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

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1 Introduction

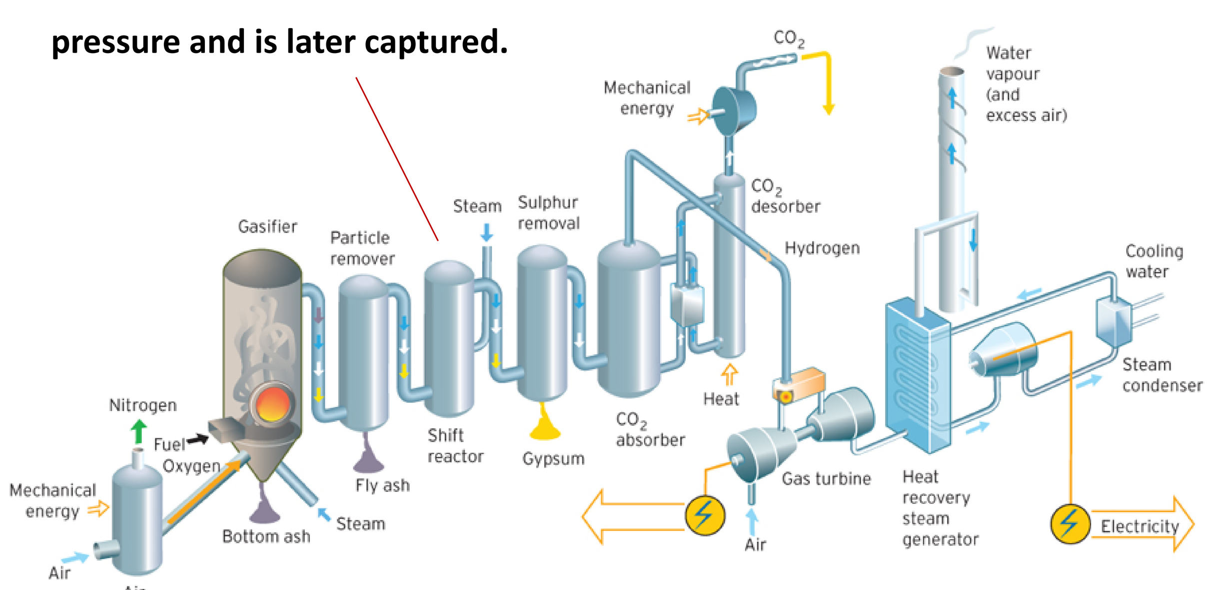
CO_2 Capture technology in IGCC process

Post-combustion capture

Inherent energy penalty in concentrating a flue gas at atmospheric pressure containing only 15%vol. CO_2 into pure CO_2 at high pressure.

Pre-combustion capture

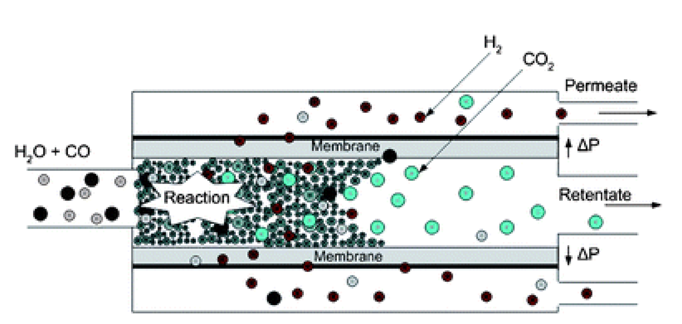
Water-gas-shift (WGS) reaction: syngas is shifted to produce additional hydrogen and convert the carbon monoxide into CO_2, which is at a high pressure and is later captured.



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

Membrane reactor technology for WGS reaction

- ✓ equilibrium shift and CO conversion enhancement
- ✓ CO_2 is concentrated at high pressure (30–35 bar)



Ref.: Energy Environ. Sci., 2010, 3, 268-278

H_2 selective membranes

1) Palladium alloy
2) Zeolite
3) Silica based
4) Carbon molecular sieve

Major issues:

- relatively low H_2 permeance and H_2/CO_2 selectivity
- limited H_2 purity and recovery in the permeate stream

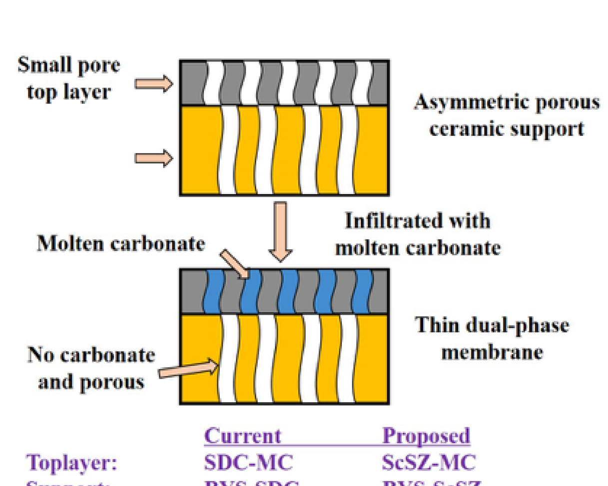
Objective

- developing a novel tubular membrane reactor (MR) made of CO_2 permeable membranes (CO_2 permeance > 2000 GPU and CO_2 selectivity > 500) for high-temperature and high-pressure WGS reaction.
- producing high-pressure H_2 and CO_2 streams with a purity over 90% and 99%, respectively.

2 Dual-phase membranes

Characteristics

- ✓ composed of a porous ceramic phase and a molten carbonate (MC) phase
- ✓ an infinite CO_2 selectivity with high CO_2 permeance at 600-900ºC

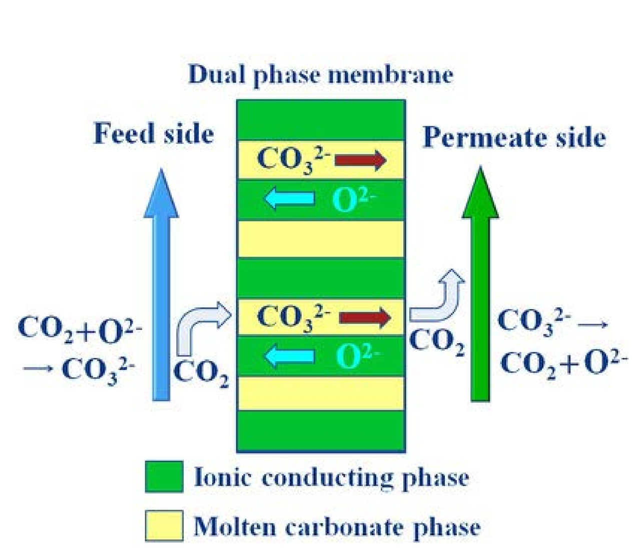


CO_2 transport through dual-phase membrane

$$J_{CO_2} = \frac{KT}{4F^2L} ln \frac{P'_{CO_2}}{P''_{CO_2}}$$

F is Faraday constant, L is membrane thickness, and K, the total conductance is related to the ratio of volume fraction to tortuosity, carbonate or oxygen ionic conductivity of carbonate (sub c) and ionic-conducting ceramic (sub i) phase.

$$K = \frac{(\varepsilon/\tau)_c\sigma_c(\varepsilon/\tau)_i\sigma_i}{(\varepsilon/\tau)_c\sigma_c + (\varepsilon/\tau)_i\sigma_i}$$



3 Recent progress in ceramic-carbonate dual-phase MRs

Ceramic-carbonate dual-phase (CCDP) membrane

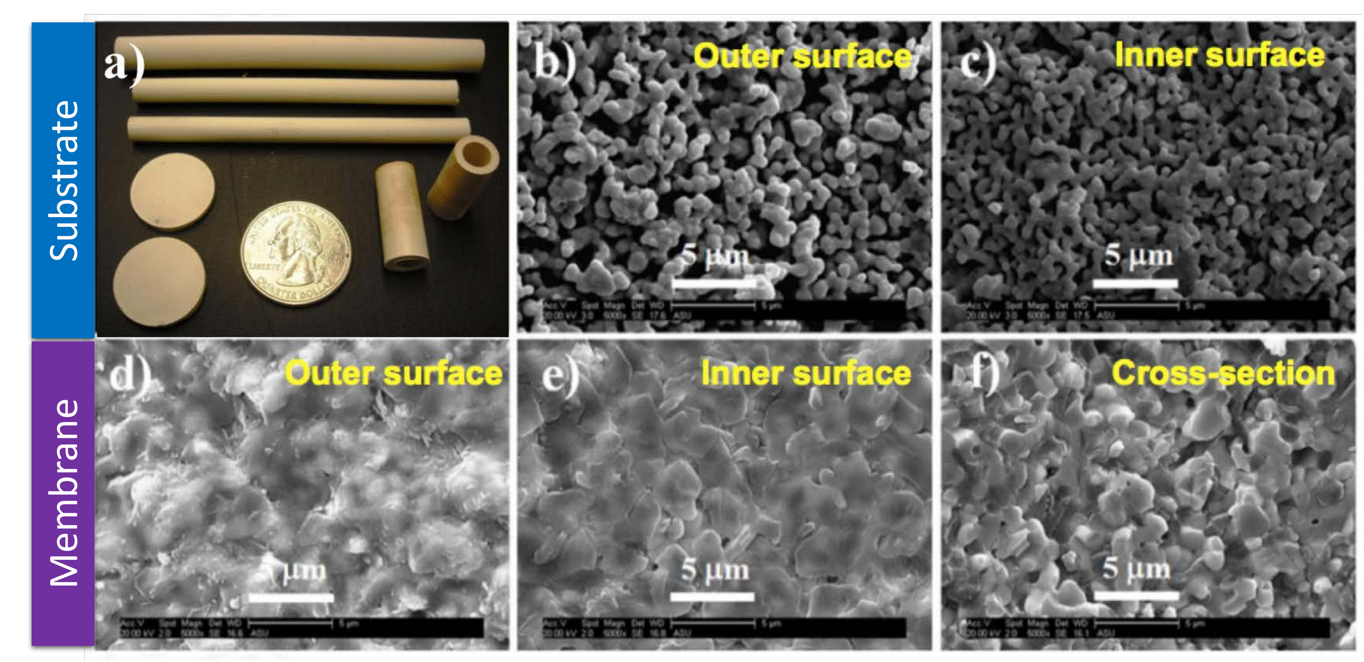
Substrate geometry

Disk membrane
Tubular membrane
Symmetric thick membrane
Asymmetric thin membrane

Ceramic phase materials

$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF)
Yttria-stabilized zirconia (YSZ)
$Sm_{0.2}Ce_{0.8}O_{1.9-\delta}$ (SDC)
$Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$ (BYS)
$La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.65}Al_{0.05}O_{3-\delta}$ (LCGFA)

Morphology of dual-phase membrane

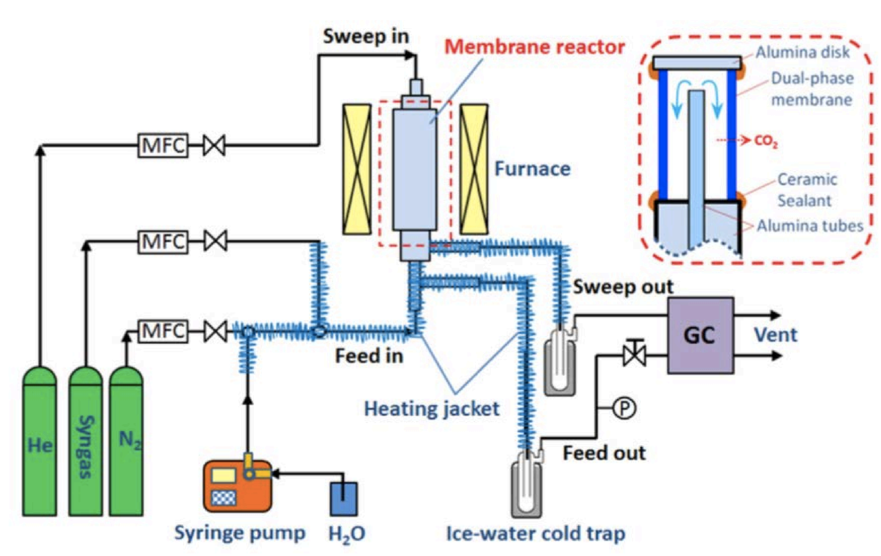


Tubular CCDP-MRs for high-temperature WGS

Ref.: J. Membr. Sci., 2016, 520, 907-913.

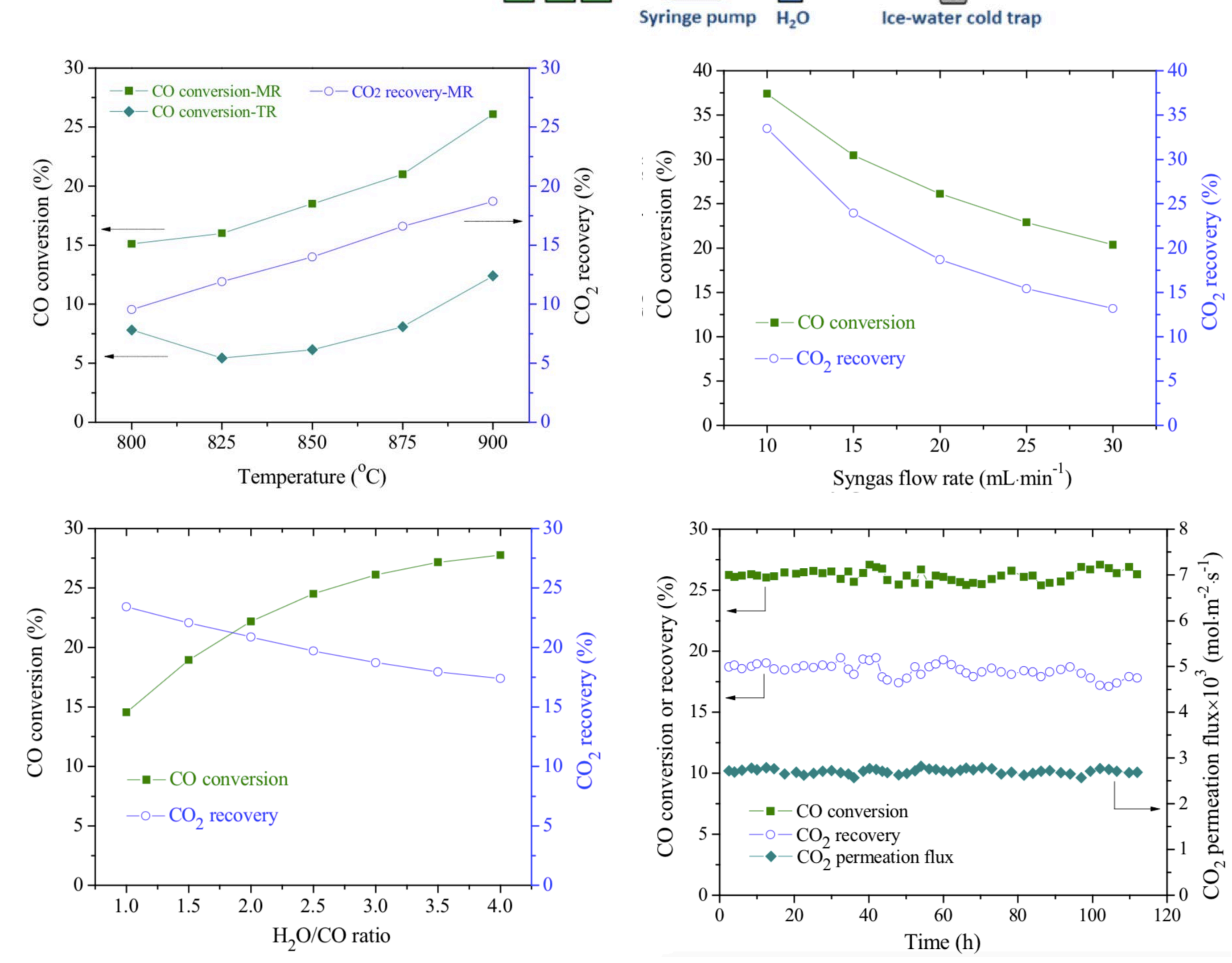
Membrane:

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.

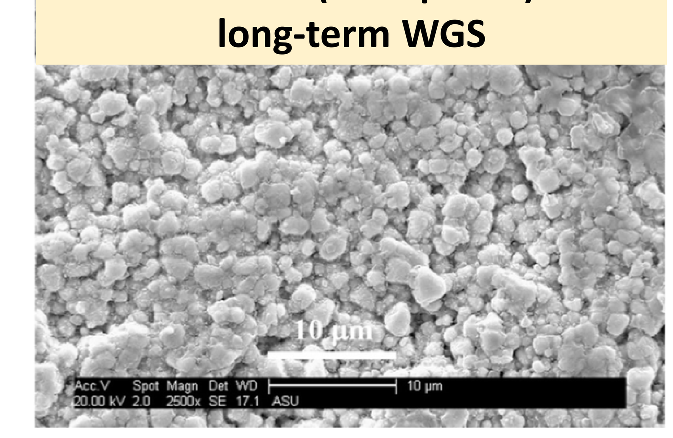


Reaction conditions:

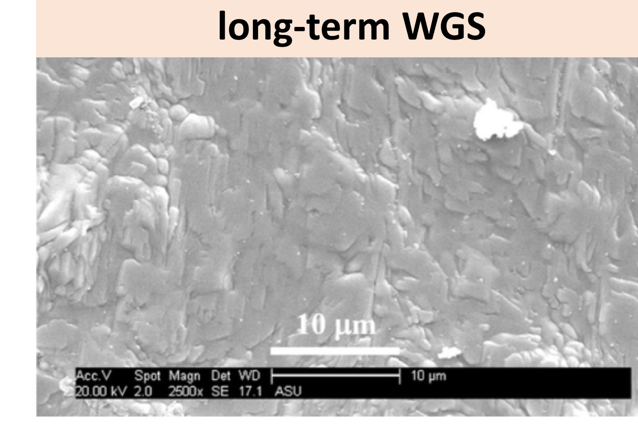
Temperature: 800-900ºC;
Feed, Sweep side pressure: 1 atm;
Simulated syngas: 49.5% CO, 36% CO_2, 10% H_2 and 4.5% N_2;
Feed side flow rate: syngas 10-30 mL·min^{-1} and N_2 10 mL·min^{-1},
Steam to CO molar ratio 1.0-3.0;
Sweep side flow rate: He 60 mL·min^{-1}.



outer surface (sweep side) after long-term WGS



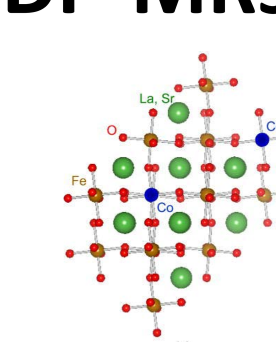
Inner surface (reaction side) after long-term WGS



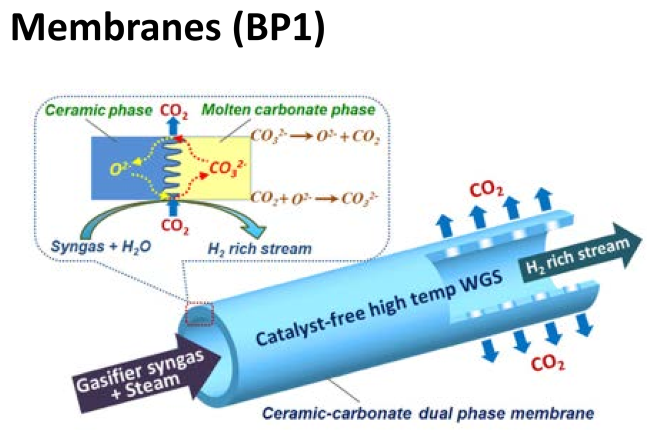
4 Scope of the further research for CCDP-MRs

Research Tasks to be Performed

Task 1.0 Project Management and Planning (BP1 and BP2)
Task 2.0 Synthesis and Characterization of Dual-Phase Membranes (BP1)
Task 3.0 High Temperature, High Pressure CO_2 Permeation Studies (BP1)
Task 4.0 Development of Improved Ceramic-Carbonate Dual-Phase Materials and Membranes (BP1)
Task 5.0 Study on CO_2 Permeation Properties of CCDP Membranes (BP1)
Task 6.0 Fabrication and Characterization of CCDP Tubular Membranes (BP2)
Task 7.0 Modeling and analysis of CCDP membrane reactor for WGS (BP2)
Task 8.0 Studies on WGS in Improved Dual-Phase Membrane Reactors (BP2)
Task 9.0 Process Design and Techno-Economic Analysis (BP2)



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



5 Conclusions

- ☑ We propose a novel process for CO_2 pre-combustion capture that is applying a ceramic-carbonate dual phase membrane reactor with CO_2 selective membrane for high-temperature WGS.
- ☑ Our work experimentally demonstrated that CCDP-MRs could offer a strong improvement in the CO conversion and the CCDP membranes show good CO_2 permeation flux and high thermal and chemical stability under WGS reaction.
- ☑ Further studies will be mainly focused on the development of new membrane materials.

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