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

primary project goal

Arizona State University (ASU), in collaboration with the University of South Carolina (USC), are developing technology for a high-temperature, high-pressure, ceramic-carbonate dual-phase (CCDP) membrane reactor. The reactor is intended to perform the water-gas shift (WGS) reaction on syngas (maximizing hydrogen [H_2] content of the syngas) while simultaneously separating a high-purity carbon dioxide (CO_2) stream from the reactor for capture. The project goal is to design and fabricate CCDP membranes with improved CO_2 permeance and mechanical strength for testing in a laboratory-scale reactor with simulated coal-derived syngas, with results informing a mathematical model used to support process design and a techno-economic analysis (TEA) for a scenario of incorporation of a CCDP membrane reactor in a full-scale integrated gasification combined cycle (IGCC) plant.

technical goals

- Synthesize chemically and thermally stable CCDP membranes with CO_2 permeance greater than 2,000 gas permeation units (GPU) (6.5×10^{-7} mol/m^2·s·Pa), CO_2/H_2 selectivity greater than 500, and resistant to poisoning from hydrogen sulfide (H_2S) to the extent that CO_2 flux drops less than 5% after 24 hours of exposure to typical levels of H_2S.
- Fabricate tubular CCDP membrane modules suitable for lab-scale WGS reactor operation (i.e., functional and durable at temperatures in excess of 700°C) and at pressures in excess of 20 atmosphere (atm), and experimentally verify performance at simulated syngas flow rate of 0.25 kg per day equivalent to 0.007 kilowatt-thermal (kWth).
- Determine CCDP membrane WGS reactor process conditions/protocols enabling 99% carbon monoxide (CO) conversion for the WGS reaction, 90% CO_2 recovery, 99% purity of the CO_2 permeate stream, and 90% purity of the H_2 retentate stream.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification-based power plant (for shifting the syngas toward primarily H_2 and CO_2) and downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas could be replaced, in whole, by a novel WGS shift reactor that integrates CO_2-selective CCDP membranes and WGS catalyst. Within the CCDP membrane WGS reactor, CO_2 would be withdrawn directly from the reaction chamber, efficiently increasing the driving force for the WGS reaction to completion. As such, the multiple stages of the conventional WGS unit are replaced by a single, elegantly performing reactor. This process concept, with the

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Ceramic-Carbonate Dual-Phase Membrane Reactor for CO_2 Capture from Coal Syngas

participant:
Arizona State University

project number:
FE0031634

predecessor projects:
N/A

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partners:
University of South Carolina

start date:
10.01.2018

percent complete:
90%

unified CCPD membrane reactor (depicted in callout) replacing the multistage conventional WGS process and amine absorption unit (both within red dotted line), is depicted in Figure 1.

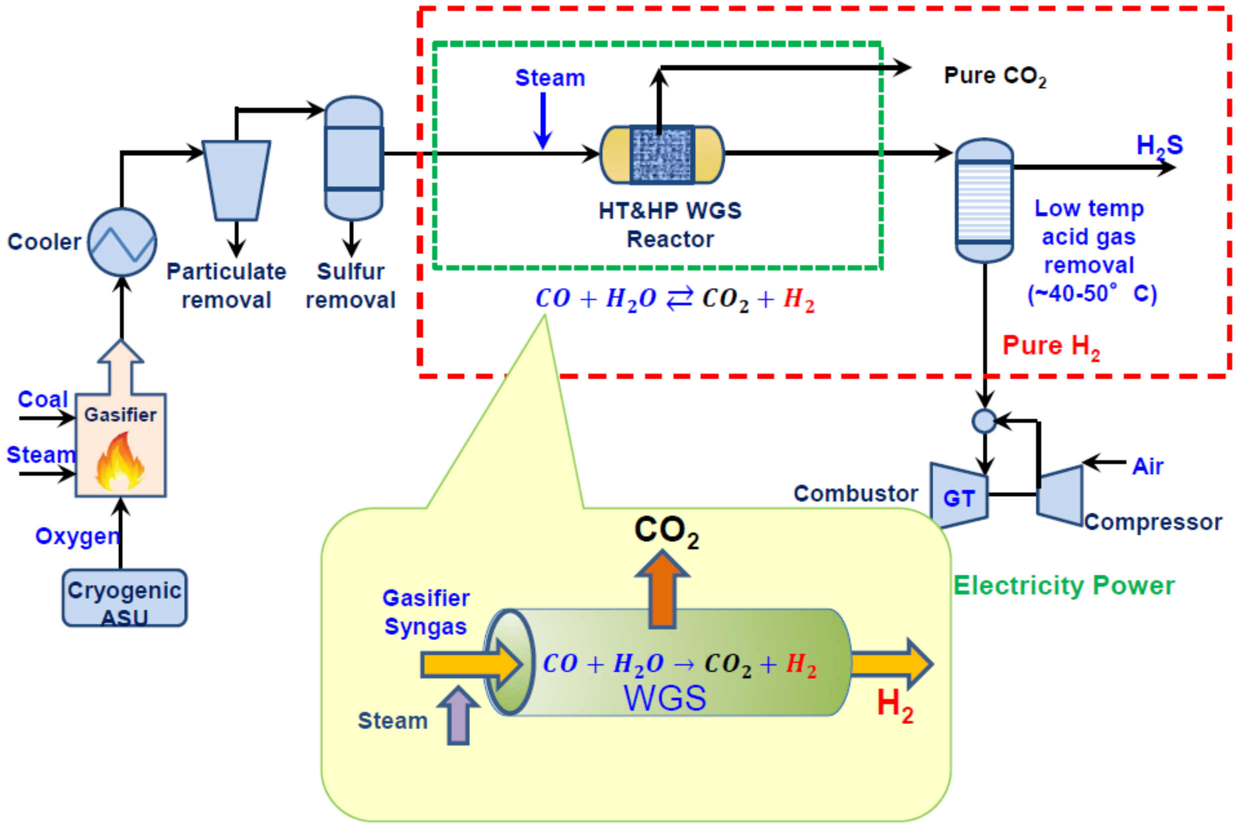


Figure 1: CCDP membrane reactor for WGS reaction and CO_2 capture in context of coal gasification plant cycle.

CCDP membranes are composed of a porous ceramic phase as the structural support matrix, infiltrated with a molten carbonate phase, as illustrated in Figure 2. At working temperatures of 600–900°C, the CCDP membrane possesses extremely high CO_2 selectivity and high CO_2 permeance.

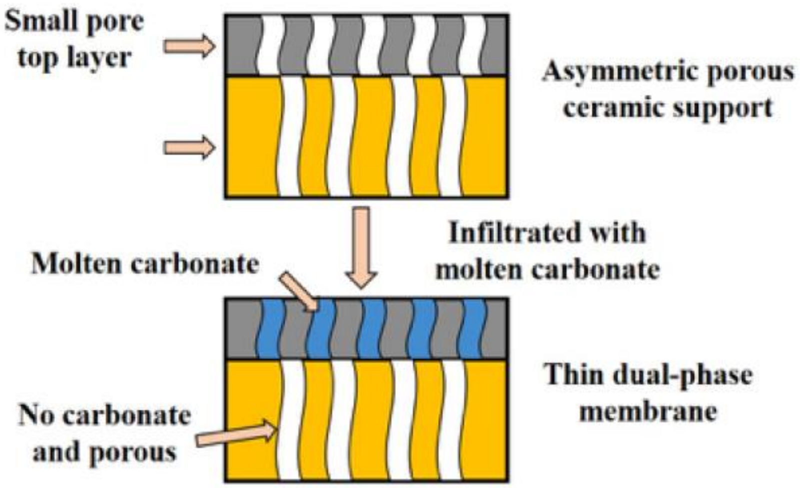


Figure 2: Physical structure of CCDP membrane.

Scanning electron microscopy (SEM) images of actual CCDP membranes are shown in Figure 3. Note that the bright areas in the SEM images are the ceramic phase, while dark zones consist of carbonate mixture. These illustrate the formation of a dense, highly gas-tight dual-phase membrane, which has been verified by pre- and post-infiltration gas permeation measurements.

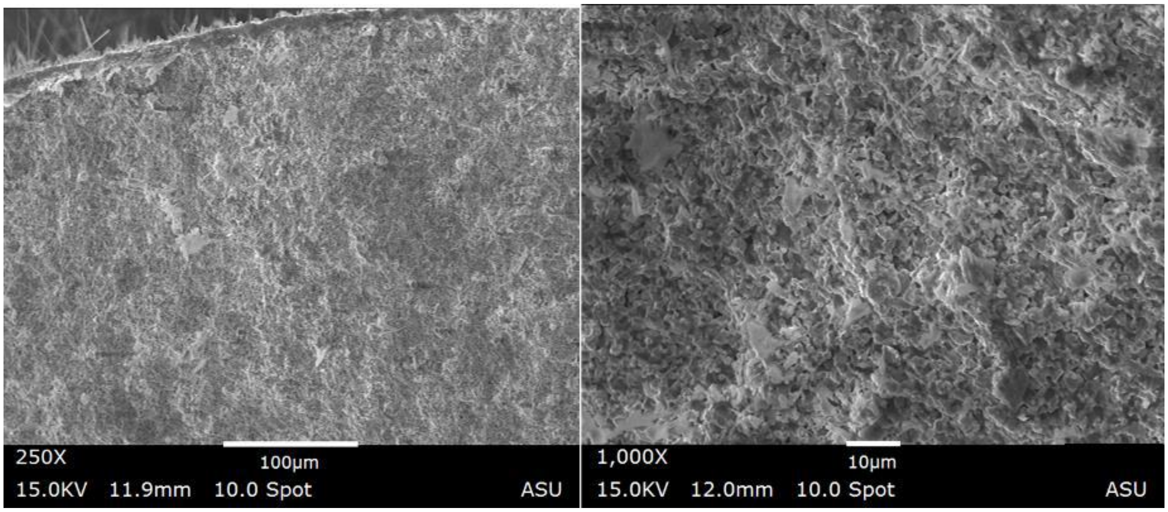


Figure 3: SEM images of CCDP membrane cross-section at 250x (left) and 1,000x (right).

The high selectivity and permeance for CO_2 in the CCDP membrane are a result of the electrochemical transport mechanism illustrated in Figure 4. At elevated process operating temperatures, CO_2 tends to form carbonate ions (CO_3^{2-}) by combining with oxygen ions (O^{2-}), the latter readily transporting through the ionically conducting ceramic phase in the membrane. At the same time, carbonate ions readily transport through the molten carbonate phase in the opposite direction. Syngas on the feed side is at high pressure, resulting in high partial CO_2 pressure on that side. The permeate side is at ambient pressure (and possibly swept), resulting in low partial CO_2 pressure. The CO_2 partial pressure differential provides the driving force for the ionic transport behavior in the membrane. High CO_2 permeance values are expected for the CCDP membrane if the functional layer is made of suitably thin (10–100 µm) ceramic with high oxygen ionic conductivity.

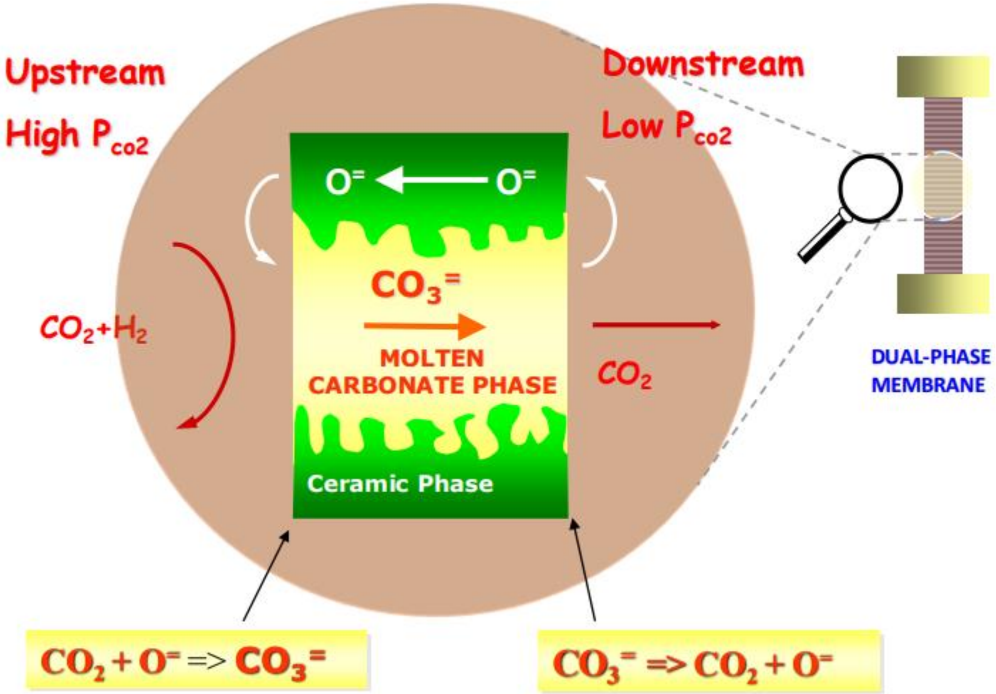


Figure 4: CO_2 separation mechanism in CCDP membrane.

The novel choice of ceramic-carbonate membrane in a WGS reactor overcomes various problems observed with possible alternatives. Theoretically, H_2 could be removed from the WGS reactor through H_2-selective membranes, which would also constitute removal of product of the WGS reaction to drive conversion forward to completion. Inorganic membranes with good H_2 perm-selectivity at high temperatures do exist, and include amorphous microporous carbon; amorphous silica; microporous crystalline zeolite; and dense, perovskite-type, proton-conducting ceramics. However, all of those choices are hampered by one or more serious issues, including insufficient H_2 permeance (particularly at the elevated temperatures involved in the WGS reactor), poor H_2 stability, poor hydrothermal stability, and membrane fabrication difficulty and high cost, which translate into high costs for a membrane WGS reactor solution. Finally, organic membranes of any type are simply incapable of application at the high operating temperatures involved. Considering these shortcomings, a CO_2-selective ceramic-carbonate membrane offers a favorable choice for this application.

An important aspect of technology development for the CCDP membrane concerns optimizing the choices of ceramic and carbonate materials deployed in the membrane, characterization of membrane morphologies and properties, and membrane fabrication. For the ceramic phase of the membrane, desired characteristics include high ionic conductivity, long-term chemical stability in presence of characteristic syngas species and contaminants (particularly H_2S), compatibility with molten carbonate, and controllability of pore size and porosity.

ASU has previously investigated several ceramics for application in the CCDP membrane. The ceramics are in the family of perovskite- or fluorite-structured metal oxides with oxygen vacancy defects:

- $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF)
- Yttria-stabilized zirconia (YSZ)
- $La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.65}Al_{0.05}O_{3-\delta}$ (LCGFA)
- $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (Samarium Doped Ceria [SDC]). Note: Figure 3 SEM images are of an SDC-based membrane.
- $Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$ (BYS)

ASU has evaluated SDC as a choice for the ceramic phase of the membrane, and has also investigated a Sc_2O_3-doped ZrO_2 (ScSZ). ScSZ avoids the tendency to form compounds with sulfur that is characteristic of cerium (Ce)-containing ceramics. Fabrication methods for the latter have been optimized to deliver the desired microstructure. The ethylenediaminetetraacetic acid (EDTA)-citric acid method is effective; this involves dissolving Sc_2O_3 in nitric acid and mixing with $ZrO(NO_3)_2$, to which EDTA and citric acid are added to the stirred solution in sequence. The solution is pH adjusted and then heated until a clear, viscous gel is formed after water evaporation. The gel is dried and calcined, resulting in almost pure-phase ScSZ with good microstructure.

Tubular membranes for incorporation in modules are formed by establishing thin layers on suitable supports. The ScSZ-based CCDPs are established on BYS support tubes by dip coating them in ScSZ slurry, sintering, and infiltrating the molten carbonate (MC). Essential steps are diagrammed in Figure 5.

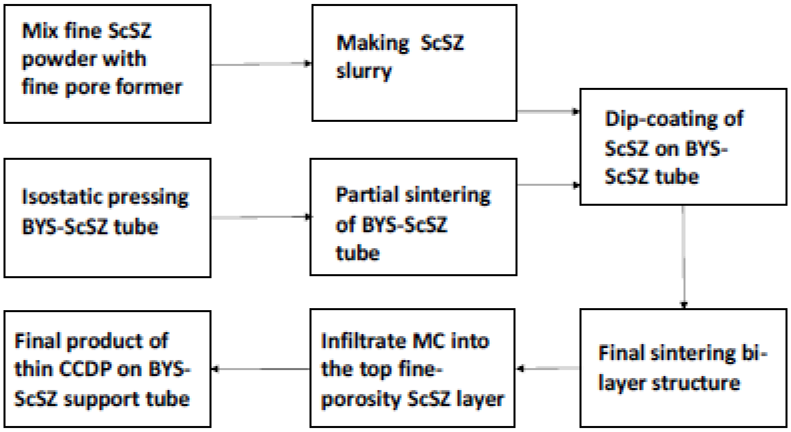


Figure 5: Tubular CCDP membrane fabrication.

For the molten carbonate phase, mixtures of common alkali metal carbonates (i.e., $Li_2CO_3/Na_2CO_3/K_2CO_3$) have been found to be suitable. Varying ratios of the alkali metal carbonates have been evaluated (e.g., a Li/Na/K ratio of 43.5/31.5/25 offers both relatively low melting point [less than 400°C] and good carbonate ion conductivity [1.24 S/cm]). In current work, a binary eutectic mixture of 52% Li_2CO_3 and 48% Na_2CO_3 (MC) is being used with both the SDC and ScSZ ceramics.

Figure 6 depicts the ScSZ-MC membrane tubes along stages of fabrication.

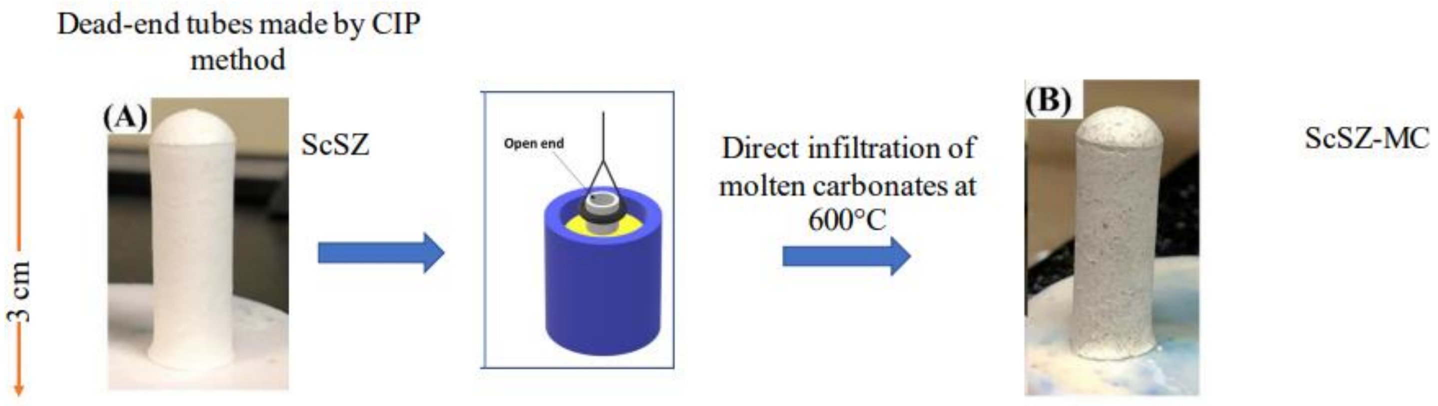


Figure 6: Sc-doped ZrO_2(ScSZ)—(52/48 Li/Na$)_2CO_3$(MC).

An apparatus for characterizing CCDP membrane performance at high temperature and feed pressures has been developed and is operated in laboratory-scale work, as depicted in Figure 7. Synthetic syngas can be mixed up and flowed to the tubular reactor module enclosed in a high-temperature furnace, while resulting gas compositions of permeate and retentate can be measured in a gas chromatograph. The fabrication of the tubular membrane reactor module itself is a challenge, with a notable point of development concerning seals able to withstand the high-targeted operating pressures and temperatures.

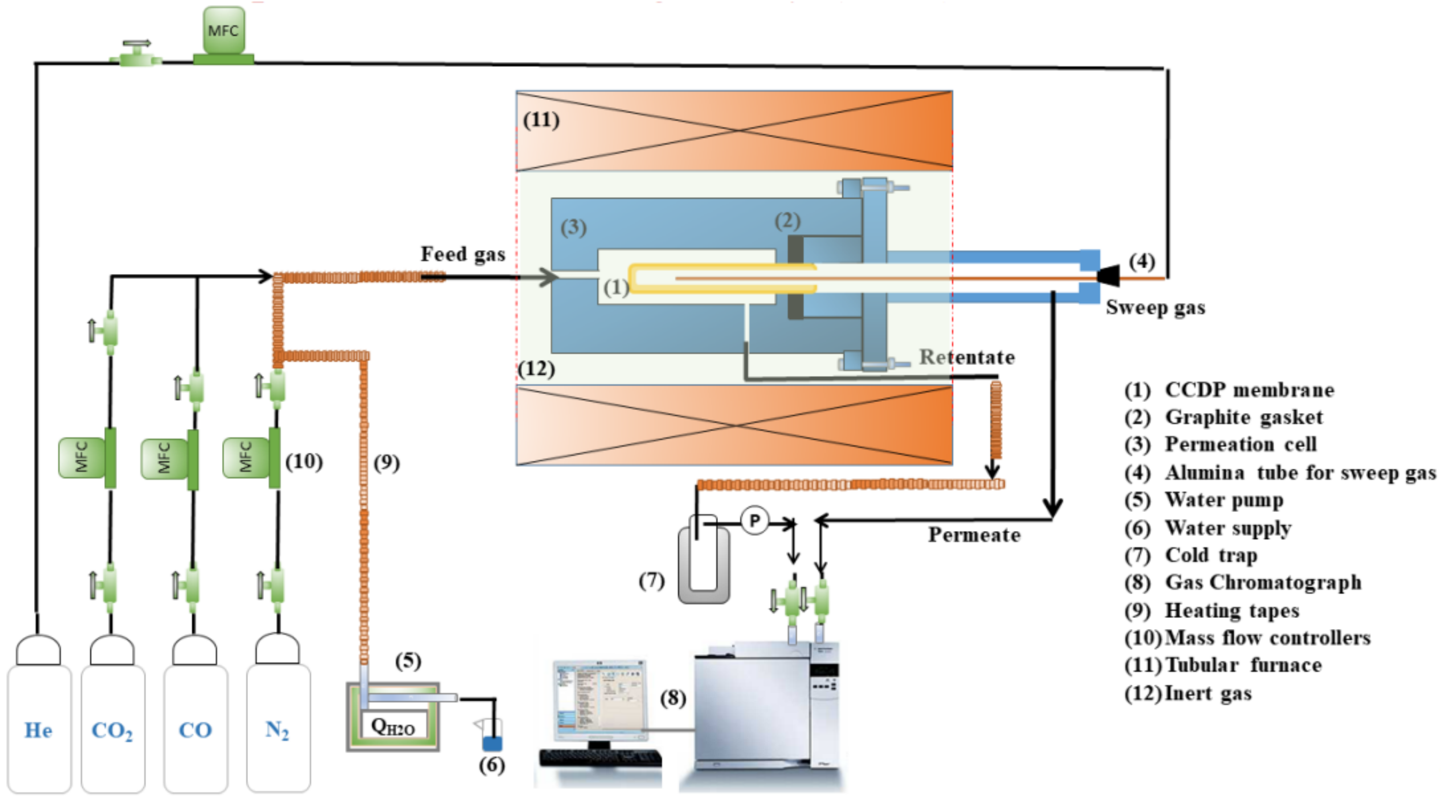


Figure 7: Laboratory-scale apparatus for CCDP membrane CO_2 permeation studies.

With this test bed, various experiments and evaluations are possible, which provide invaluable data for optimizing membrane and module materials and fabrication methods. For example, the reactor module with SDC ceramic infiltrated with Li_2CO_3/Na_2CO_3/K_2CO_3 carbonate mixture (SDC-MC) was evaluated under the following test conditions:

- Temperature: 700–950°C.
- Feed pressure: 1–20 atm.
- Sweep-side pressure: vacuum to 1 atm.

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

Results of CO conversion as a function of temperature, syngas flow rate, and ratio of steam to CO are shown in Figure 8, along with behavior of CO conversion, CO_2 permeation, and flux over long-term, steady-state operation. At feed pressure of 7 atm, temperature of 850°C and space velocity of 225 hr^{-1}, CO conversion of 95% has been achieved in the CCDP membrane reactor. Such conversion is significantly higher than the equilibrium CO conversion under the same conditions (62%). The CCDP membrane under such conditions also offers CO_2 permeation flux of 0.56 cm^3(STP)/min.cm^2.

Also, the test bed allows long-term testing to evaluate changes to morphology of CCDP that may occur. For example, Figure 9 shows the high-pressure side of the SDC membrane (left), the SDC-MC infiltrated membrane (center), and the SDC-MC after high-temperature and high-pressure operation.

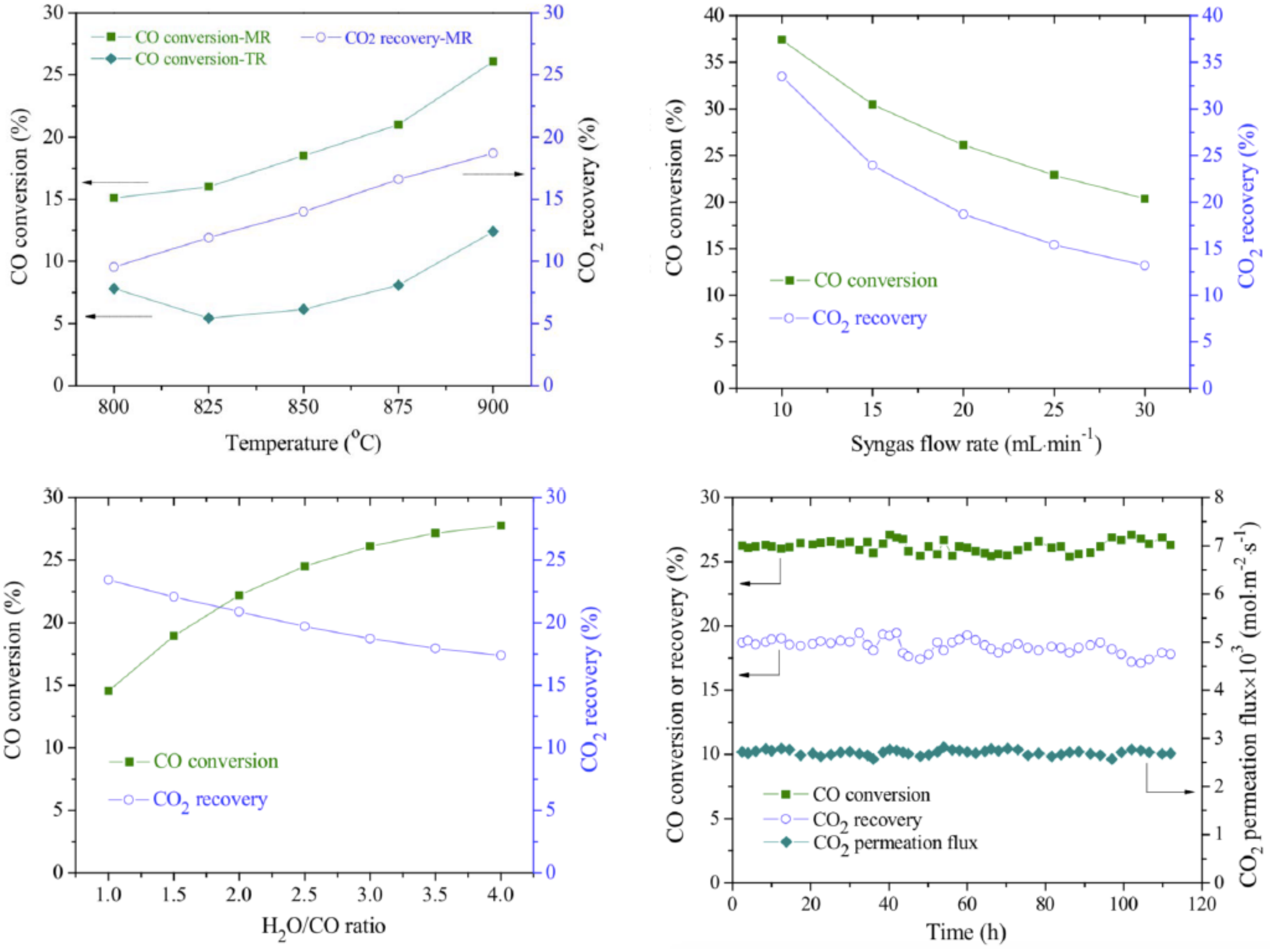


Figure 8: Measurements from tubular CCDP modules in high-temperature WGS testing (1 atm feed).

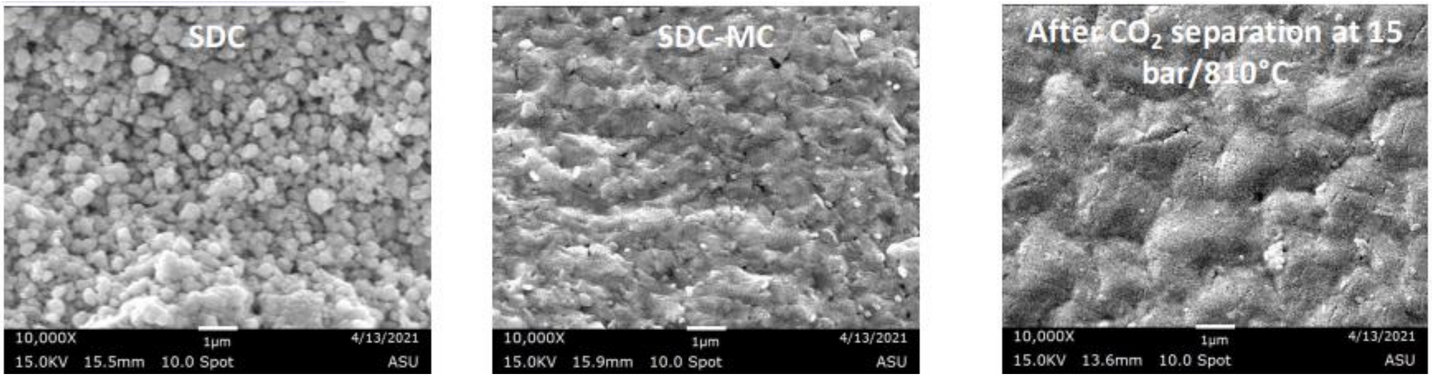


Figure 9: SEM images of high-pressure side of SDC membrane (left); SDC-MC (center); SDC-MC after high-pressure CO_2 permeation (right).

The CCDP membrane reactor has been evaluated for effectiveness in WGS conversion of simulated syngas. The CCDP membrane tubes are surrounded by a Co-Mo-Mg$(AlO_2)_2$-based shift catalyst, as shown in Figure 10. Testing has involved both SDC-MC membranes with catalyst on contaminant-free syngas, and with ScSZ-MC tubular membranes with syngas containing H_2S.

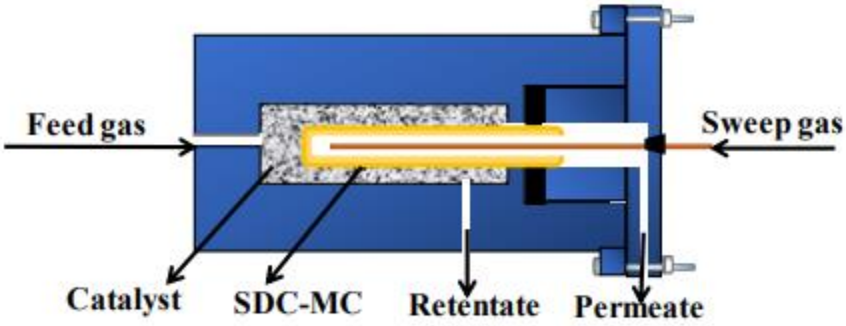


Figure 10: WGS reaction in membrane reactor with Co-Mo-Mg$(AlO_2)_2$-based shift catalyst.

WGS reaction testing with contaminant-free synthetic syngas successfully showed 95% CO conversion in the SDC-MC membrane reactor. The new ScSZ-based, H_2S-resistant CCDP membranes were fabricated in tubular configuration, with CO_2 permeance measured at 2,000 GPU and stability assessed under 30 atm transmembrane pressure drop.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
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)	Sc-doped ZrO_2 (ScSZ) (42.5/32.5/25 Li/Na/K)$_2CO_3$ (MC)
Materials of Fabrication for Support Layer	—	BYS	BYS
Nominal Thickness of Selective Layer	µm	1,500	50-200
Membrane Geometry	—	tubes	tubes
Maximum Trans-Membrane Pressure	bar	1	30
Hours Tested without Significant Degradation	hour	120	>200
Manufacturing Cost for Membrane Material	$/m^2	1,000	500
Membrane Performance			
Temperature	°C	700-900	700-900
CO_2 Pressure Normalized Flux	GPU	300-600	>2,000
CO_2/H_2O Selectivity	—	>500	>500
CO_2/H_2 Selectivity	—	>500	>500

CO_2/H_2S Selectivity	—	>500		>500
Sulfur Tolerance	ppm	<5 ppm		>400 ppm
Type of Measurement	—	mixed-gas		mixed-gas
Proposed Module Design				
Flow Arrangement	—		Counter-current	
Packing Density	m^2/m^3		50-200	
Shell-Side Fluid	—		Retentate, H_2-rich flow	
Syngas Gas Flowrate	kg/hr		0.005-0.01	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90	99	~1
H_2 Recovery, Purity, and Pressure	%/%/bar	99	90*	~ 10
Pressure Drops Shell/Tube Side	bar		10-30	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		~1,000	

* Gasifier, coal feedstock, and upstream unit operation (e.g., syngas pretreatment) specifications dependent.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivity should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – At temperatures above 600°C, the separation of H_2 and CO_2 through CCDP membranes is governed by ionic transport of carbonate ion in MC phase in meso/macropores and oxygen ion in the ceramic phase support.

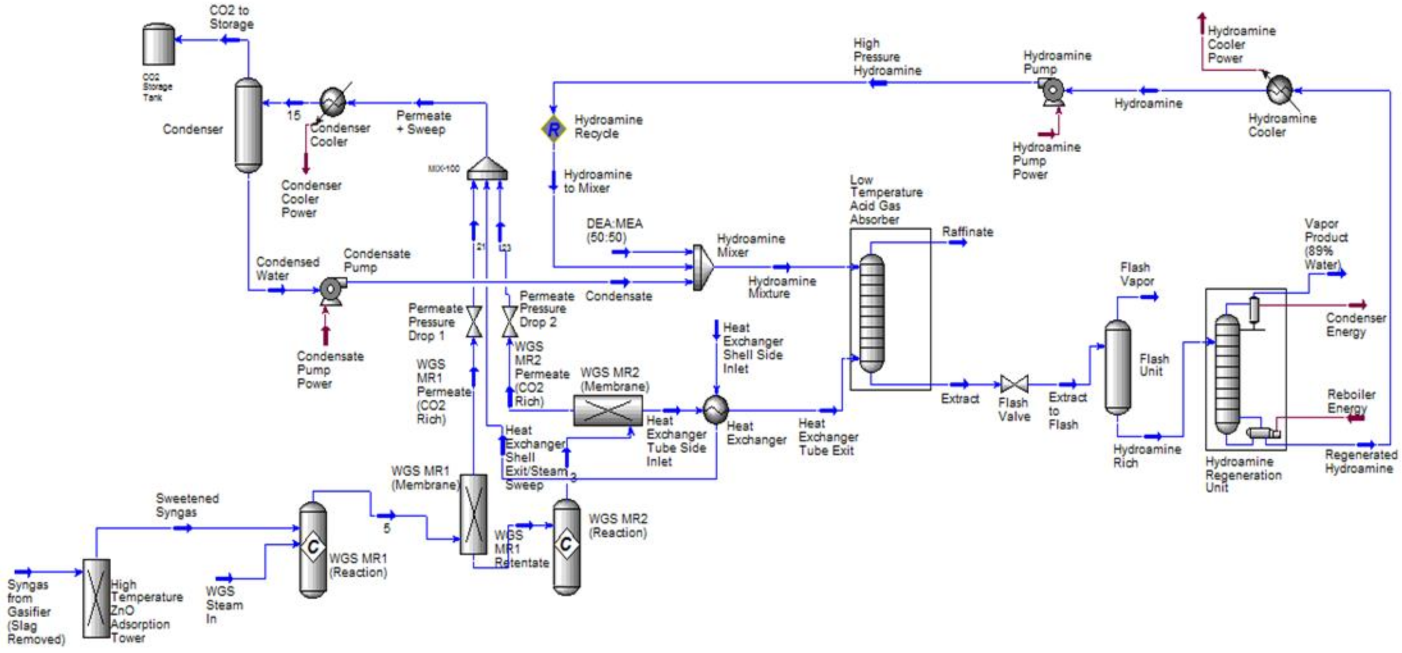
Contaminant Resistance – The developed CCDP membranes have resistance to syngas contaminants such as H_2S.

Syngas Pretreatment Requirements – Particulate removal is required.

Membrane Replacement Requirements – The multiple-tube membrane bundle is intended to operate in the membrane reactor continuously over 1,000 hours without replacement.

Waste Streams Generated – There are no waste streams generated in the flowsheet. All potential waste streams are recycled and used in the process somewhere.

Process Design Concept –



Proposed Module Integration – The composition of the gas mixture is assumed:

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
435	1500	11.6	26.7	0.08	2.8	25.7	33.6	>400

technology advantages

- The membrane reactor process could replace a conventional two-stage WGS reactor system requiring intercooling and a separate CO_2 capture unit, with a single WGS membrane reactor unit with potential for energy efficiency increase and equipment cost savings.
- WGS reactors containing CO_2-selective membranes to recover CO_2 have potential to achieve higher H_2 delivery to the turbine in an IGCC cycle than if H_2 were being selectively recovered from the syngas stream.
- Carbon dioxide removal through a membrane process in a WGS reactor retains the H_2 at high pressure, maximizing the efficiency of the combustion turbine in an IGCC cycle.
- Tubular membranes can be fabricated into robust and stable multiple-tube modules at a high packing density.

R&D challenges

- ScSZ has poor carbonate wettability making it difficult to infiltrate carbonate and achieve stability.
- Gas leakage through membrane from unsealed pores (imperfect carbonate infiltration).
- High-temperature stability of membrane bundle components and seals.
- Deterioration of strength of membrane tubes in use.
- CCDP thermal stability and poison resistance maintained at high pressures (greater than 20 atm) and temperatures (700–900°C).
- Removal of particulate matter from the hot syngas to reduce its potential impact on the membrane lifetime.
- Cost reductions for the membrane module materials if the technology is to become economically viable.

status

A laboratory-scale module of the high-temperature and high-pressure CCDP-based WGS membrane reactor has been successfully realized incorporating SDC-MC tubular membranes, which involved development of new seals to avoid leakage. WGS reaction testing with contaminant-free synthetic syngas successfully showed 95% CO conversion in the membrane reactor. The new ScSZ-based, H_2S-resistant CCDP membranes were fabricated with CO_2 permeance measured at 2,000 GPU and stability under 30 atm transmembrane pressure drop. However, the ScSZ has poor wettability with molten carbonate making the ScSZ-MC CCDP membrane unstable. The WGS reaction in H_2S-resistant configuration will be studied with simulated coal-gasified syngas contaminated with H_2S, with CO conversion targeted at 99%.

available reports/technical papers/presentations

“High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture,” presented by Jerry Lin, Arizona State University, 2021 NETL Carbon Management Research Project Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Lin_ASU.pdf*

“High-Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture,” presented by Oscar Ovalle-Encinia, Arizona State University, 2019 NETL CO_2 Capture, Utilization, Storage, and Oil & Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/O-Ovalle-Encinia-ASU-Ceramic-Carbonate.pdf*

“High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture,” Kick-off meeting presentation, November 2018. *https://netl.doe.gov/projects/plp-download.aspx?id=10558&filename=High+Temperature+Ceramic-Carbonate+Dual-Phase+Membrane+Reactor+for+Pre-Combustion+Carbon+Dioxide+Capture+.pptx*

“High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-combustion Carbon Dioxide Capture,” presented by Lie Meng, Arizona State University, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/L-Meng-ASU-High-Temperature-Ceramic-Carbonate-Dual-Phase-Membrane.pdf*

Ovalle-Encinia and J. Y.S. Lin, “High-pressure CO_2 permeation properties and stability of ceramic-carbonate dual-phase membranes”, *J. Membr. Sci*., 646, 120249 (2022).

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