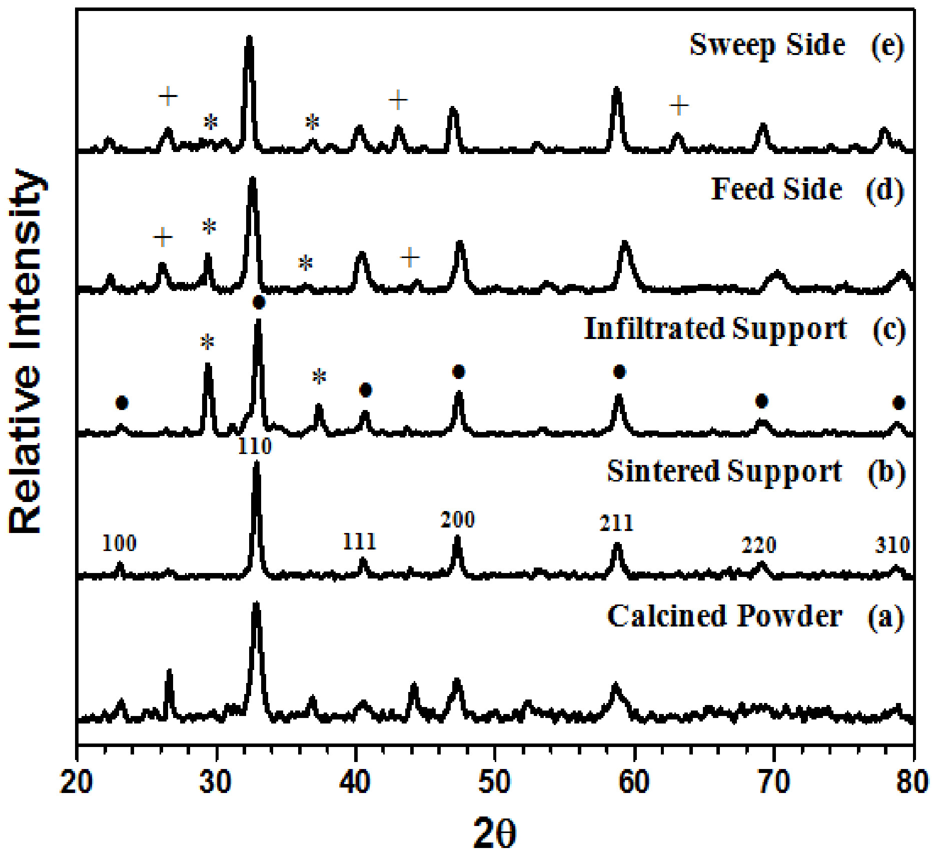
After Infiltration

Helium permeance: 10^{-10} mol/m^2·s·Pa

Pore diameter: n/a (dense)

18

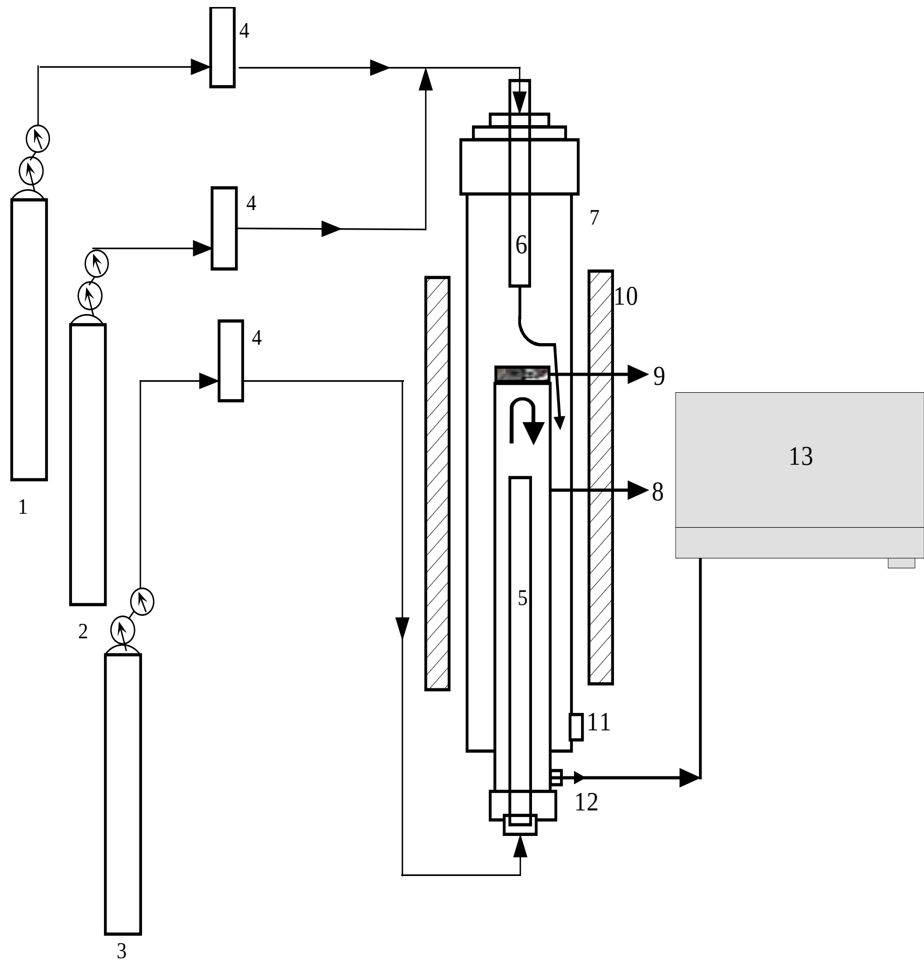
XRD Analysis of LSCF



- **LSCF is rhombohedral perovskite in structure**
- **Lattice parameters: least squares regression**
  - **a = b = 5.45Å**
  - **c = 13.21Å (hexagonal system)**
  - **Cell volume: 340.28Å^3**
  - **α = β = 90°, γ = 120 °**
- **XRD confirms complete infiltration of the support**
  - **● Perovskite phase**
  - **+ "New" Carbonate phases (i.e., $SrCO_3$) and $LiCoO_2$**
  - *** Molten Carbonate**

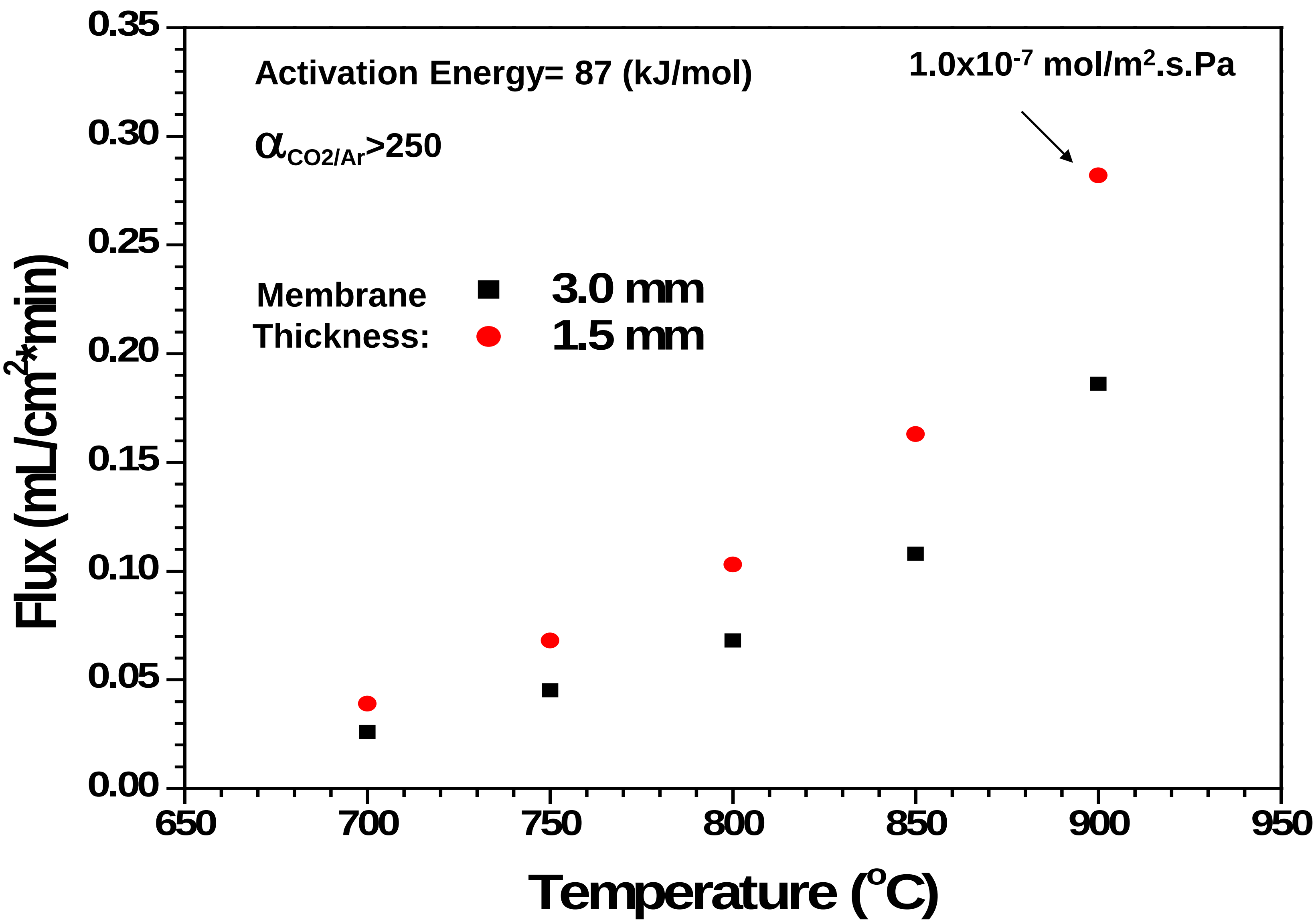
High Temperature Permeation Schematic

- **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

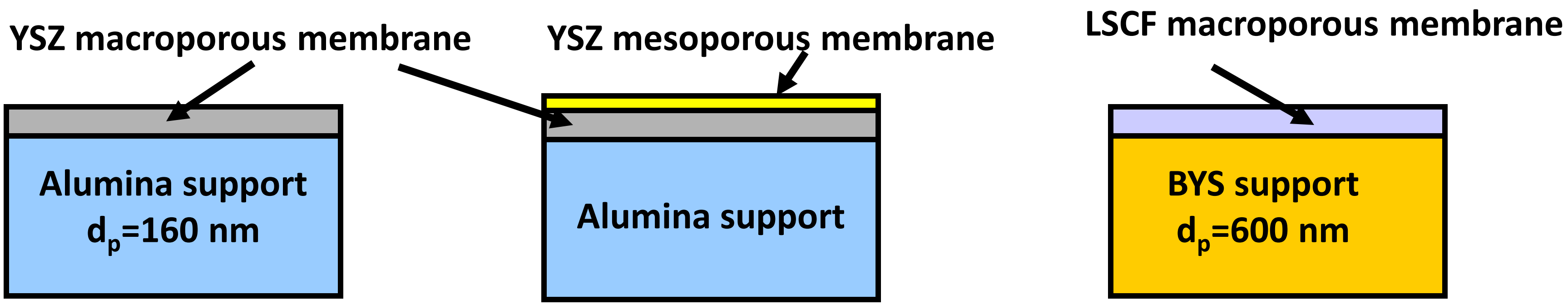
Experimental Results

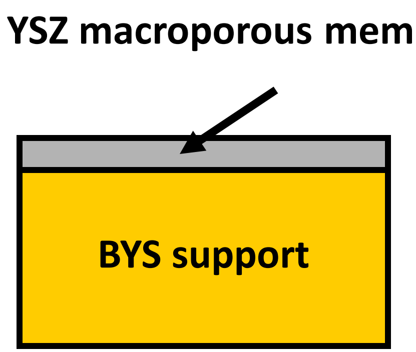


21

Synthesis of Thin Dual-Phase Membranes

Multi-Layer Porous Supports





YSZ: Yttria Stabilized Zirconia

BYS: Bi-Y-Sm oxide

LSCF: La-Sr-Co-Fe oxide

Synthesis of Porous Base Supports

Alumina support

1. 2.0 g of commercial alumina powder mixed with 0.20g of PVA solution
2. The alumina and PVA mixture is evenly placed into a 20.0 mm stainless steel die-mold
3. The powder is pressed in the mold at 150 MPa for 5 minutes
4. The support is carefully removed from the die and dried at 40°C and 60% RH for 1 day
5. Alumina support is sintered for 30 hours at 1150°C with programmable procedure

BYS support

1. Metal nitrate precursors of Bismuth, Yttria and Samarium are weighed out in a molar desired ratio
2. Citric acid method is used to make BYS powder
3. BYS powder is mixed with PVA solution and evenly placed into a stainless steel die-mold
4. The powder is pressed in the mold
5. After drying at 40°C and 60% RH for 1 day, the support is sintered to obtain porous disks

Synthesis of Suspension/Sol for Coating Thin Porous Layers

YSZ suspension

- YSZ powders mixed with HNO_3 (pH=3-4) at a weight ratio of 1:2
- → Ultrasonically treated and ball milled for 7 d
- → More HNO_3(pH=3-4) was added to adjust powder and solvent ratio to 10wt%

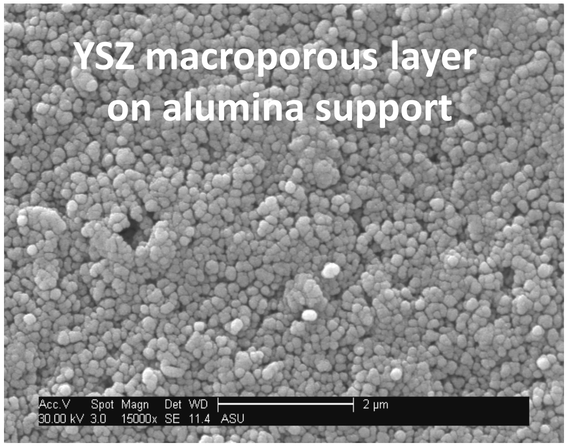
YSZ sol

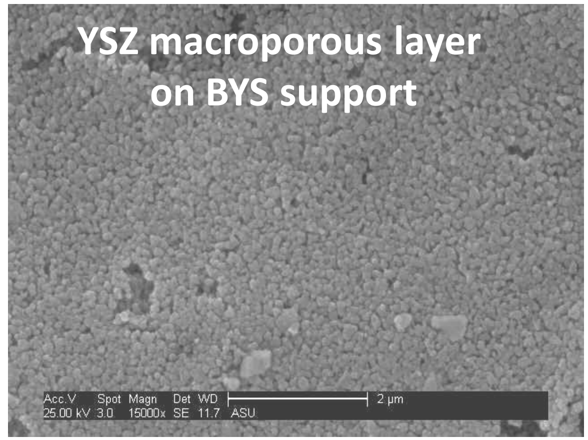
- Zirconium n-propoxide is mixed with isopropanol at 50°C
- → The solution is kept stirring at 70°C where hydrolysis and condensation reaction happened
- → The solution was filtered and filter cake was washed
- → The filter cake was peptized with HNO_3 and refluxed at 90-110°C
- → Stable zirconia sol mixed with $Y(NO_3)_3$ and PVA

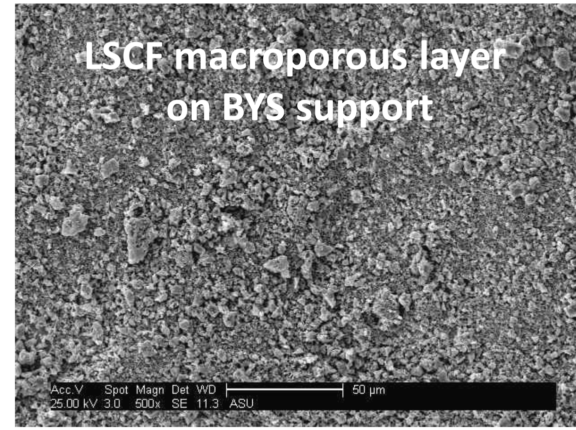
LSCF suspension

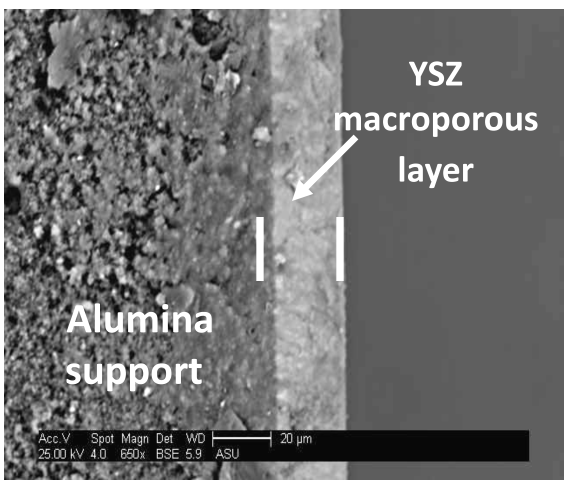
- Metal Nitrate precursors of La, Sr, Co and Fe are weighed out in a 6:4:2:8 molar ratio (LSCF6482)
- → Add excess citric acid and 1000 mL and heat the solution at 105°C until a brick-red gel remains
- → After drying the remnants was self ignited at 400°C to remove the organics
- → The powder is then heated to 900°C and then ball milled for 7 d
- → LSCF powders were mixed with ethanol and polyethylene glycol

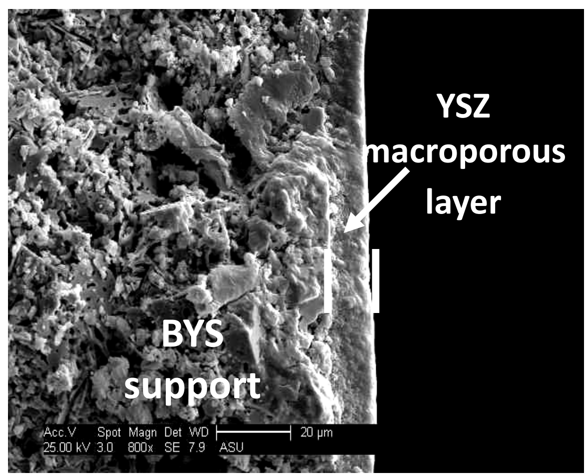
SEM Images of Composite Membrane

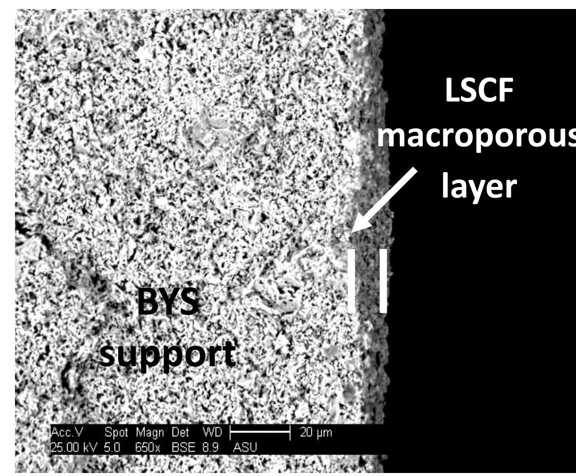




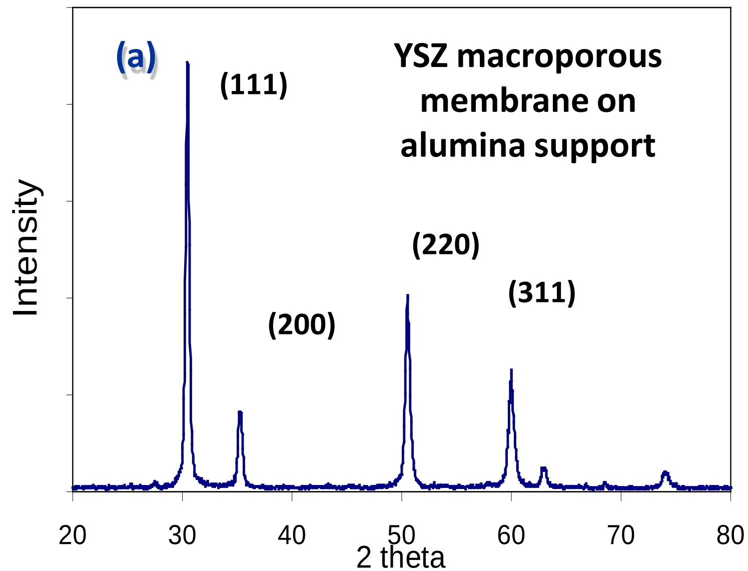


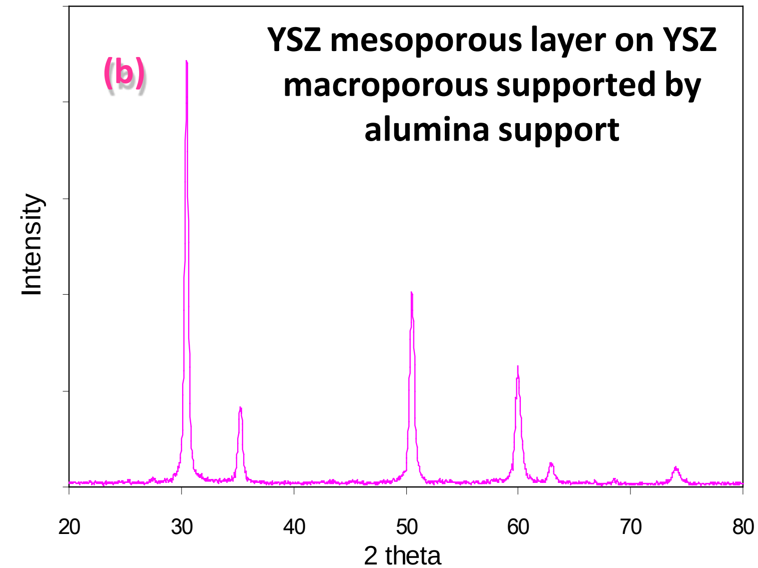


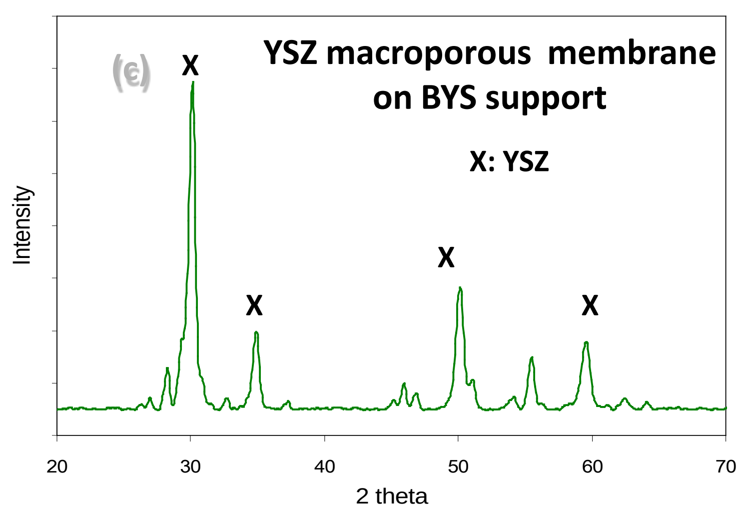




XRD Patterns of Composite Membranes







No XRD peaks for the alumina (Figure a) indicating a thickness of the YSZ coated on alumina disk of at least 10 μm

No difference between XRD patterns of YSZ mseoporous and YSZ macroporous layers (Figure b) indicating same phase structure

Index of YSZ (Figure c) indicating its coating on BYS support

Results of Molten Carbonate Infiltration

Support / Properties	YSZ macroporous membrane on alumina	YSZ mesoporous membrane on alumina	YSZ macroporous membrane on BYS	LSCF macroporous membrane 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 ermeance 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 $mol/m^2 \cdot Pa \cdot s$	$<10^{-9}$	$<10^{-9}$	Experiment in progress	Experiment In progress

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

- LSCF-Carbonate dual-phase membrane disks prepared
- Prepared dual-phase membranes showed desired CO_2 permeance and selectivity
- Multiple-layer ionic conducting porous supports prepared, and coating thin dual-phase membrane in progress
- Year 1 milestones met

Acknowledgement

- Department of Energy
  - National Energy Technology Laboratory

    Arun Bose (DoE Project Manager)