High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

Award No: DE-FE0031634

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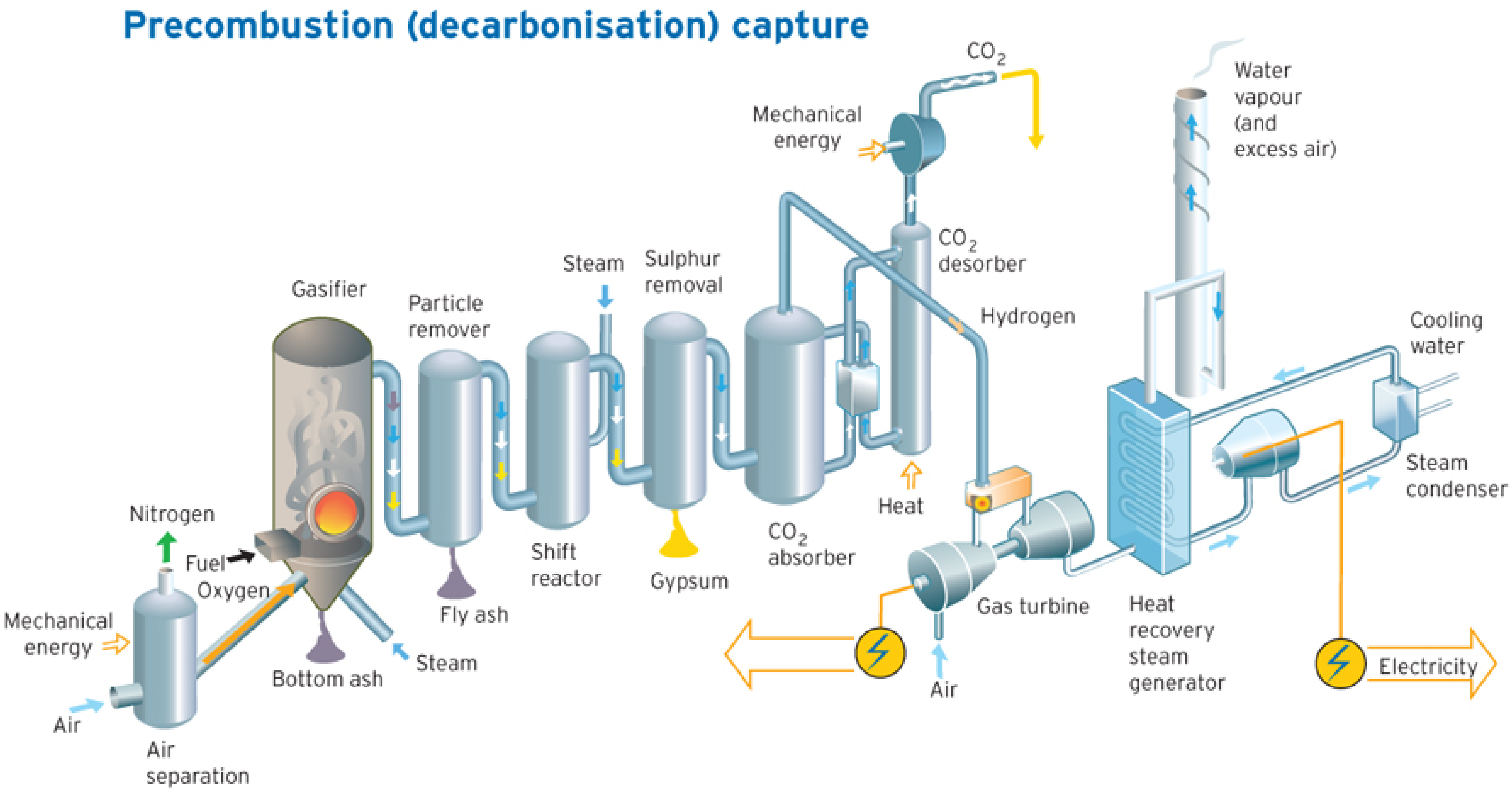
Project Kick-off Meeting
Nov.8, 2018

Background

and

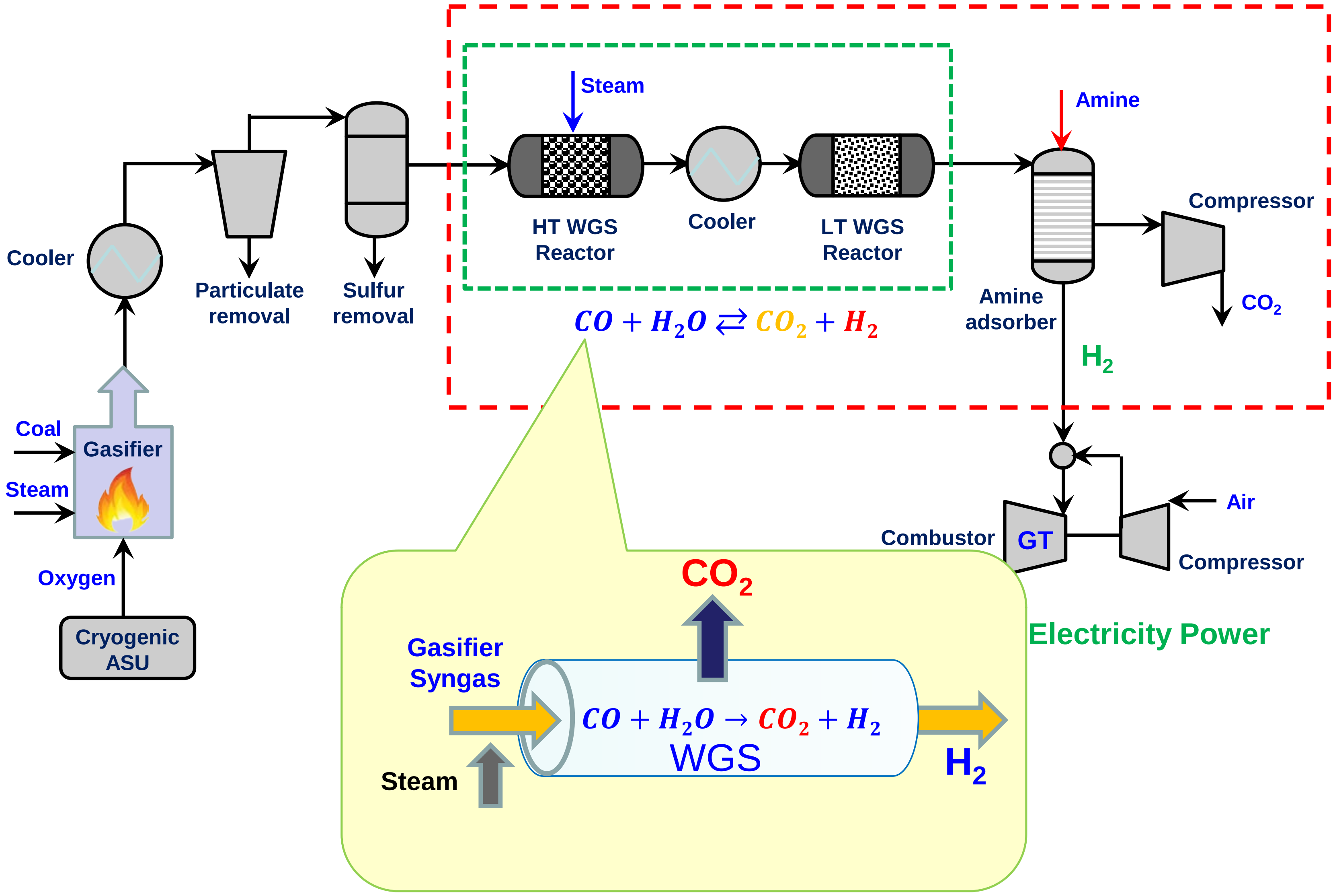
Preliminary Results

IGCC with Pre-Combustion CO_2 Capture Method

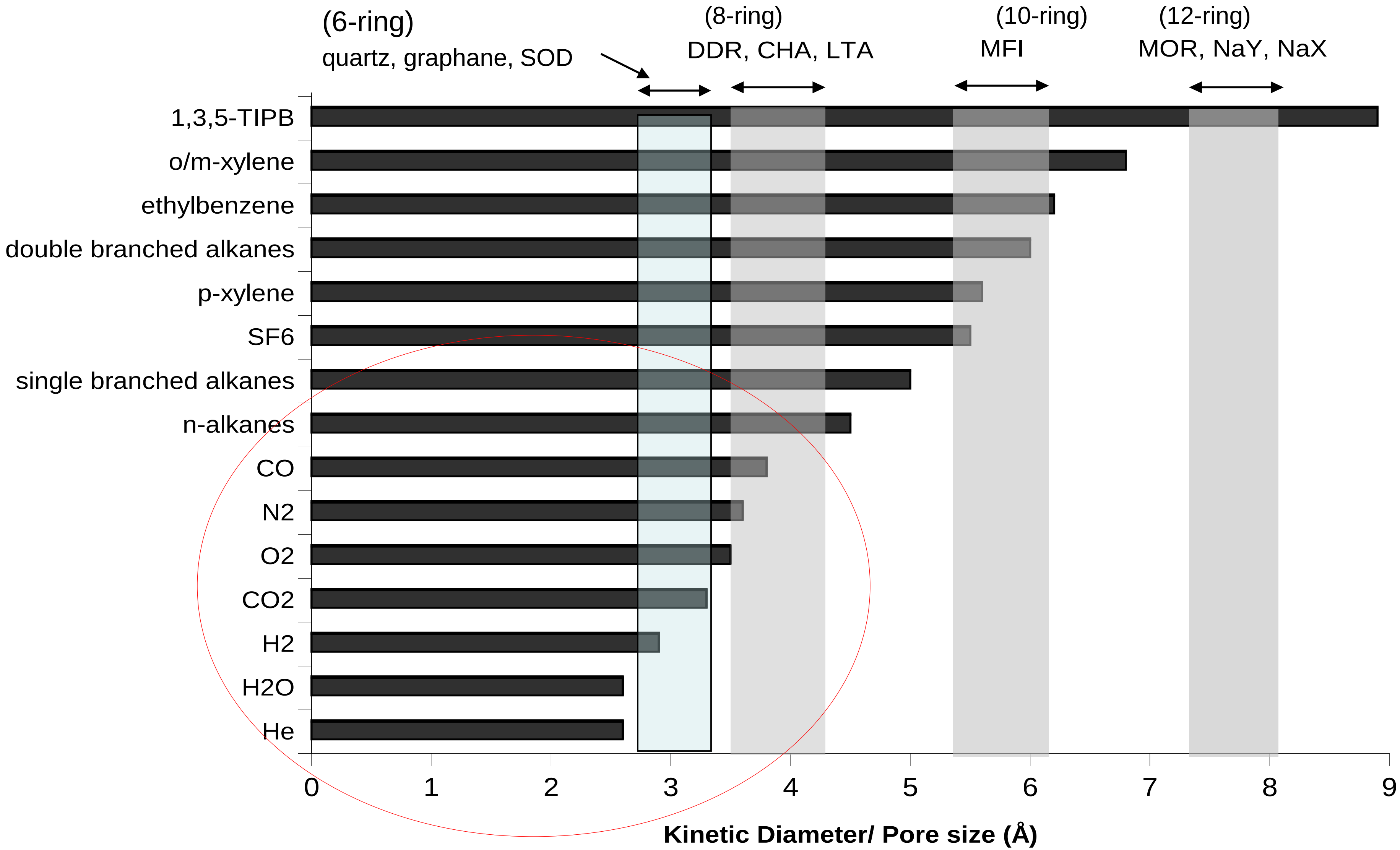


Ref.: CLIC Innovation Oy’s Carbon Capture and Storage R&D program / Finland

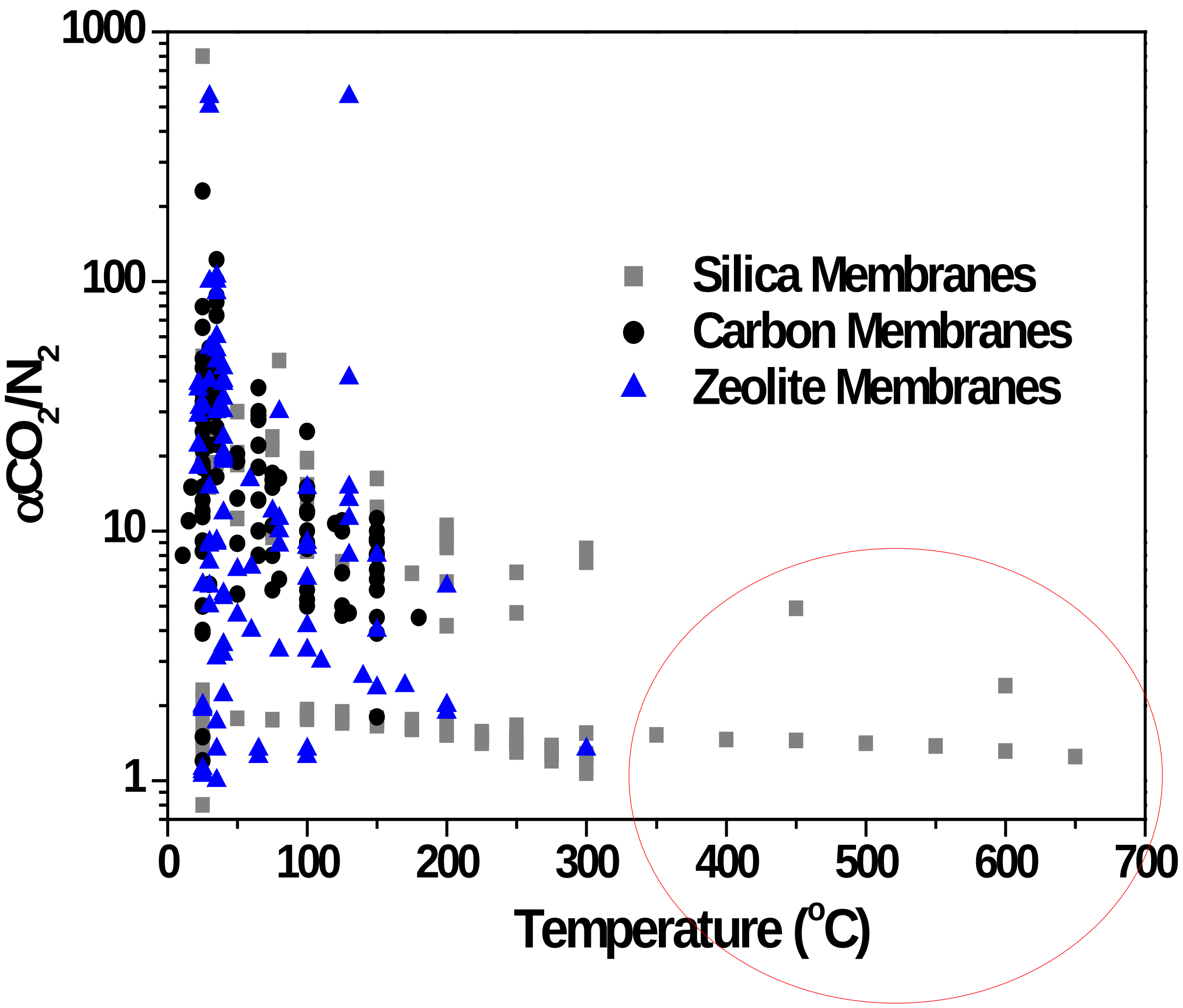
Membrane Reactor for H_2 Production and CO_2 Capture



Crystalline Microporous Materials vs Molecular Size



CO_2 Perm-Selective Inorganic Membranes



- **Microporous silica, carbon and zeolite membranes separate 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 temperature**

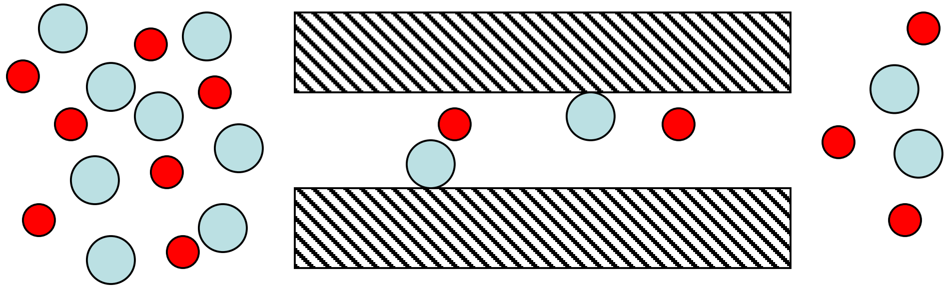
M Anderson, HB Wang & YS Lin, *Review Chem. Eng.*, 28, 101 (2012)

Diffusion-Controlled Permeation

F = [Solubility][Diffusivity]

Diffusion Dominating

(non-adsorbing, or high temperature)



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

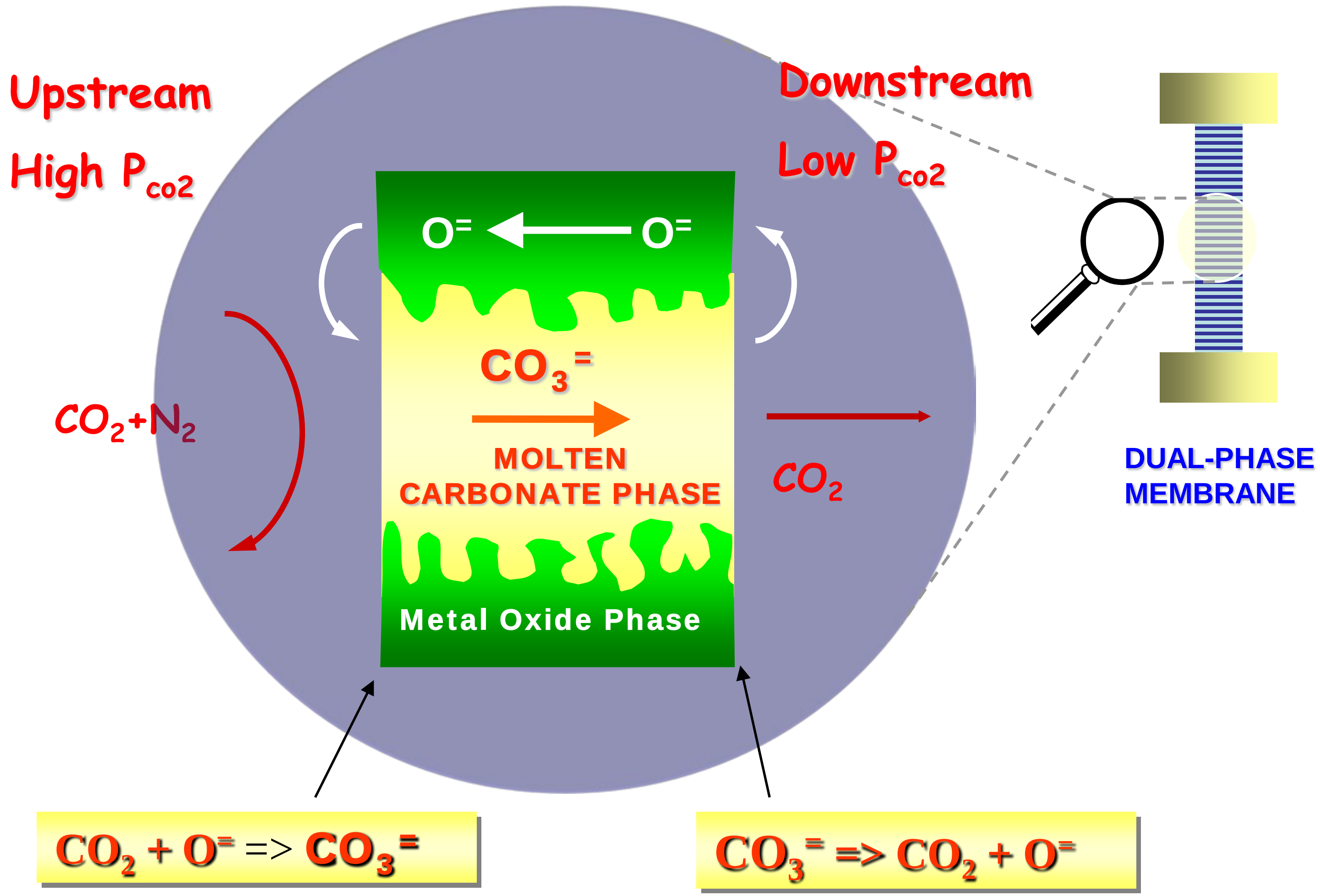
At high temperature (>300°C) solubility difference diminishes:

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 (CCDP) Membrane



M Anderson & YS Lin, Proc. *ICIM2006*, pp. 678-681 *(2006)*; *J. Membr. Sci*. 357, 122*(2010)*

Molten Carbonate

	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

Carbon Dioxide Permeation Flux-Theory

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

Total conductance

Membrane thickness

Experimental conditions

For SDC-carbonate membrane

$$J_{CO_2} = \frac{K' RT}{4F^2 L}[P'^{n}_{CO_2} - P''^{n}_{CO_2}]$$

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

TT Norton, B Lu & YS Lin, , *J. Membr. Sci. 467*, 244 (2014)

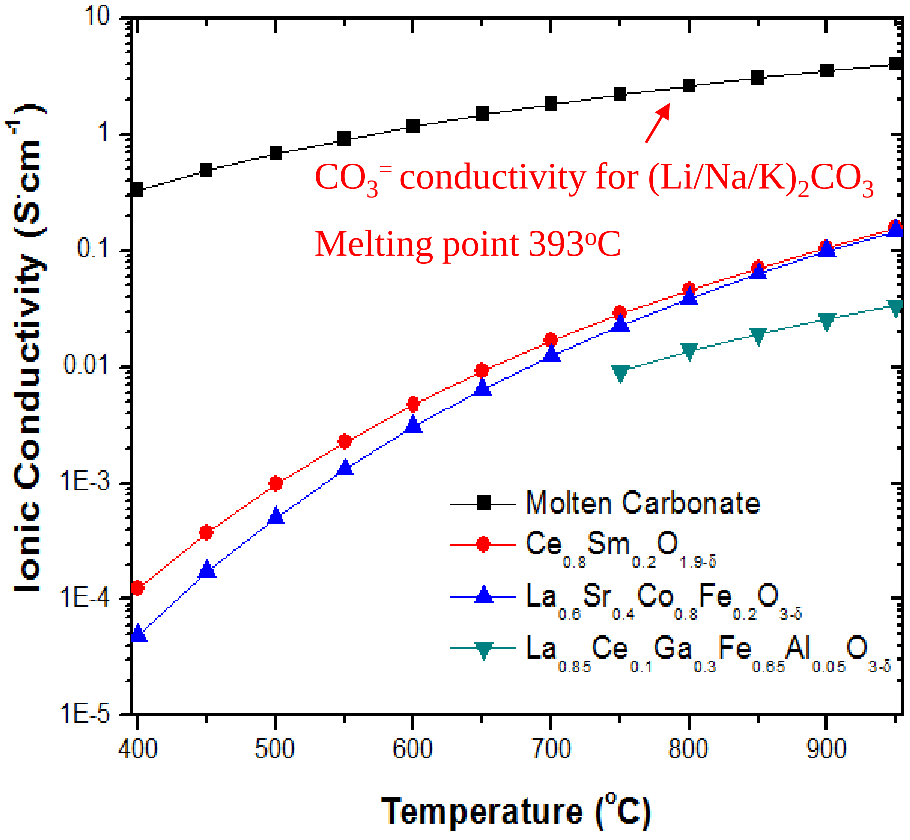
Selection of Materials

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

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

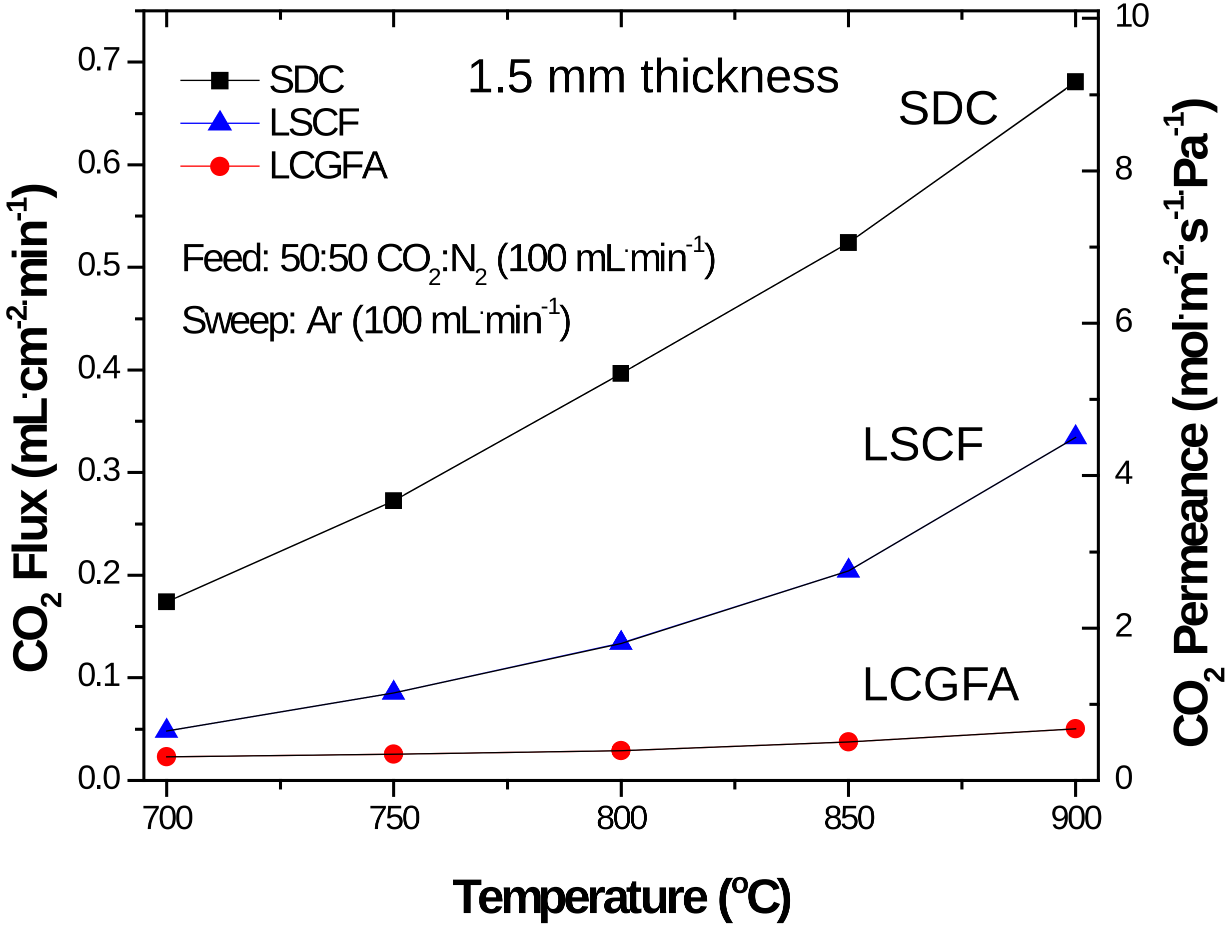
$La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.6}Al_{0.1}O_{3-\delta}$ (LCGFA)

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



Perovskite or Fluorite Structured Metal Oxides with Oxygen Vacancy Defects

Carbon Dioxide Permeation through CCDP Membranes

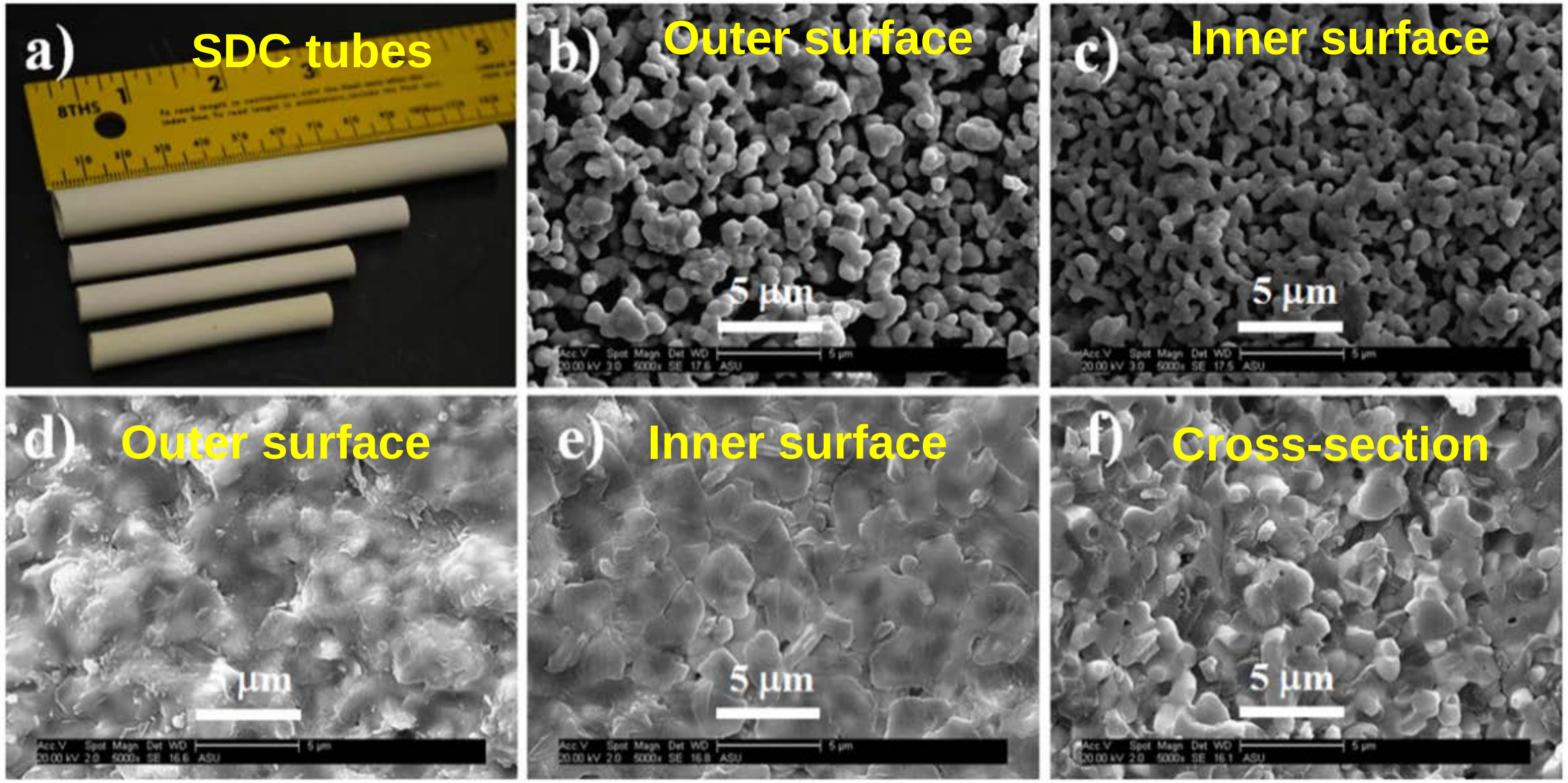


CO_2 permeation flux is proportional to oxygen ionic conductivity of the ceramic phase

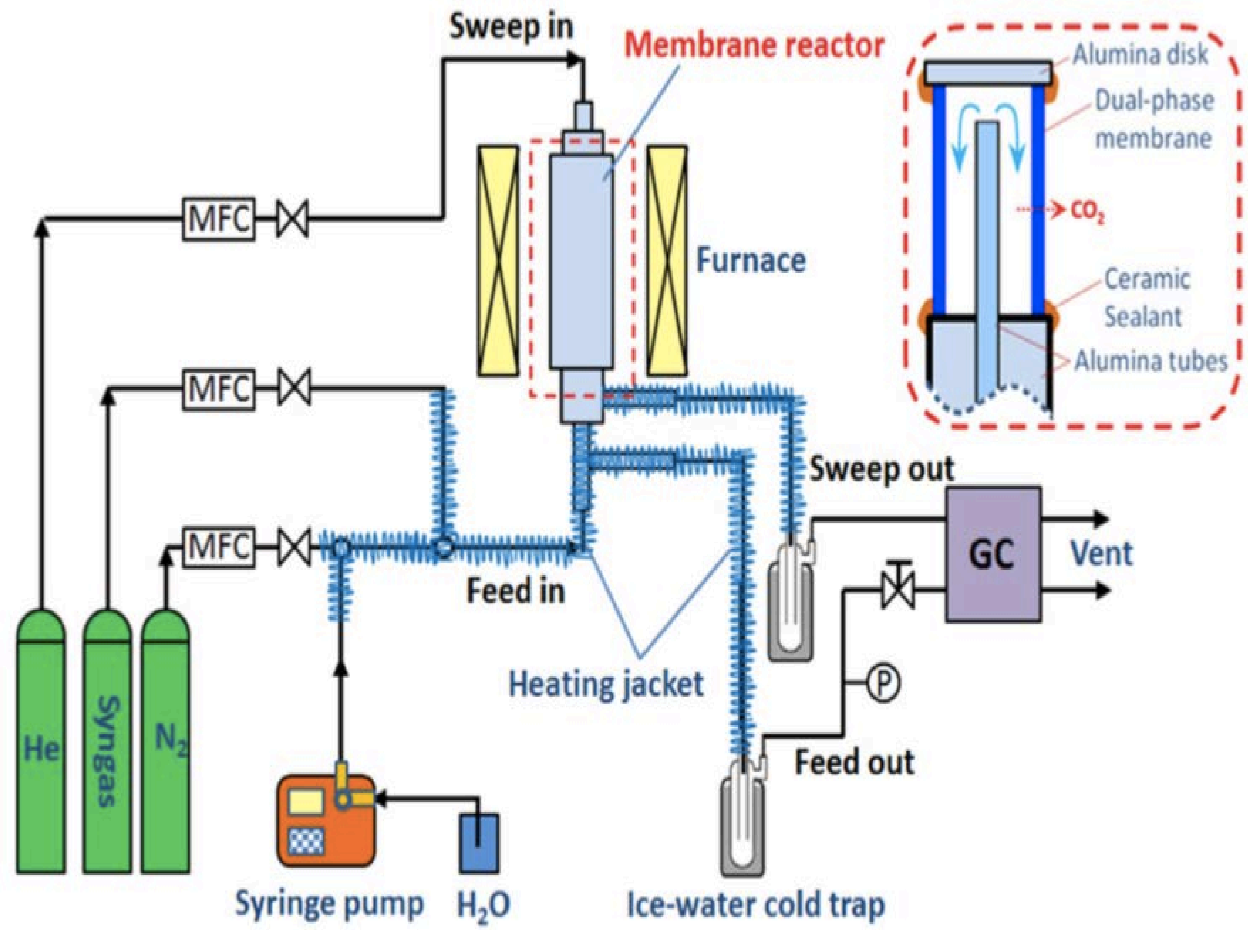
Morphology of Tubular CCDP membrane

Support

CCDP
Membrane



WGS with CO_2 Capture on CCDP Membrane Reactor



Membrane:

Ceramic: SDC;

Carbonate:

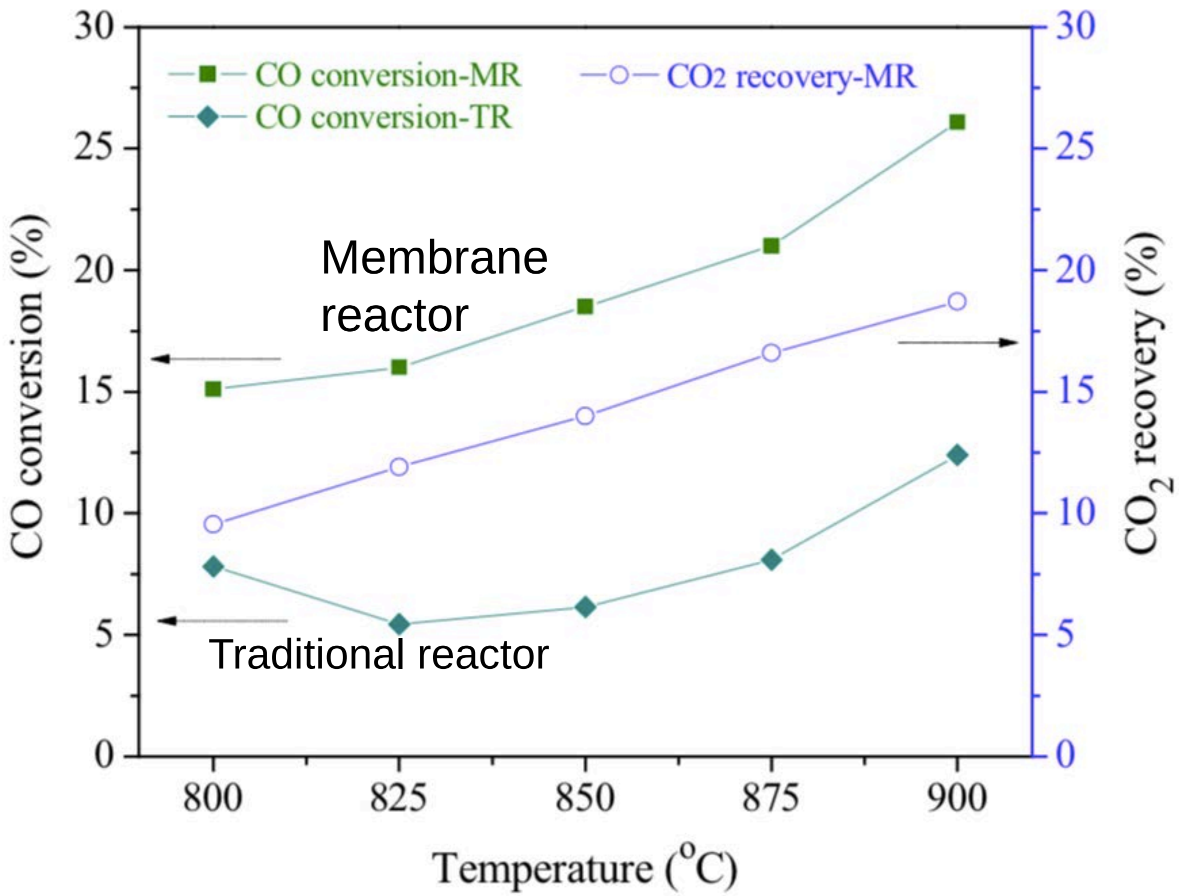
- **$Li_2CO_3/Na_2CO_3/K_2CO_3$**
- **Outer diameter: 1.1cm;**
- **Inner diameter: 0.8cm;**
- **Thickness: 1.5 mm;**
- **Effective length: 2.5 cm;**
- **Catalyst: No.**

***Reaction conditions*:**

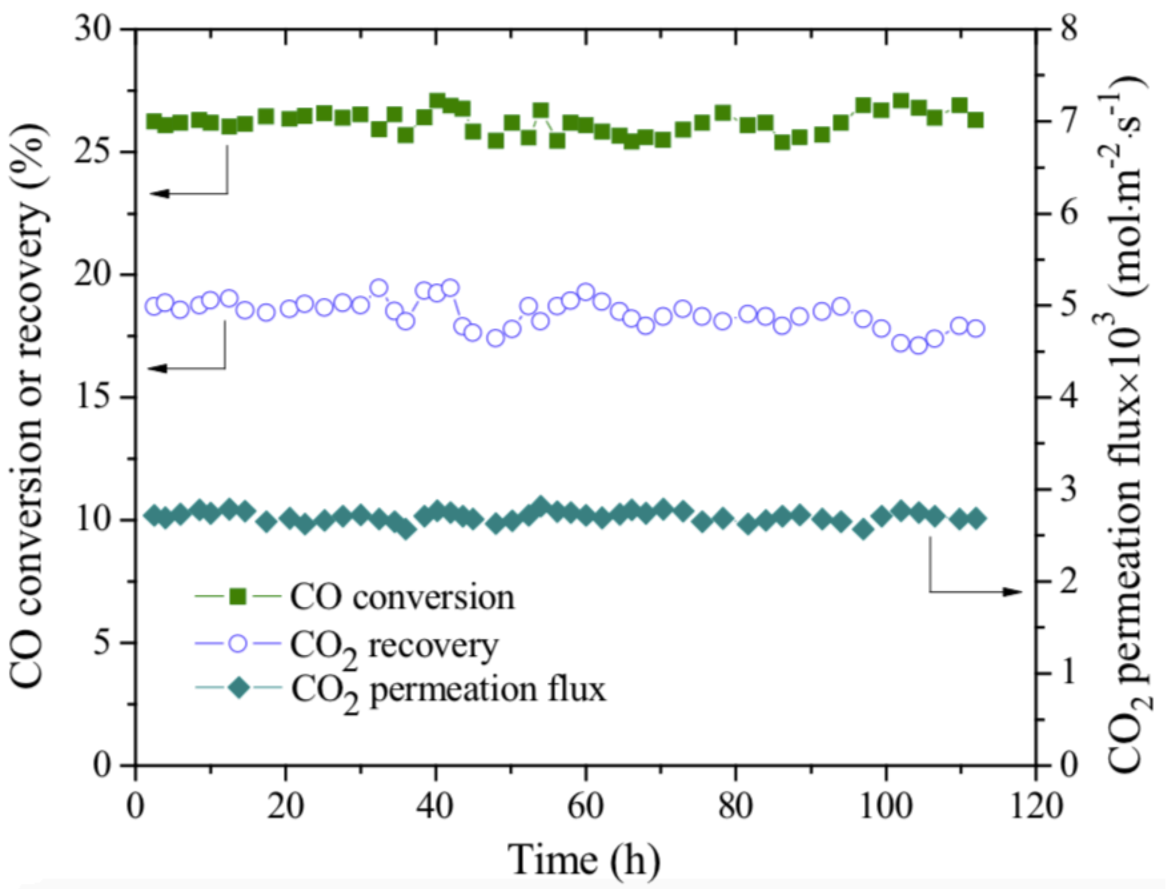
- **Temperature: 800-900^{o}C;**
- **Feed, Sweep side pressure: 1 atm;**
- **Simulated syngas: 49.5% CO, 36% CO_2, 10% H_2 and 4.5% N_2;**
- **Feed side flow rate: syngas 10-30 mL·min^{-1} and N_2 10 mL·min^{-1} ,**
- **Steam to CO molar ratio 1.0-3.0;**
- **Sweep side flow rate: He 60 mL·min^{-1}.**

Results of Catalyst-Free WGS with CO_2 Capture in Membrane Reactor

Conversion and CO_2 Recovery



Performance stability



Effect of Pressure on WGS in CCDP Membrane Reactor

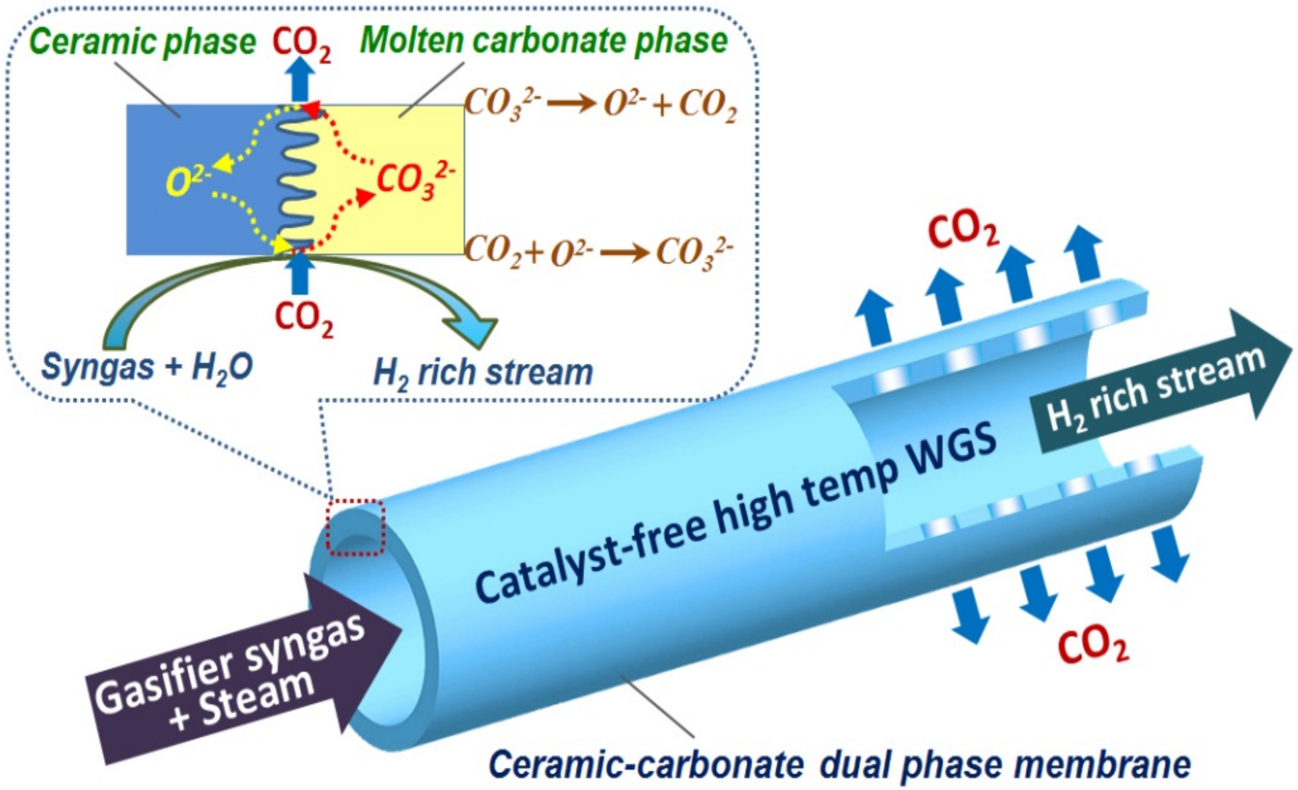
WGS reaction in a 1.5 mm thick disk CCDP membrane reactor at 700ºC without catalyst.*

- Thickness of CCDP disk membrane ~ 1.5 mm.
- Feed side: CO flow rate 10 ml/min, N_2 flow rate 40 ml/min, $H_2O/CO=3.0$;
- Sweep side: He flow rate 100 ml/min.
- Pressure at permeate sides is 1 atm

Feed pressure (bar)	CO conversion (%)	CO_2 recovery (%)
1	44.4	2.8
2	55.7	8.1
3	61.2	11.5
4	65.0	13.8
5	67.3	15.5

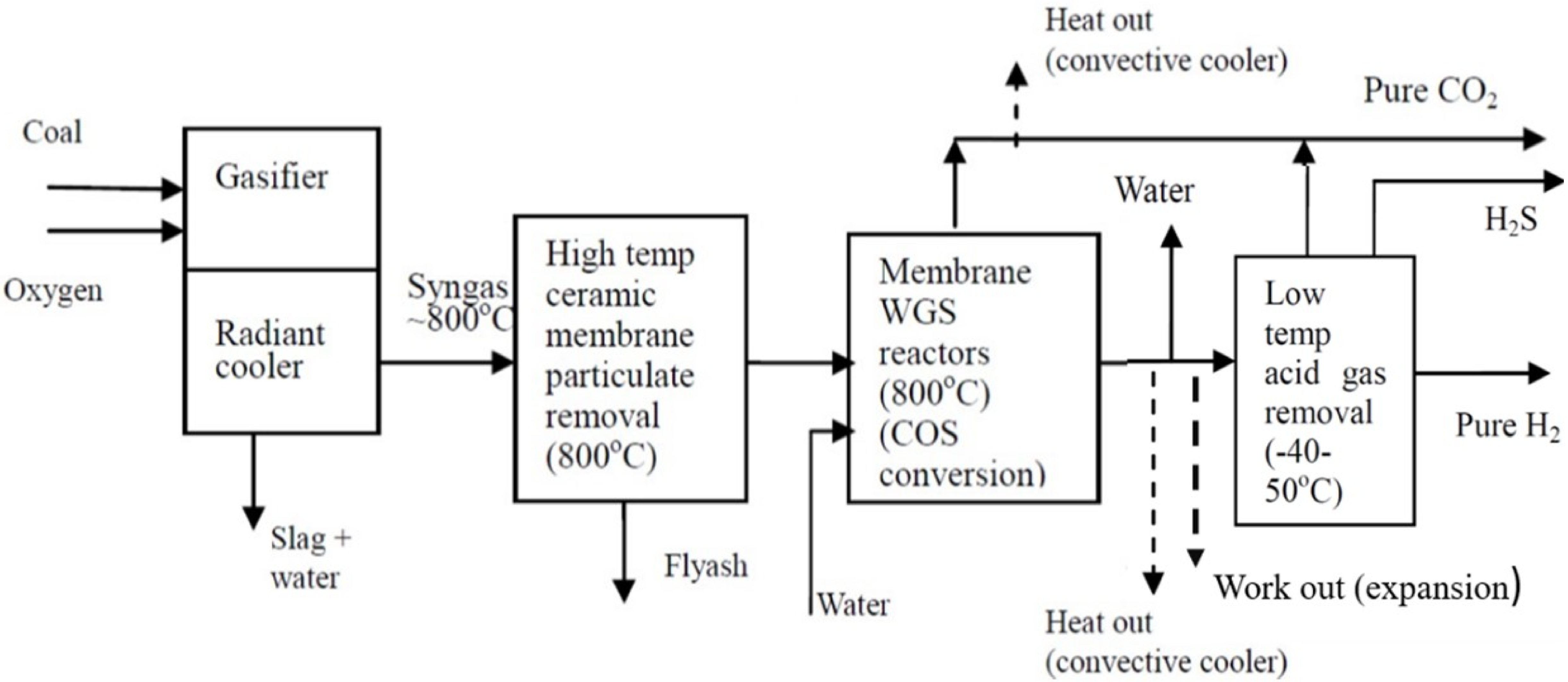
Proposed Improved Membrane Reactor for WGS with CO_2 Capture

Improved CCDP Membrane Reactor for WGS with CO_2 Removal



- High temperature catalyst-free WGS reaction (earlier work on Pd membrane reactor by NETL)
- **CCDP membrane reactor for WGS reaction at high pressure with CO_2 removal**
- **Sulfur resistant CCDP membrane with improved CO_2 permeace**
- **WGS with simulated syngas feed**

Block-flow diagram of high temperature CCDP membrane reactor with CO_2 capture for IGCC power plant



Membrane Material Properties

	Measured/ Estimated Performance	Projected Performance
Materials of Fabrication for Selective Layer	$Ce_{0.8}Sm_{0.2}O_{2-\delta}$(SDC)-(42.5/32.5/25 Li/Na/K)$_2CO_3$ (MC)	M-doped ZrO_2 (MSZ) (42.5/32.5/25 Li/Na/K)$_2CO_3$ (MC)
Materials of Fabrication for Support Layer (if applicable)	Same	$Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$(BYS)
Nominal Thickness of Selective Layer (μm)	1500	50-200
Membrane Geometry	Tubular	Tubular
Max Trans-Membrane Pressure	1	30
Hours tested without significant degradation in H_2S free syngas	120 hr	1000 hr
Hours tested without significant degradation in simulated syngas containing H_2S free syngas	Not tested	720 hr

Membrane Performance and Module Design

	Units	Measured/ Estimated Performance	Projected Performance
Materials of Fabrication for Selective Layer		$Ce_{0.8}Sm_{0.2}O_{2-\delta}$(SDC)-(42.5/32.5/25 Li/Na/K)$_2CO_3$ (MC)	MSZ-(42.5/32.5/25 Li/Na/K)$_2CO_3$ (MC)
Temperature	°C	700-900°C	700-900°C
Pressure Normalized Flux for Permeate (CO_2 or H_2)	GPU or equivalent	300-600 (CO_2 as permeate) (900°C)	2000-6000 (CO_2 as permeate) (900°C)
CO_2/H_2 Selectivity	-	>500	>500
Flow Arrangement	-	Co-current Flow	
Packing Density	m^2/m^3	40-60	
Shell-Side Fluid	-	Steam or Permeate	
CO conversion	%	38	99
CO_2 capture	%	35	90

Proposed Work

Project Goal

To demonstrate the high temperature and high pressure WGS membrane reactor with simulated syngas as feed, achieving one-pass

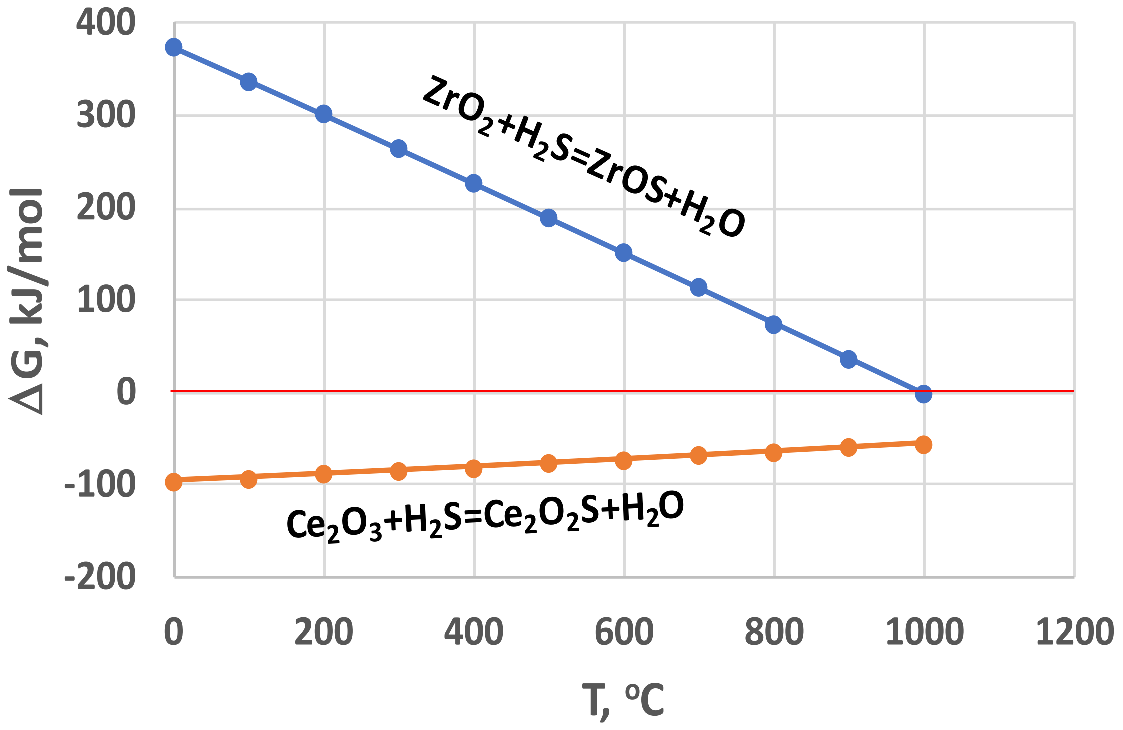
- CO conversion > 99%,
- CO_2 recovery (capture) > 90%,
- CO_2 and H_2 streams purity ~ 99% and 90%,respectively.

Developing the Improved CCDP Membranes - Materials

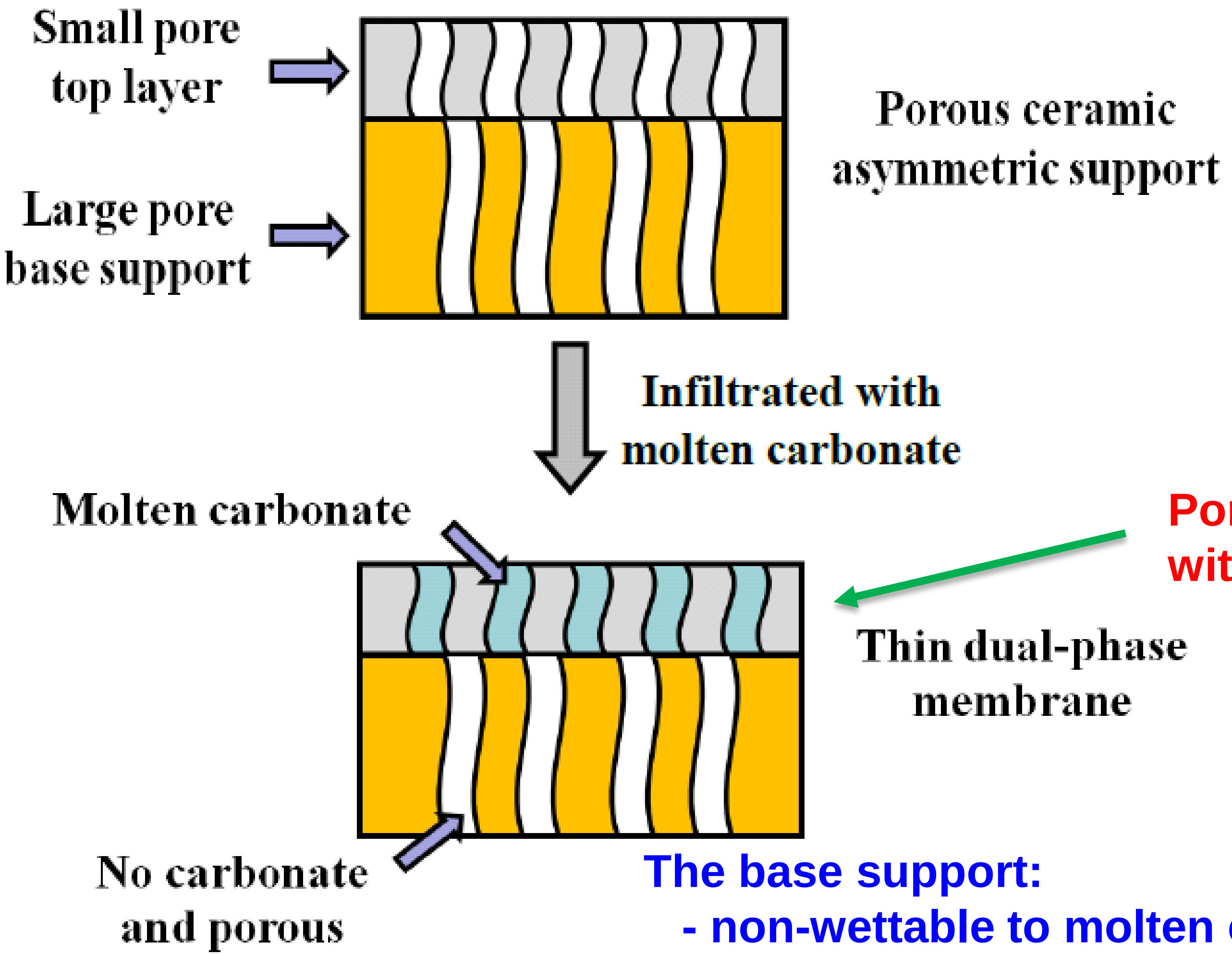
Compared to SDC-CCDP Membranes, a new CCDP membrane should have:

- CO_2 permeance 3-7 times (flux 10-40 times)
- Stable in H_2S containing coal gasifier syngas

Why ZrO_2 over CeO_2



Thin Dual-Phase Membrane to Increase Permeance

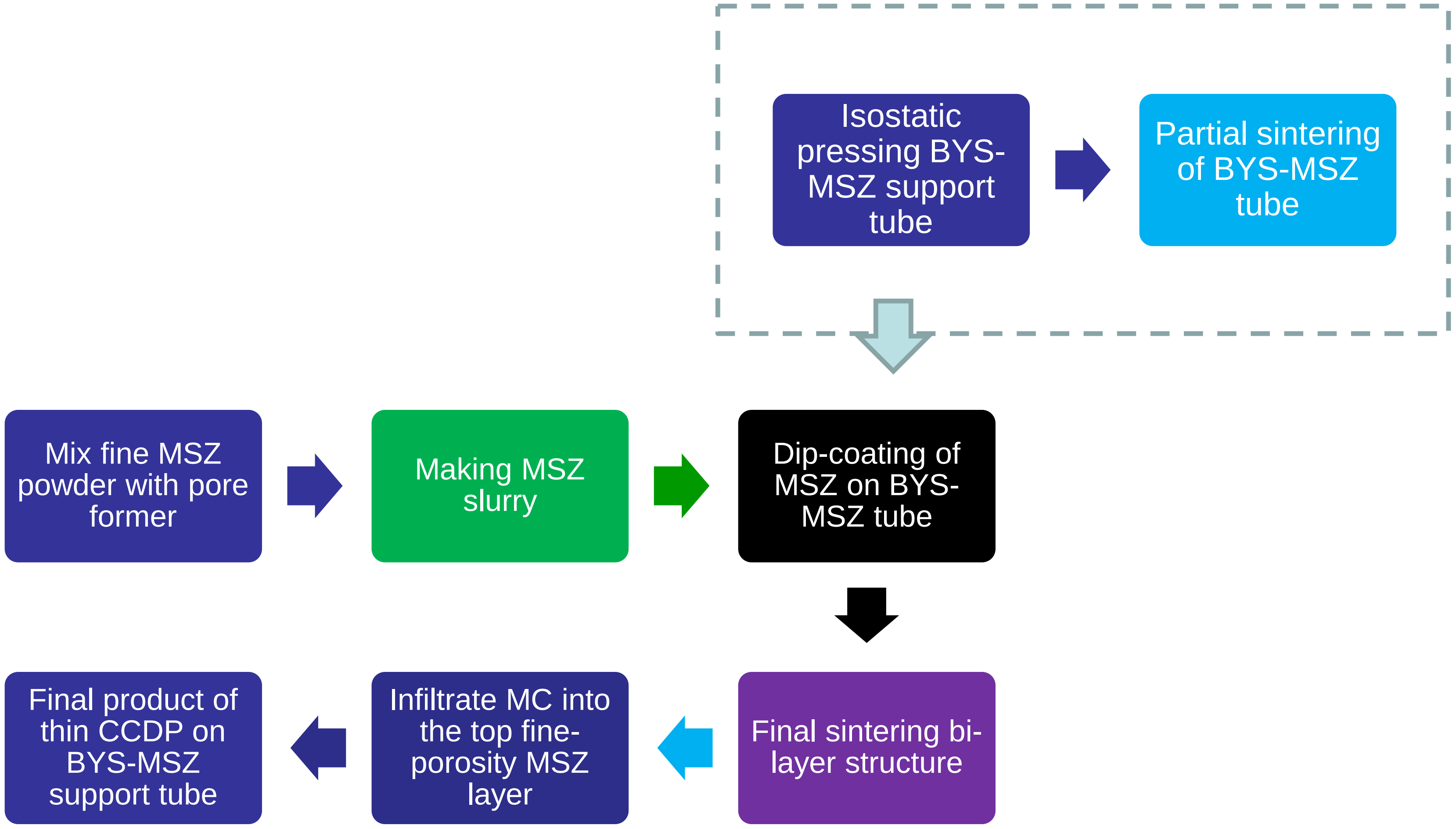


Porous MSZ layer filled with molten carbonate

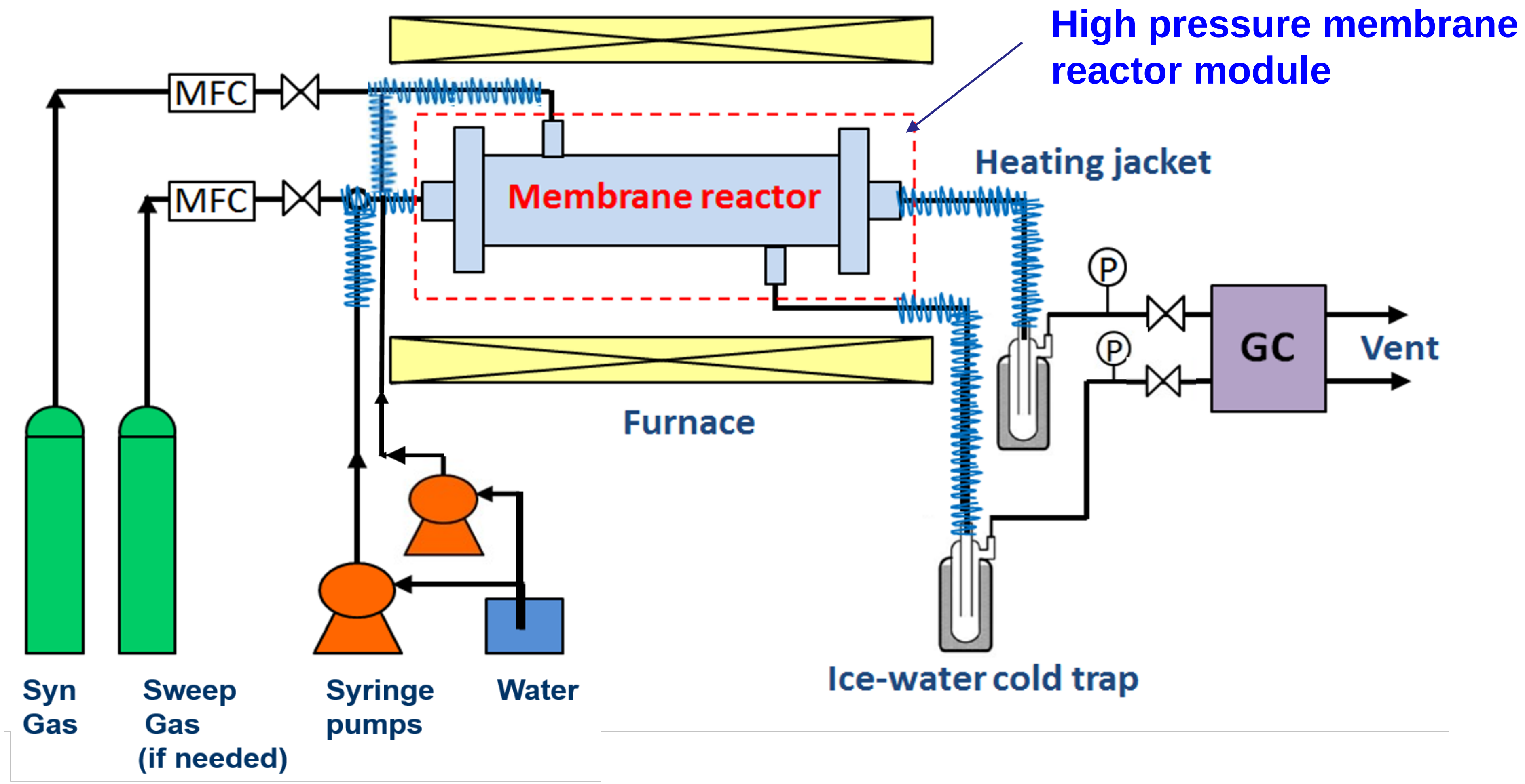
The base support:
- **non-wettable to molten carbonate**
- **oxygen ionic-conducting**

Yttria-doped-bismuth oxide (BYS)-MSZ

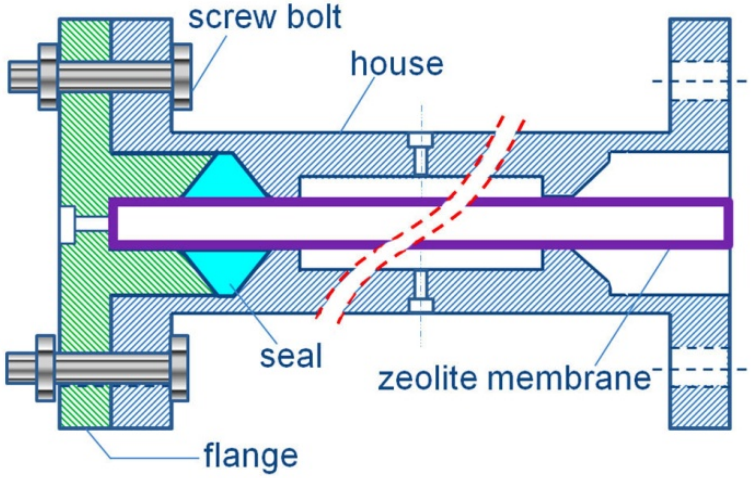
Synthesis of Thin Sc-doped ZrO_2 (ScSZ) CCDP Membrane



Studies on WGS on Improved CCDP Membrane Reactor with Simulated Syngas



High Pressure, High Temperature Membrane Module



Typical Composition of Gas from a GE Radiant Coal Gasifier

Gas	mol%
H_2	25.9
CO	26.7
CO_2	11.6
H_2O	33.6
CH_4	0.08
H_2S	0.56
COS	0.01
NH_3	0.13

- CO_2 permeation tests at high feed pressures (with simulated gasified gas, without steam)
- Stability test for up to 1 month

Modeling and Experimental Studies on WGS in CCDP Membrane Reactor

- ❑ Studying catalyst-free WGS kinetics at high temperature (700-900^{o}C) and high pressure (20-30 atm)
- ❑ Modeling and analysis of CO_2 permeation and WGS reaction kinetics to obtain key characteristics of CCDP membrane reactor for WGS to guide experiments
- ❑ WGS reaction in CCDP membrane reactor with sulfur-free syngas
- ❑ WGS reaction CCDP membrane reactor with simulated coal-gasifier syngas containing H_2S
- ❑ Identification of experimental conditions to achieve >99% CO conversion, 90% CO_2 recovery; CO_2 and hydrogen streams with respectively 99% and 90% purity (dry-base).
- ❑ Stability tests of the CCDP membrane reactors (for 1-2 months)

Process Design, Economical Analysis and EH&S Risk Assessment

- Design a WGS membrane reactor process with feed of raw syngas from a coal gasifier for a full-scale IGCC plant (550MW basis).
- Perform techno-economic analysis of the IGCC plant with the integration of WGS CCDP membrane reactor.
- The process design and techno-economic analysis follow the guideline presented in the NETL reports

Assumptions and Cost Estimation of Membrane Reactor

Parameters	**Conditions**
Coal type	Illinois 6#
Coal feed	slurry
Gasifier type	GE gasifier
Coal Consumption Rate	220,904 kg/hr
Carbon Content in Coal (dry basis)	0.70
Rate of CO in Syngas	2,296 mol/s
Rate of H_2 in Syngas	2,187 mol/s
Pressure of coal gas to WGS reactor	3 MPa
Temperature of coal gas to WGS reactor	800-950^{o}C

Deliverables of Project

Task	Deliverable Title	Anticipated Delivery Date
1.0	Project Management Plan	Update due 30 days after award. Revisions to the PMP shall be submitted as requested by the Project Officer.
3.1	WGS membrane reactor system	At the end of 9th month, the Recipient shall prepare and submit a report detailing design and operation of high temperature and high pressure WGS membrane reactor system.
4.0	Development of improved CCDP membrane	At the end of 12th month, the Recipient shall prepare and submit a report reporting new CCDP materials with desired H_2S resistant and CO_2 permeability
6.0	Fabrication of improved CCDP membrane tubes	At the 27th month, the Recipient should fabricate tubular CCDP membranes of improved composition and structure for testing in WGS membrane reactor, and submit a report documenting the properties of the membranes.
8.0	WGS reaction in CCDP membrane reactor	At the end of the project, the Recipient shall prepare and submit a report detailing the performance of WGS reaction in CCDP membrane reactor, including stability data.
9.0	Final techno-economic Analysis	At the end of the project, the Recipient shall prepare and submit a techno-economic analysis following the format and containing the information and data as defined in Appendix G of the FOA.
1.0	State Point Data Table	At the end of the project, the Recipient shall prepare and submit a complete and final State Point Data Table, appropriate to the technology being developed, following the format and containing information and data as defined in Appendix F of the FOA.
1.0	Technology Maturation Plan	At the end of the project, the Recipient shall prepare and submit a final Technology Maturation Plan following the format and containing the information and data as defined in Appendix H of the FOA.
9.0	Environmental Health and Safety Risk Assessment	At the end of the project, the Recipient shall prepare and submit an Environmental Health and Safety Assessment following the format and containing the information and data as defined in Appendix J of the FOA.

Success Criteria

At the end of Budget Period 1

- Development of H_2S tolerant CCDP membrane with CO_2 permeance of 1000 GPU and CO_2/H_2 selectivity > 500
- Establishment of high temperature and high-pressure membrane reactor (and sealing technology) and test of WGS in the reactor with CO conversion larger than 95%

At the end of the project

- Development of H_2S tolerant tubular CCDP membrane with CO_2 permeance of 2000 GPU and mechanical strength that can handle 30 am transmembrane pressure.
- Operation of the high temperature, high pressure CCDP membrane reactor for testing WGS reaction with simulated coal gasified gas at 99% CO conversion and 95% CO_2 capture rate.

Progress Updates

- Contract has been in place at ASU since October, 2018
- ASU is working on subcontract with USC
- ASU has two researchers working on the project on part-time basis. A full-time post-doctor has been hired and will start Jan.1, 2019
- USC has hired a post-doctor, starting Nov.1, 2018 for the project

Thank You!