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

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July 10, 2013
Pittsburgh, Pennsylvania

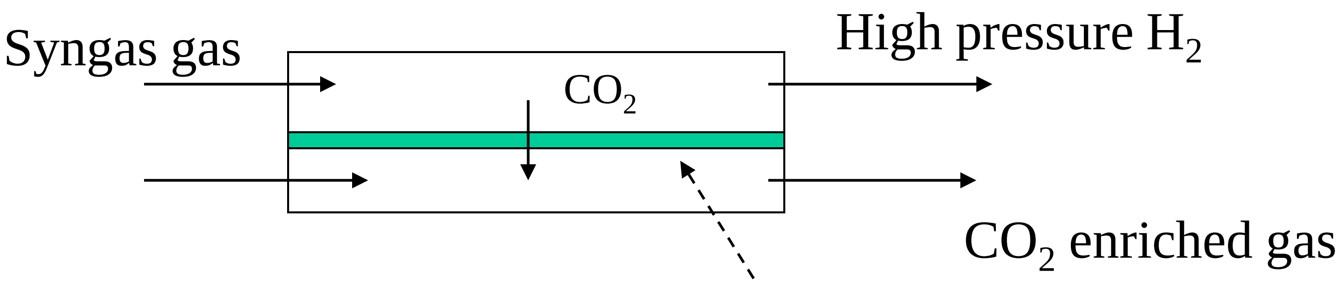
Tasks

- 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

Background

High Temperature CO_2 Selective Membranes

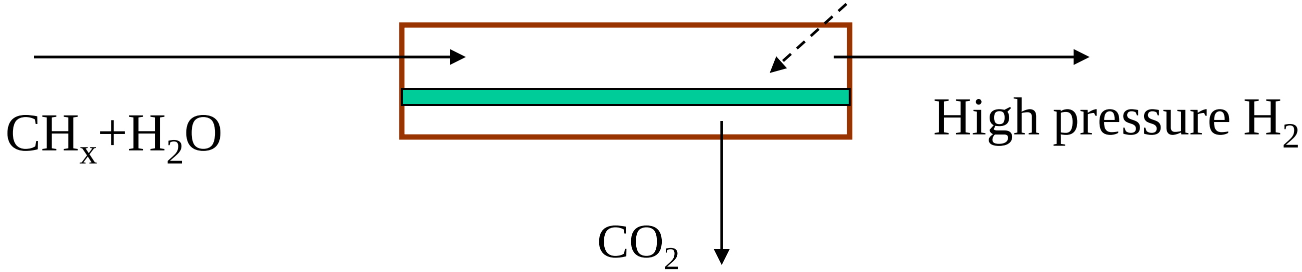
- Pre-combustion CO_2 capture at higher temperatures (400-800^{o}C)



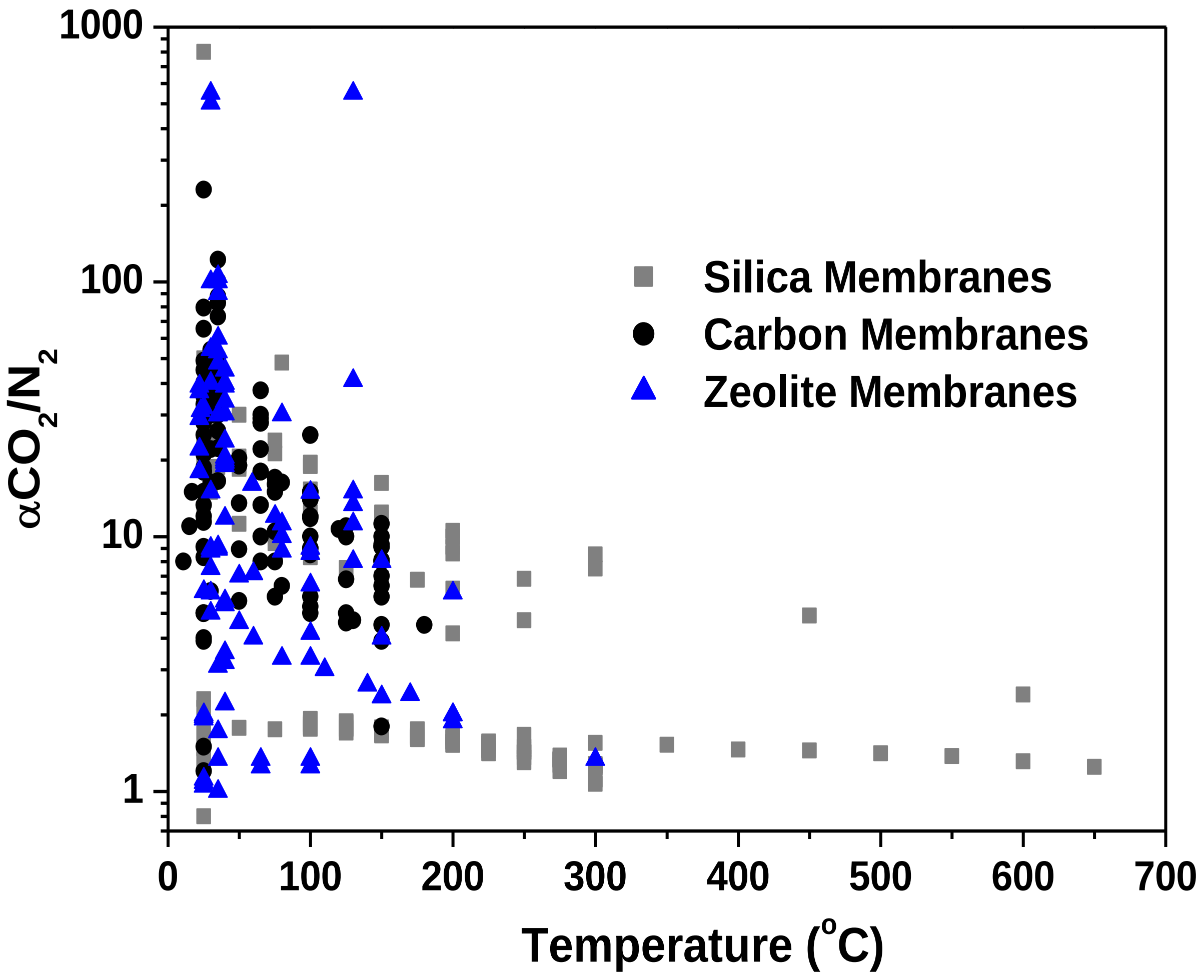
- Reforming reaction with CO_2 removal (600-900^{o}C)

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

High temp. membrane for CO_2 removal



CO_2 Perm-Selective Inorganic Membranes



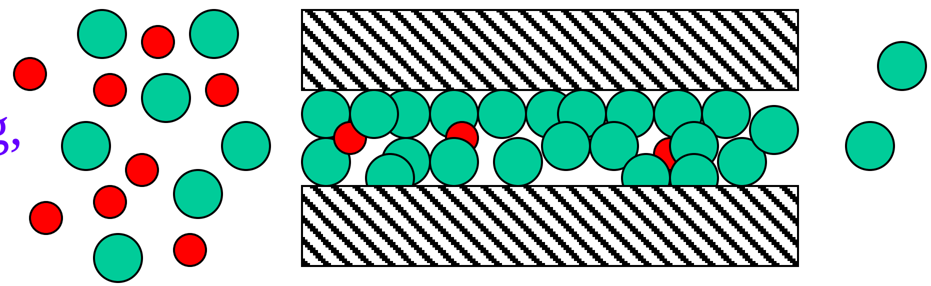
- Microporous membranes made from silicas, carbons and zeolites are capable of separating CO_2 from N_2 at low temperature
- Ultrathin, ion exchanged Y-type zeolites are best candidates for low temperature separation
- CO_2/N_2 selectivity decreases with increasing temperatures

Separation Mechanism - Adsorption & Diffusion

F = [Solubility][Diffusivity]

Adsorption Dominating

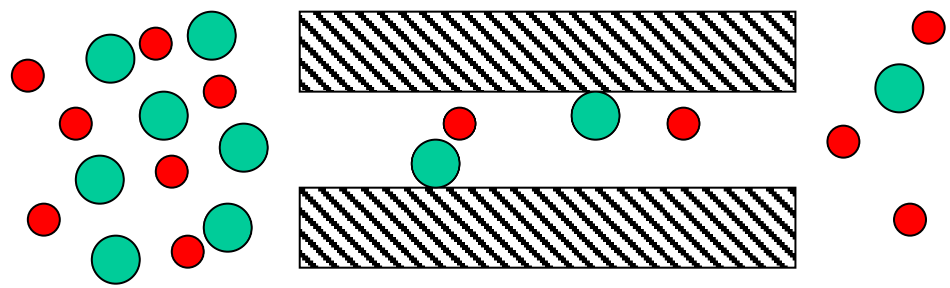
(strongly adsorbing, low temperature)



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

Diffusion Dominating

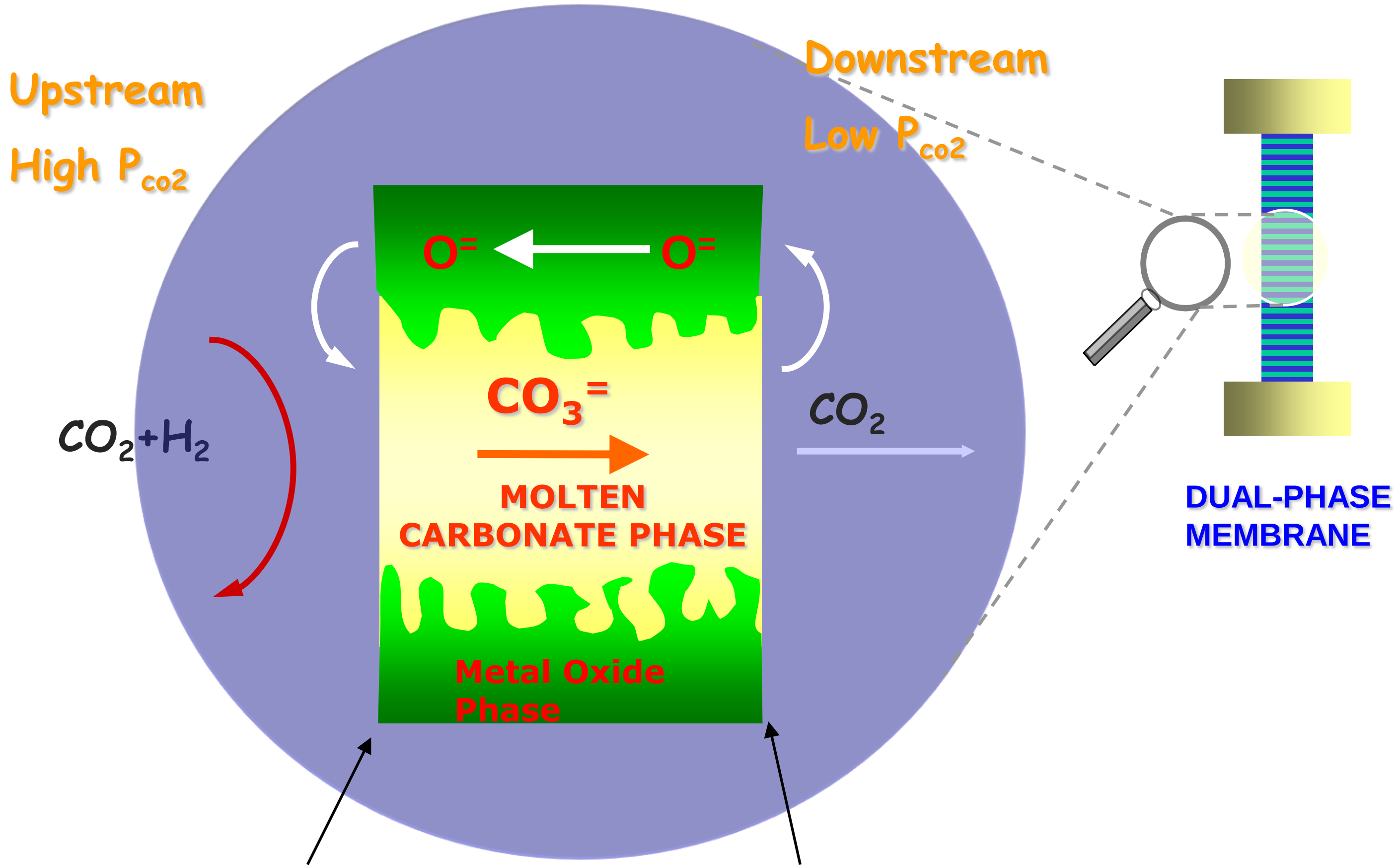
(non-adsorbing, or high temperature)



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

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

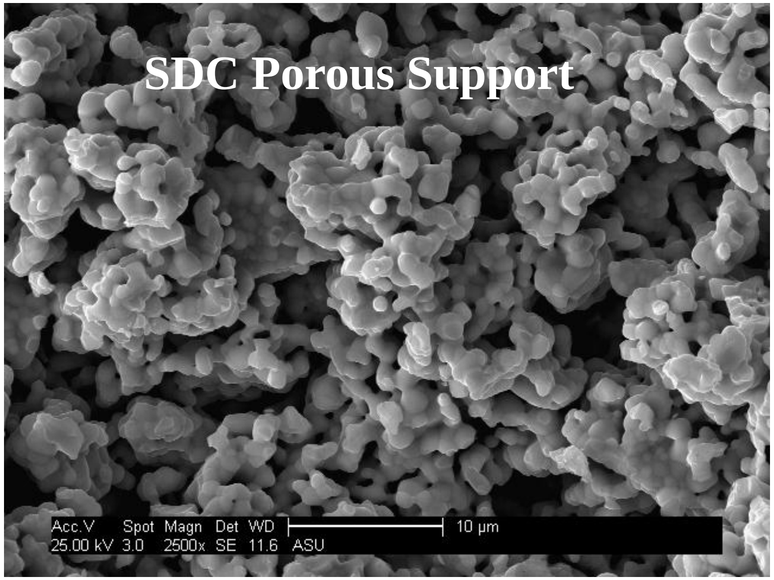
Concept of Dual-Phase Membrane



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

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

Dual-Phase Membrane Characteristics



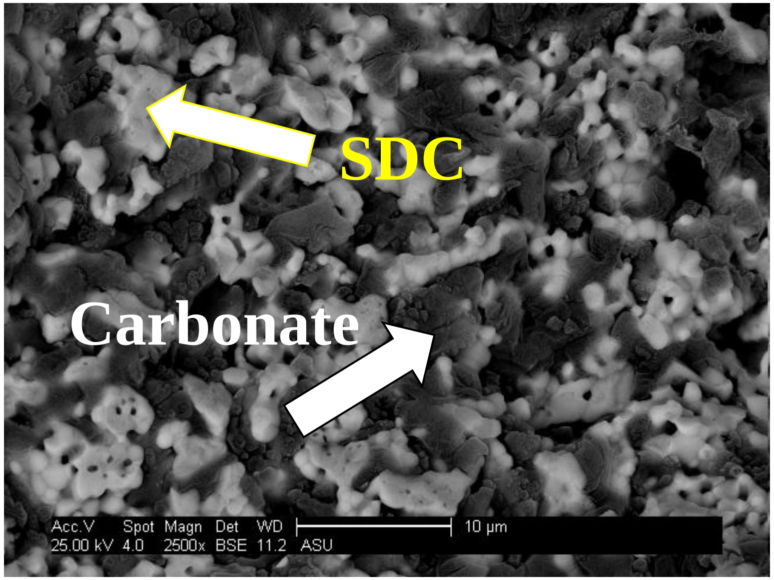
- **He permeance of support:**

  ~ 10^{-6} mol/m^2·s·Pa

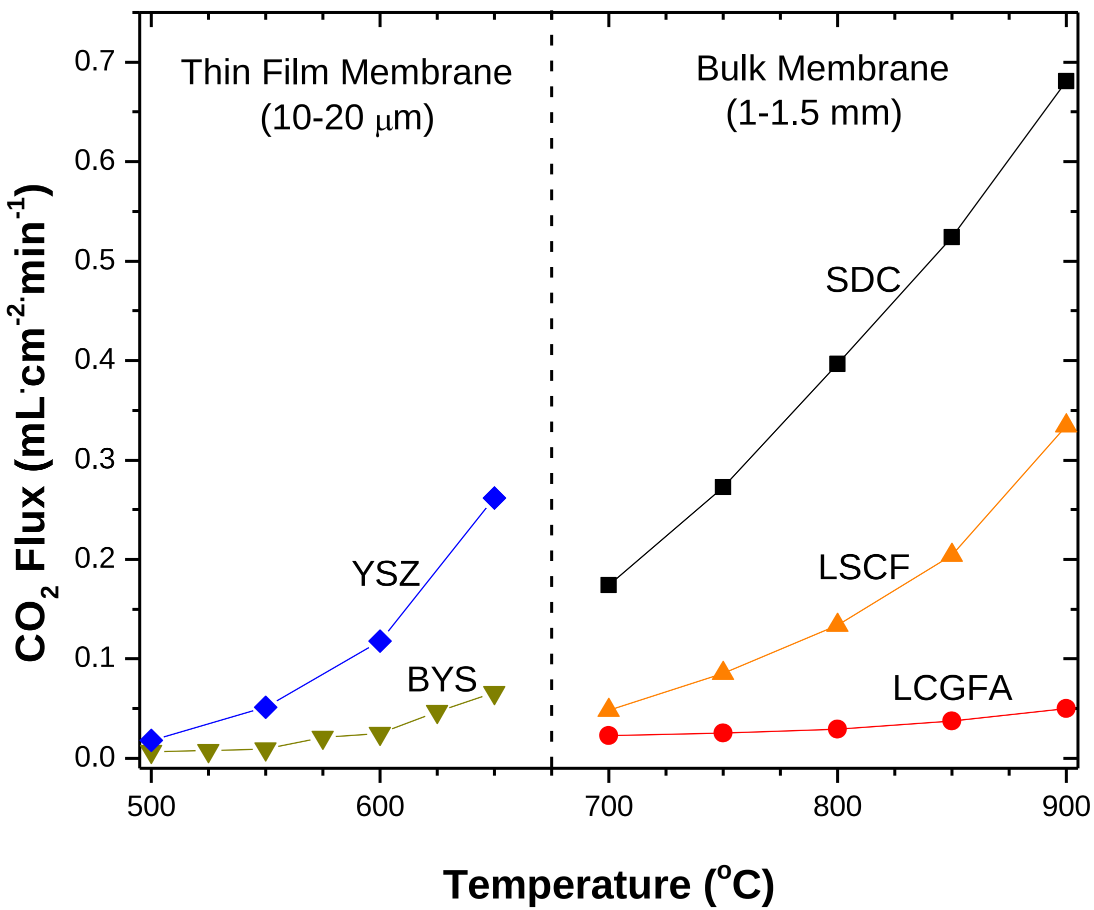
- **After infiltration of carbonate:**

  - He permeance:

  $<10^{-10}$ mol/m^2·s·Pa



Carbon Dioxide Permeance

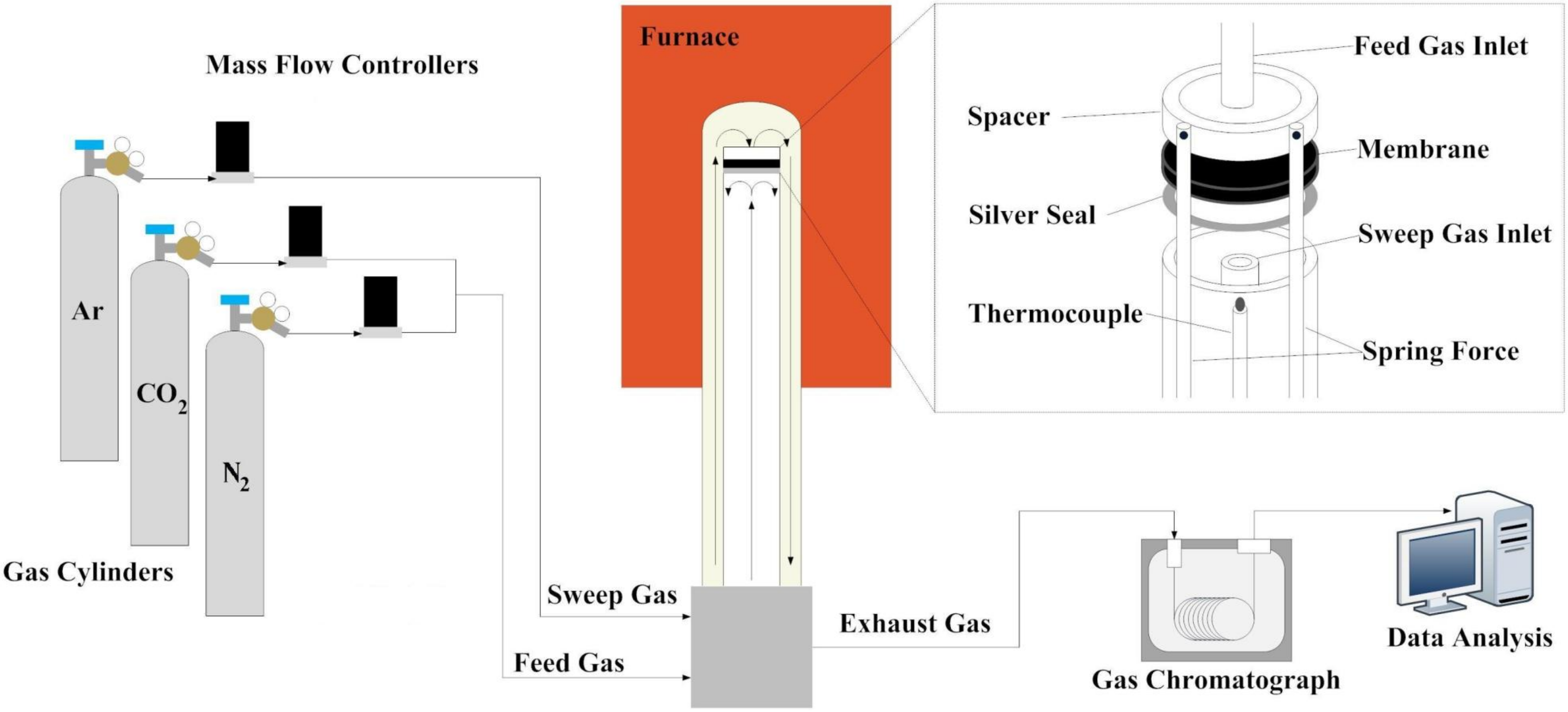


- **All ceramic supports infiltrated with Li/Na/K molten carbonate**
- **Feed CO_2 concentration of 50% (YSZ tested with 25%)**
- **Feed and sweep flow rates of 100 mL·min^{-1}**

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	$La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.6}Al_{0.05}O_{3-\delta}$

All membranes tested with 43.5/31.5/25 Li/Na/K (mol%) carbonate mixture

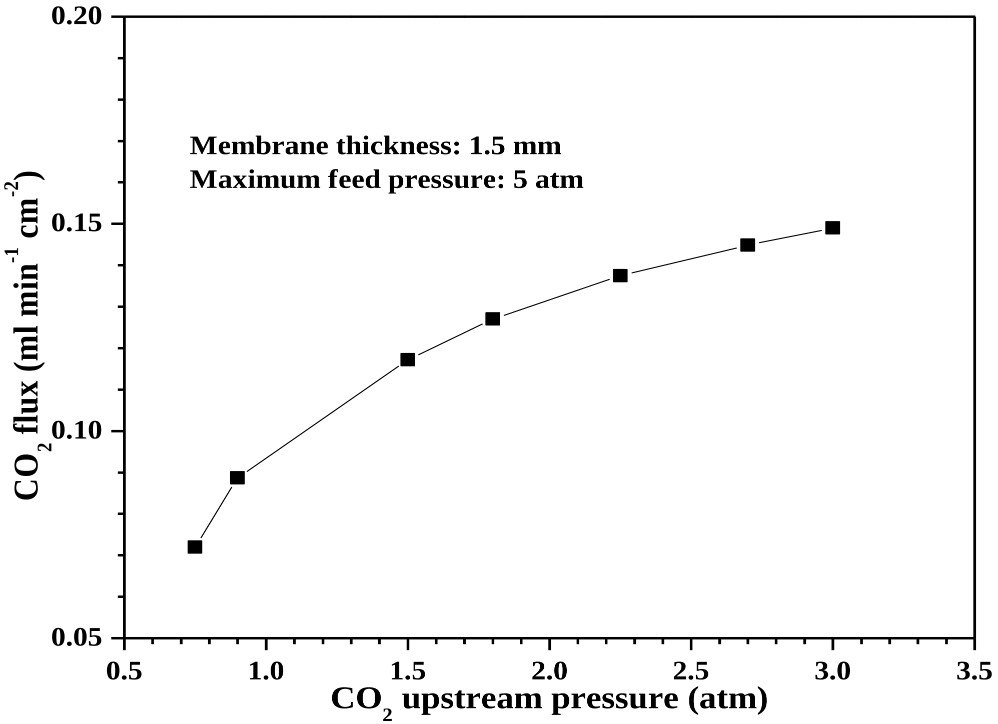
High Temperature Permeation Measurements



Progress and Current Status of Project

Part I: High pressure SDC carbonate disk membranes

High Pressure CO_2/N_2 Feed Test



Feed gas composition:
50%CO_2, 50%N_2

Feed gas flow rate:
50 ml/min

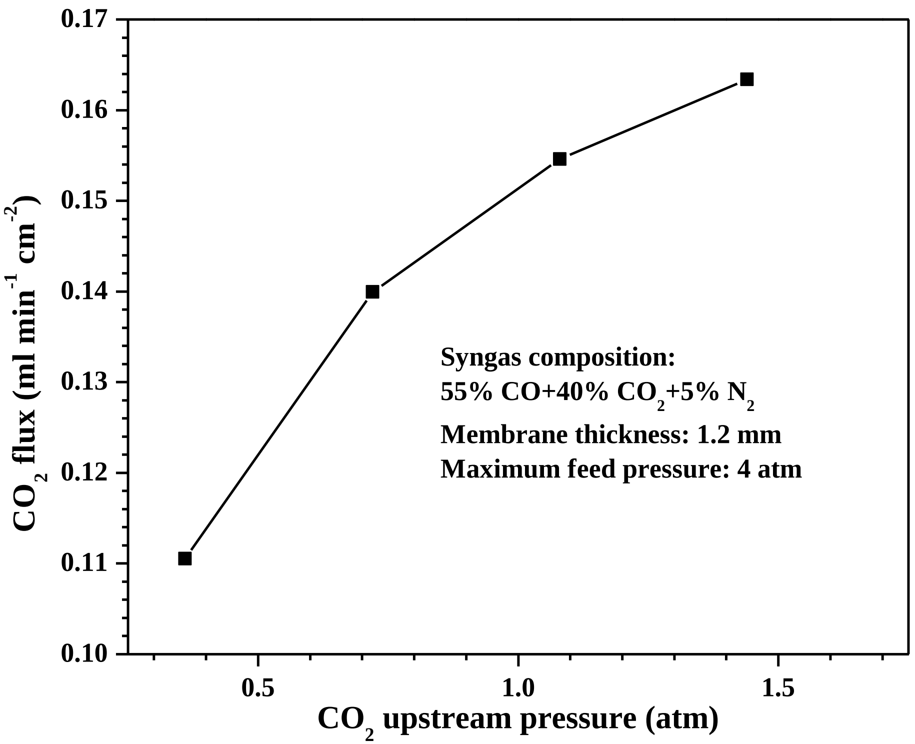
Temperature: T=700 ºC

Total Feed Pressure range:
1-5 atm

CO_2 flux increases with upstream carbon dioxide partial pressure;

The membrane exhibited good mechanical strength at high pressure.

High Pressure Syngas Feed Test



Feed gas composition:
50% CO, 35% CO_2, 10% H_2, 5% N_2

Feed gas flow rate:
50 ml/min

Temperature: T=700 °C

Total Feed Pressure range:
1-4 atm

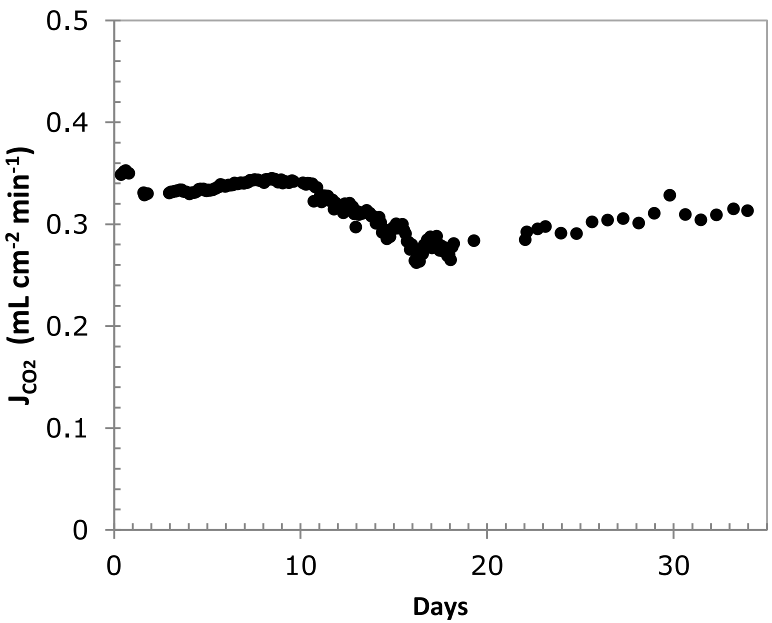
CO_2 flux did not change after normalized by thickness;

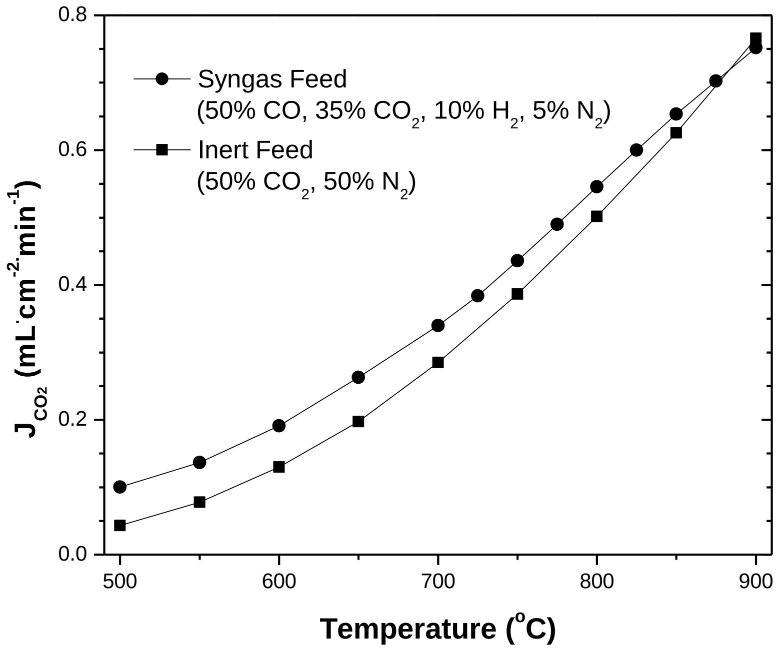
The membrane was stable in high pressure syngas.

Part II: Long term stability of SDC-carbonate disk membranes

SDC-Carbonate Membrane in Syngas

- SDC-carbonate permeation was measured with feed composition of 50% CO, 35% CO_2, 10% H_2, 5% N_2
- SDC-carbonate shows excellent stability for 35 days





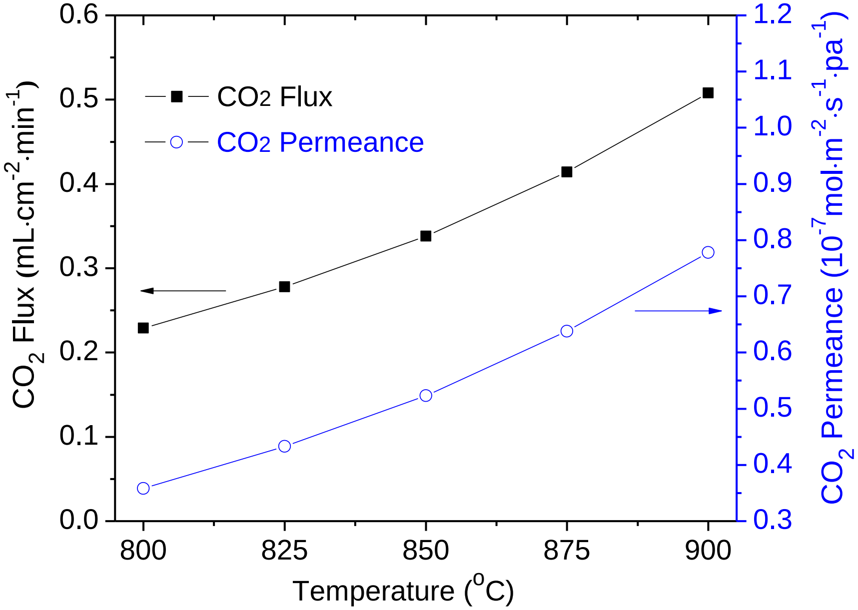
- SDC-carbonate permeation increased with exposure to syngas due to increase in driving force

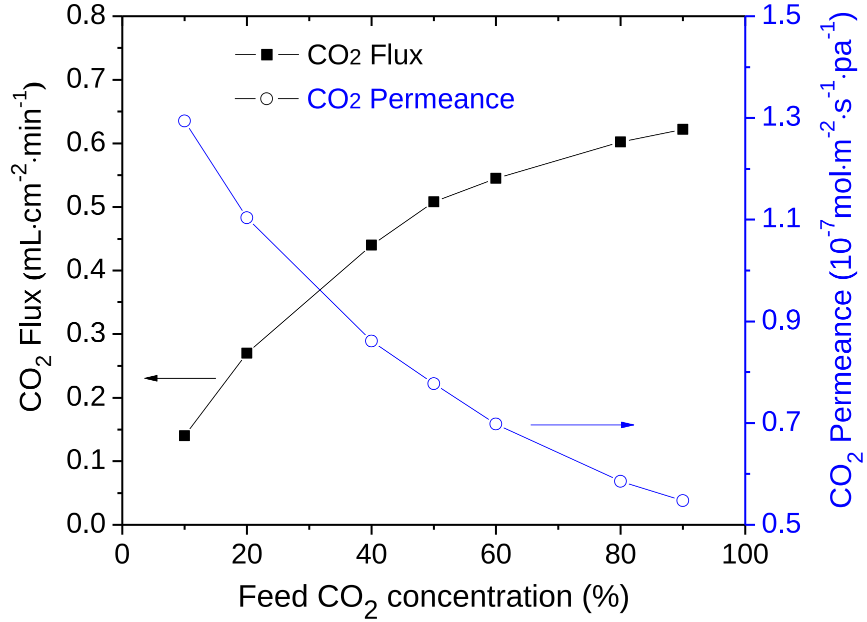
Part III: Symmetrical Tubular SDC-Carbonate Membranes

&

WGS Reaction Tests

CO_2/N_2 Separation



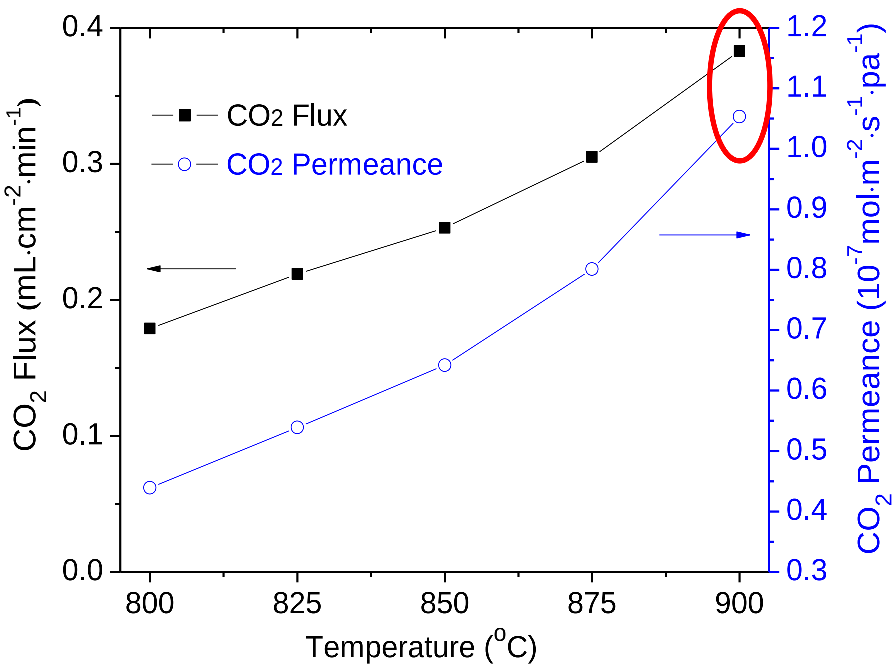


- **900 ^{o}C, CO_2 permeation flux 0.51 ml·cm^{-2}·min^{-1}, CO_2 permeance 0.78×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1}.**

- **The CO_2 flux increases with increasing the feed CO_2 concentration, while the permeance decreases.**

CO_2 Separation from Simulated Syngas

Simulated syngas (50% CO, 36% CO_2, 10% H_2 and 5% N_2) was fed to the membrane



Feed side: simulated syngas flow rate 50 $ml\cdot min^{-1}$; Sweep side: He flow rate 50 $ml\cdot min^{-1}$.

Thickness of the membrane is about 1.5 cm.

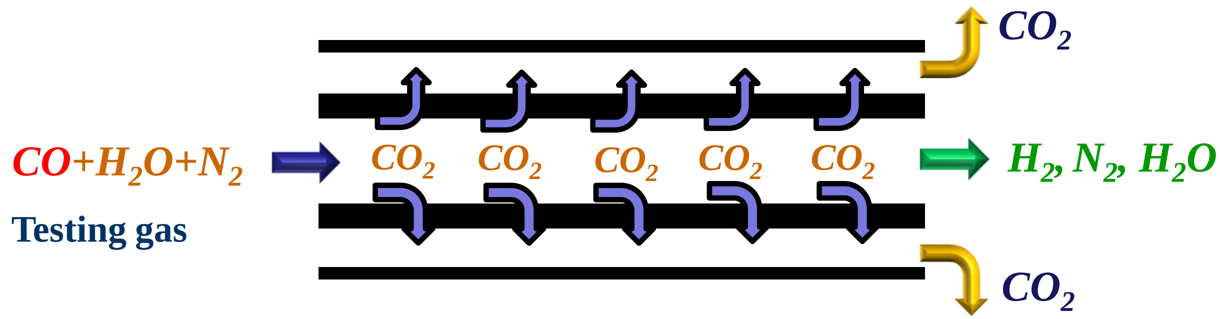
Feed	Feed CO_2 concentration	CO_2 flux ($ml\cdot cm^{-2}\cdot min^{-1}$)	CO_2 permeance ($mol\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-1}$)
Syngas	36%	0.38	1.05 10^{-7}
CO_2/N_2	40%	0.44	0.86 10^{-7}
	50%	0.51	0.78 10^{-7}

- **900°C, CO_2 separation results agree well with the data from CO_2/N_2 separation.**

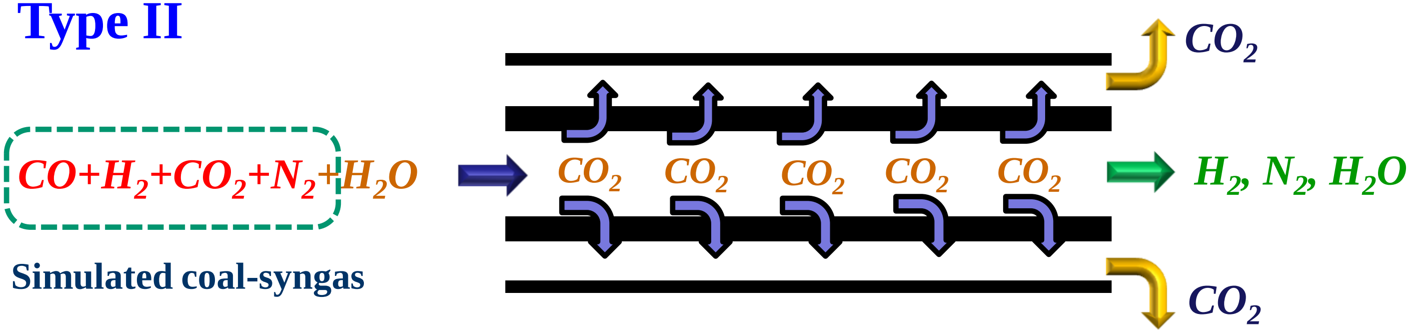
Tests in Membrane Reactor WGS Tests

Water gas shift at high temperatures

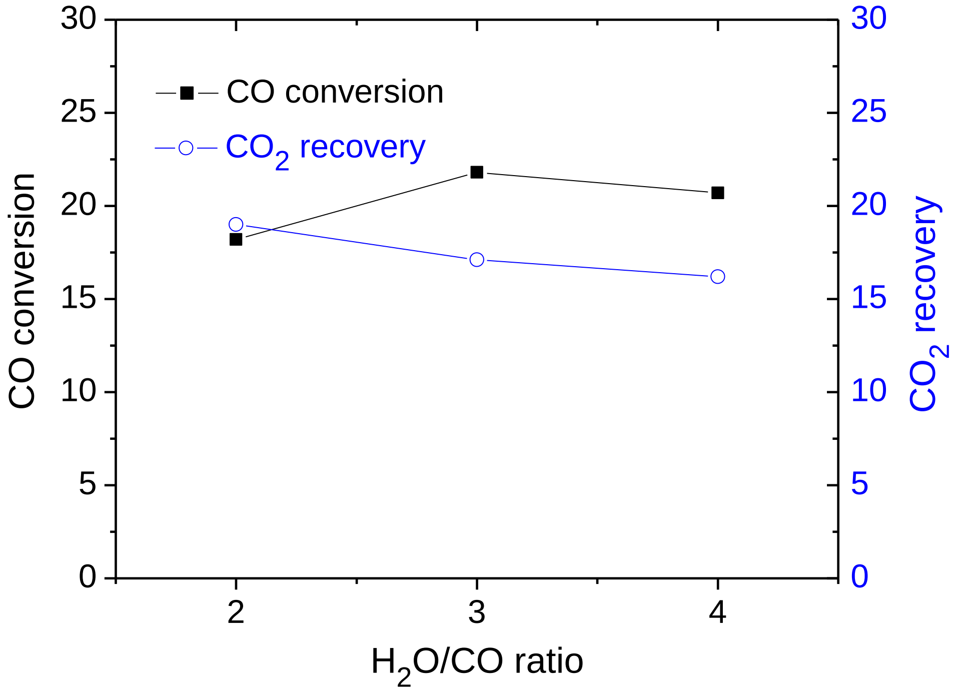
Type I



Type II



High Temperature WGS: Type I H_2O/CO Feed



Operation temperature: 800°C

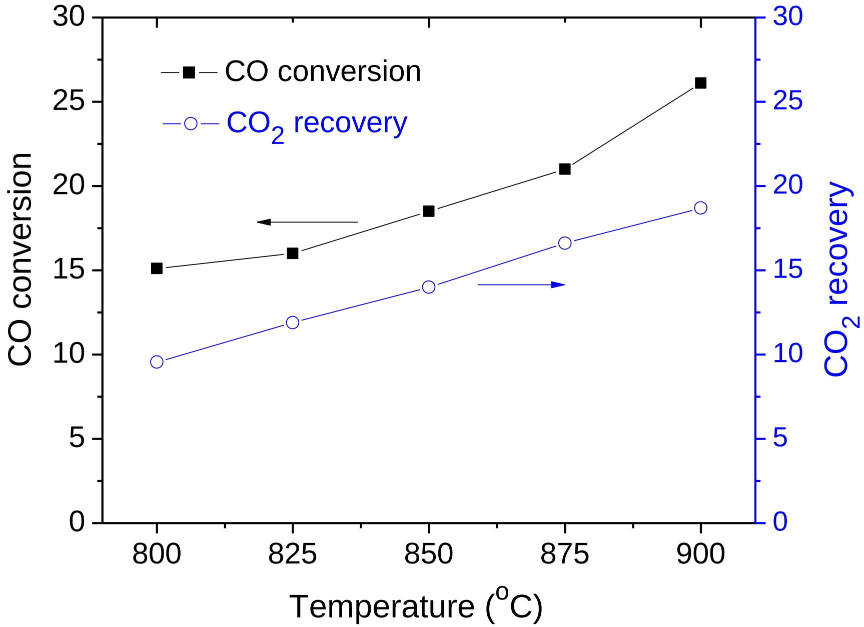
Feed Composition: 33%CO, 66% N_2
Flow Rate: 30 ml/min

Sweep:
Helium at 60 ml/min.

Thickness of the membrane is about 1.5 cm.

- **With increasing H_2O/CO ratio, the CO conversion increases first and then decreases, while the CO_2 recovery decreases;**
- **the optimized H_2O/CO ratio is 3.**

High Temperature WGS: Type II H_2O/Syngas Feed



Feed: syngas 20 ml/min, N_2 10 ml/min and H_2O to CO ratio is 3;

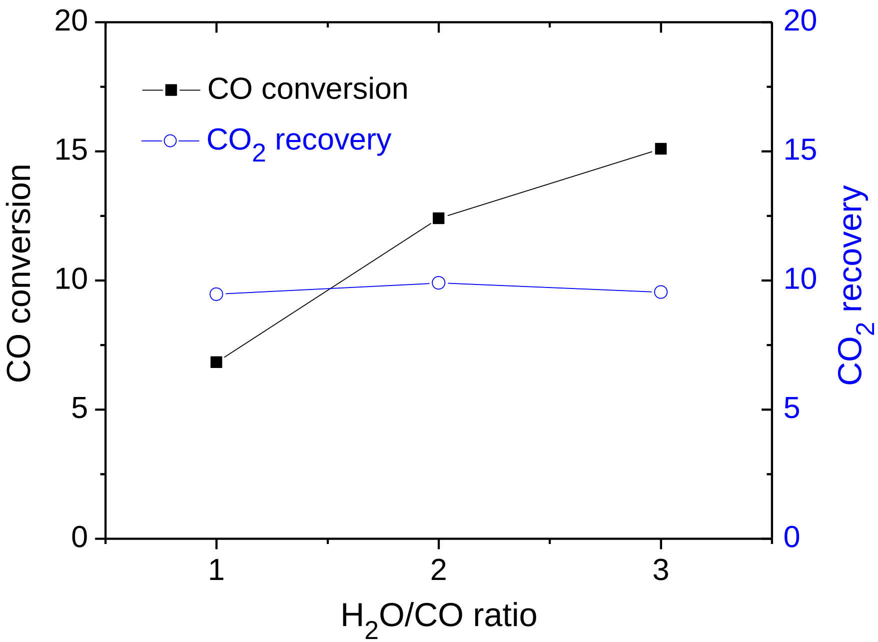
Sweep: Helium 60 ml/min.

Thickness of the membrane is about 1.5 cm.

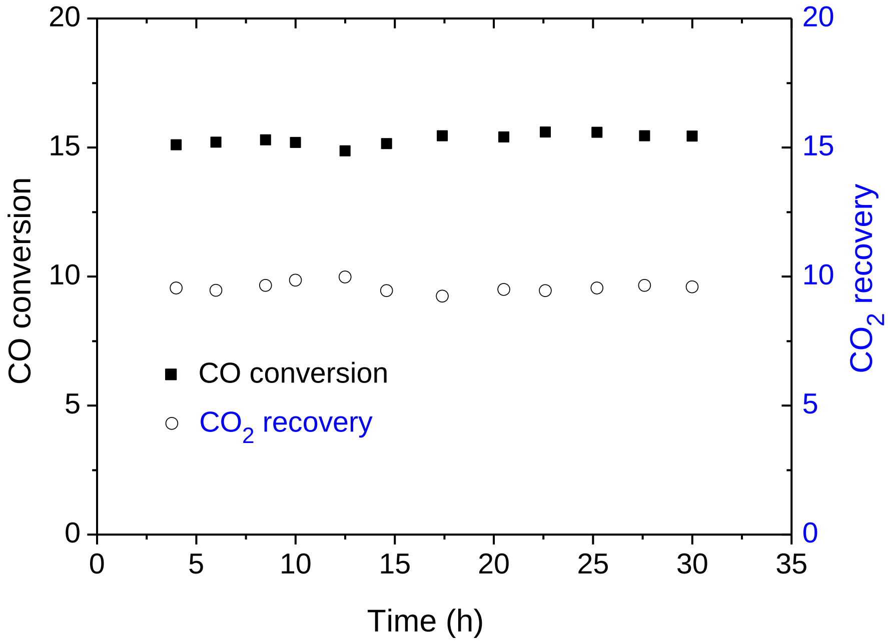
Temperature: 800°C

Feed: syngas 20 ml/min and N_2 10 ml/min, H_2O/CO ratio 1-3.

Sweep: helium 60 ml/min.



High Temperature WGS: Type II H_2O/Syngas Feed



Temperature: 800°C

Feed: syngas 20 ml/min, N_2 10 ml/min and H_2O to CO ratio is 3;

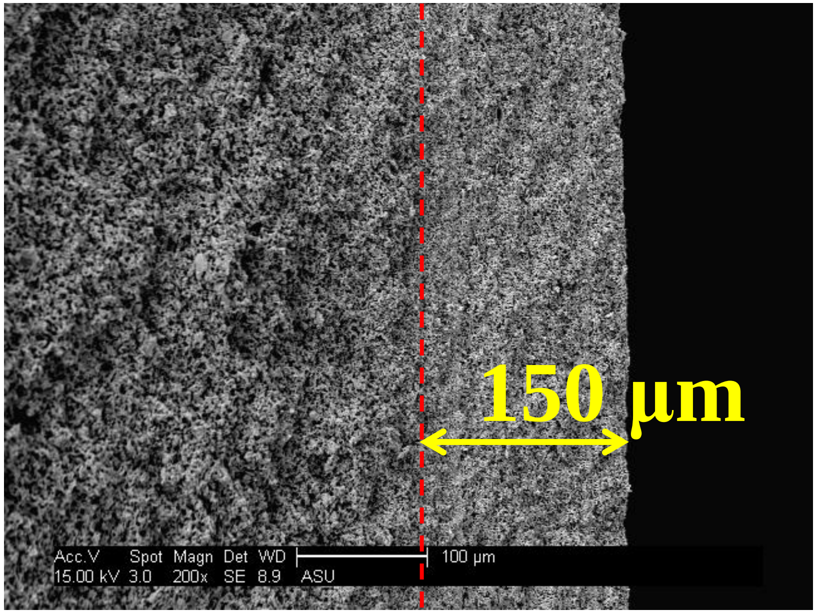
Sweep: helium 60 ml/min.

- **The CO conversion and CO_2 recovery are stable during the 30 h test;**
- **The membrane is stable under the high temperature syngas WGS environment.**

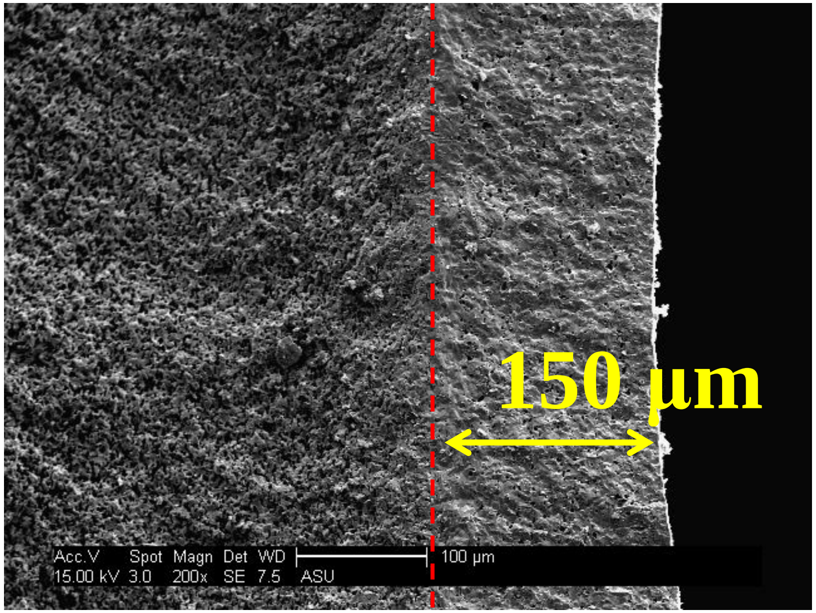
Part IV: Asymmetrical Thin Film Tubular SDC-Carbonate Membranes

Prepared by centrifugal casting method

SEM Images



SDC/SDC-BYS porous tube

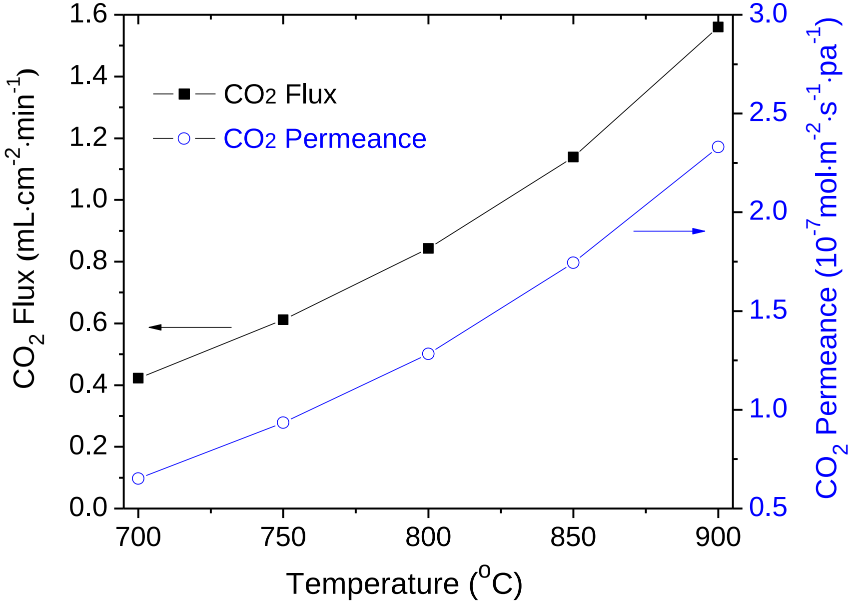


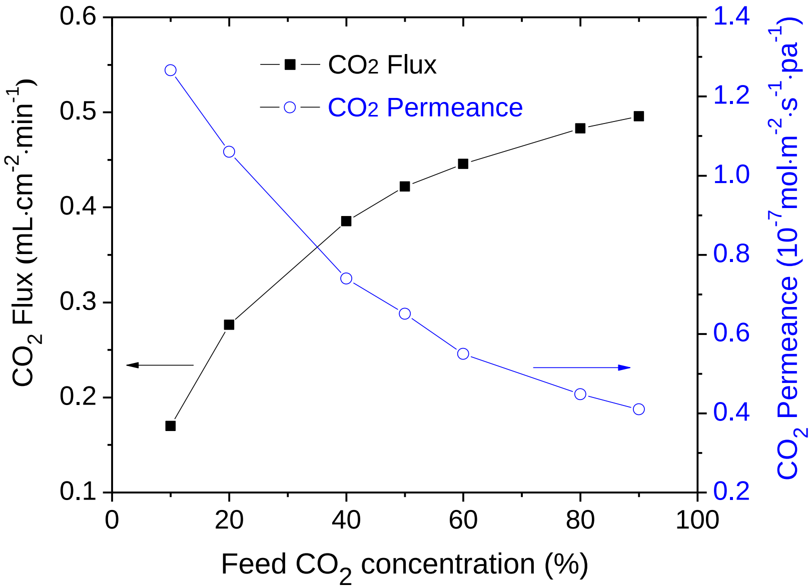
SDC/SDC-BYS membrane

- **The SDC layer bonded well with the SDC-BYS layer;**
- **After infiltration the SDC layer became dense while the SDC-BYS layer was still porous.**

CO_2/N_2 Separation Test

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}. Thickness of the membrane is about 150 μm.

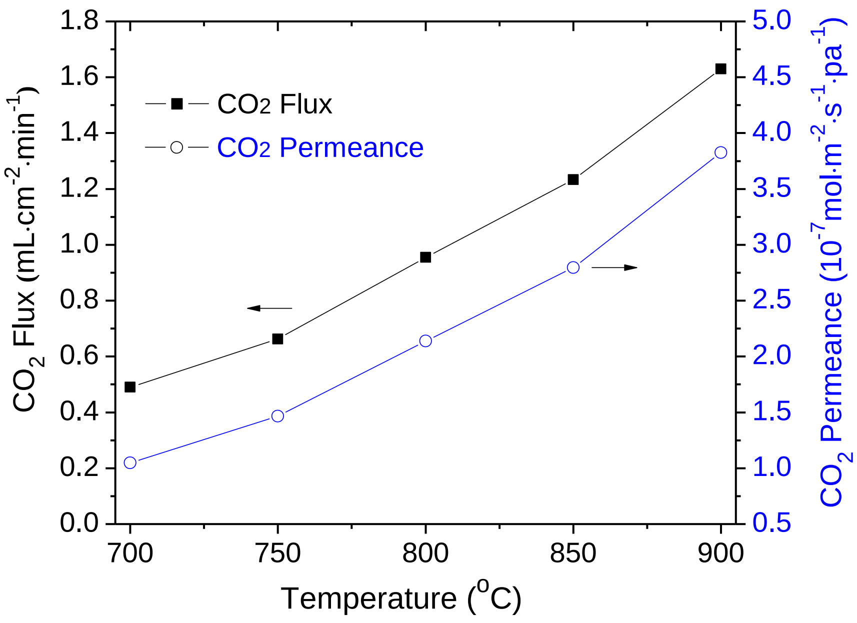




700°C, Feed side: CO_2 flow rate 5-45 ml·min^{-1}, CO_2 and N_2 total flow rate 50 ml·min^{-1};

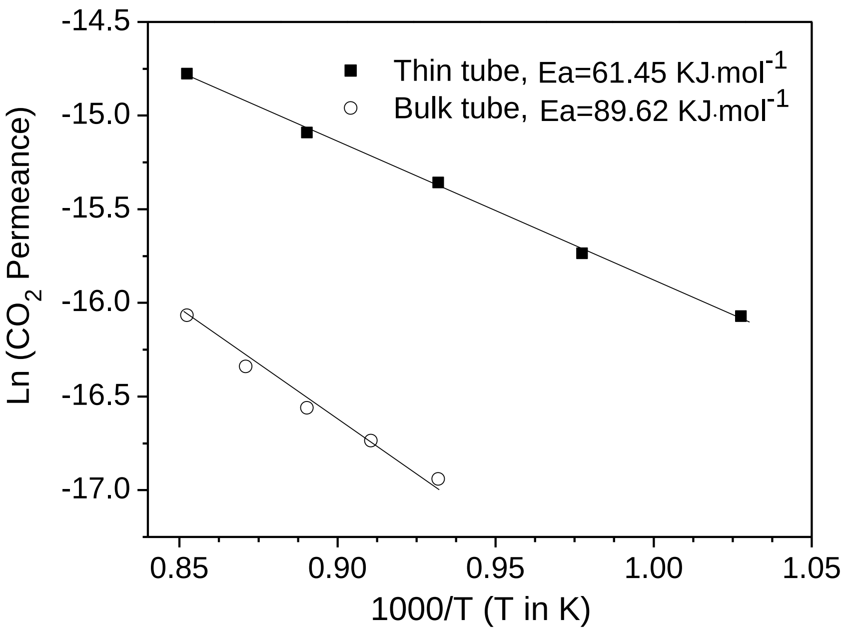
Sweep side: He flow rate 50 ml·min^{-1}.

CO_2 Separation from Simulated Syngas

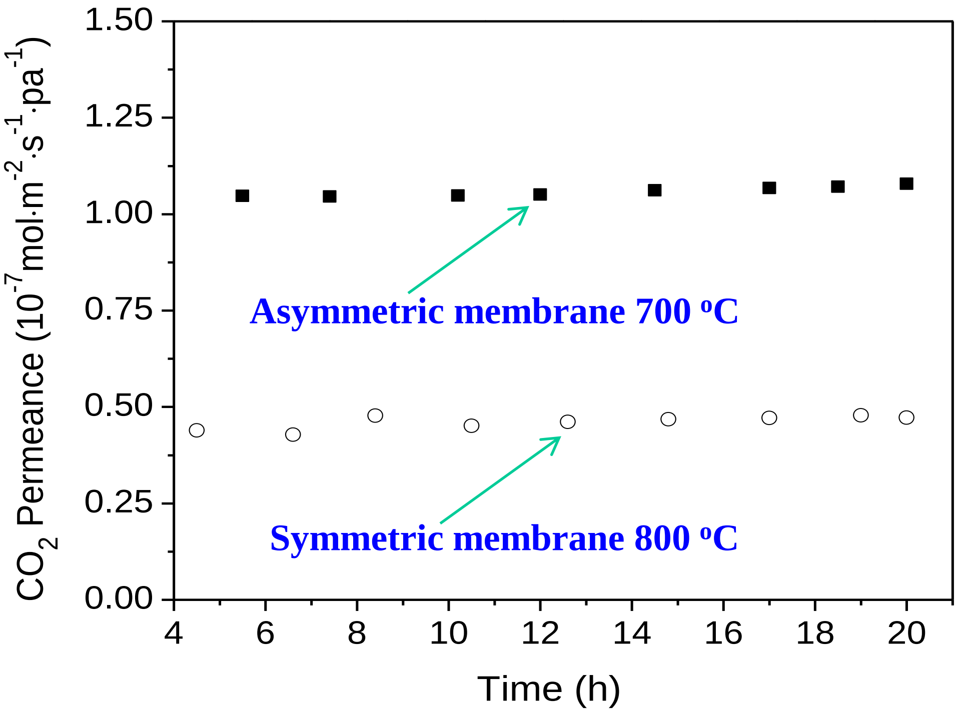


Feed side: syngas flow rate 100 ml·min^{-1}; Sweep side: He flow rate 100 ml·min^{-1}. Thickness of the membrane is about 120 mm.

Feed side: syngas flow rate 100 ml·min^{-1}; Sweep side: He flow rate 100 ml·min^{-1}.



CO_2 Separation from Simulated Syngas



Feed side: Syngas at 50 ml/min;

Sweep side: He at 50 ml/min.

- **Asymmetrical, thin membrane has much higher permeation flux than thick membranes.**
- **CO_2 permeance of the membrane is stable during the operating period;**
- **This membrane is potential for the application in pre-combustion CO_2 capture.**

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

- SDC-carbonate (disk and tubular) membranes prepared showing excellent CO_2 selectivity, CO_2 permeance with syngas feed
- SDC-carbonate membrane has shown feasibility for high temperature water gas shift reaction with simulated coal-gas feed
- SDC-carbonate membranes shows long-term stability of more than one month at 700^{o}C
- 150 μm dual-phase membrane successfully prepared on tubular support and tested in syngas conditions showing improved performance and stability