Pressure Driven Oxygen Separation

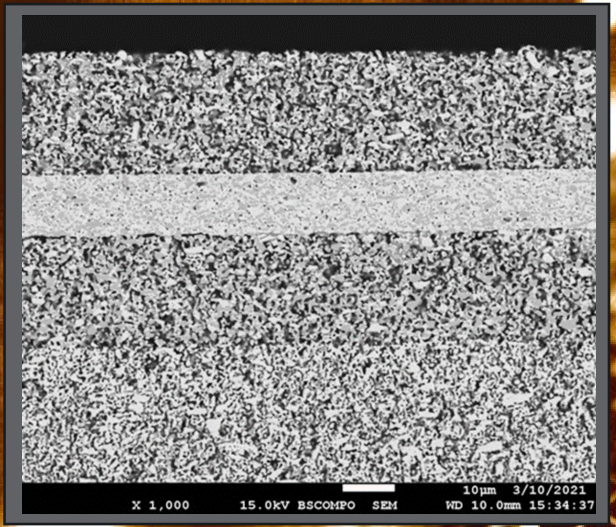
FWP-73130

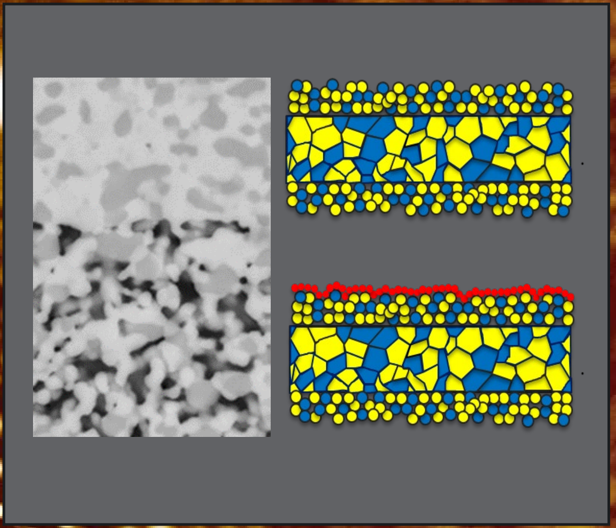
David Reed, Jon Helgeland, Greg Coffey, and Pepa Matyas

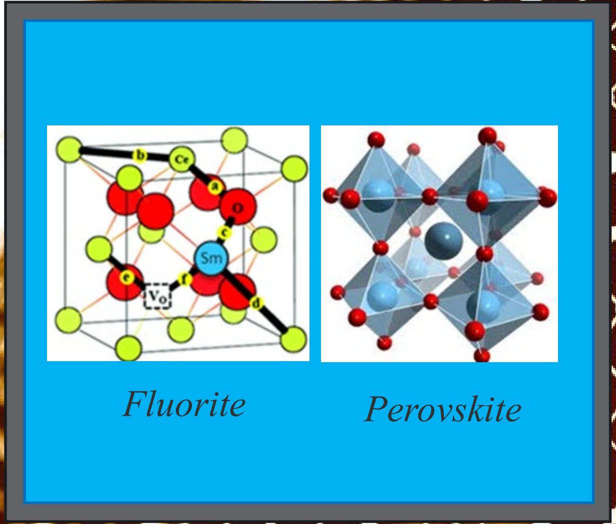
Pacific Northwest National Laboratory
Richland, WA

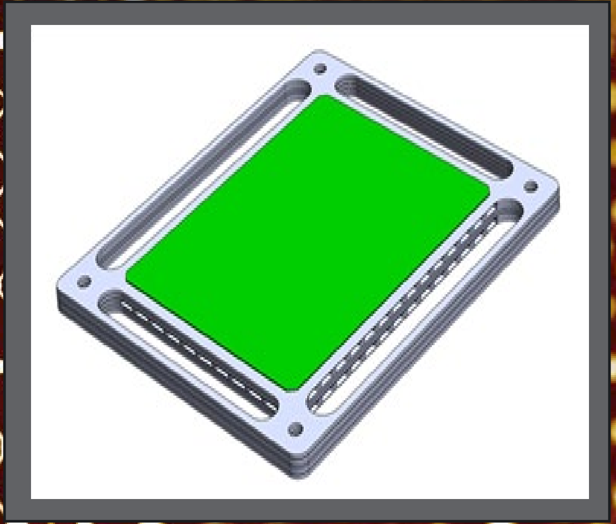
Spring R&D Project Review Meeting

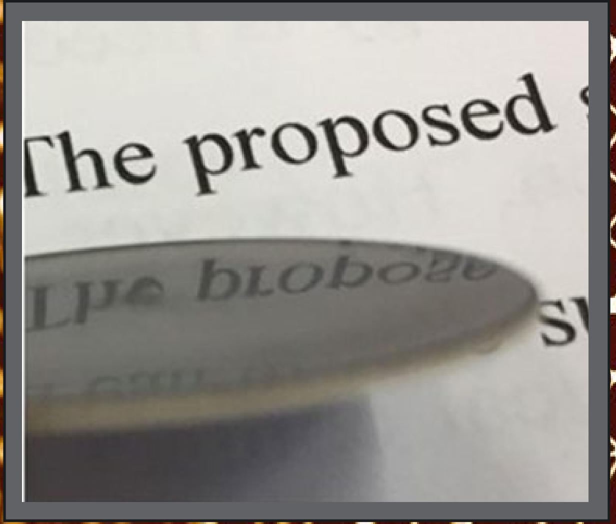
May 2, 2022

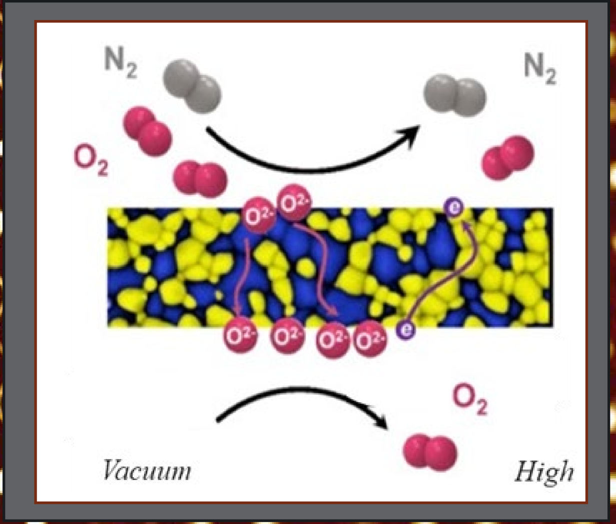












Pressure Driven Oxygen Separation

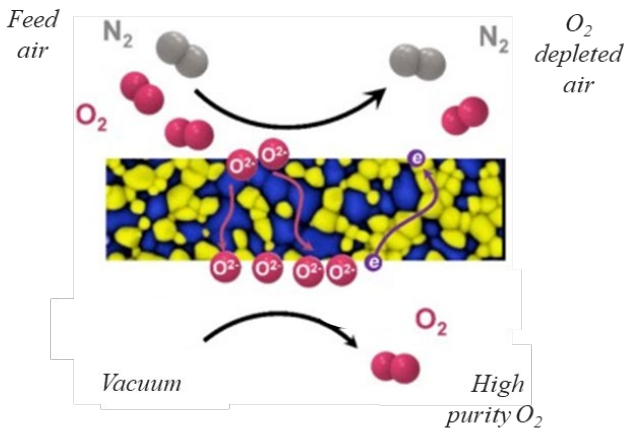
Outline

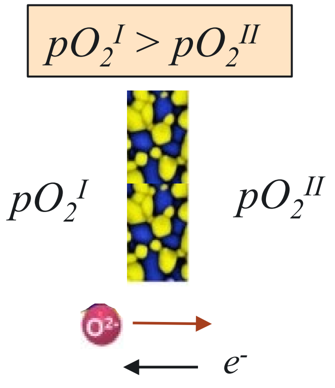
- Project Description and Objectives
- Project Background
- Critical Factors for Project Success
- Project Update
- Next Steps

Project Description and Objectives

The overall goal of the proposed effort is to develop a small scale, modular air separation unit providing 10-40 tons/day of high purity oxygen to a 1-5 MW gasifier at low cost and high efficiency

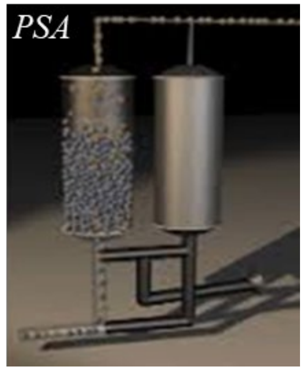
- Mixed conducting two phase material capable of separating oxygen at 700-800°C.
- Planar membrane/support structure
- Utilize the difference in oxygen partial pressure across the membrane to drive oxygen from air, <u>no electrical energy needed for oxygen separation</u>



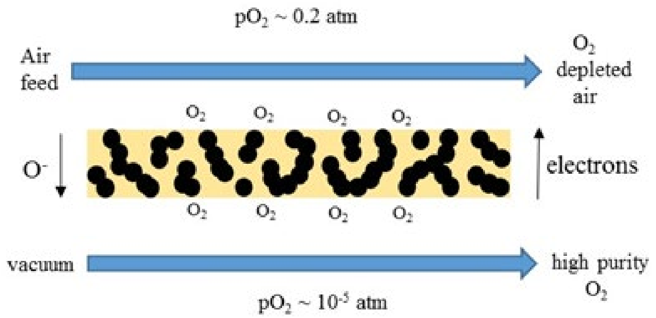


Oxygen Separation Techniques

- **Cryogenic Air Separation** – mature
  - Low energy demand at high capacity (4000 T/day)
  - Energy demand very high at low capacity (i.e., 10-40 T/day)
  - Very high purity (99+)
- **Pressure Swing Adsorption (PSA)** – mature
  - Economical at lower capacities (i.e., 300-400 T/day)
  - Purity ~ 90 - 93%
- **Polymer Membranes** – mature
  - Low purity (~ 40%)



- **Ceramic Membranes** – R&D
  - High purity (99+)
  - Thermal integration
  - Can be economical depending on oxygen permeability
  - Examples: OTM (Oxygen Transport Membrane)
    ITM (Ion Transport Membrane)

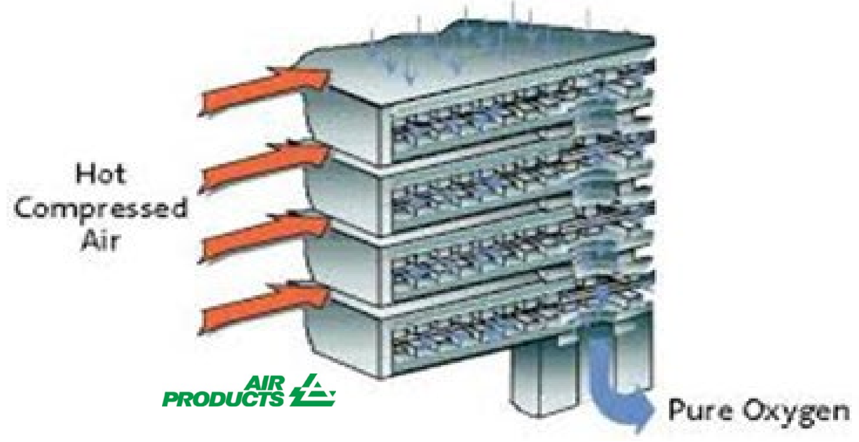


Proposed Ceramic Membrane Technology

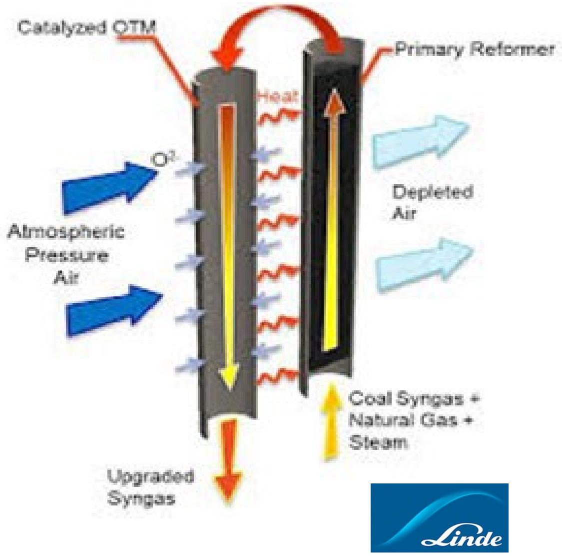
<u>Planar</u> vs Tubular Design

- Ease of manufacturing
- High surface area
- Increased sealing surface area
- Medium temperature (700-900°C)
- Two phase composite membrane (σ_i and σ_e)
- SOFC design experience at PNNL

Planar Design

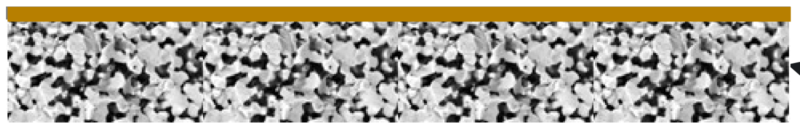


Tubular Design



Proposed Ceramic Membrane Technology

Bilayer Structure



Thin composite membrane (~ 10 μm)

Porous support (~ 0.5-1mm)

Composite membrane

- Dense
- High σ_i and σ_e
- Compatible with glass seal
- Inexpensive fabrication
- No electrodes

Porous Support

- ~ 50% dense
- TEC match to membrane
- Mechanical integrity
- Co-fired w/ membrane

Design will leverage SOFC stacks developed at PNNL

Proposed Ceramic Membrane Technology

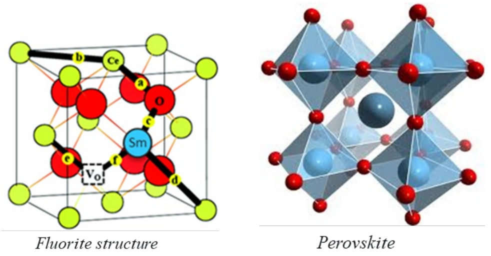
Factors Critical for Project Success

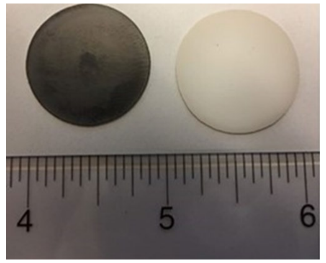
- **Low-cost materials** to enable market penetration and maximize energy efficiency
- **Minimize interactions** between ionic and electronic conducting phases
- **Co-sinter thin composite membrane on low cost porous supports** with minimal warping and cracking
- Design a planar stack architecture with **low-cost fabrication processes**

Proposed Ceramic Membrane Technology

Year 1

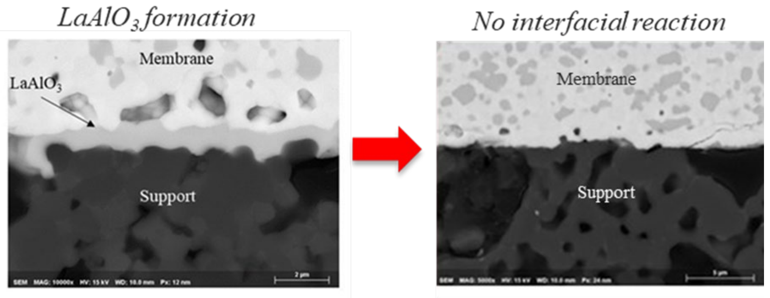
Membrane and Support Characterization
Bilayer Characterization
Membrane Oxygen Permeability

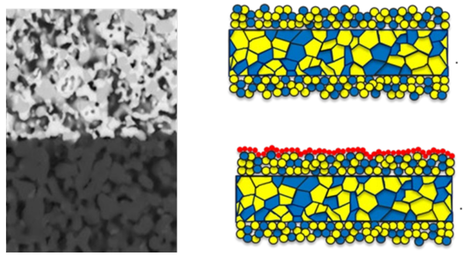




Year 2

Bilayer Interactions
Oxygen Permeability Optimization
(Barrier layers, Catalysts)
Preliminary Stack design



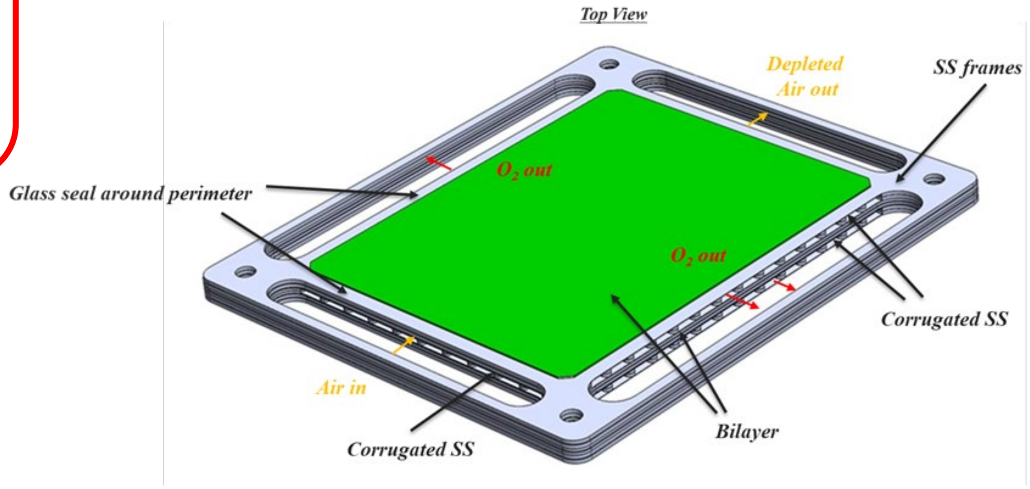


Year 3

Scale up ~ 50 cm^2
Cell assembly w/ stainless frames & glass seals
Oxygen Permeability Optimization
Cost Analysis

Year 4

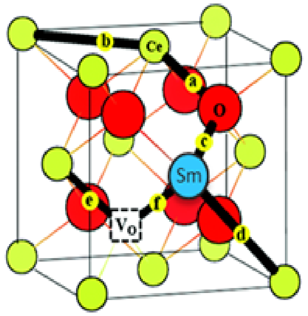
Scale up to 400 cm^2
Cell assembly w/ stainless frames & glass seals
Oxygen Permeability Optimization
Prototype
Cost Analysis



Composite Membrane Characterization

Ionic Conductor

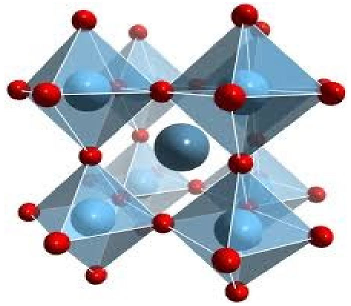
- Doped CeO_2
- $Sm_{Ce}' \rightarrow 2[V_O^{\circ\circ}]$



Fluorite structure

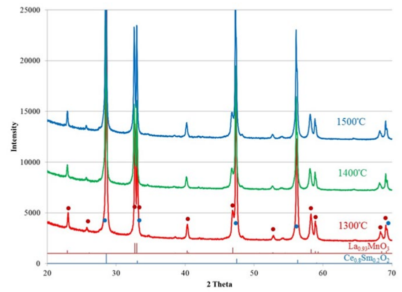
Electronic Conductor

- Doped $LaMnO_3/LaFeO_3$
- Acceptor doped p-type

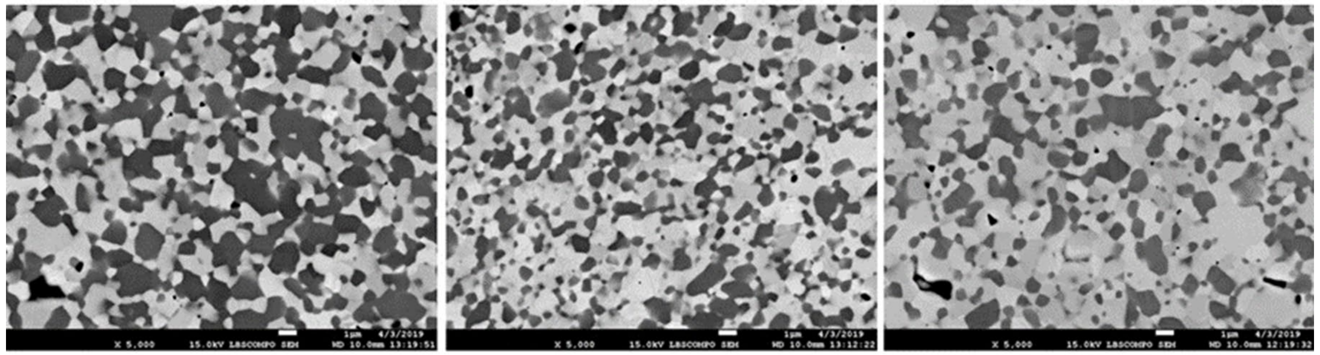

Perovskite

Microstructure Control

- Minimize stress during sintering, hermetically sealed, controlled thermal expansion limited interaction during sintering to maximize oxygen permeability



50/50 60/40 70/30



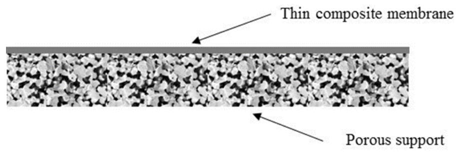
SDCC

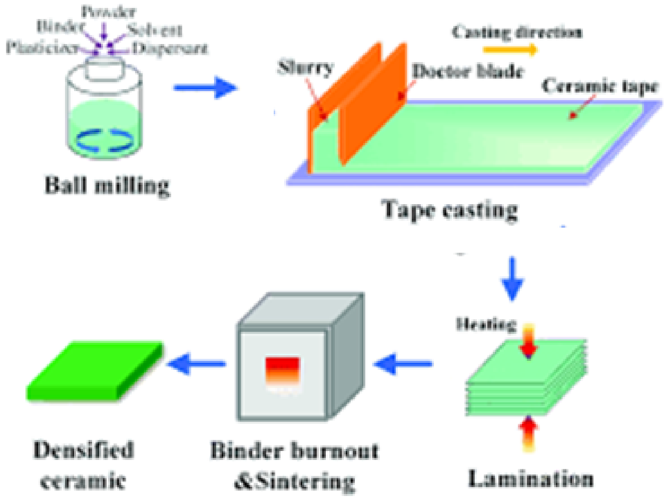
LM90

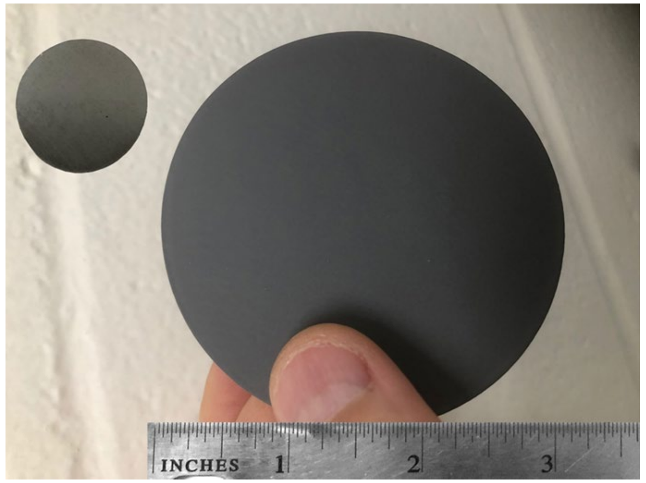
Conductivity

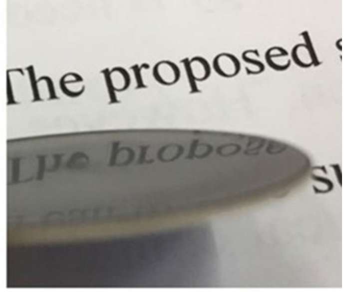
- Electrical conductivity controlled by perovskite phase, $\sigma_e \sim 4$ orders of magnitude greater than ionic conductivity (σ_i)
- ~ 2/3 σ_i value used in composite calculations
- Percolation in both phases

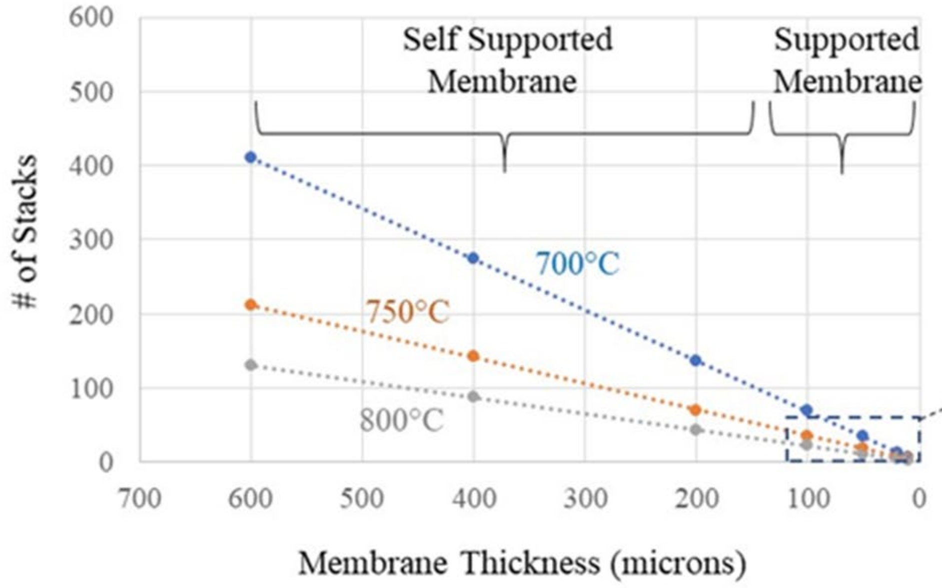
Bilayer Characterization

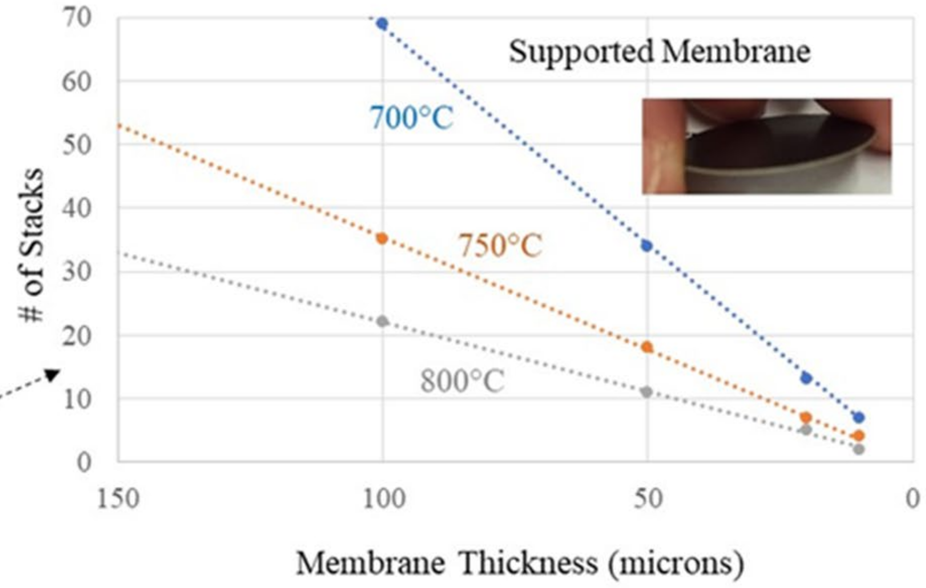










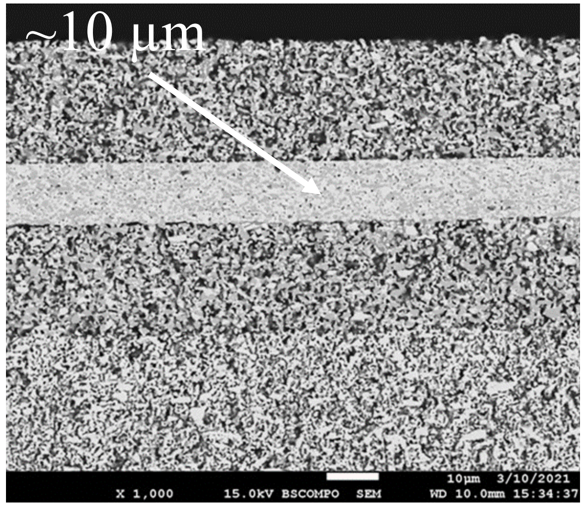


- A realistic number of stacks for producing 10 T/day of O_2 → the membrane thickness needs to be on the order of 10-15 μm.

Membrane will need to be supported → Bilayer Structure

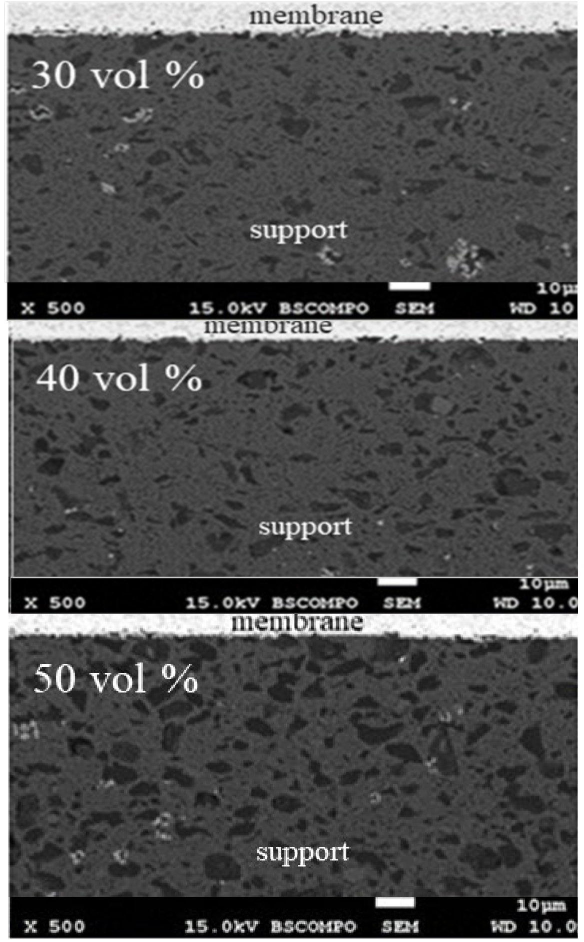
Bilayers with Controlled Microstructures

Membrane Thickness



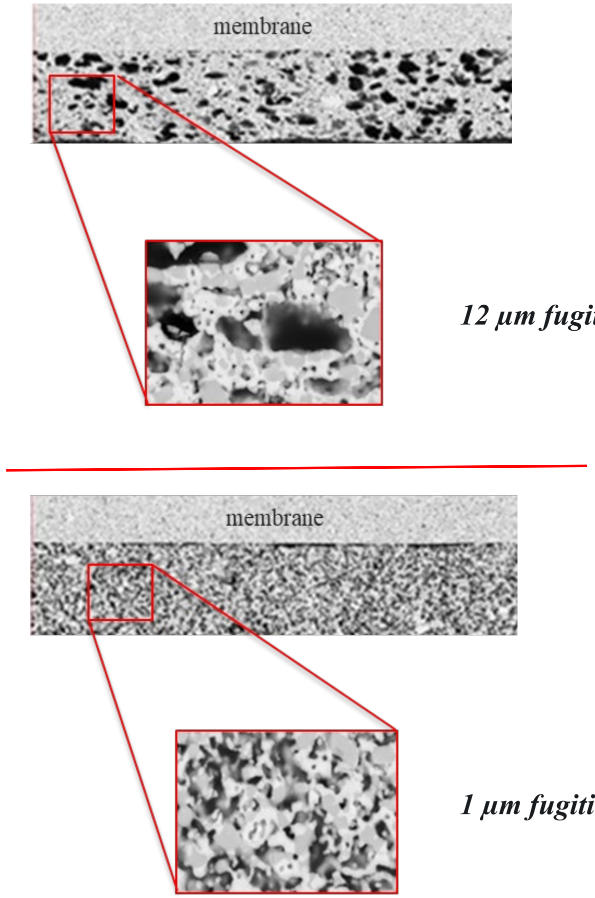
Tailor the membrane thickness by controlling the casting thickness

Vol % Porosity



Tailor porosity by controlling the amount of fugitive phase used in tape cast suspension

Size & distribution of Porosity



12 µm fugitive phase

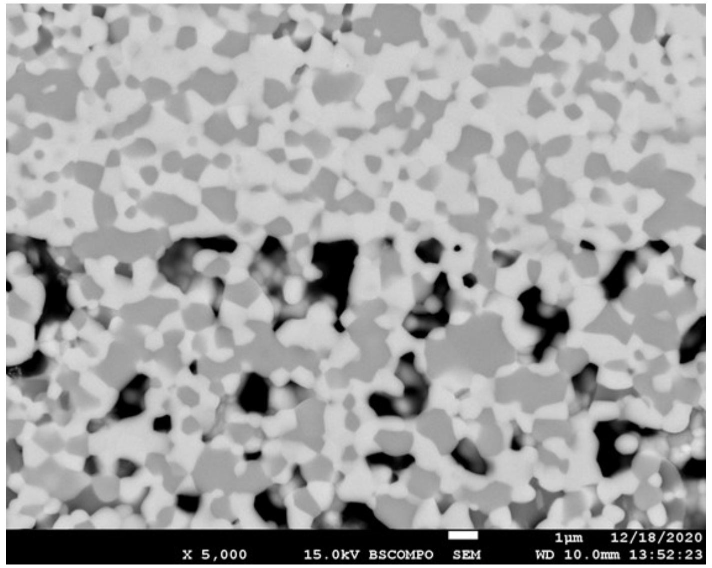
1 µm fugitive phase

Tailor size & distribution of porosity by controlling size of the fugitive phase

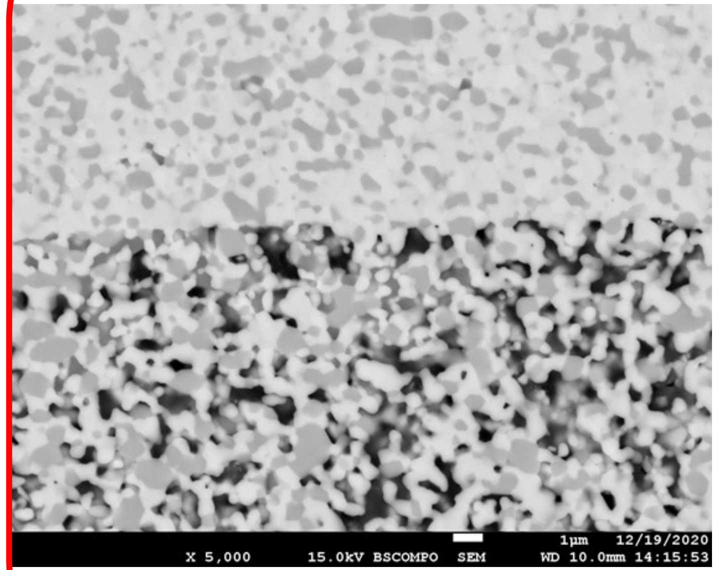
Densification of Membrane During Co-firing

Gd doped CeO_2 w/ $La_{0.75}Sr_{0.2}MnO_3$

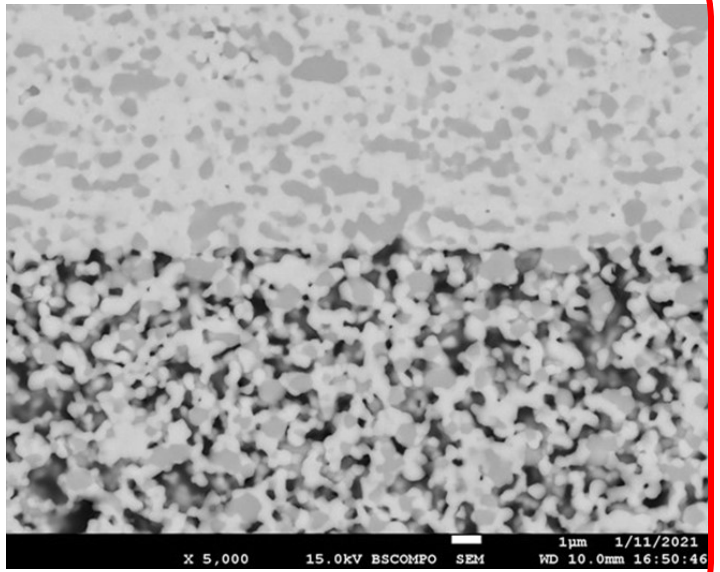
1375°C



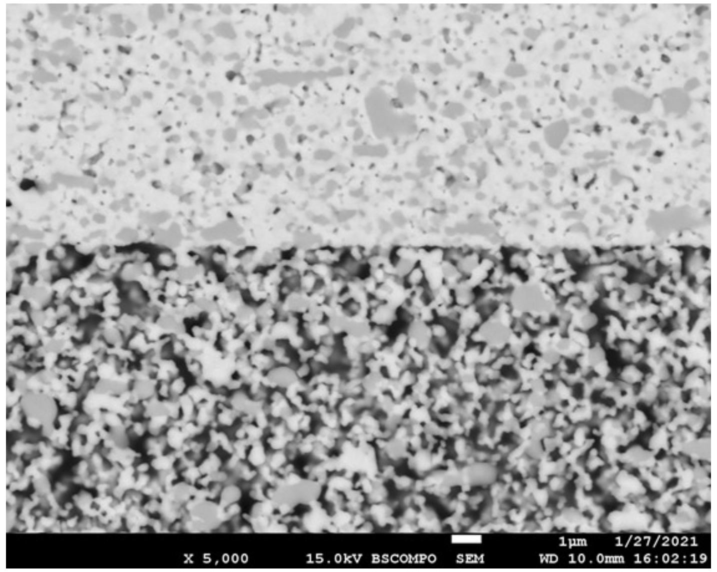
1325°C



1300°C



1275°C



Sintering Temperature

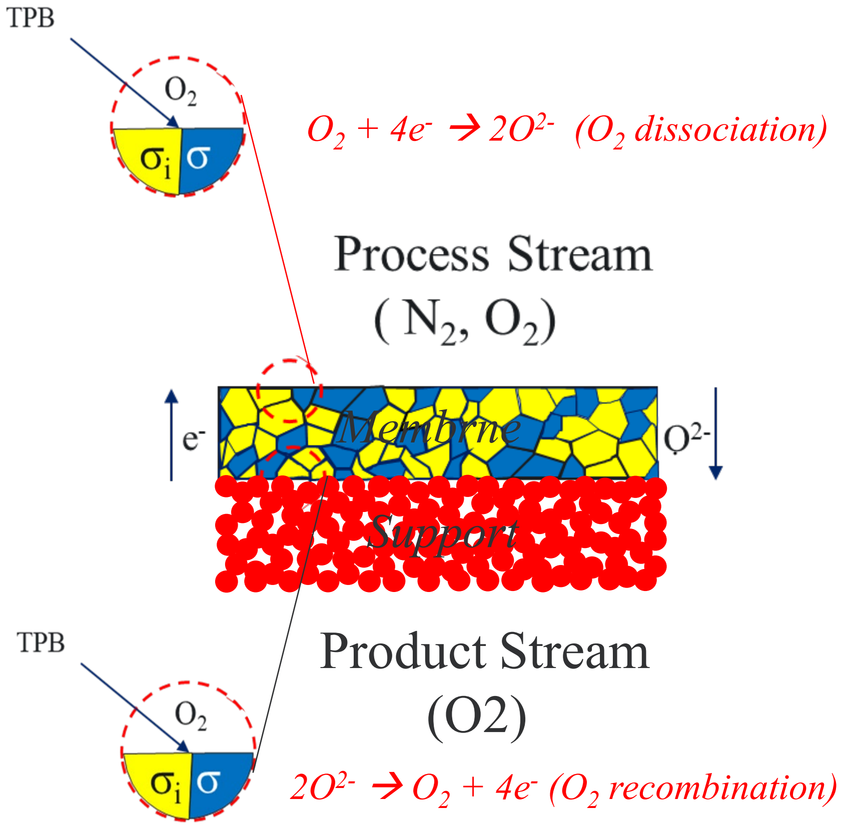
- Dense Membrane
- Larger grains
- Reduced number of TPBs
- Greater interaction/ diffusion of ions

- Dense Membrane
- Finer grains
- Increased number of TPBs
- Less interaction/ diffusion of ions

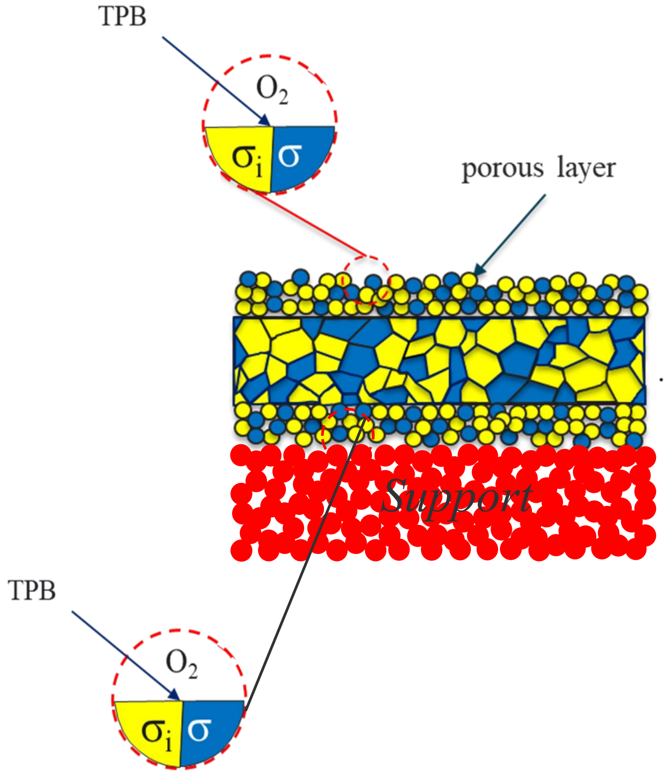
- Porous Membrane
- Finest microstructure
- Potentially non-hermetic
- Reduced strength

Bilayer Microstructure Designs

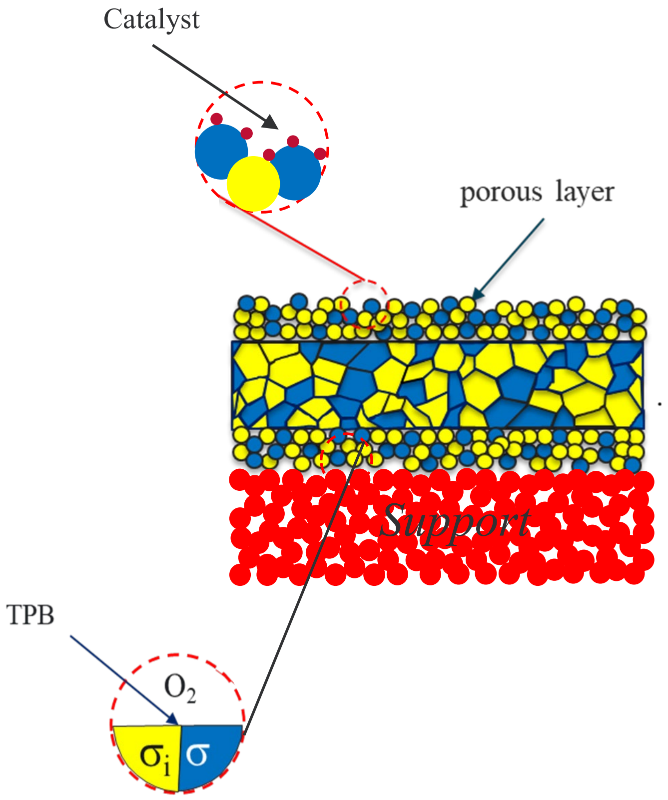
Planar Membrane	*w/ Barrier Layers*	*w/ Barrier Layers & Catalyst*



- Reaction area - 2-D surface
- Surface dominated – reduced thickness



- Expanded reaction area - 3-D surface
- Improve reaction kinetics – increased number of TPBs on both sides

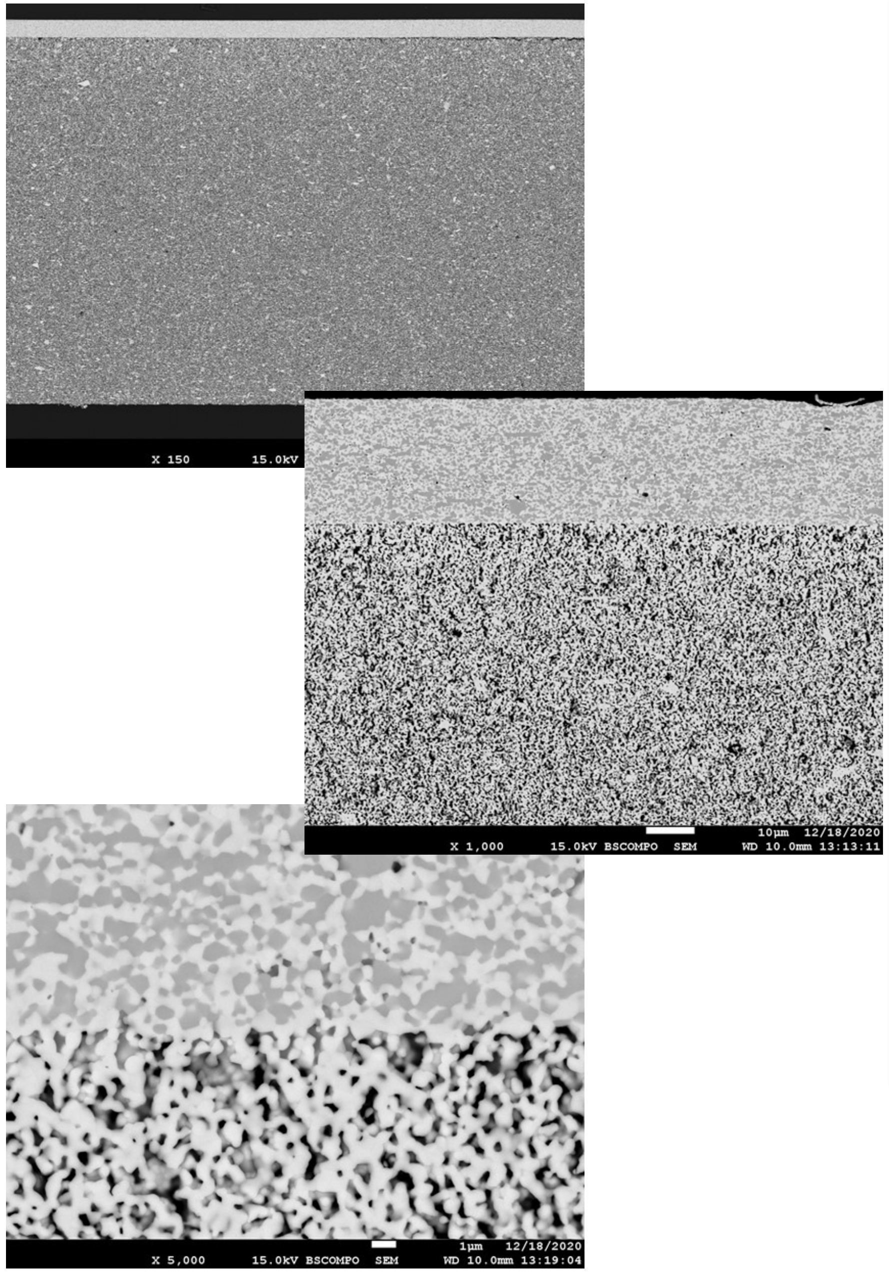


- Expanded reaction area - 3-D surface
- Further improve reaction kinetics – use of know catalyst at TPBs

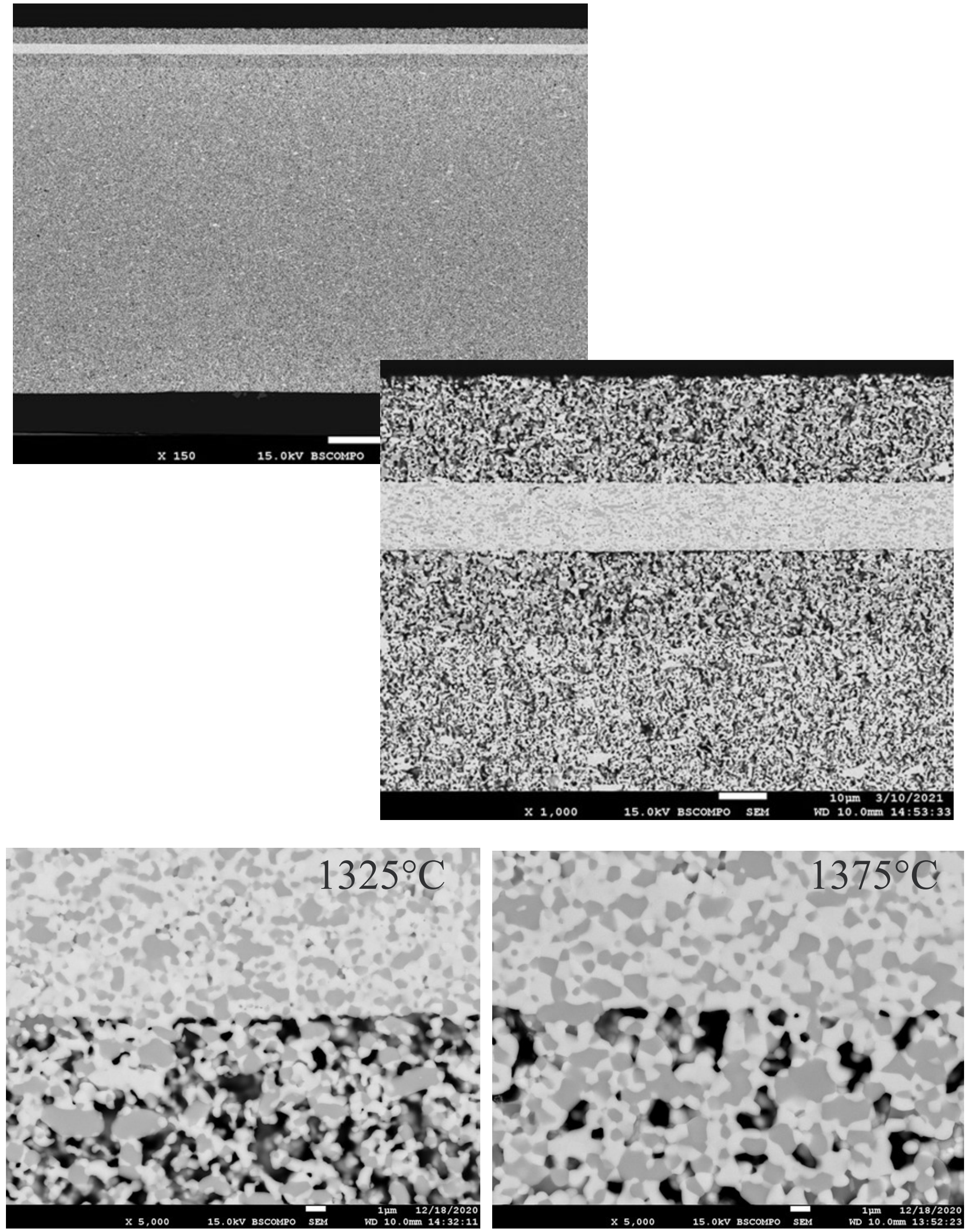
Bilayer Microstructures

Gd doped CeO_2 w/ $La_{0.75}Sr_{0.2}MnO_3$

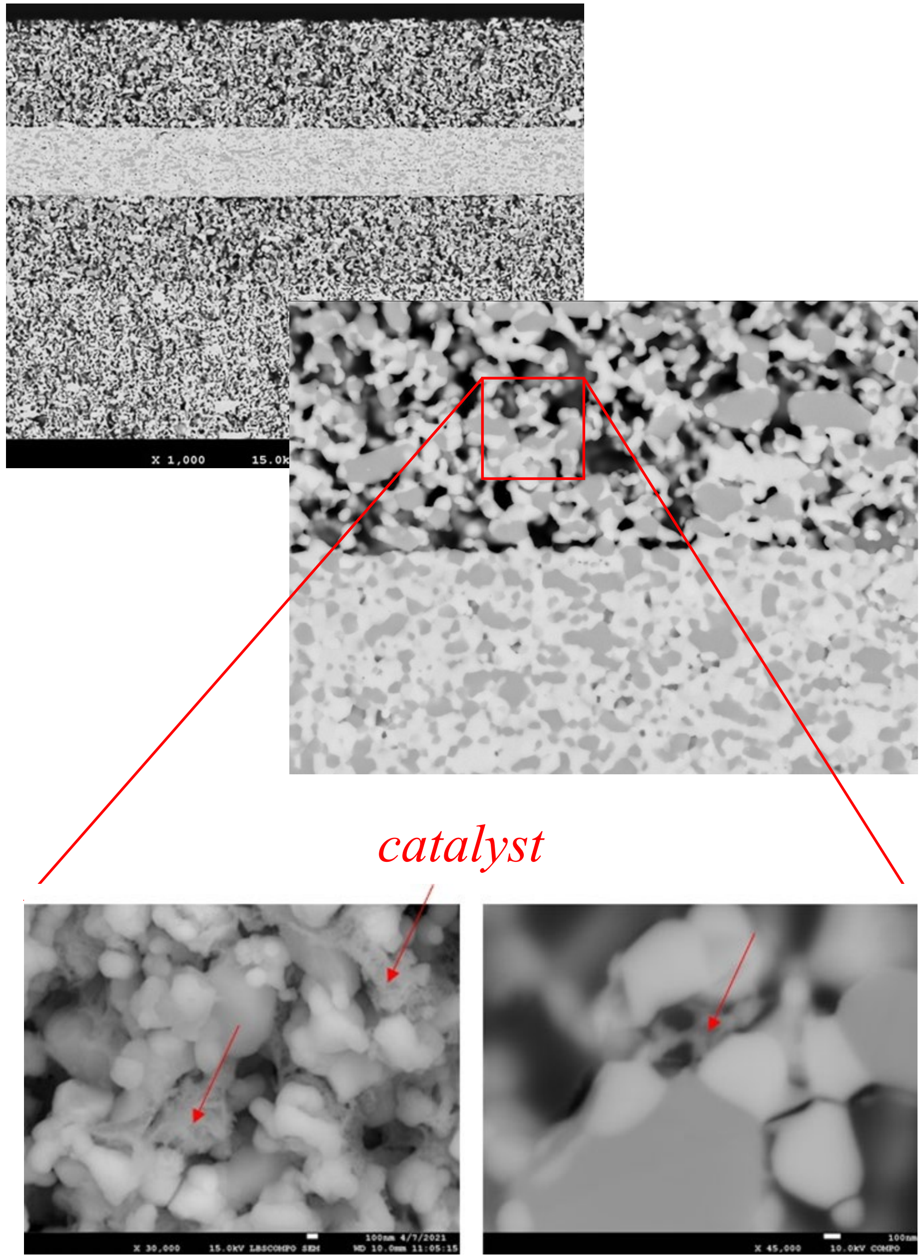
Planar Membrane



w/ Barrier Layers



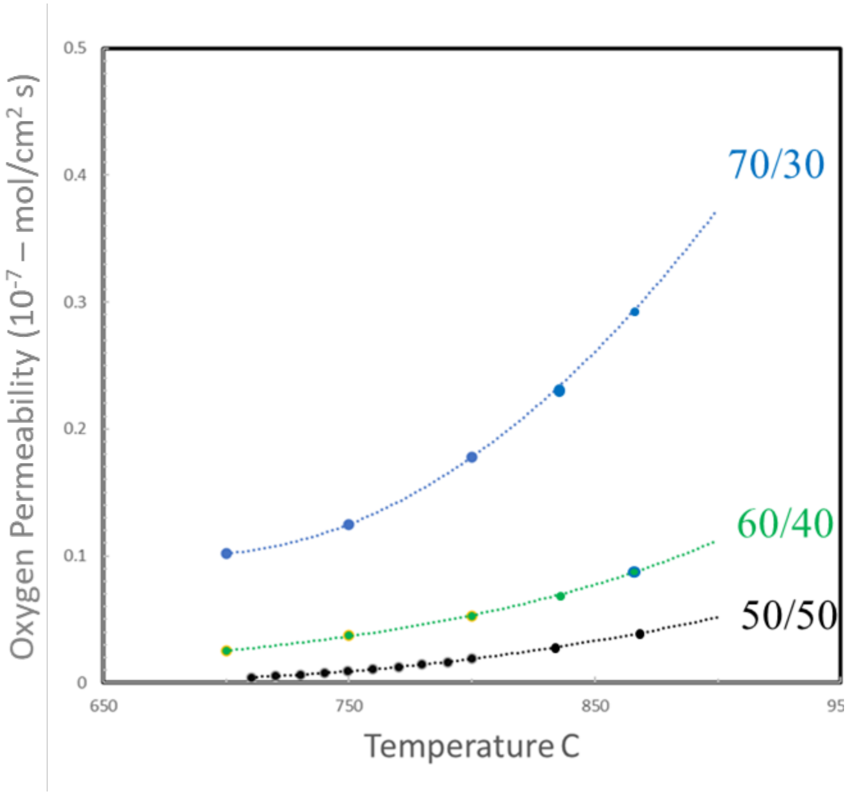
w/ Barrier Layers & Catalyst



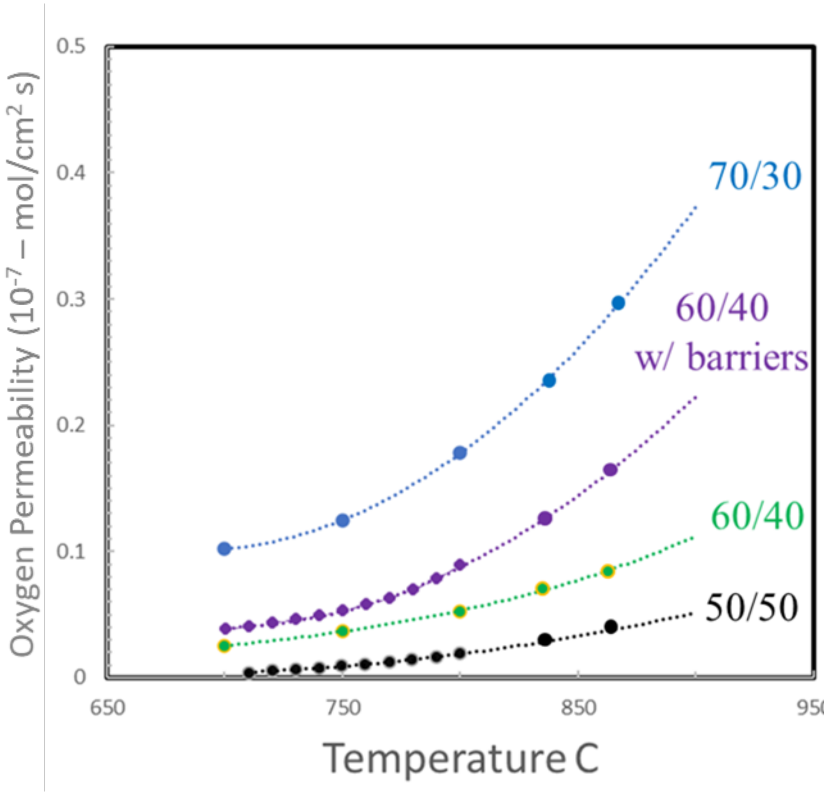
Bilayer Permeability

Gd doped CeO_2 w/ $La_{0.75}Sr_{0.2}MnO_3$

Planar Membrane

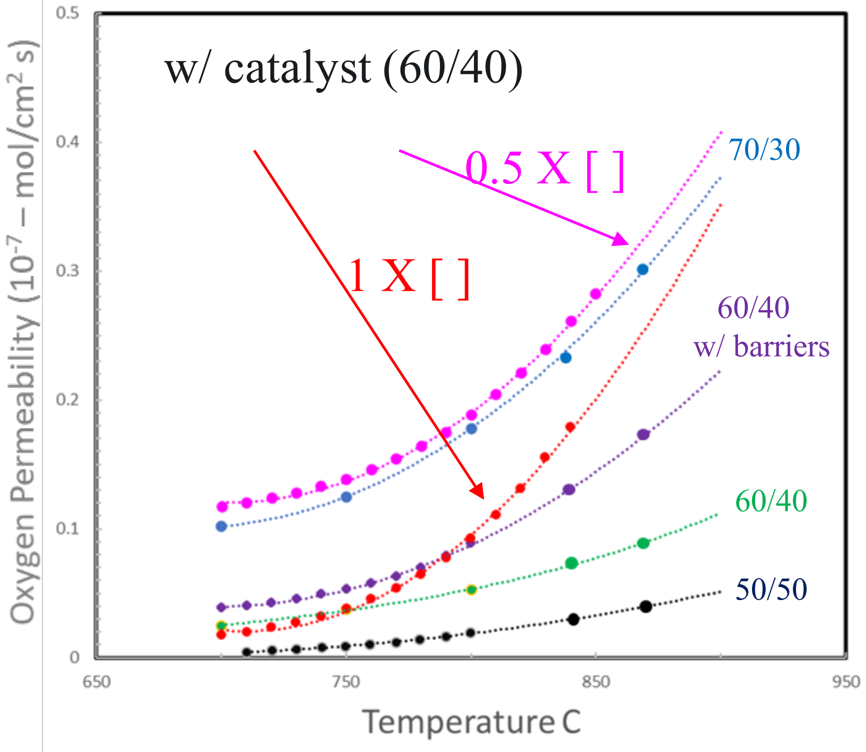


w/ Barrier Layers



w/ Barrier Layers & Catalyst

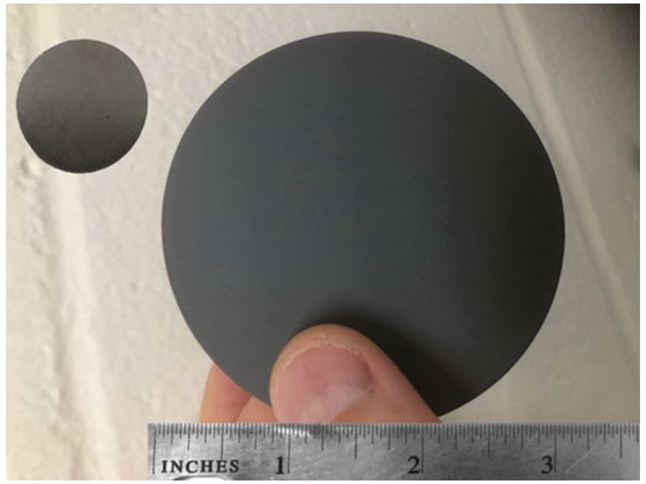
Catalyst is CeO_2

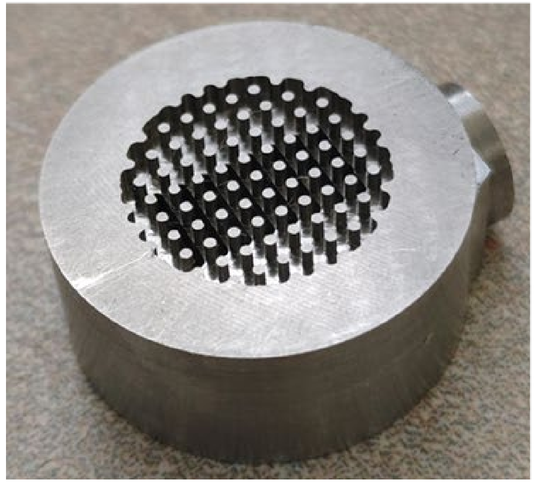


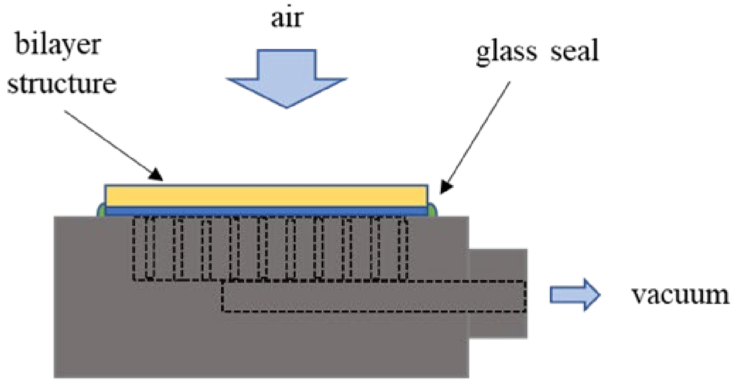
Recent Results

Bilayer Scale Up

- Fabricate 3” diameter bilayers that are flat and crack free capable of measuring the O_2 permeability





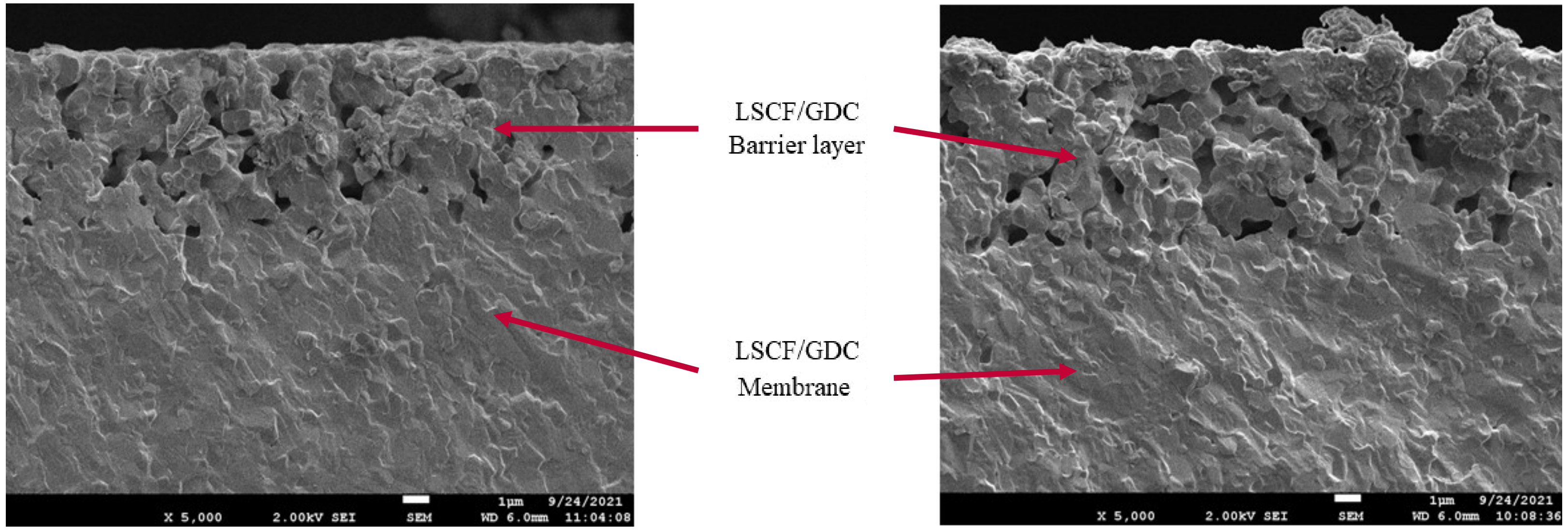


Additional Membrane Composition

- Sr and Co doped $LaFeO_3$ (LSCF) and GDC – LSCF/GDC
- Lower densification temperature (1150°C) than LSM/GDC (1300-1325°C)
- LSCF has mixed conductivity and higher catalytic activity than LSM
- LSCF has a higher thermal expansion than LSM
- Takes some development – not a simple drop in replacement

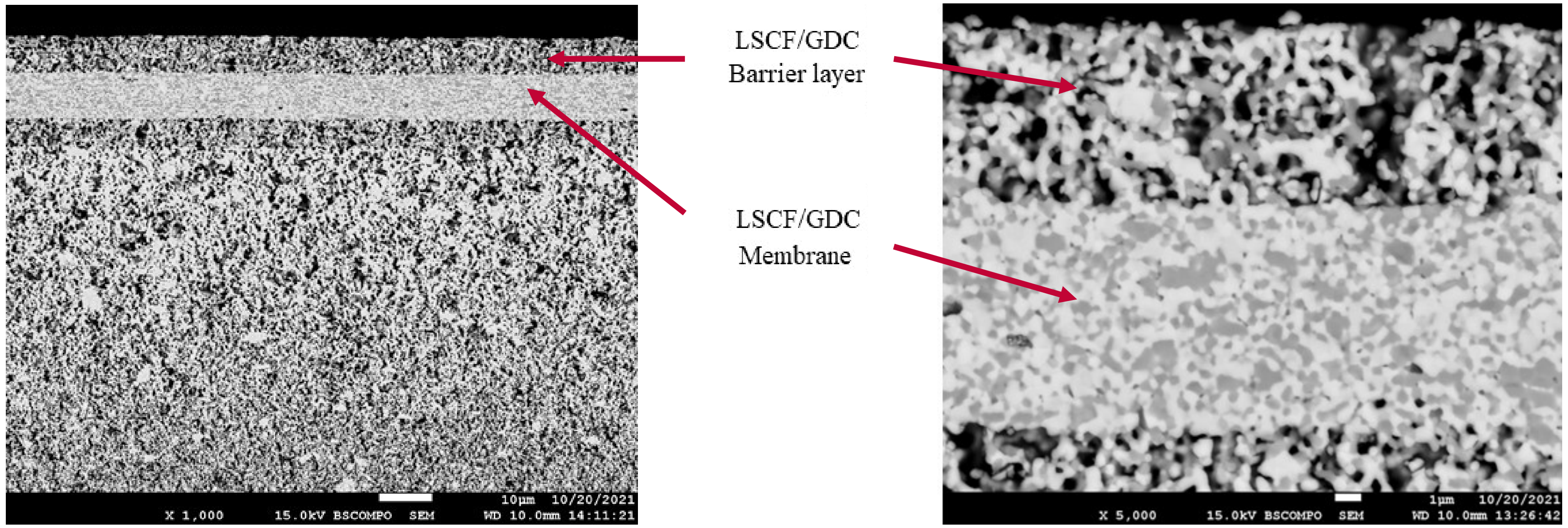
Bilayer Microstructures

Gd doped CeO_2 w/ $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$



- <u>Sintered at 1325°C</u>
- Barrier layer densified, dense membrane

→ Limited O_2 permeability



- <u>Sintered at 1150°C</u>
- open Barrier layer, dense membrane

→ O_2 permeability under test

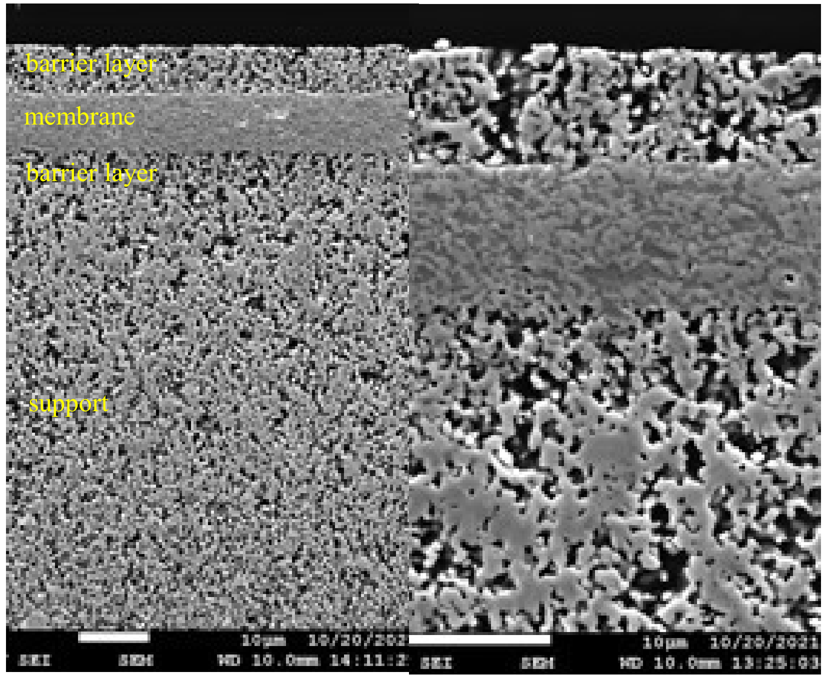
Pacific Northwest
NATIONAL LABORATORY

Bilayer Microstructures

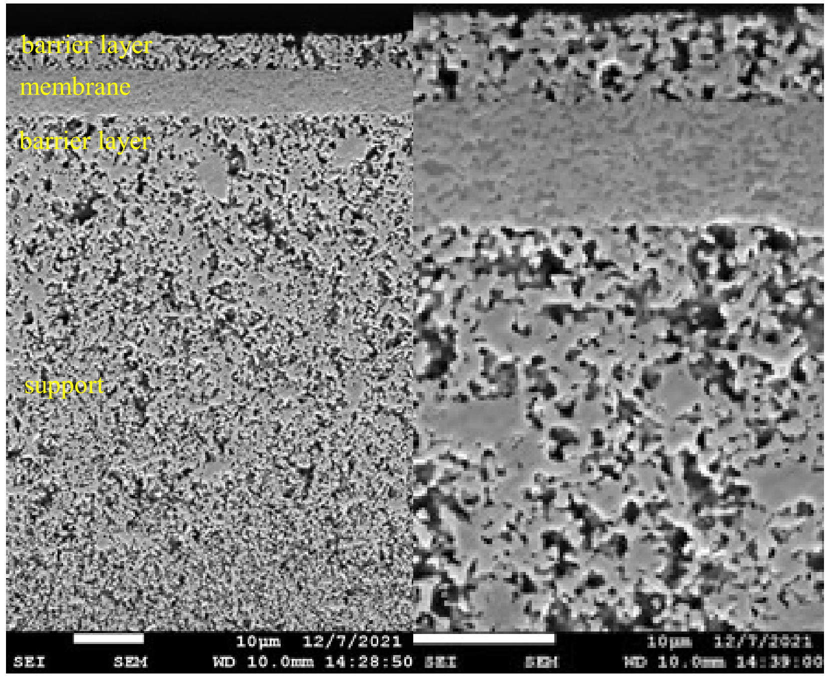
Sintering Study - Gd doped CeO_2 w/ $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$

- Open Barrier layer
- Dense membrane

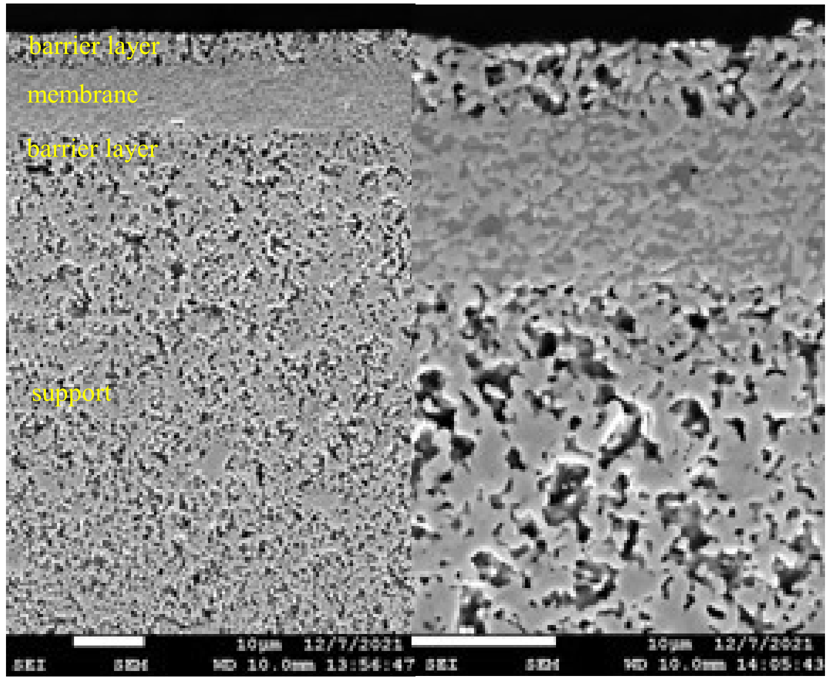
1150°C



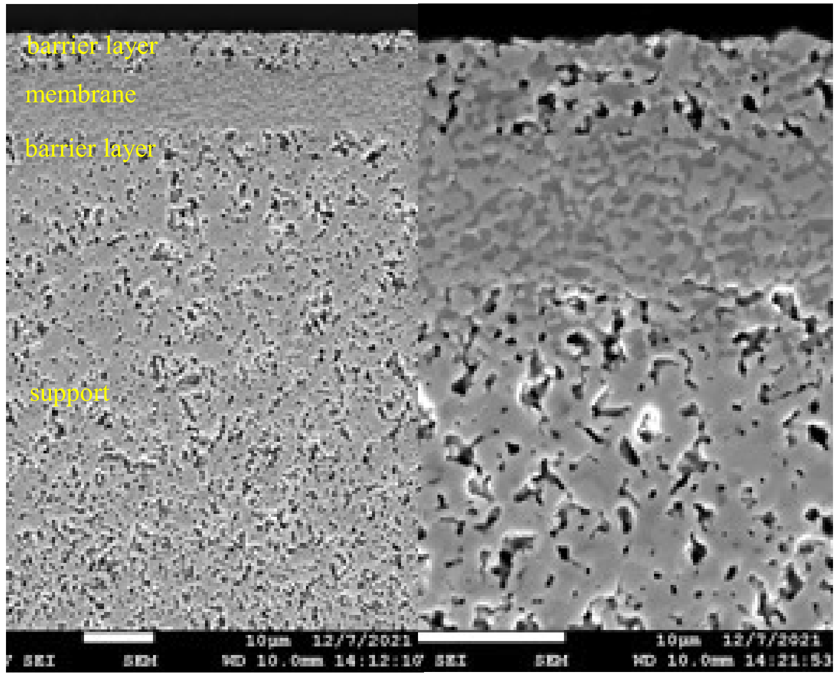
1175°C



1200°C



1225°C



- Denser Barrier layer
- Dense membrane

Pacific Northwest
NATIONAL LABORATORY

Catalyst Nanoparticle Infiltration

Catalyst Composition

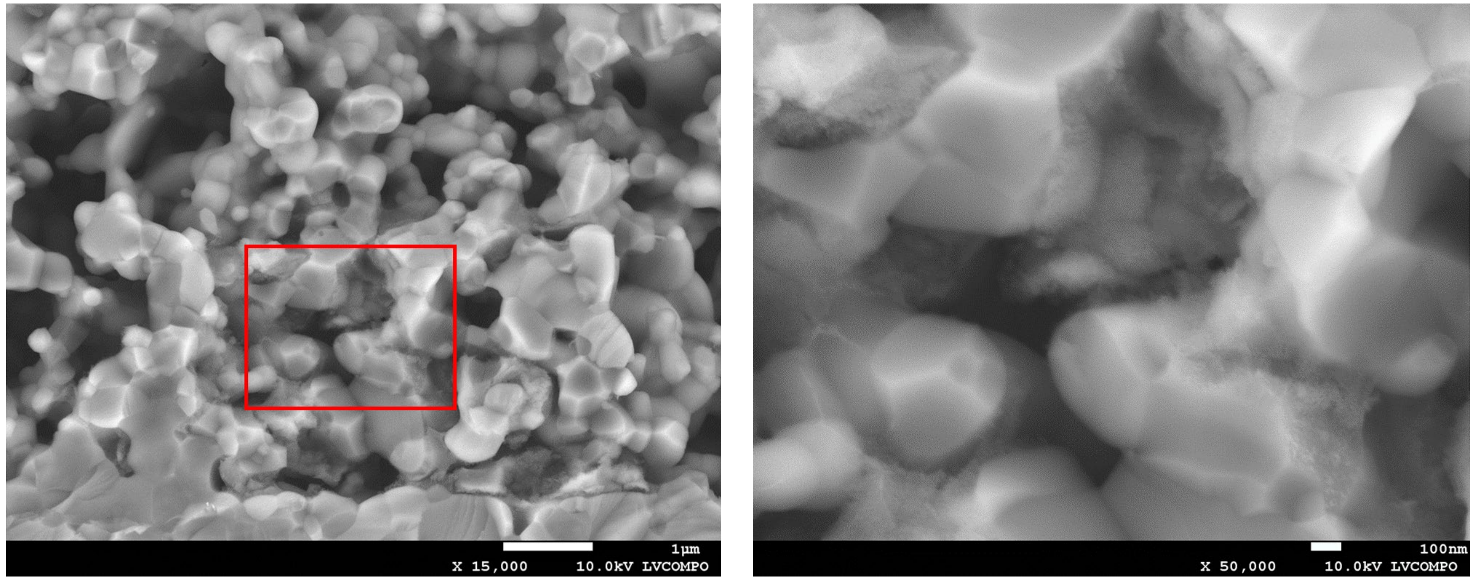
- Doped CeO_2
- $LaCoO_3$ based

Catalyst Optimization

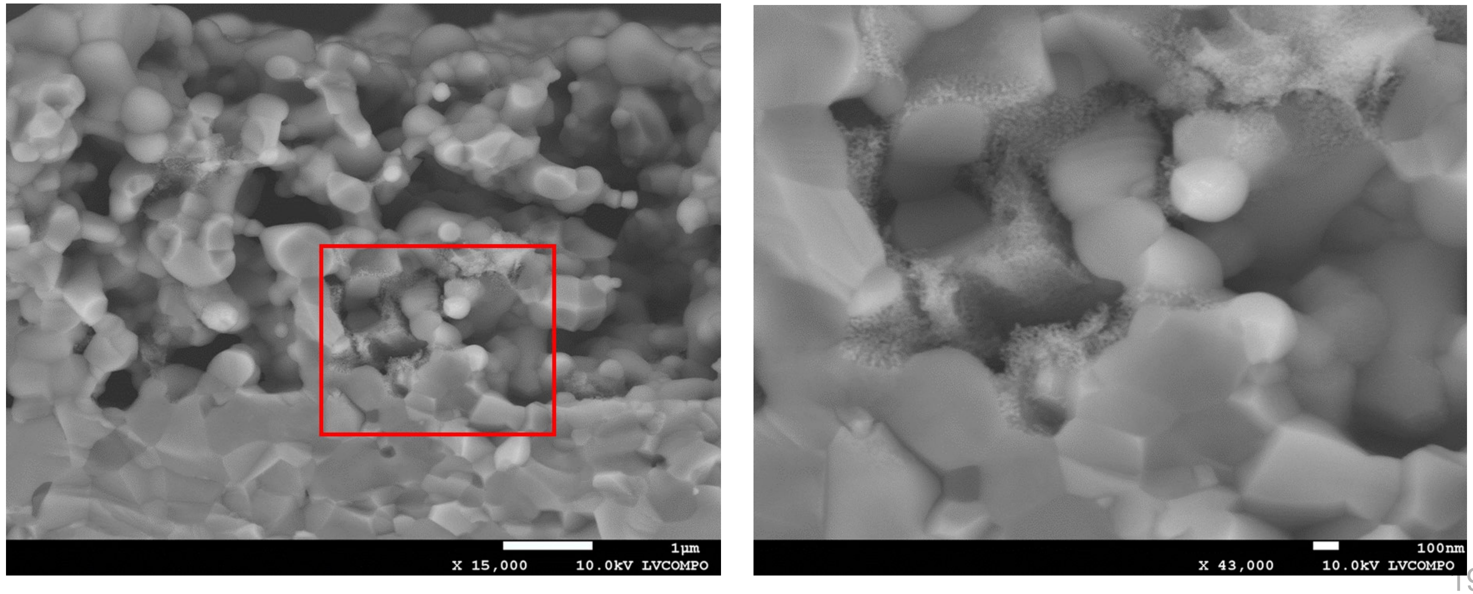
- Concentration and size/distribution of particles
- Coverage
- Deposition technique
- Heat treatment temperature
- Fabrication Temp
- LSM and LSCF based

Catalyst ↔ O_2 Permeability Relations

CeO_2 – lower heat treatment temp

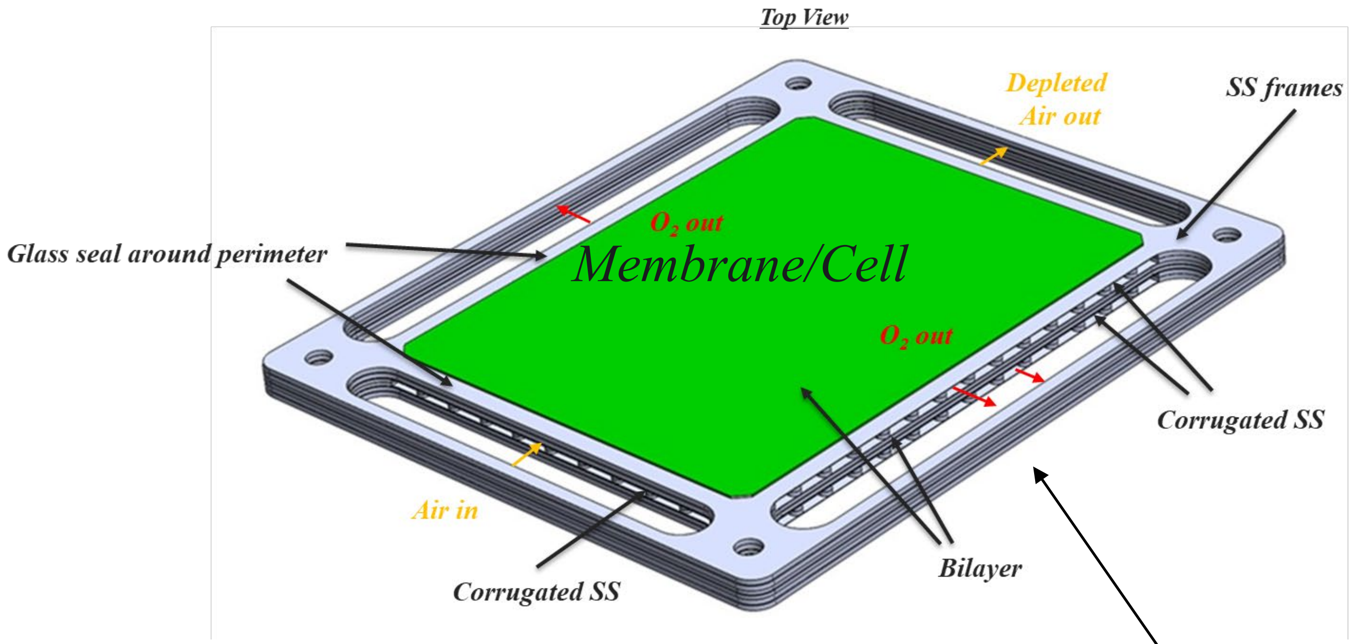


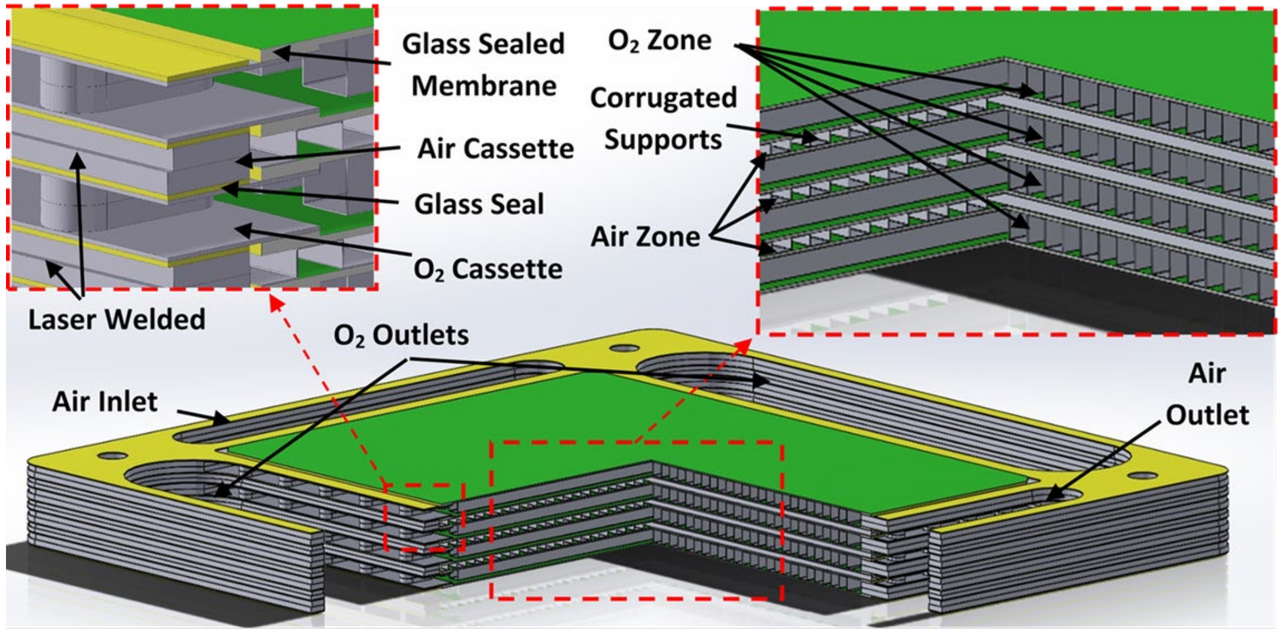
CeO_2 – higher heat treatment temp



3 Cell Demonstration Stack Build

- *Membrane/Cell Active area = 56 cm^2 (7.5 cm x 7.5 cm)*
- *Barium aluminosilicate-based glass seal*
- *Stainless frames and corrugated supports*

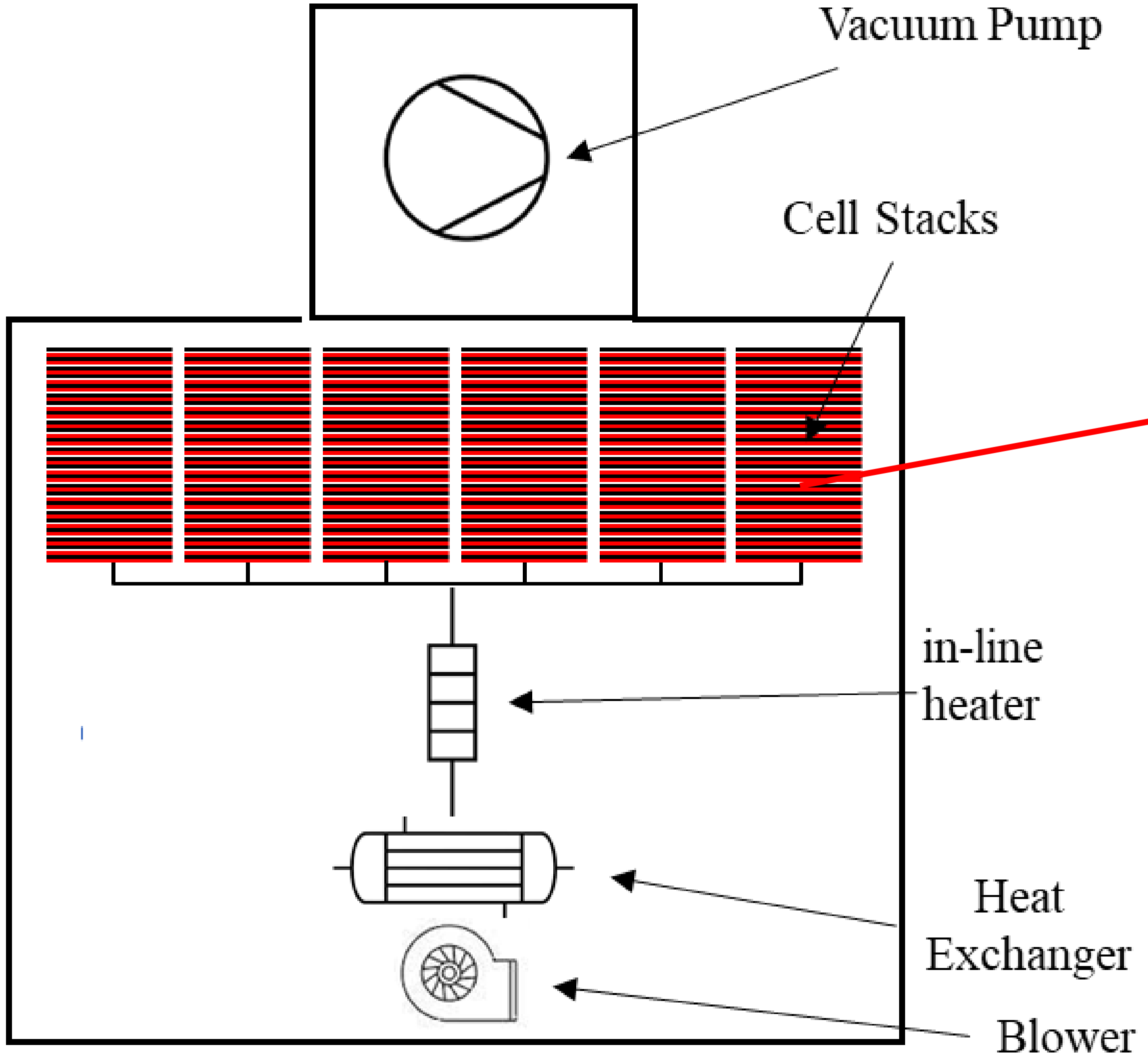


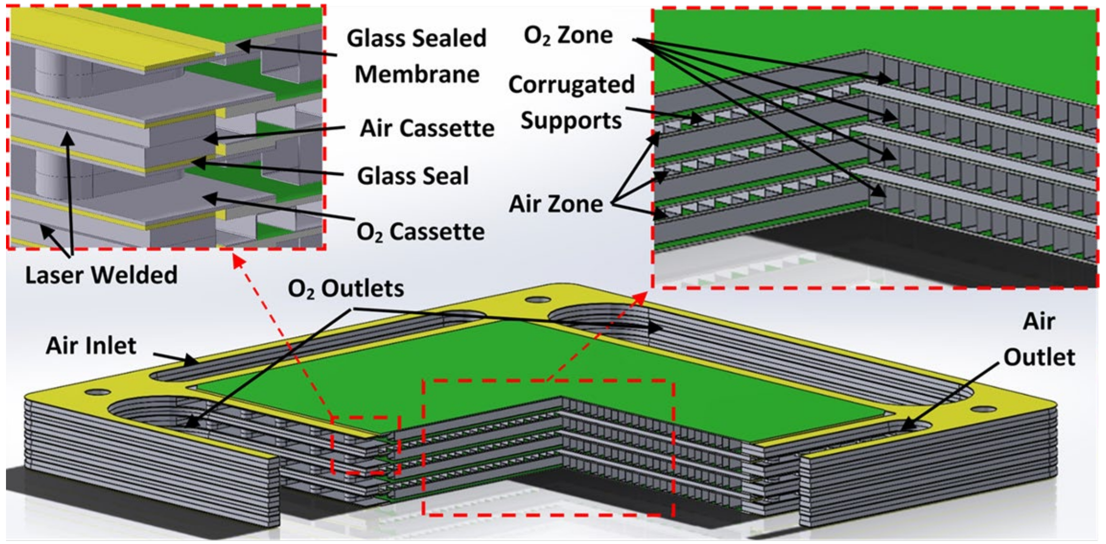


CFD Optimization on Stack Design

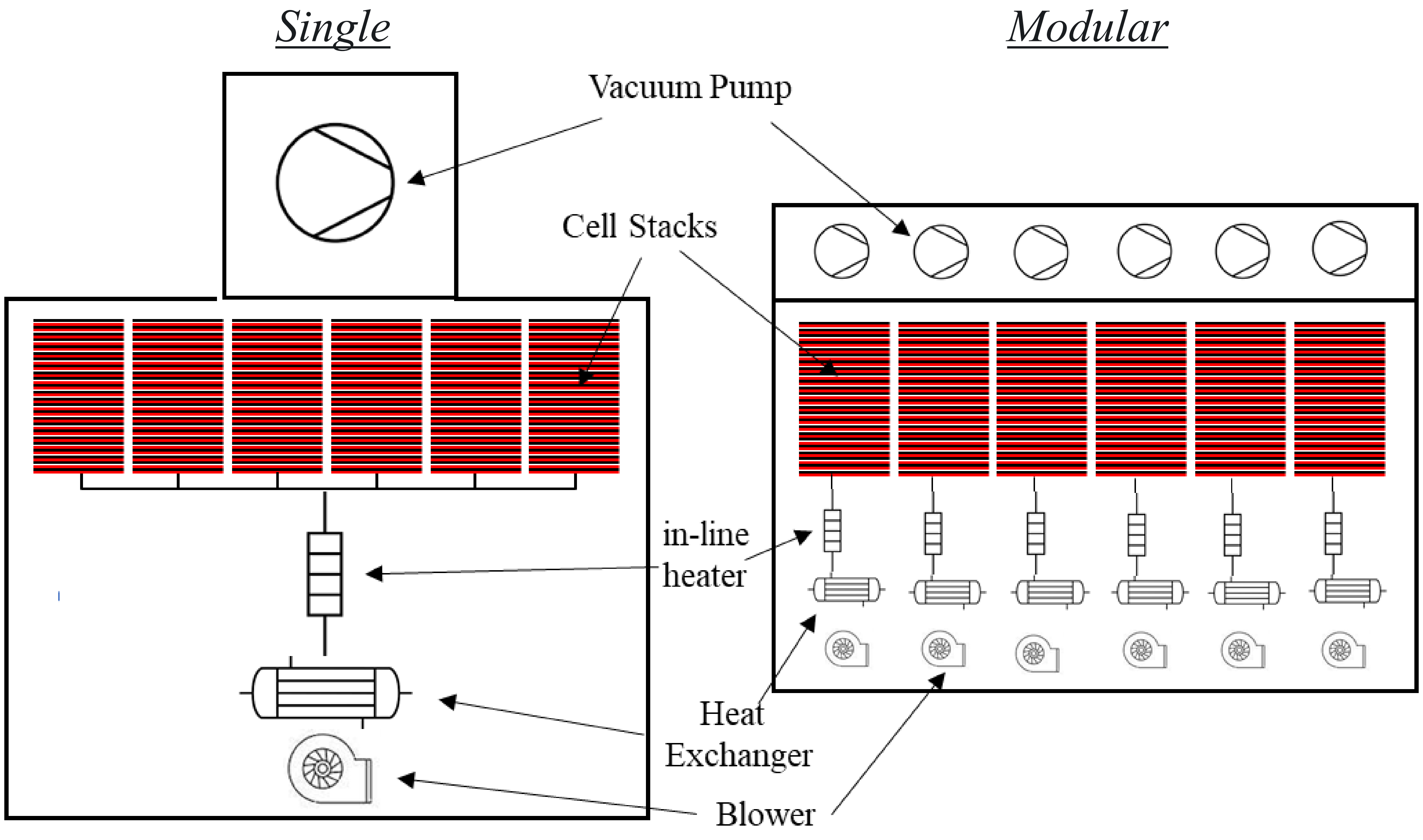
- Higher O_2 permeability
- Efficient operation of pumps
- Reduced stress on gaskets and membrane

System Design





System Design



- Simple design
- Equipment limitations
- Single point for system failure
- System downtime

- Improved reliability
- Higher capital costs?
- Equipment options

Ceramic Membrane Technology
Milestone Review

ID	Description	Planned/ Expected Completion Date	Actual Completion Date	Verification Method
M1	Verify support material is proper composition	12/31/2021	12/17/2021	Measure the hardness of the support layer and ascertain if there is sufficient hardness to withstand attrition and breakage during installation and operation.
M2	Evaluate other oxides (i.e. TiO_2) as the support structure	12/31/2021	12/20/2021	Evaluate other non-reacting oxides, such as titanium dioxide (TiO_2), if the MgO is too soft.
M3	Air pre-treatment step	3/31/2022	3/14/2022	Determine if a pretreament step is needed in the process to remove particulates and oil impurities to prevent fouling in the heat exchanger and membrane module.
M4	Proper heat exchanger and vacuum pump designs	3/31/2022	3/17/2022	Consult various designers of heat exchangers and vacuum pumps to insure proper sizing, cost, and limitations to intended designs.
M5	O_2 permeation for 3" diameter (~50 cm^2)	5/30/2022	4/14/2022	Develop and implement a test plan to conduct O2 permeation measurements to support accelerating scaleup of bilayer membranes for stack production.
M6	3 cell stack fabrication (56 cm^2)	9/30/2022		Demonstrate a stack build utilizing 7.5 cm x 7.5 cm bilayer structures with low cost frames and glass seals.
M7	Techno-economic analysis	9/30/2022		Identify and secure resources to complete a preliminary TEA to obtain an indication of costs versus state-of-the-art, specifically using previous technologies developed using this similar technology. Develop cost as a function of membrane performance and modular system design

Project Accomplishments

- Reduced sintering temperature during co-firing to reduce interactions (both LSM and LSCF based)
- Good membrane conductivity – significant oxygen flux can be achieved in composites for designing an economic modular oxygen separation unit
- Thermal expansion match between all components (composite membrane, composite support, glass-ceramic seal, 400 series stainless steel frame)
- Inexpensive materials of construction, ability to scale using traditional inexpensive thick film techniques
- Good mechanical strength/flexibility in porous support
- Ability to fabricate very thin dense membrane (10-15 μm) on flat, crack free porous supports
- Ability to control tape cast composite microstructures with controlled properties
- Modular system approach with improved reliability

Acknowledgements

The authors wish to thank Evelyn Lopez, David Lyons, and Jai-Woh Kim from DOE Office of Fossil Energy for their support of this project.