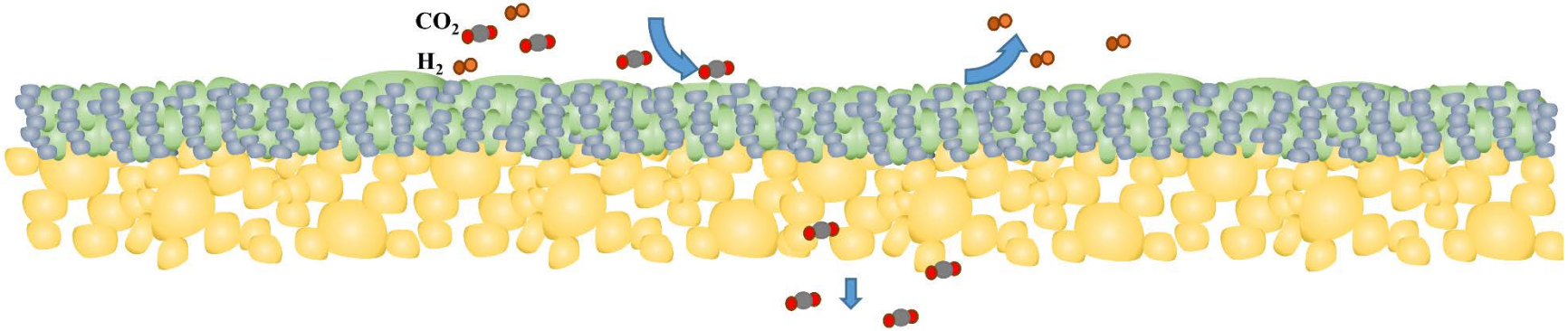
High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

DOE Award: DE-FE0031634



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Tempe, Arizona

2019 NETL CO_2 Capture, Utilization, Storage, and Oil & Gas Technologies Integrated Review Meeting

August 27, 2019, Pittsburgh, Penn

Overview

Timeline

- ✓ Project start date:
  Oct. 1, 2018
- ✓ Project end date:
  Sep. 30, 2021
- ✓ Budget Periods:
  I: 10/1/2018-3/31/2020
  II: 4/1/2020-9/30/2021

Budget

- ✓ Total project funding
  - ❑ DOE **$800,000**
  - ❑ Cost-share: **$200,007**
  - ❑ Total**: $1,000,007**

Research Area 1

- ✓ Lab-Scale CO_2 Capture Development and Testing on Simulated Syngas

Partners

- ✓ Arizona State University (ASU)
- ✓ University of South Carolina (USC)

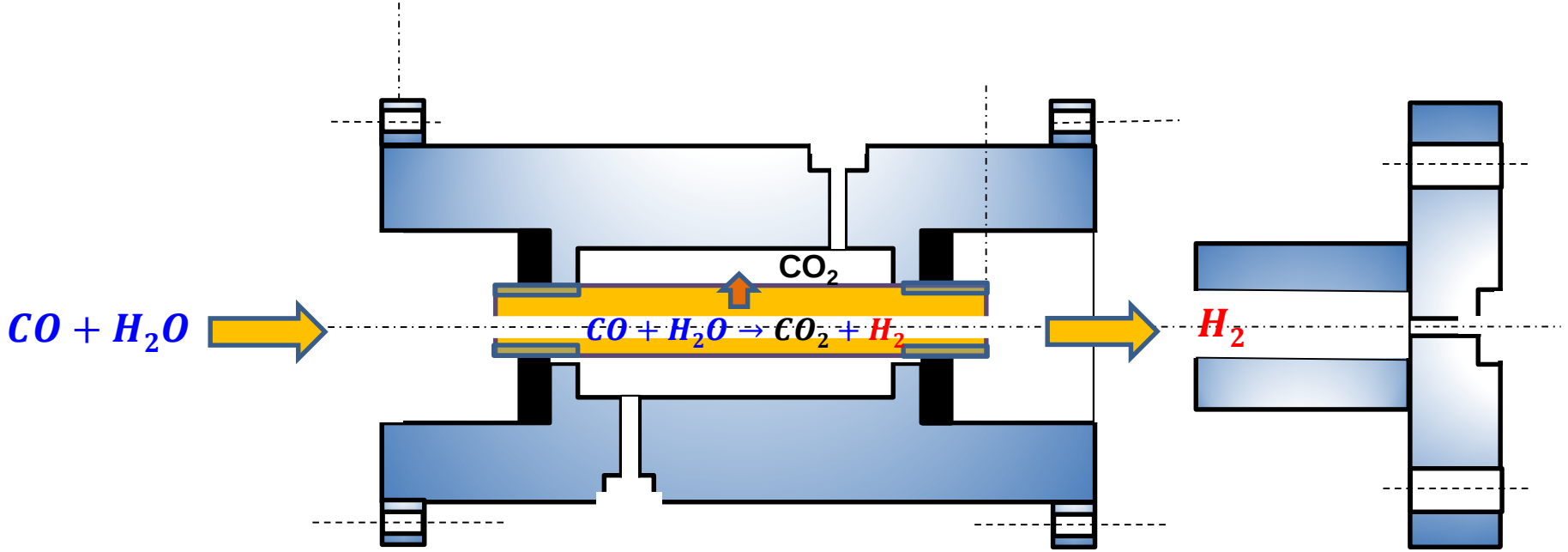
Project Objectives

- To synthesize the chemically/thermally stable Ceramic Carbonate Dual-Phase (CCDP) membranes.
  - ✓ CO_2 permeance > 2000 GPU ($6.5x10^{-7}$ mol/m^2·s·Pa)
  - ✓ Selectivity > 500
  - ✓ Resistant to H_2S
- To fabricate tubular CCDP membrane reactor modules.
  - ✓ High-temperature >700 ° C
  - ✓ High-pressure > 20 atm
  - ✓ WGS membrane reactor applications.
- To identify experimental conditions for WGS.
  - ✓ 99% purity of CO_2 stream
  - ✓ 90% purity of H_2 stream

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

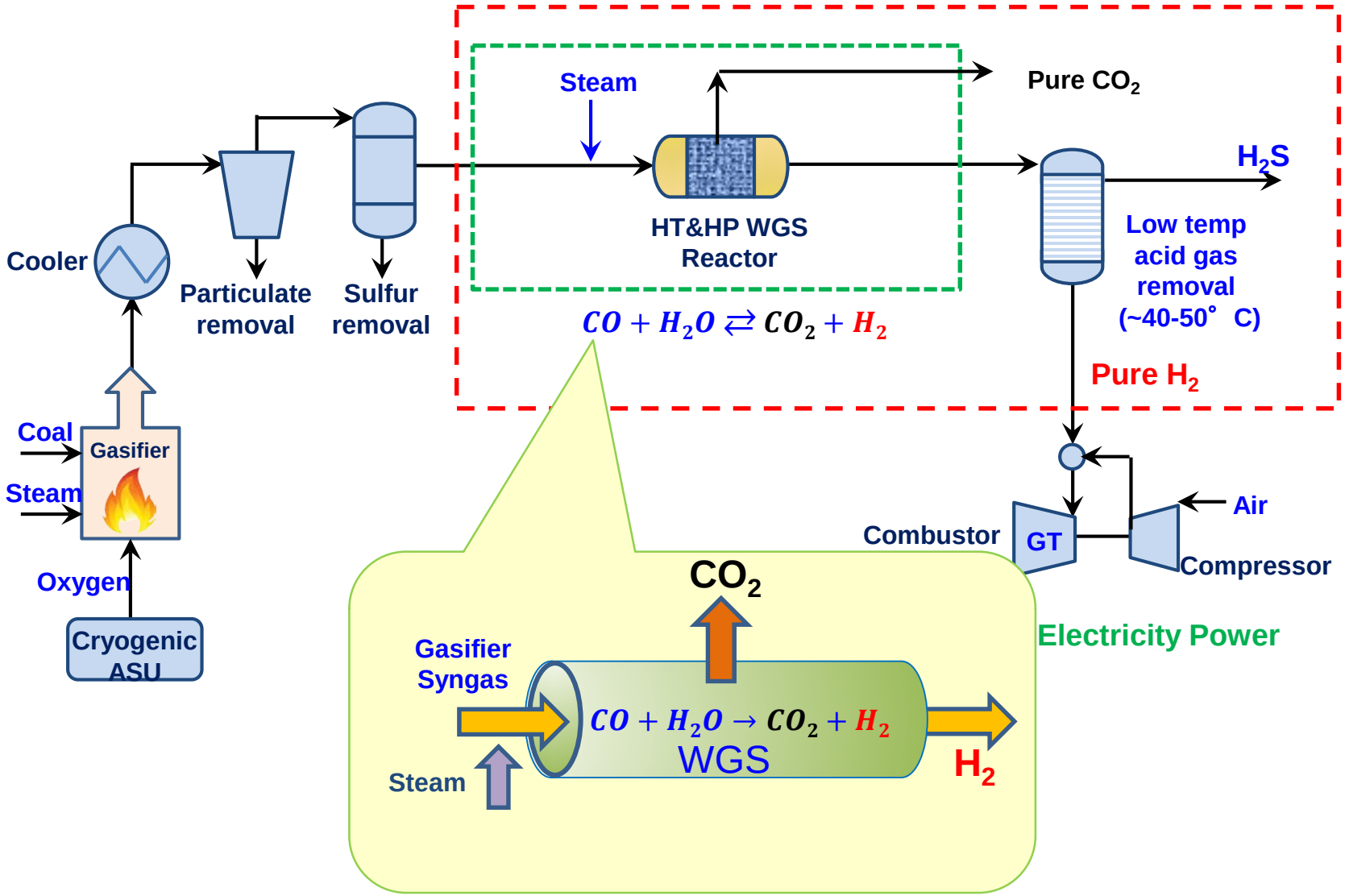
Task description

Synthesis of Ceramic Tubular and Disk Supports	Fabrication of Symmetric and Asymmetric Membrane	Lab-scale module for tubular membrane & HT/ HP seals	CO_2 Permeance at HT and HP & Stability Tests	Studies on Experimental and Modeling WGSR	Process Design and Techno-Economic Analysis



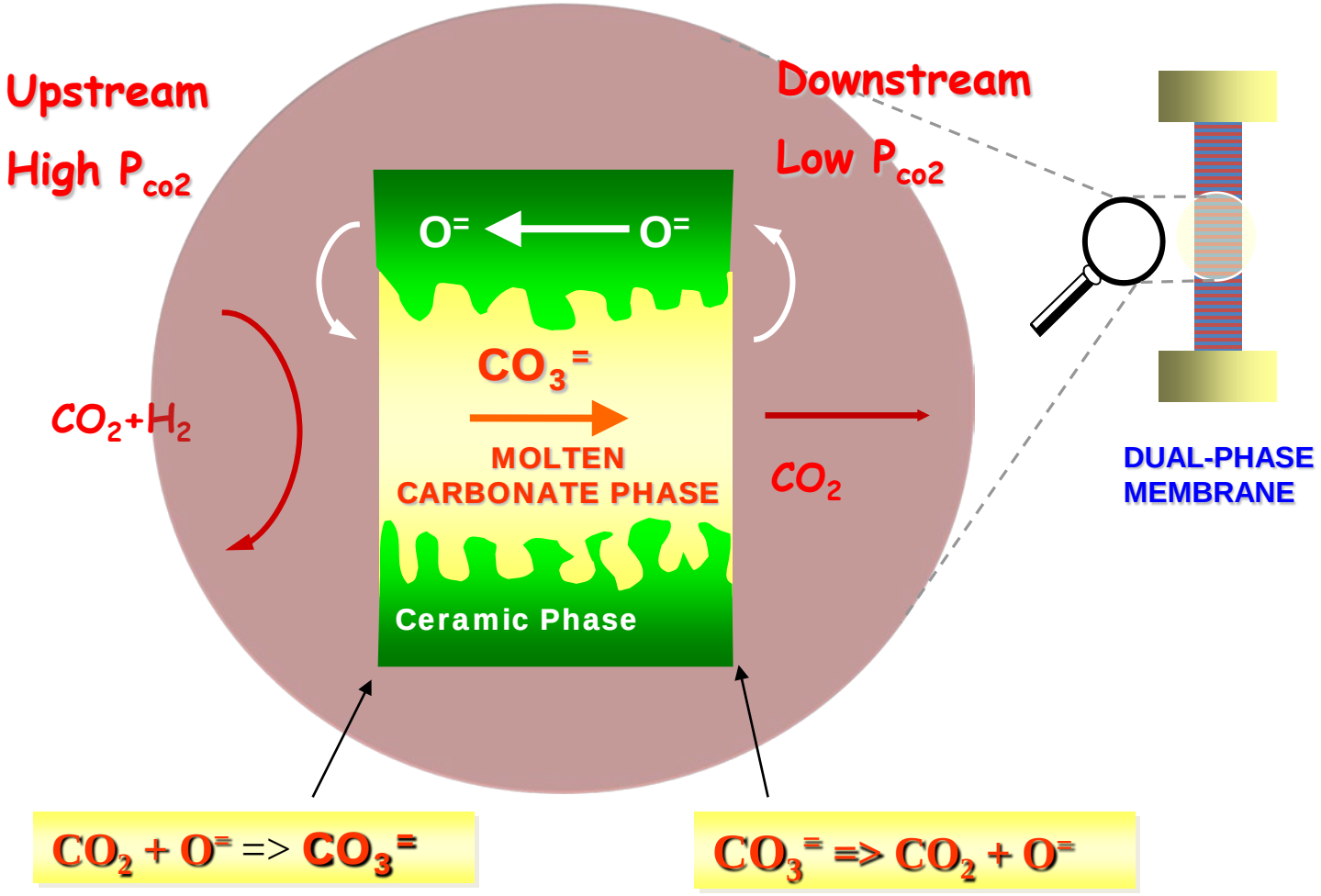
Background: IGCC process with Pre-combustion CO_2 Capture

- One single reactor
- Improvement of kinetic of WGSR at 900° C
- Improvement of thermodynamics by separating CO_2



Background

Concept of Ceramic-Carbonate Dual-Phase (CCDP) Membrane



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

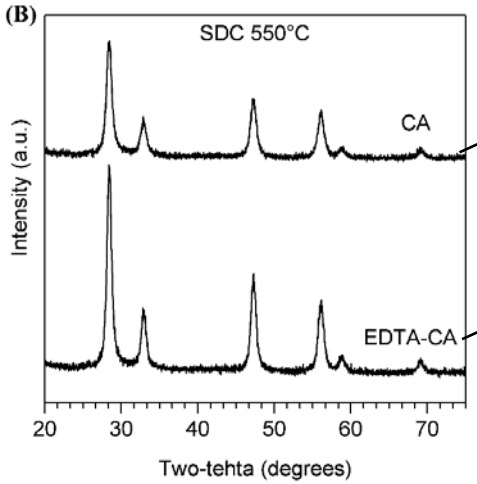
Progress and Accomplishments

- Project Management and Planning **(Task 1.0)**
- Synthesis and Characterization of SDC-MC Membranes **(Task 2.0)**
- High Temperature, High Pressure CO_2 Permeation Studies **(Task 3.0)**
  - Construction of high temperature and high pressure CO_2 permeation/separation setup **(Subtask 3.1)**
- Development of Improved Ceramic-Carbonate Dual-Phase Materials and Membranes **(Task 4.0)**
  - Synthesis of ScSZ with desired microstructure **(Subtask 4.1)**
  - Characterization of ScSZ disks **(Subtask 4.2)**
- Study on CO_2 Permeation Properties of ScSZ-MC Membranes **(Task 5.0)**
  - Study of the effect of temperature and CO_2 concentration on flux **(Subtask 5.1)**

SDC

- ❑ **High oxygen ion conductivity**
- ❑ **Chemically/thermally stable under reductive atmosphere**
- ❑ **Synthesized and characterized in our lab for a long time**

❑ **Pure ionic conductivity: Sm-doped CeO_2 (SDC)**



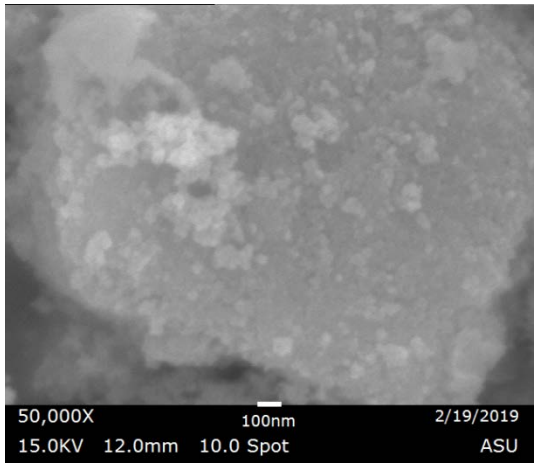
<D>=8.9nm

<D>=17nm

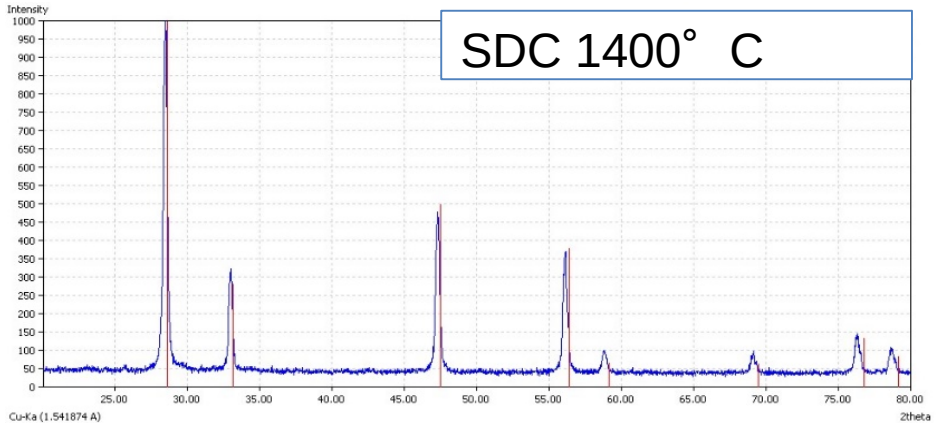
a=5.43804 Å
(5.411 Å for CeO_2)

CA (500 ° C)

❑ **Agglomerates of ~ 1µm made of particle < 10 nm**



❑ **Thermal stability of SDC support**

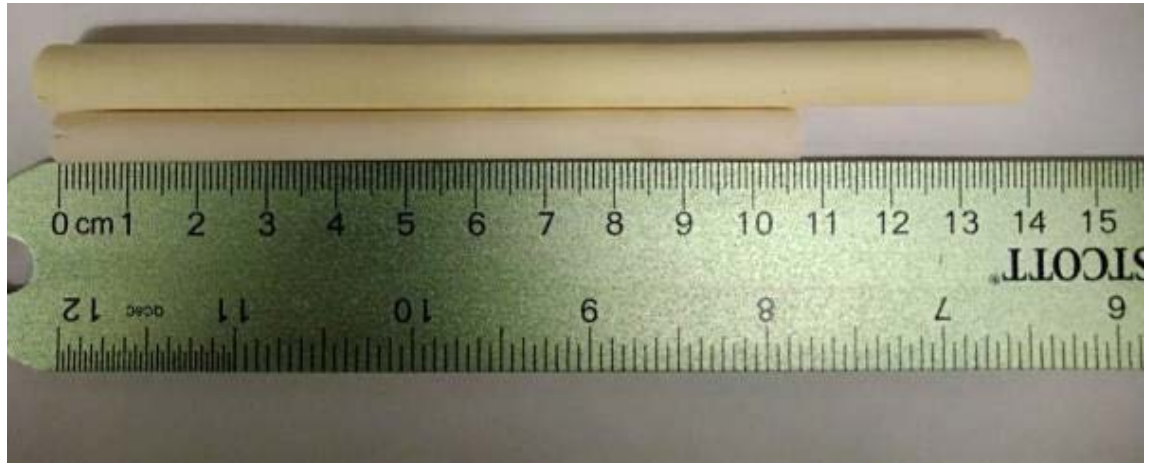


Progress and Accomplishments

Task 2.0: Synthesis and Characterization of SDC-MC Membranes

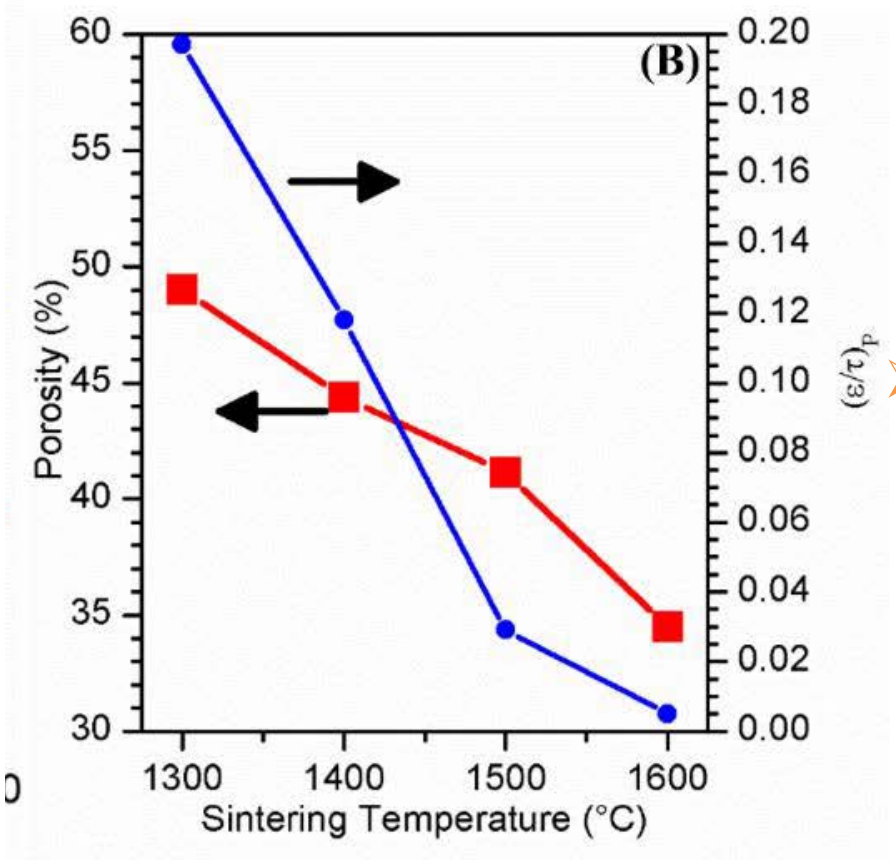
- SDC tubular supports by the Centrifugal Casting (CC) method
- Development of a module for high rate centrifugation
- Design of highly efficient sintering process
- Long, straight and uniform-circumference tubes

➢ **Initial stage of tubes fabrication**

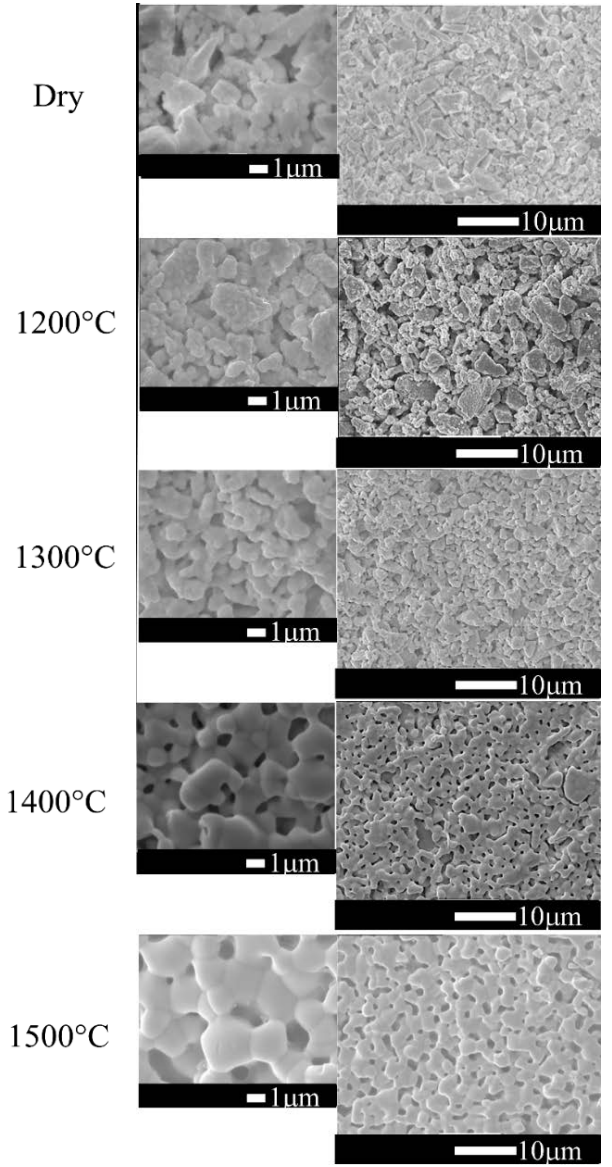


➢ **Tubes Fabrication improved**

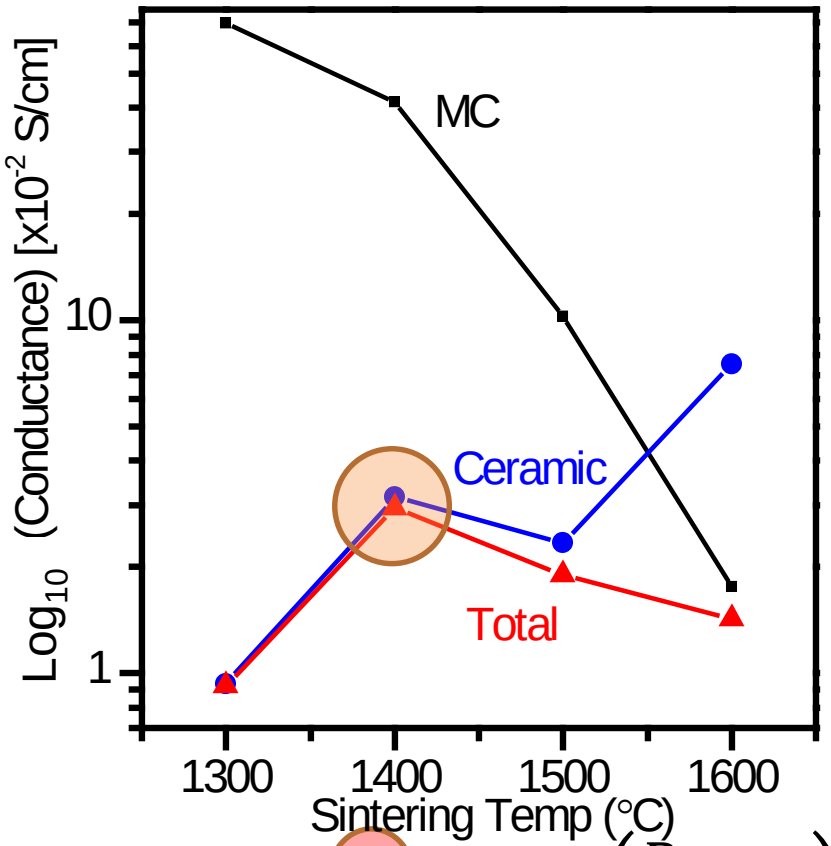
- **Microstructure of SDC tubular supports modified with different sintering temperature**



- **Porosity**
- **Tortuosity**
- **Average grain size**
- **Solid volume fraction**

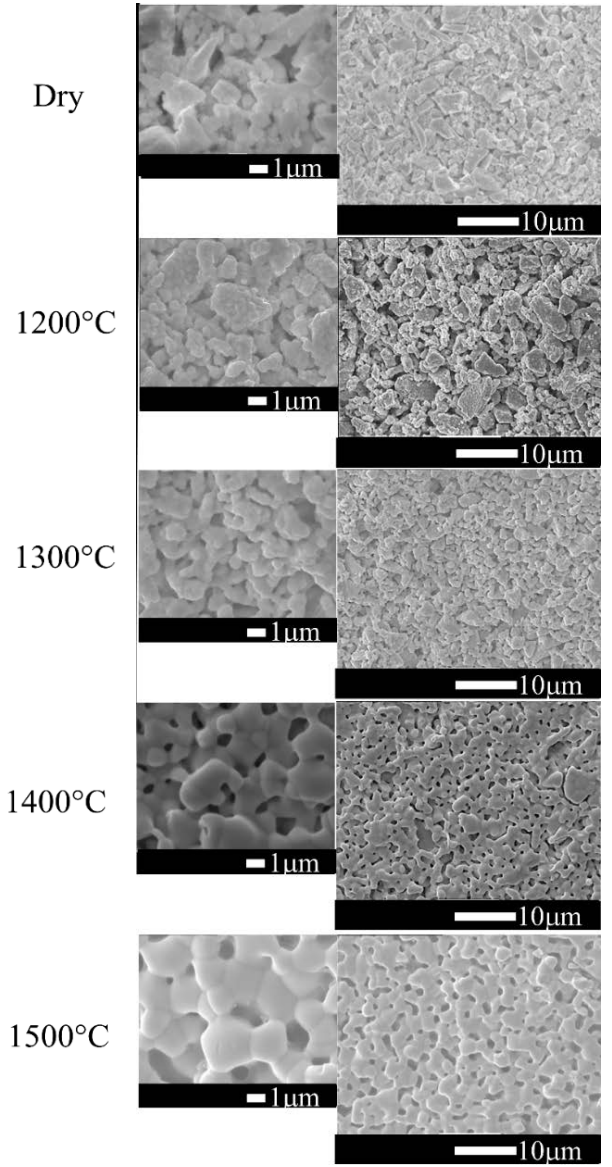


❑ **Microstructure of SDC tubular supports modified with different sintering temperature**



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

- **Porosity**
- **Tortuosity**
- **Average grain size**
- **Solid volume fraction**



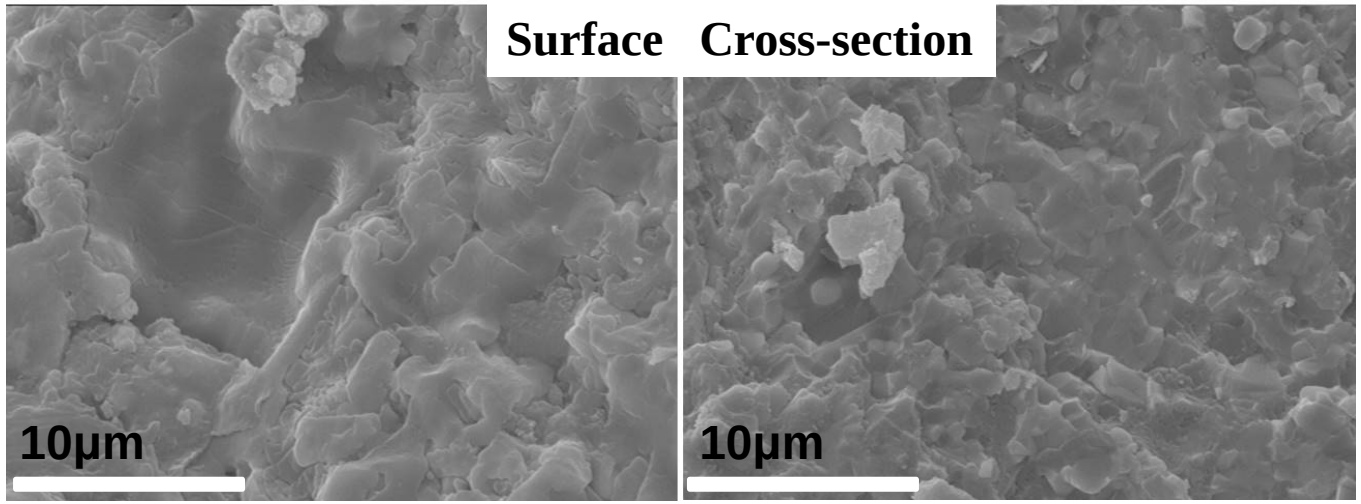
Progress and Accomplishments

Task 2.0: Synthesis and Characterization of SDC-MC Membranes

❑ Molten carbonates Infiltration at 550° C

Carbonates mixture	Li/Na/K	Li/K	Li/Na	Na/K
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

❑ Gas-tight membrane (He permeance: $<1.22\times10^{-10}$ mol·m^{-2}·s^{-1}·Pa^{-1})

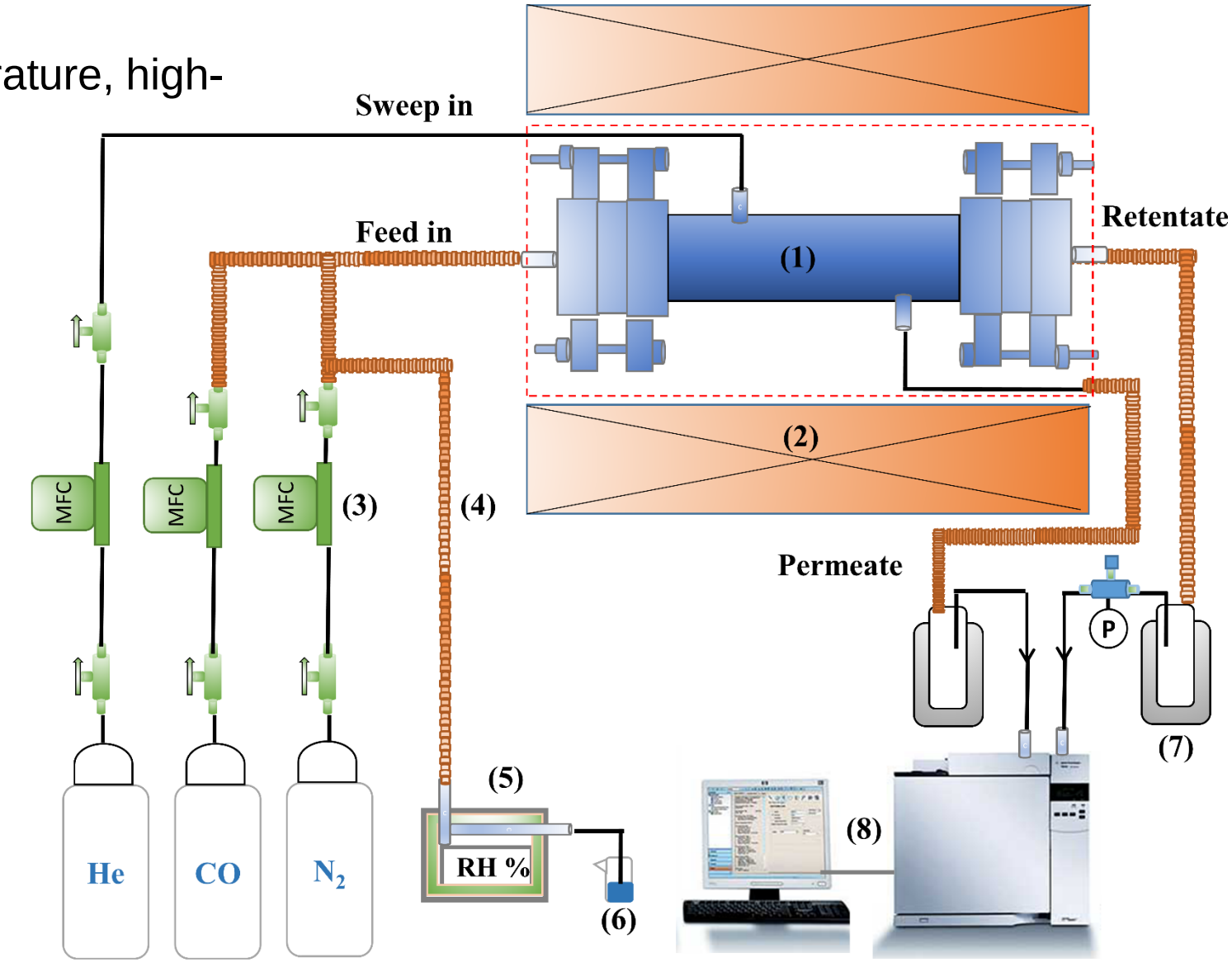


Progress and Accomplishments

Task 3.0: High Temperature, High Pressure CO_2 Permeation Studies

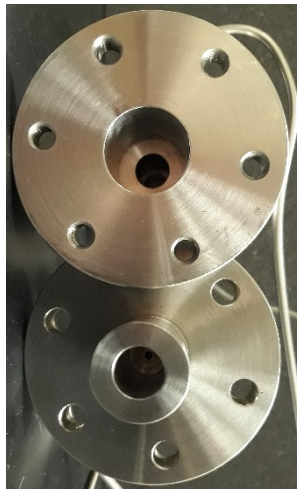
Schematic diagram of high-temperature, high-pressure gas permeation set-up:

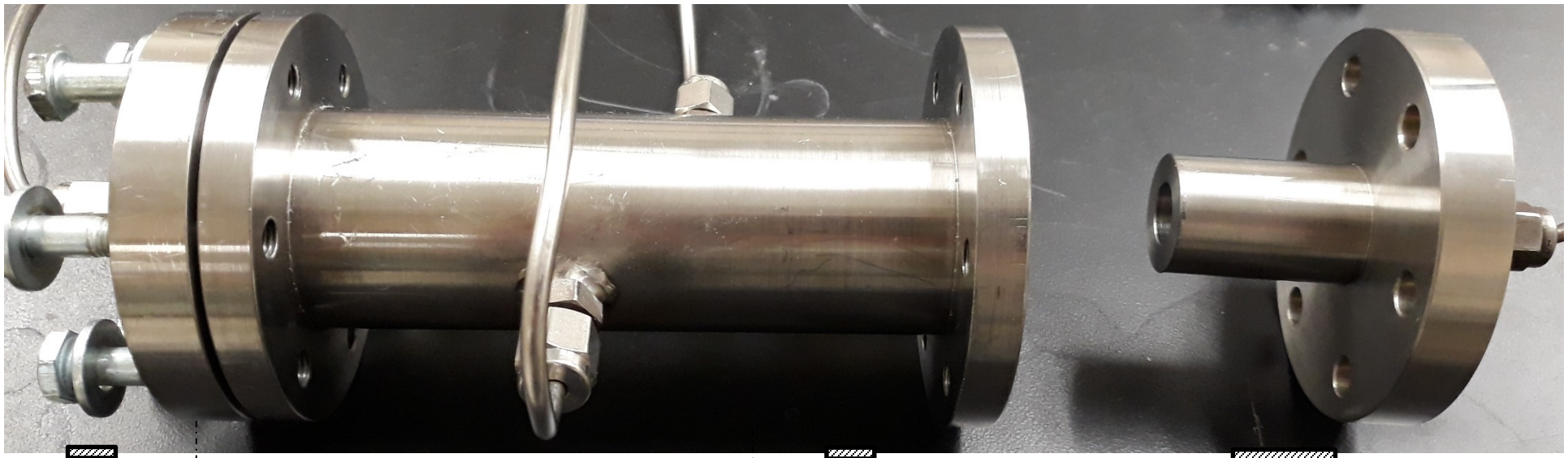
(1) **module**
(2) high temperature furnace
(3) mass flow controller
(4) heating jacket
(5) water pump
(6) water
(7) steam trap
(8) GC system
(P) fine valve

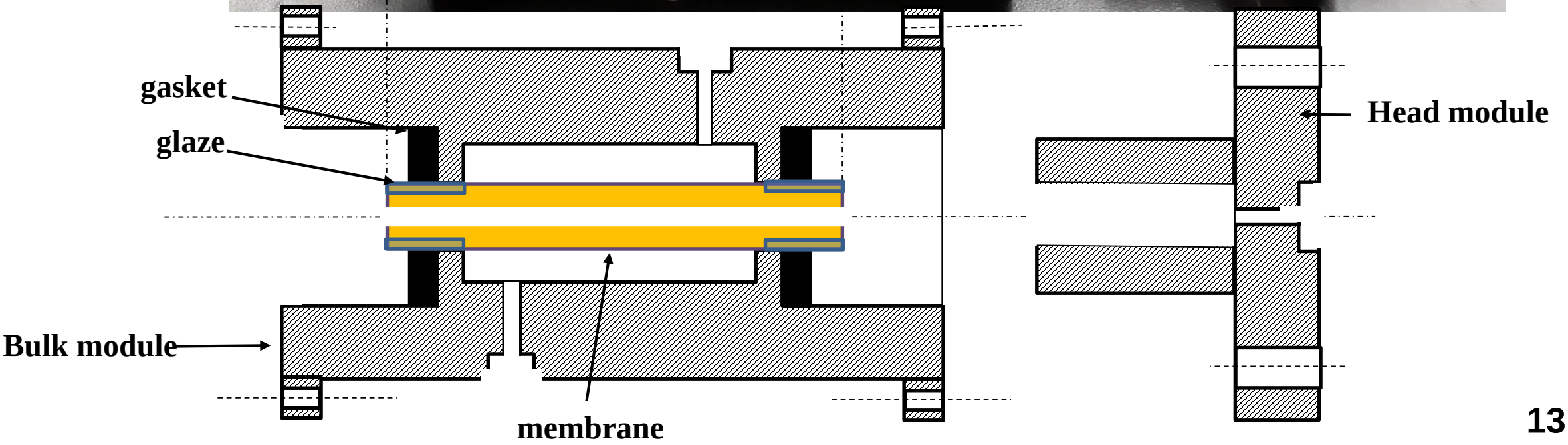


Progress and Accomplishments

Task 3.1: Construction of High Temperature and High Pressure CO_2 Permeation/Separation setup







Progress and Accomplishments

Task 3.1: Construction of High Temperature and High Pressure CO_2 Permeation/Separation setup

❑ Seals tested at high temperature

- ✓ Graphite
- ✓ Strip-metal graphite
- ✓ Flexible metal-graphite
- ✓ Home-made glaze
- ✓ Commercial glaze

❑ Seal tested at high pressure

- ✓ Graphite
  - o Leak % <4%
  - o Stable at temp ~700˚ C
  - o Pressure ~14 bar

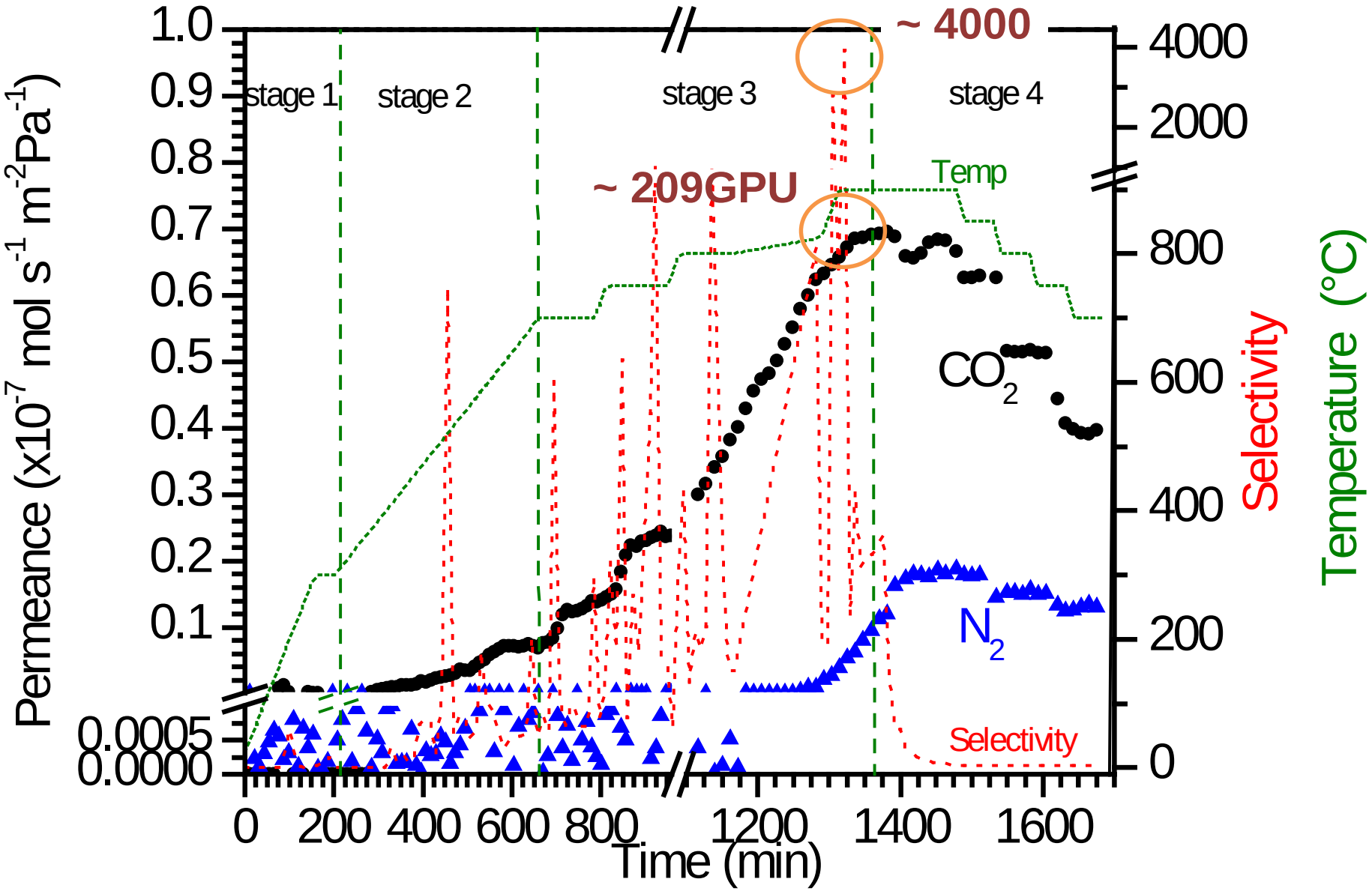
❑ Best seal performance

- ✓ Flexible metal-graphite
  - o Leak % <0.1%
  - o Stable temp ~ 900˚ C

Progress and Accomplishments

Task 4.0: Development of Improved Ceramic-Carbonate Dual-Phase Materials and Membranes

- ✓ **Seal is stable up to 900° C**
- ✓ **CO_2 Permeance Improved (thickness 2mm)**
- ✓ **Best selectivity at 900° C (~4000)**

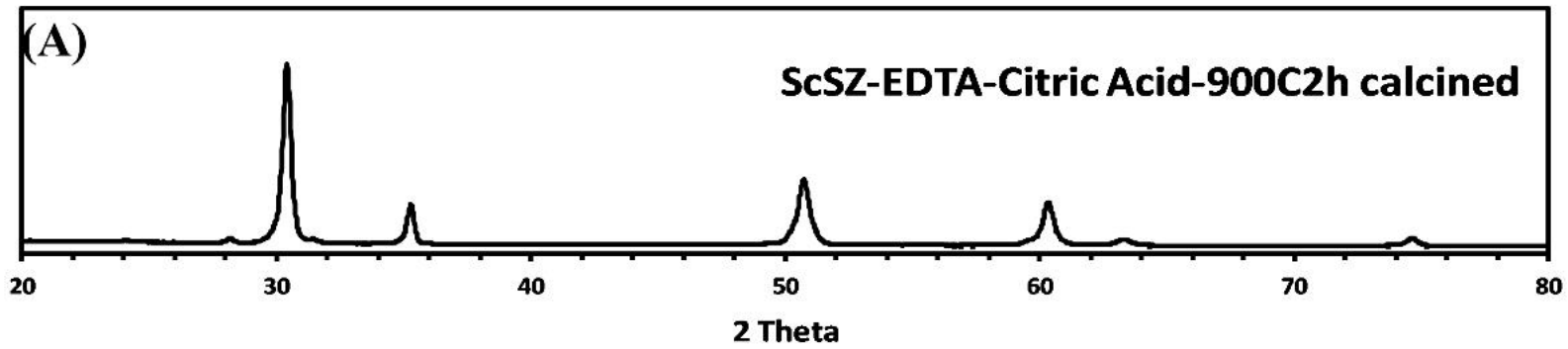


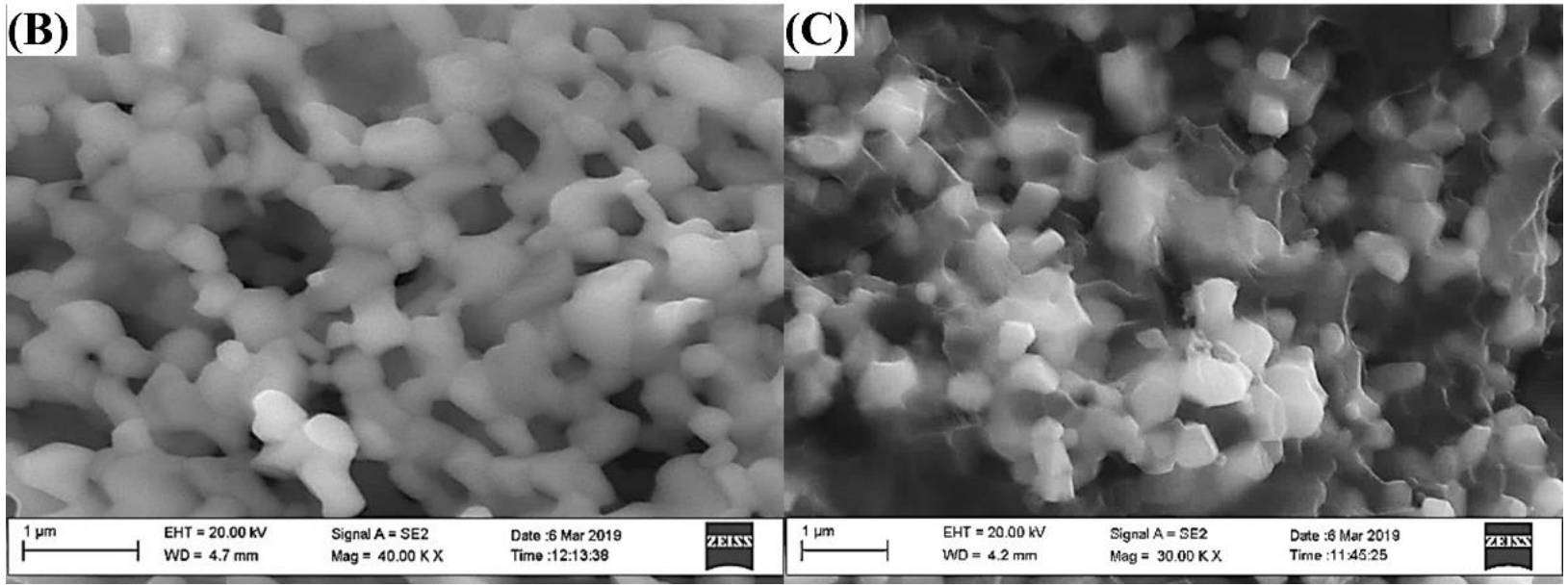
Progress and Accomplishments

Task 4.1: Synthesis of ScSZ with desired microstructure

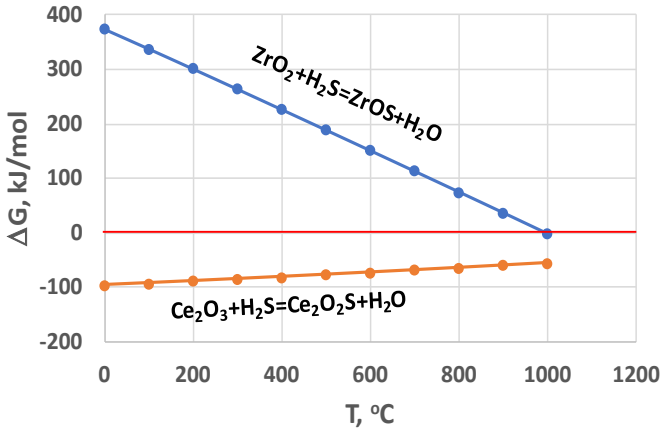
Task 4.2: Characterization of ScSZ disks

ScSZ powders synthesized via EDTA-citric acid method

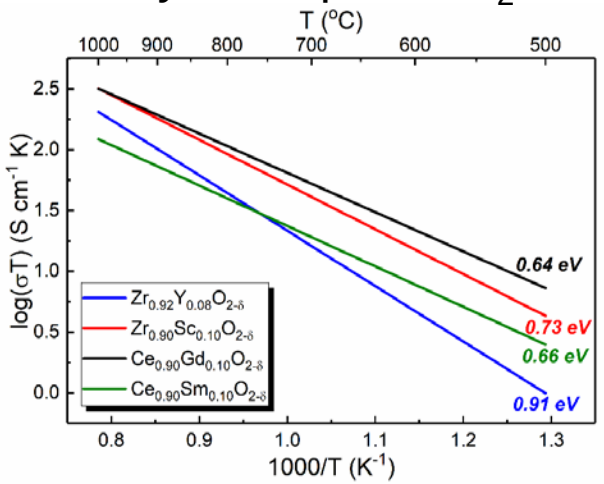




Why ZrO_2 over CeO_2



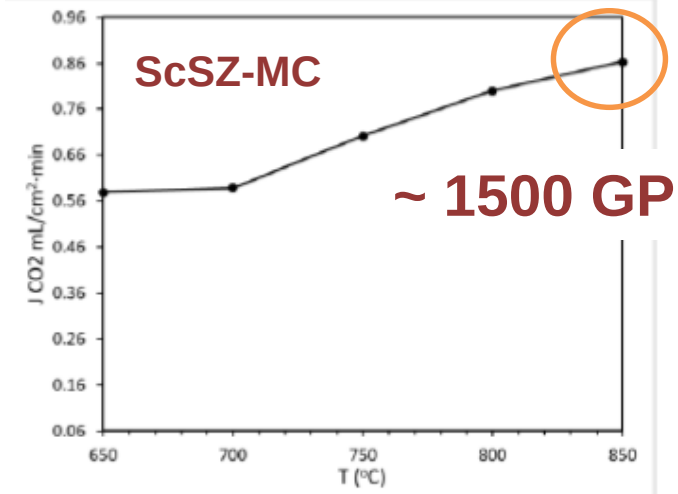
Why Sc-doped ZrO_2

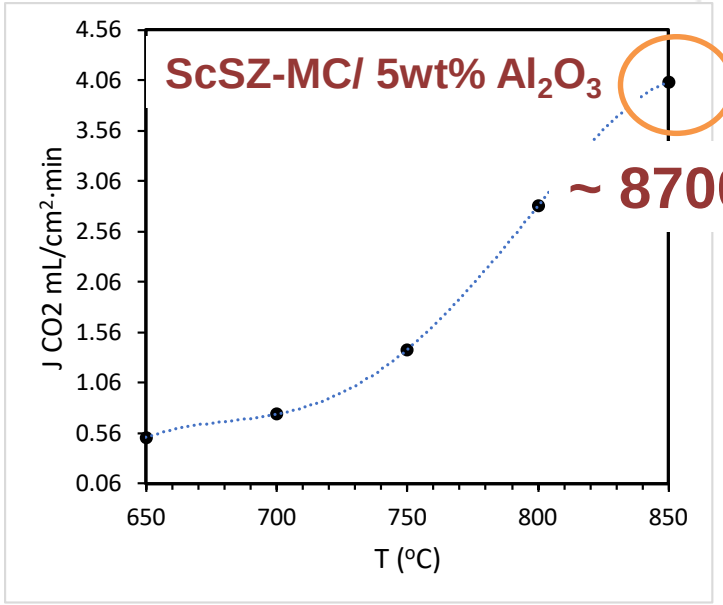


Progress and Accomplishments

Task 5.0: Study on CO_2 Permeation Properties of ScSZ-MC Membranes

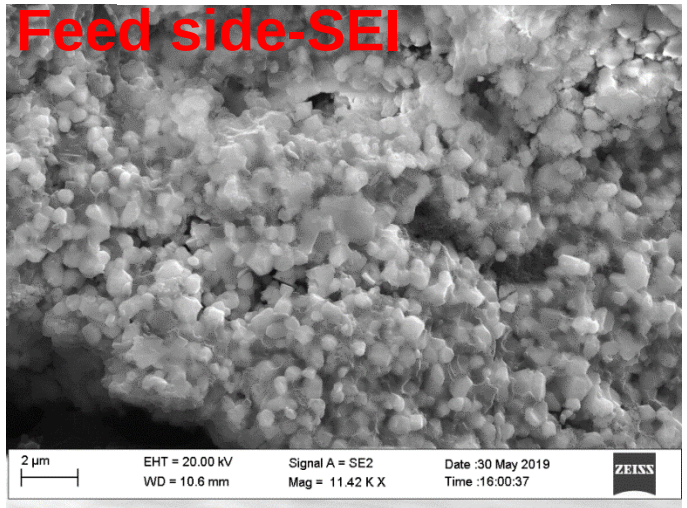
Task 5.1: Study of the effect of temperature and CO_2 concentration on flux



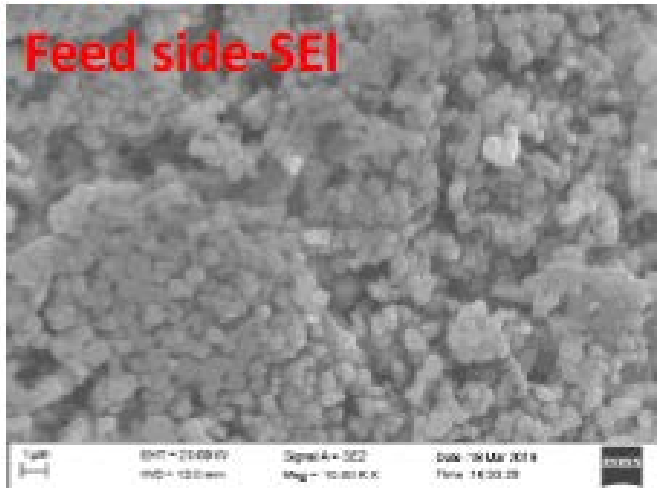


- $Li_2CO_3+Al_2O_3=2LiAlO_2+CO_2$
- N_2 leakage~2-3% at T>650°C
- Na_2CO_3 is locally abundant, thus it is transformed to solid phase
- $LiAlO_2$ improves the wettability to MC

ScSZ-MC/ 5wt% Al_2O_3



ScSZ-MC



Future Work

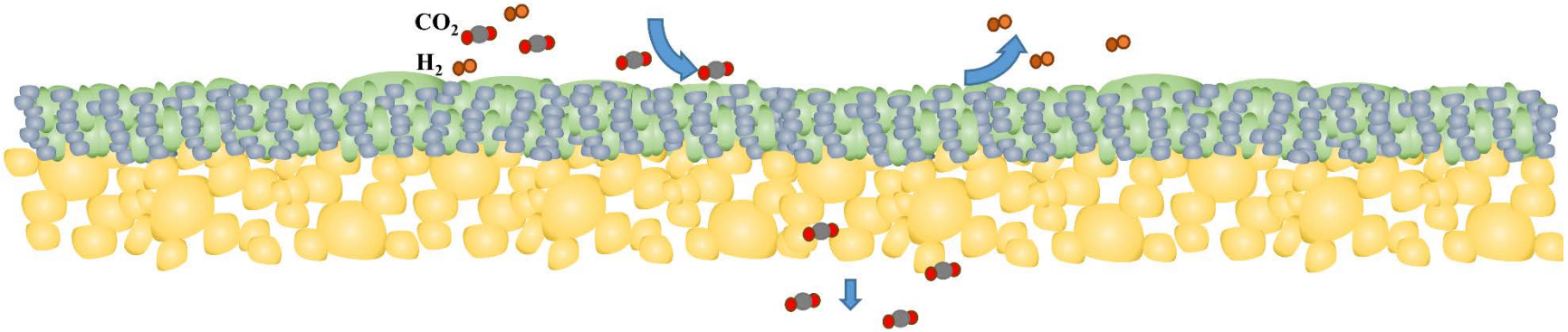
- Task 3.0 High Temperature, High Pressure CO_2 Permeation Studies
  - **High pressure** CO_2 permeation and separation **study**
  - **Modeling** and analysis **of CO_2 Permeation**
- Task 5.0 Study on CO_2 Permeation Properties of **ScSZ-MC Membranes**
  - **Flux stability study**
- Task 6.0 - **Fabrication** and Characterization of **Sc-ZrO_2 Tubular Membranes**
- Task 7.0: **Modeling** and analysis of CCDP membrane reactor for **WGSR**

Conclusions

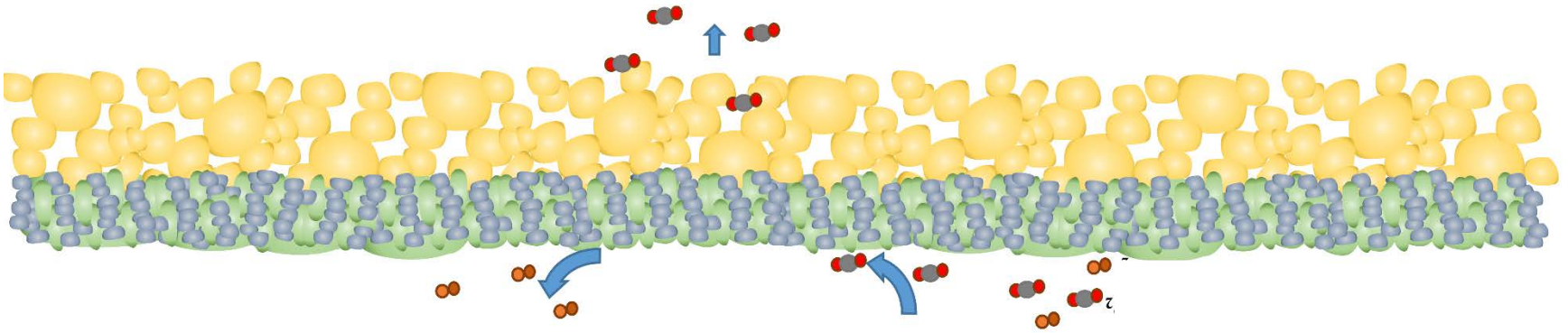
- The module for high-temperature, high-pressure WGS membrane reactor and CO_2 separation was successfully built.
- High-pressure and high-temperature seal was developed for avoiding leaks.
- SDC tubular membranes were tested at high temperatures, with selectivity of at least 4000.
- ScSZ disk membranes were tested at high temperatures with high CO_2 permeation flux of 8700 GPU.

Acknowledgement

- Financial support: U.S. Department of Energy and National Energy Technology Laboratory (Federal Grant: DE-FE0031634).
- Project manager: Andrew O'Palko
- Collaborators:
  - ✓ Prof. Kevin Huang
  - ✓ Dr. Shichen Sun



Thank You!



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