Pacific Northwest
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Pressure Driven Oxygen Separation

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Richland, WA

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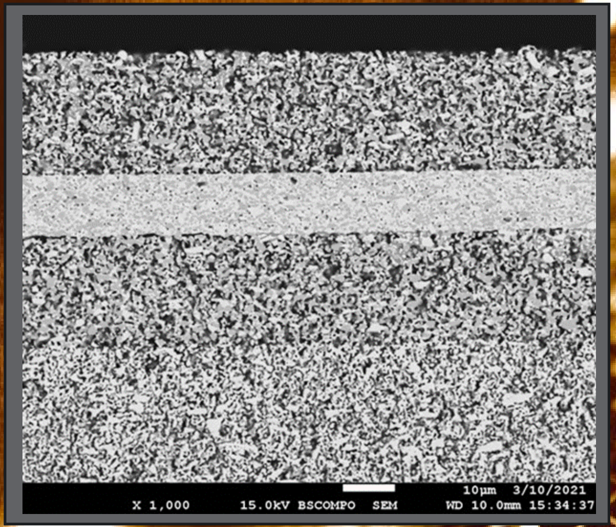
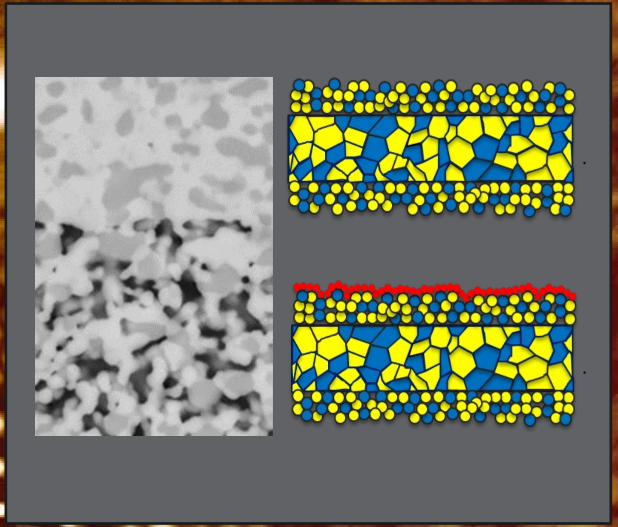
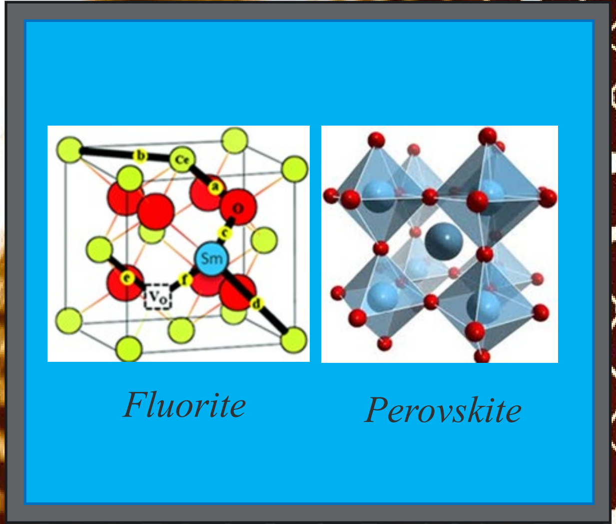
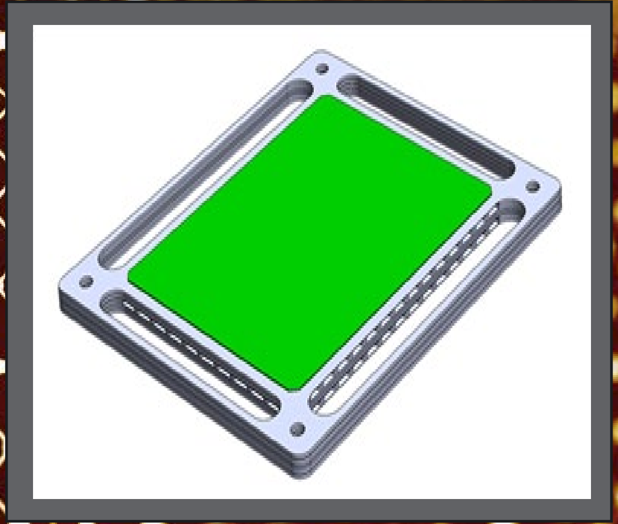
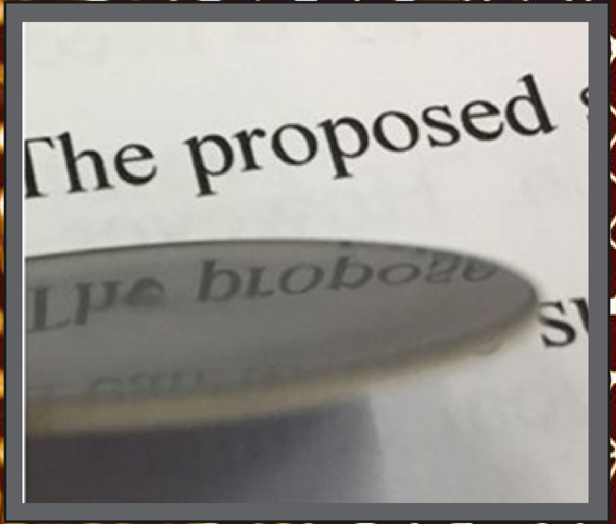
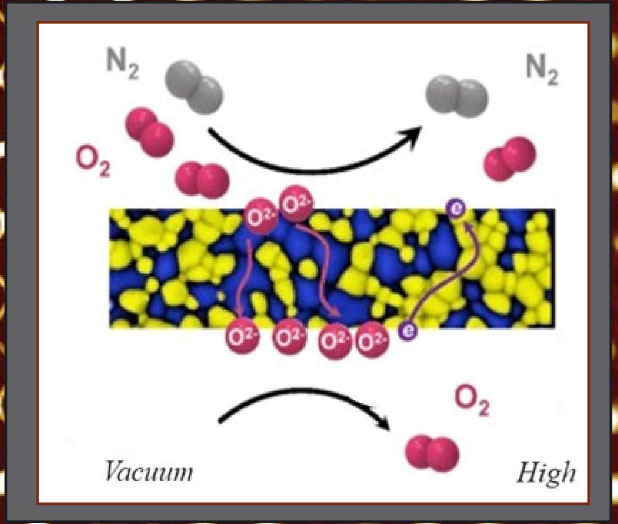




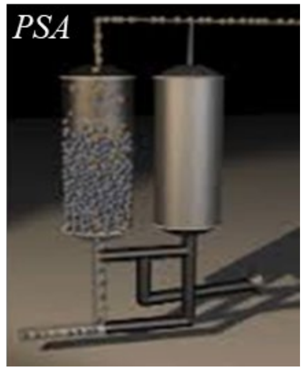






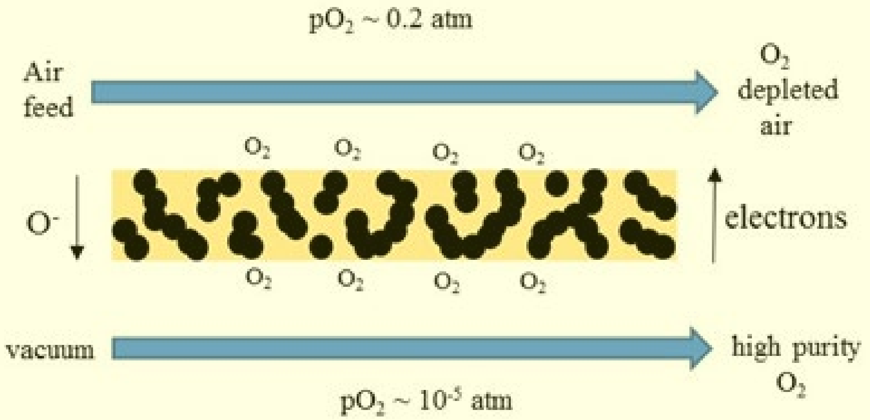


Oxygen Separation Techniques



- **Cryogenic Air Separation** – mature
  - Very high purity (99+)
  - Low energy demand at high capacity (4000 T/day)
  - Energy demand very high at low capacity (i.e., 10-40 T/day)
- **Pressure Swing Adsorption (PSA)** – mature
  - Purity ~ 90 - 93%
  - Economical at lower capacities (i.e., 300-400 T/day)
- **Polymer Membranes** – mature
  - Low purity (~ 40%)
- **Pressure Driven Oxygen Separation with Ceramic Membranes** – R&D
  - High purity (99+), ~10 T/day
  - Thermal integration
  - Can be economical depending on oxygen permeability
  - Examples: OTM (Oxygen Transport Membrane)

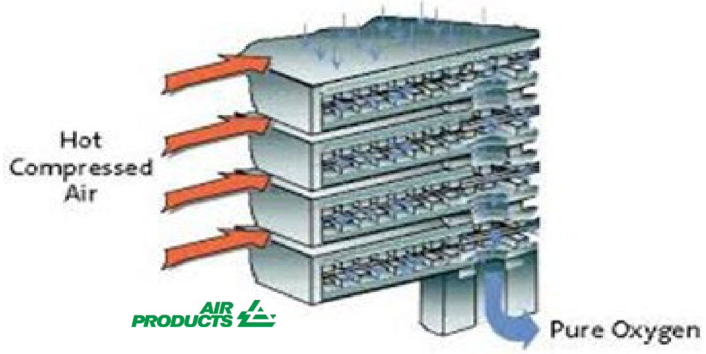
    ITM (Ion Transport Membrane)

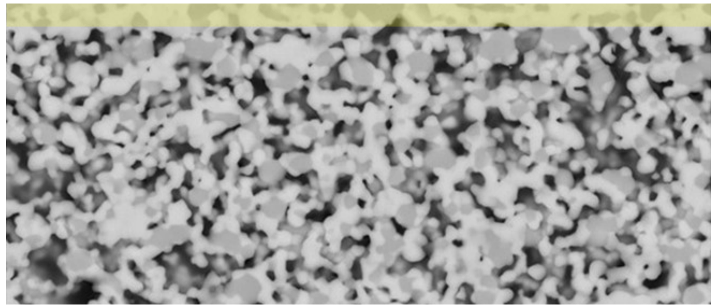


Project Objective

Develop a small scale and modular air separation unit providing 10 T/day of high purity oxygen to a 1-5 MW gasifier at low cost and high efficiency

- Planar design with bilayer structure (membrane/support)



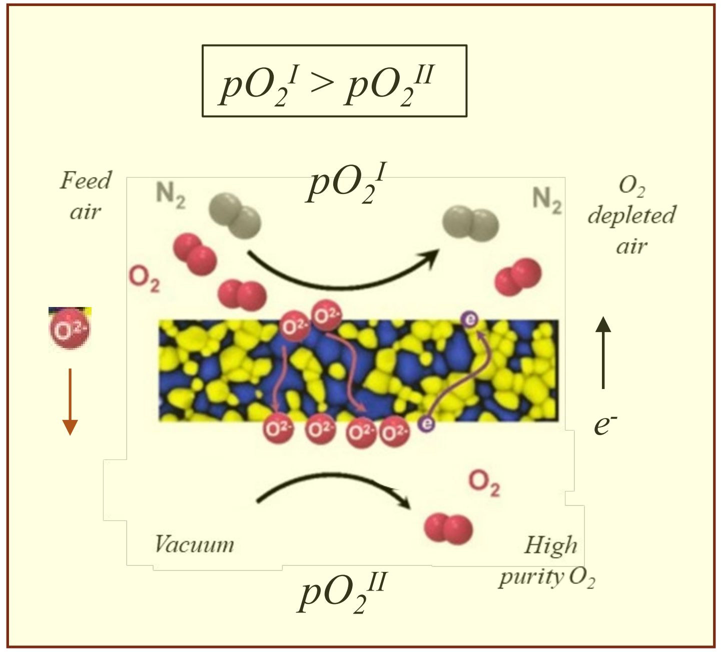


← Thin composite membrane (~ 10 μm)

← Porous support (~ 0.5-1mm)

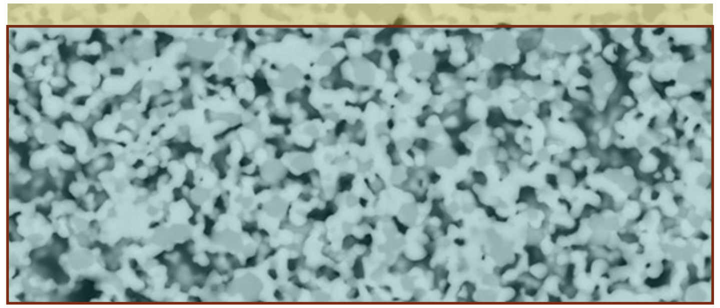
- Composite membrane made of mixed conducting two phase material capable of separating oxygen at 700-800°C

- Utilize the difference in oxygen partial pressure across the membrane to drive oxygen from air (*no electrical energy needed for oxygen separation)*



Proposed Ceramic Membrane Technology

- Planar design with bilayer structure -



Composite membrane

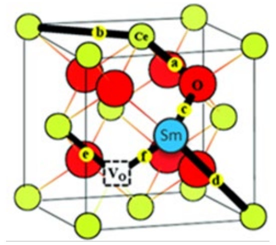
- ➢ Dense
- ➢ Two phase composite
  - High σ_i
  - Sufficient σ_e
- ➢ Similar TEC
- ➢ Limited interaction during firing
- ➢ Compatible with glass seal
- ➢ Inexpensive fabrication
- ➢ No electrodes

Porous Support

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

Ionic Conductor

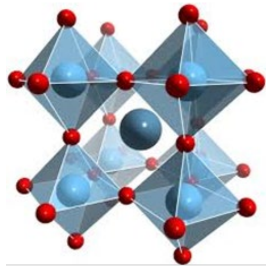
- Doped CeO_2



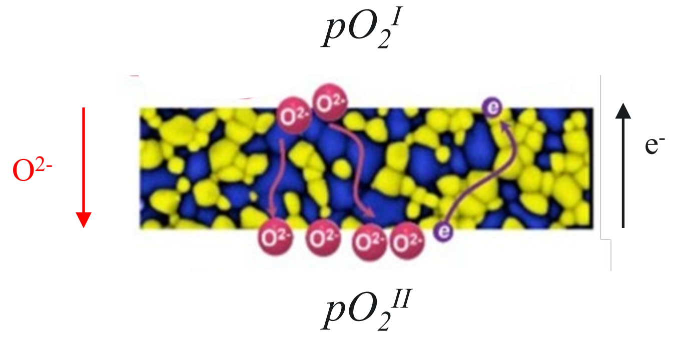
Fluorite structure

Electronic Conductor

- Doped $LaMnO_3$
- Doped $LaFeO_3$



Perovskite

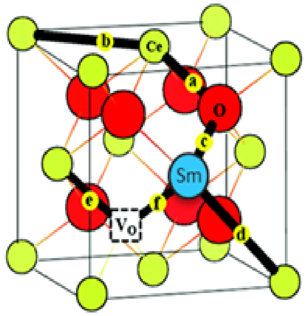


Composite Membrane

- Microstructure Control/Conductivity -

Ionic Conductor

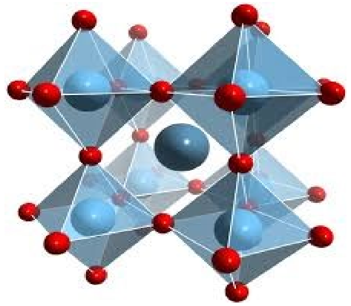
- Doped CeO_2
- $Sm_{Ce}' \rightarrow 2[V_O^{\circ\circ}]$



Fluorite structure

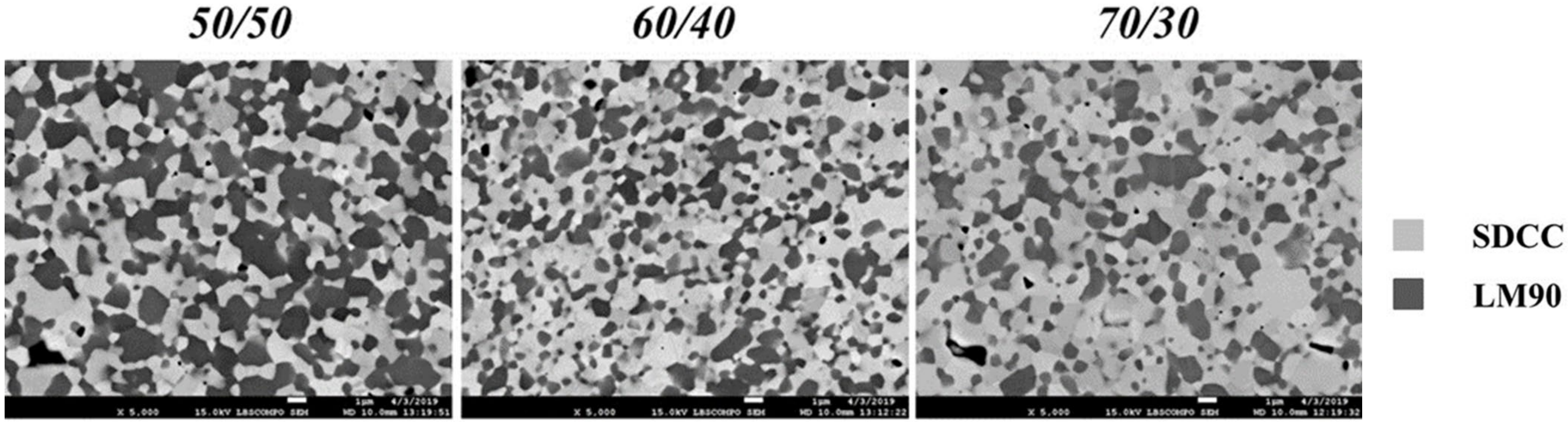
Electronic Conductor

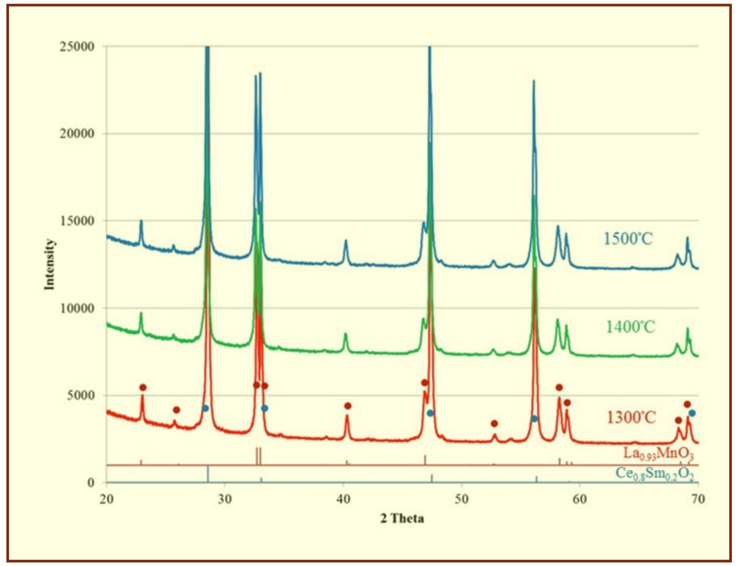
- Doped $LaMnO_3/LaFeO_3$
- Acceptor doped p-type



Perovskite

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



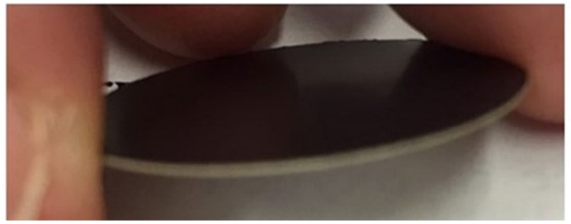


➢ Electrical conductivity (σ_e) controlled by perovskite phase, σ_e ~ 4 orders of magnitude greater than ionic conductivity (σ_i) - σ_i for pure ceria phase ~0.07 S/cm at 800°C and 0.03 S/cm at 700°C

➢ ~ 2/3 σ_i value used in composite calculations

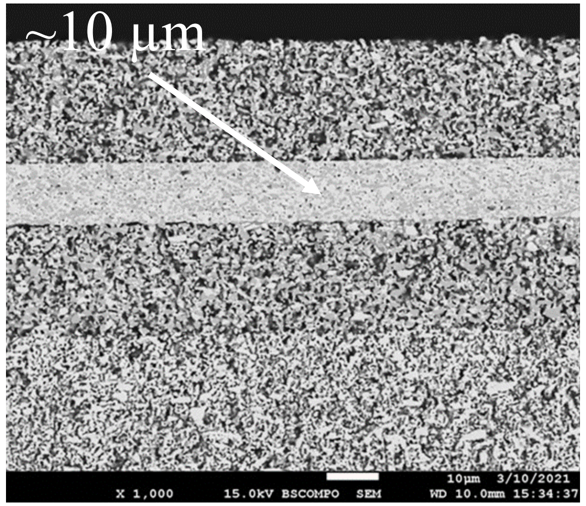
➢ Percolation in both phases

Bilayers with Controlled Microstructures



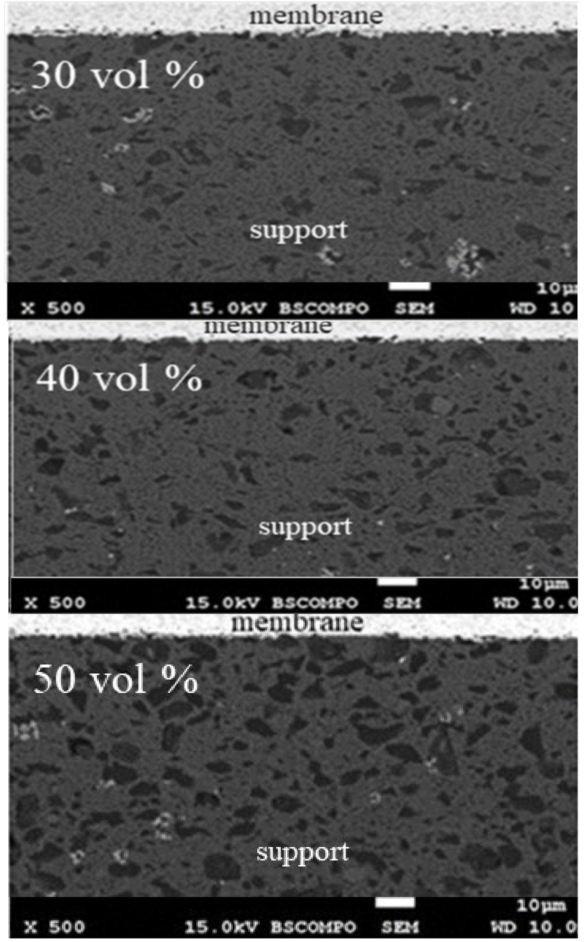
Tailor the **membrane thickness** by controlling the casting thickness

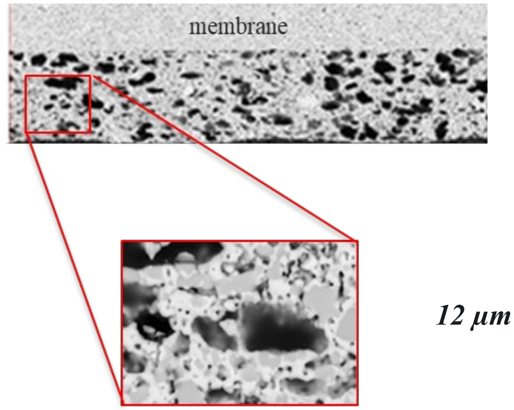
- Dense and thin membrane to maximize the oxygen permeability



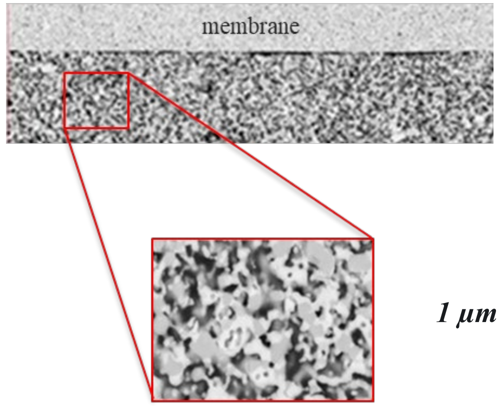
Tailor **amount of porosity** and the **size/distribution of pores** in the **support** by controlling the amount and particle size of fugitive phase used in tape cast suspension

- Thick and porous support to provide mechanical integrity and maximize gas diffusion





12 µm fugitive phase



1 µm fugitive phase

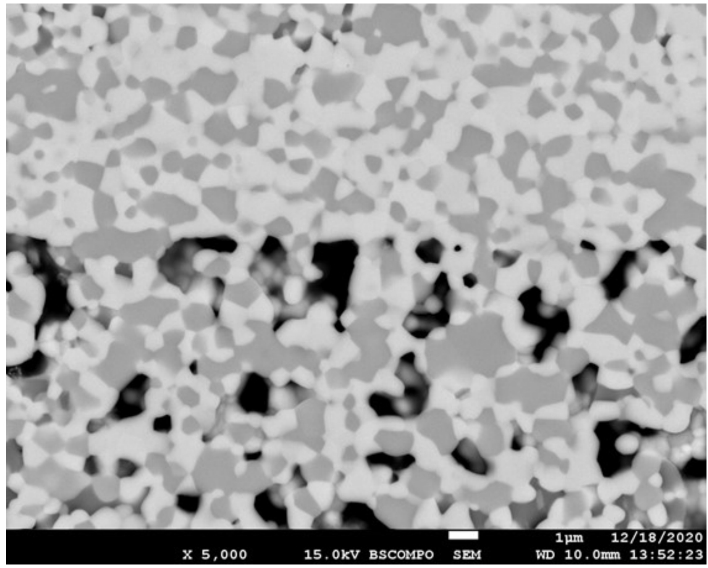
- **Limited interaction during co-sintering**
- **Match sintering shrinkage**

Densification of Membrane During Co-firing

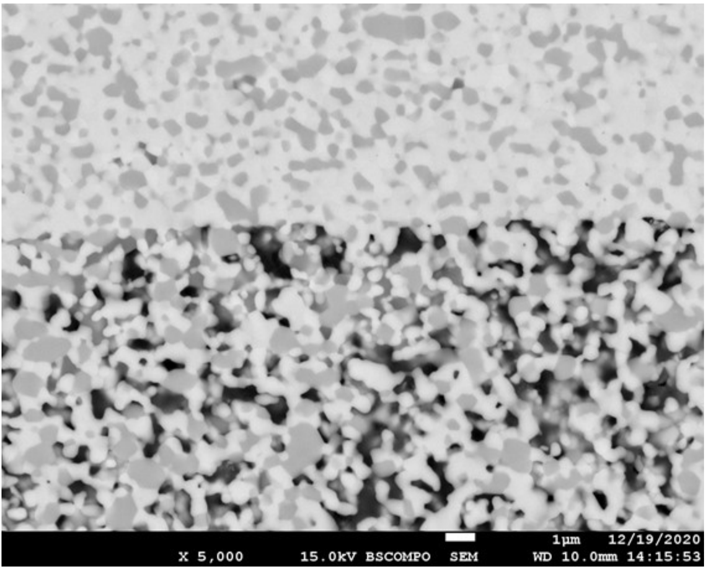
Gd doped CeO_2 w/ $La_{0.75}Sr_{0.2}MnO_3$

Sintering Temperature

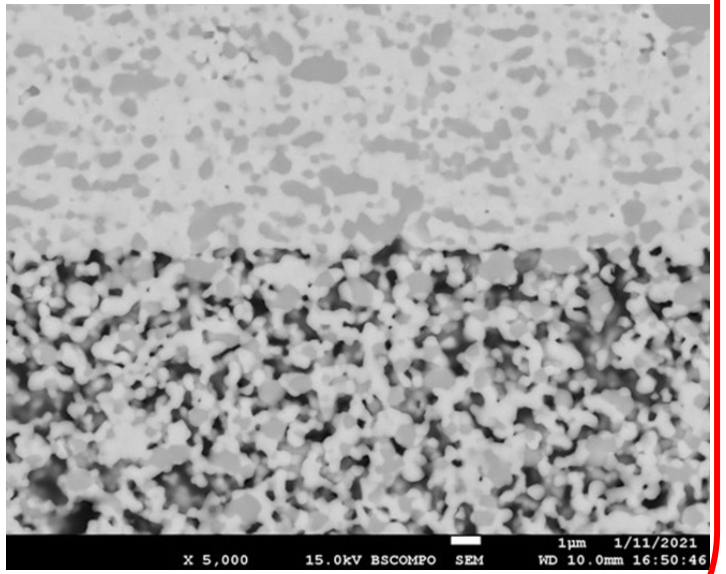
1375°C



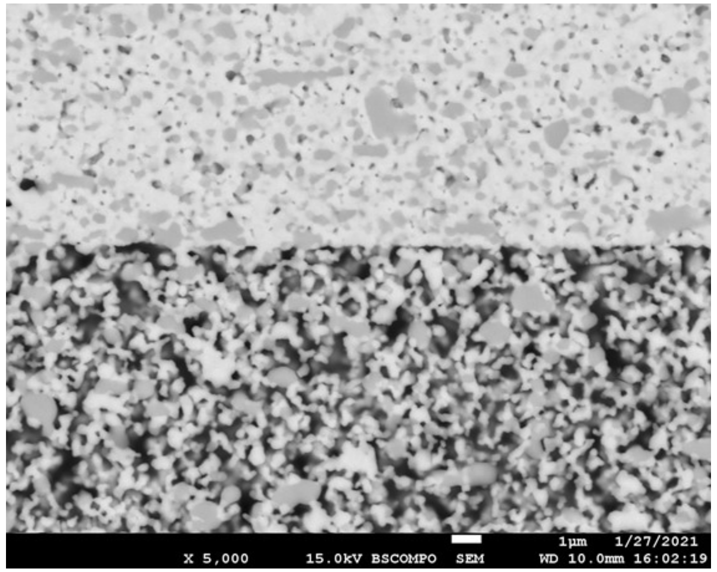
1325°C



1300°C



1275°C



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

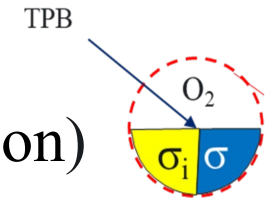
- Dense Membrane
- Finer grains
- Increased number of TPBs
- Less interaction/ diffusion of ions

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

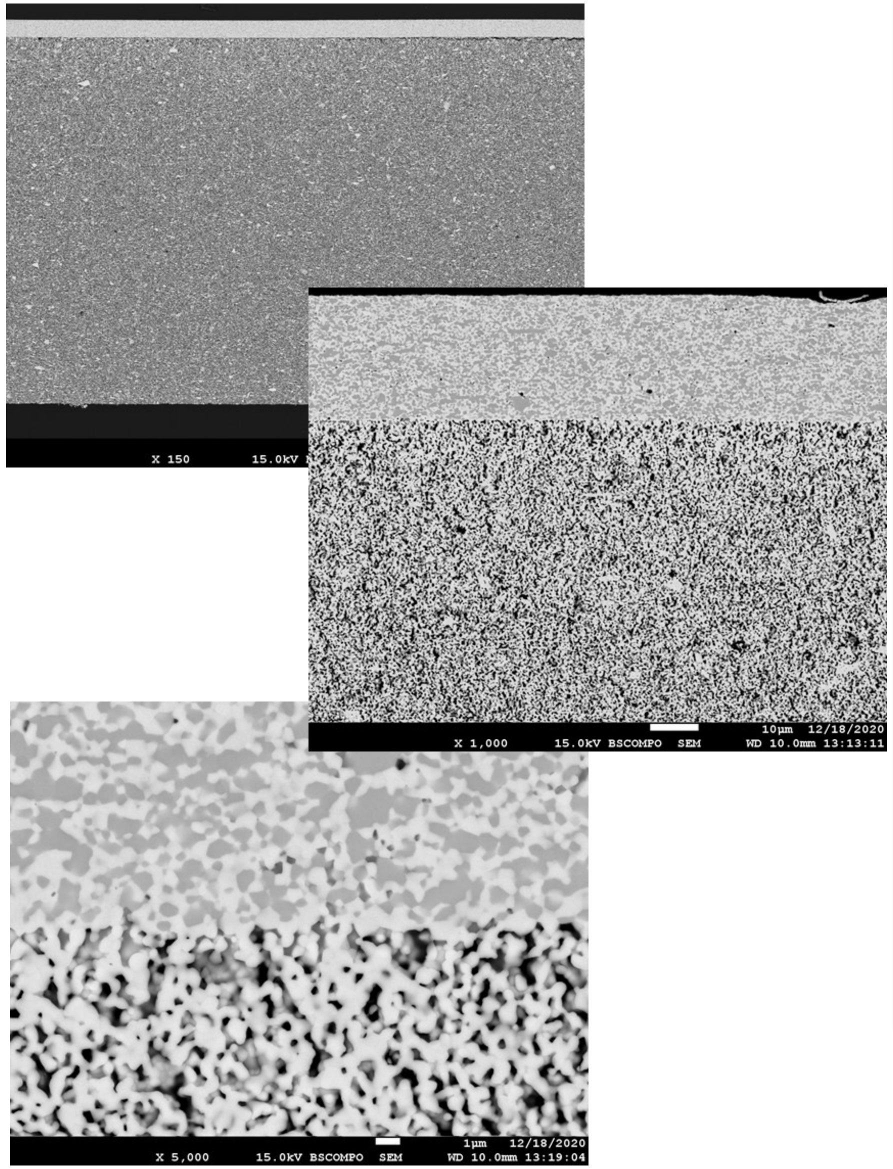
Bilayer Microstructures

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

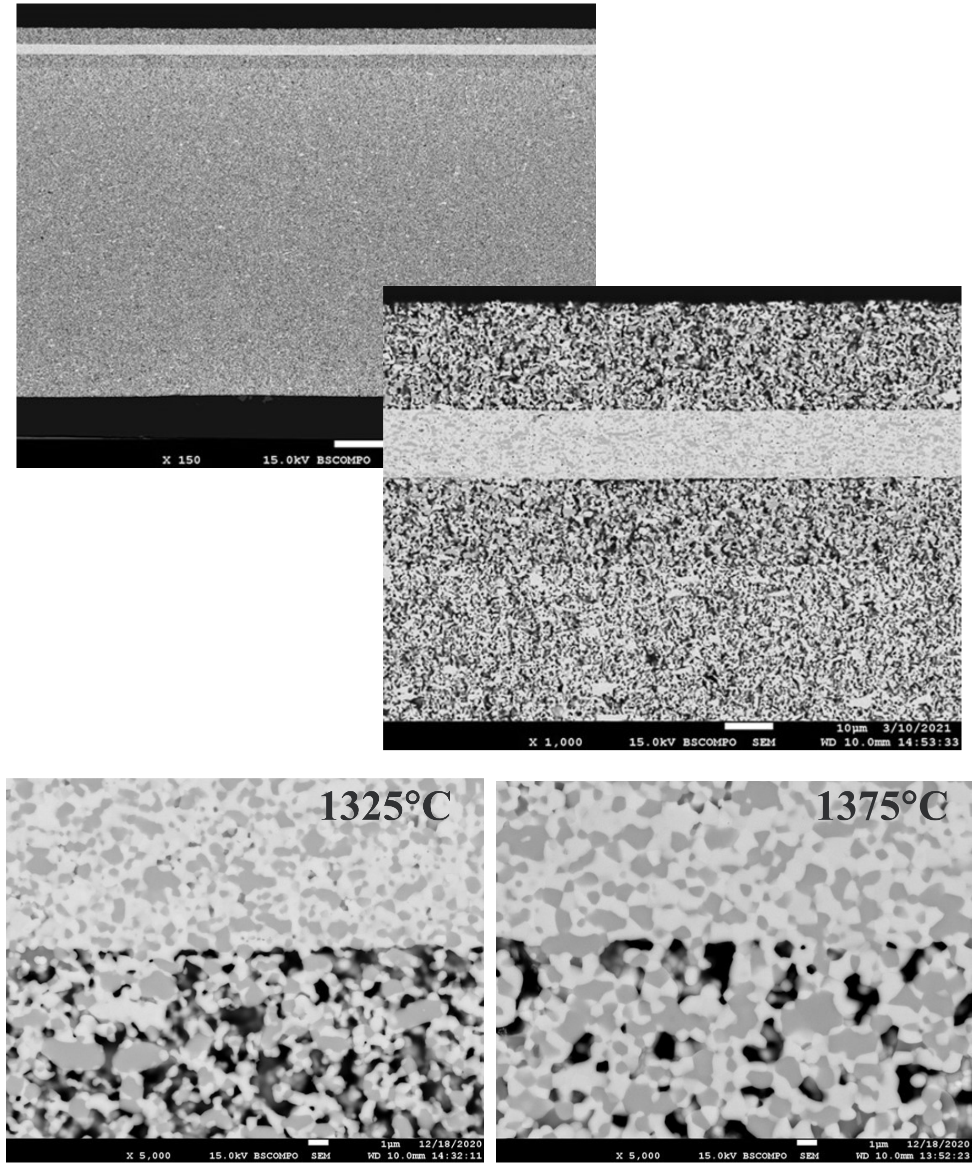
➡ Expanded reaction area improves reaction kinetics (O_2 dissociation/recombination)



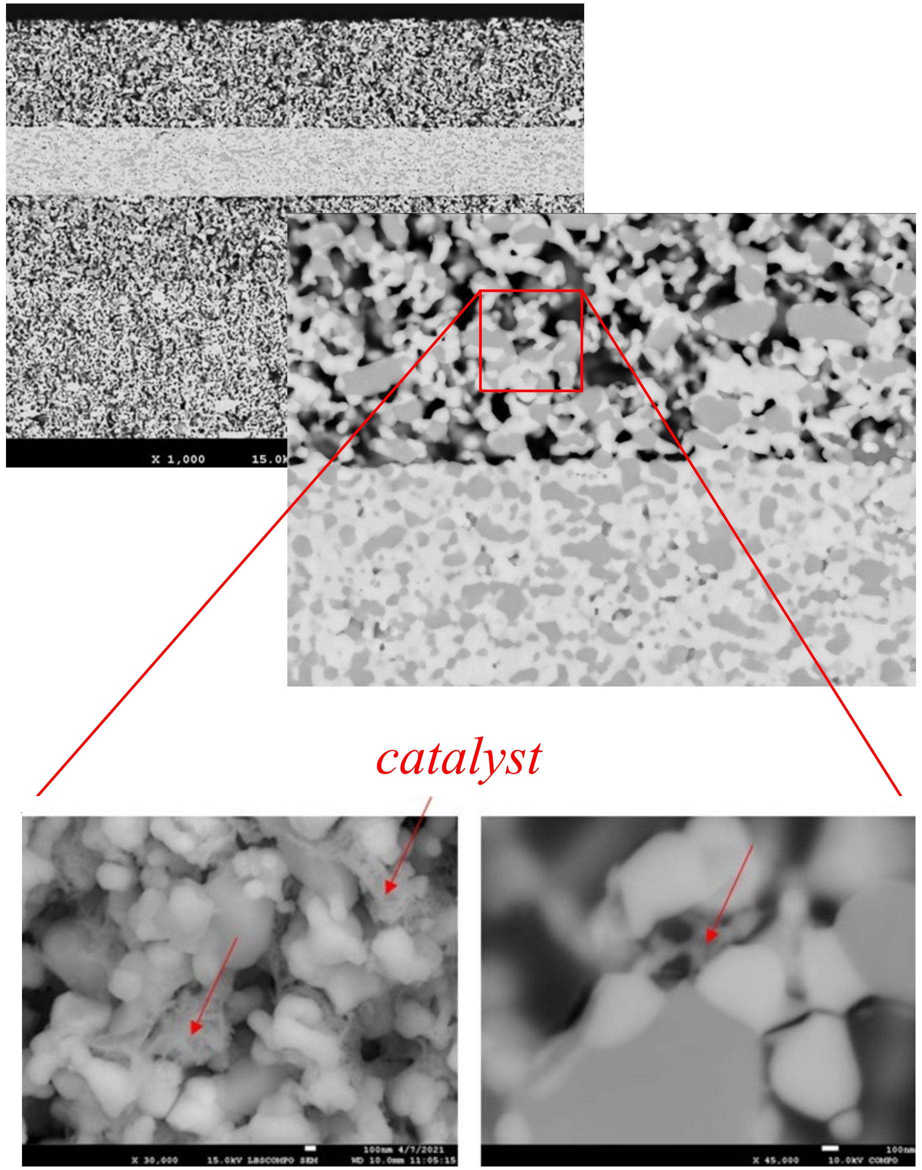
Planar Membrane



w/ Barrier Layers

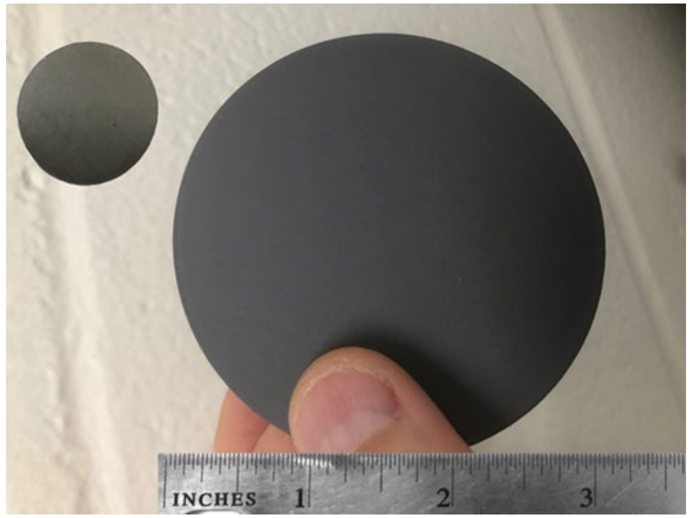


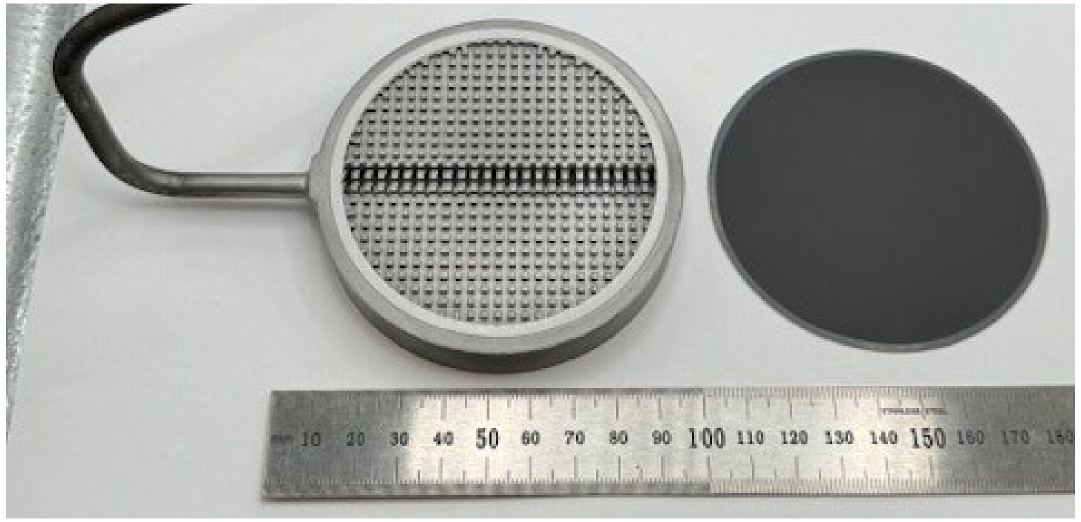
w/ Barrier Layers & Catalyst



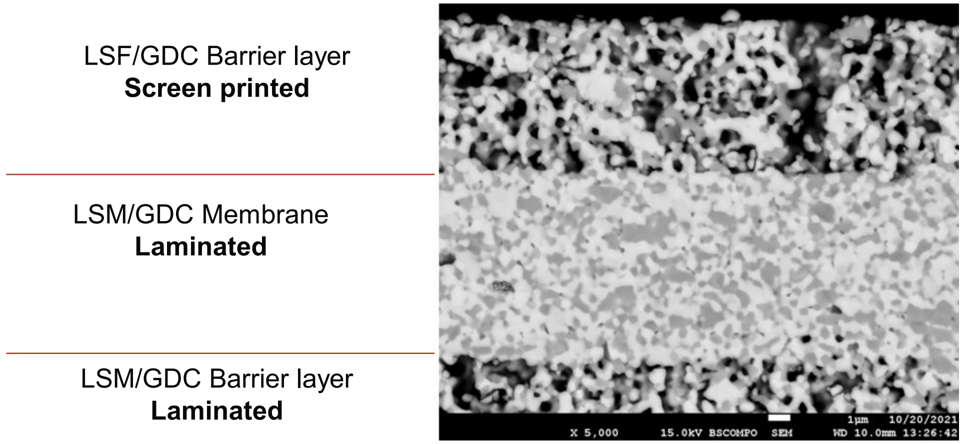
Bilayer Scale Up and Membrane/Barrier Composition

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





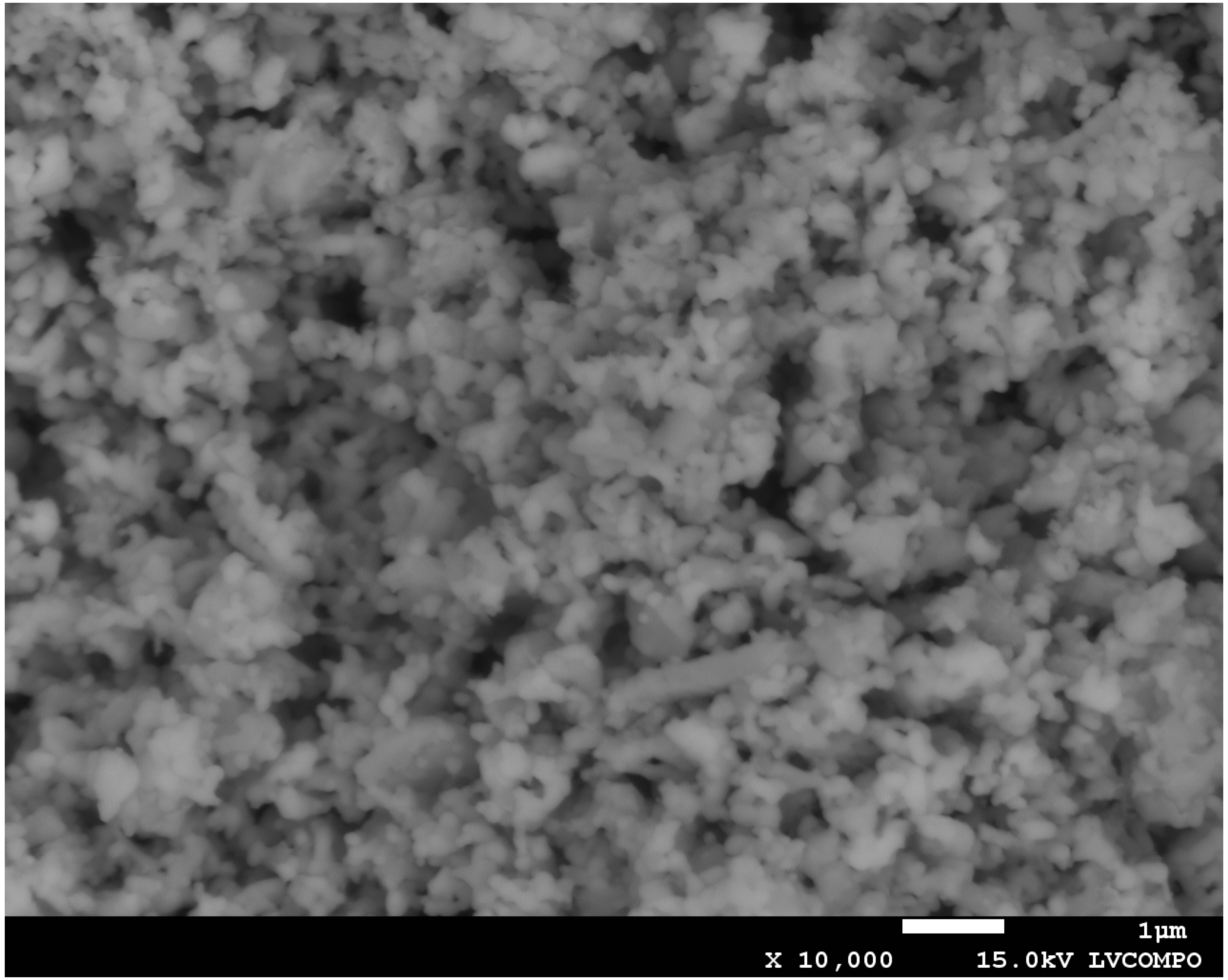
- Membrane composition (dense)
  - LSM/GDC (sintered at 1300-1325°C)
- Barrier (porous)
  - LSM/GDC (laminated) and LSCF/GDC (screen printed
  - LSCF has mixed conductivity and higher catalytic activity than LSM
  - Heat-treatment at 1000°C



Catalyst Nanoparticle Infiltration by Ultrasonic Dispersion

Catalyst Composition

- Doped CeO_2 ($Sm_{0.2}/Ce_{0.8}$) →
- $LaCoO_3$ based

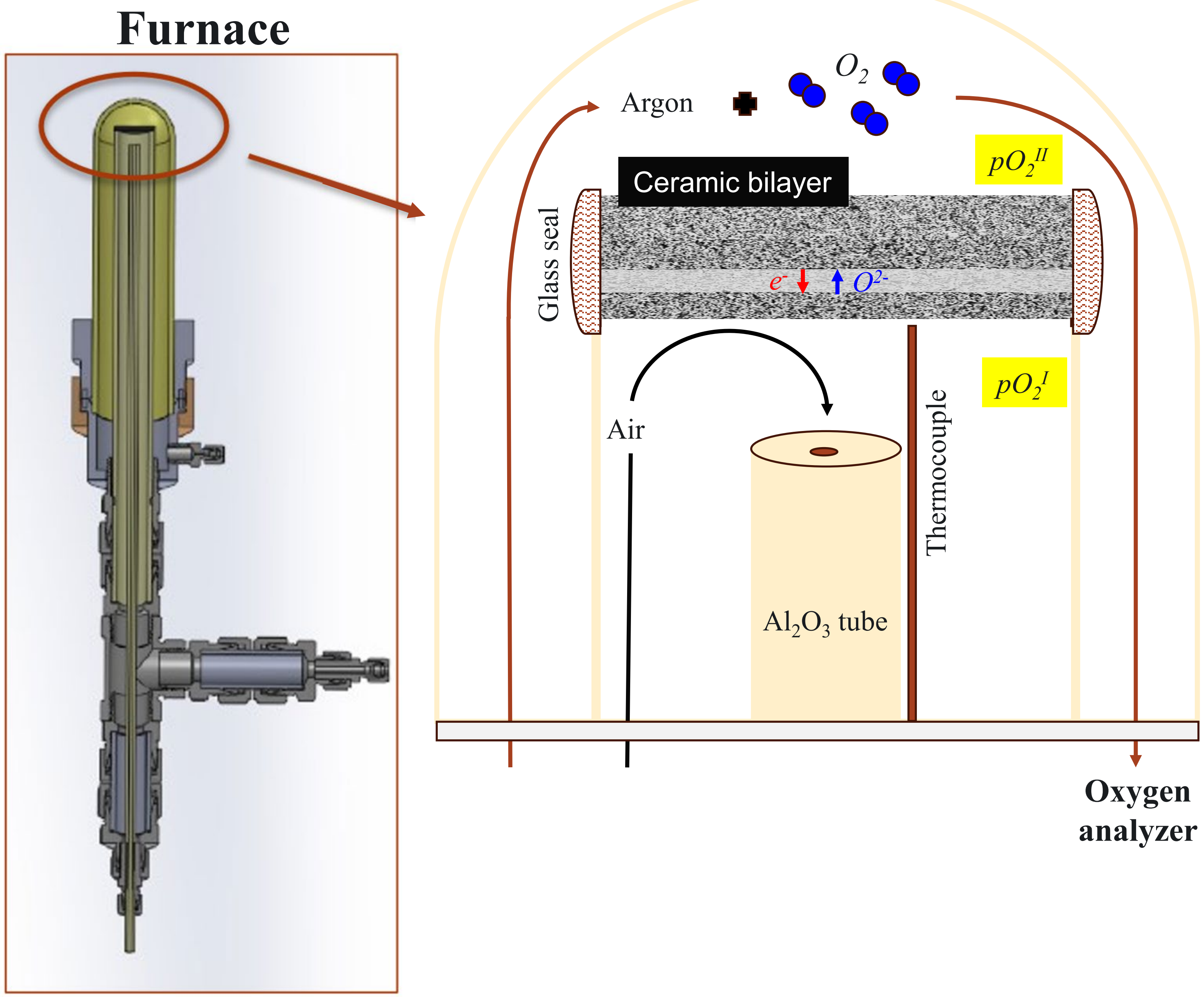


Catalyst Optimization

- Composition
- Concentration of particles
- Size and distribution of particles
- Heat treatment temperature

Catalyst ↔ O_2 Permeability Relations

Small-Scale Oxygen Permeation Testing

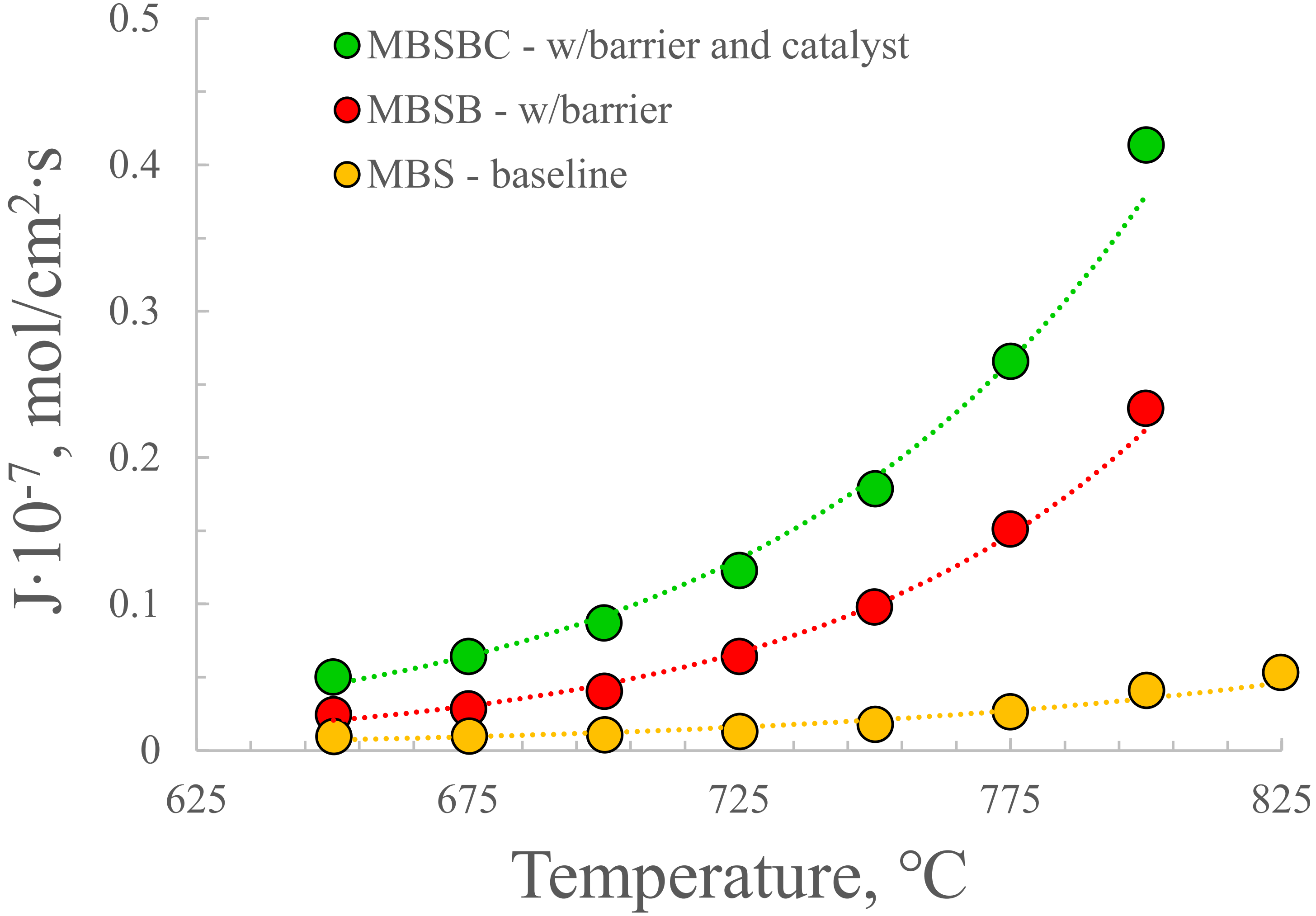


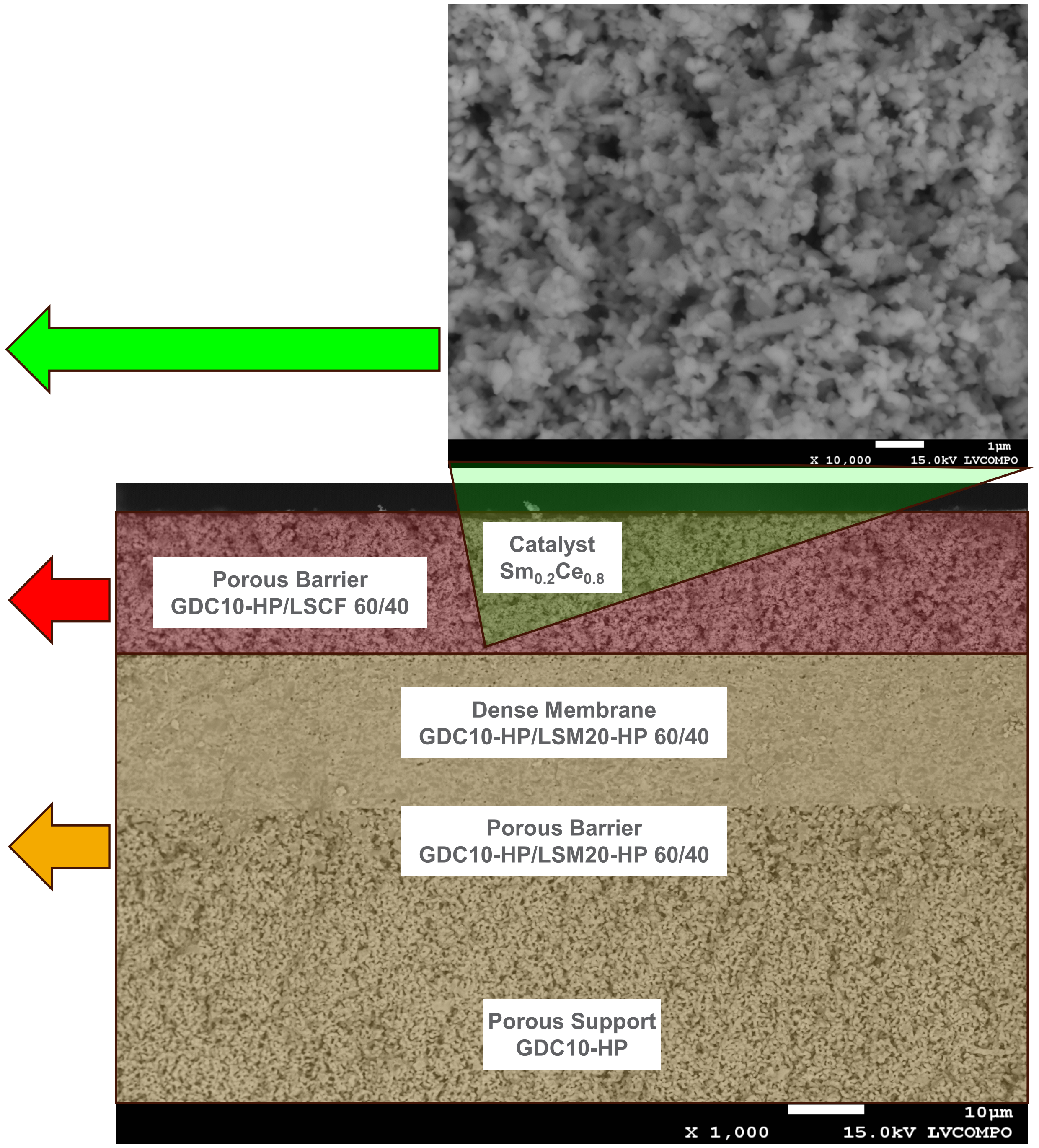
- Ceramic bilayers – ⌀ **0.75″**
- Driving force - $\boldsymbol{pO_2^{I} > pO_2^{II}}$
- Real-time measurement of O_2 concentration
- Fully automated and quick test

- **Impact of composition and thickness**
  - Membrane and barrier layers
- **Impact of catalyst** (infiltrated particles)
  - Composition, size, and distribution
  - Concentration

Small-Scale Oxygen Permeation Testing

Oxygen flux



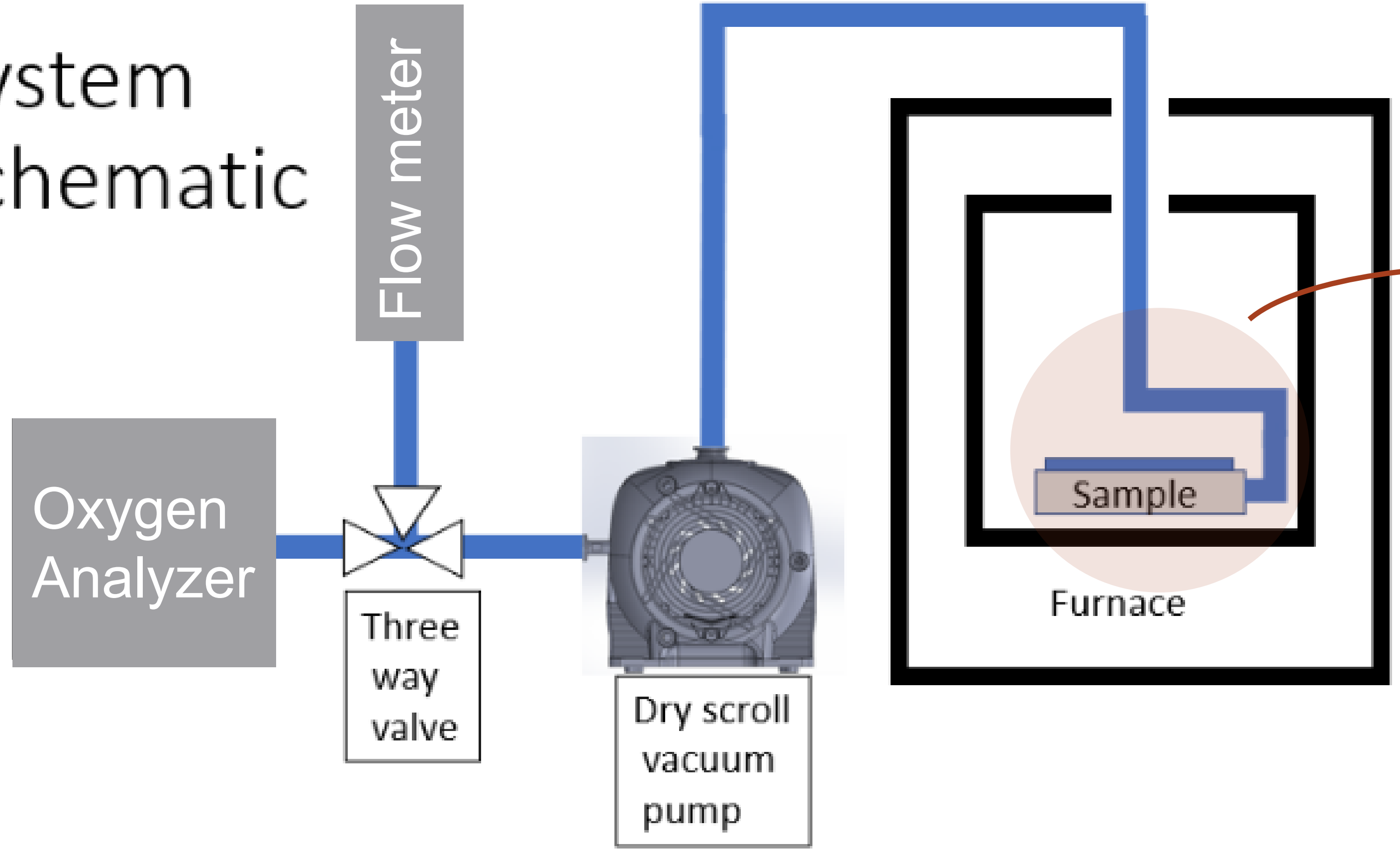


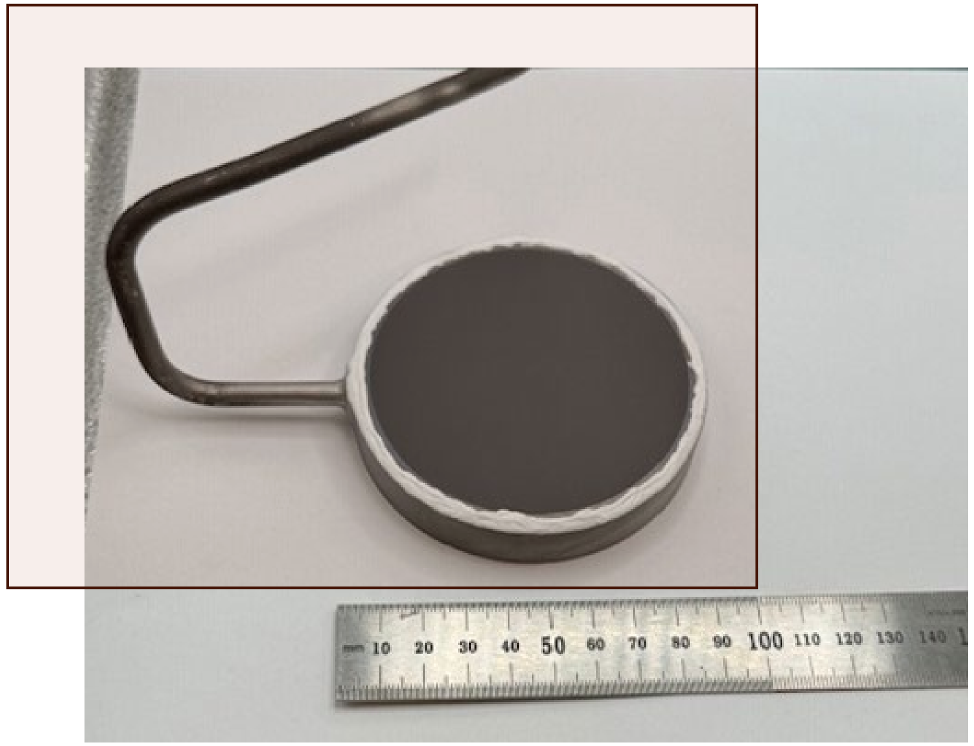
Large-Scale Oxygen Permeation Testing

- Ceramic bilayers – ⌀ **3″**
- Driving force - ***$pO_2^I > pO_2^{II}$ and vacuum***
- Real-time measurement of O_2 concentration
- Time consuming

- **Bilayer performance under realistic conditions**
  - Permeability as a function of temperature
  - Mechanical robustness
- **Glass seal design and performance**

System schematic

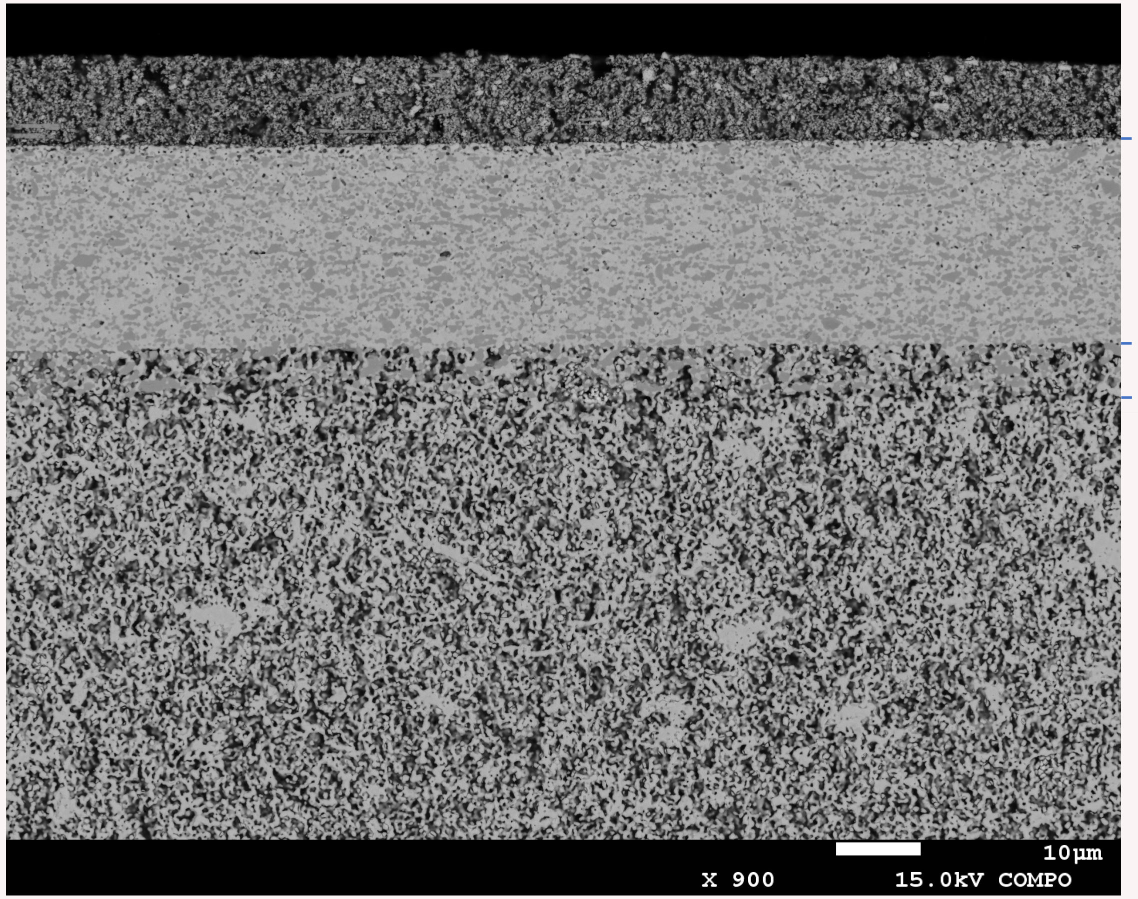




Large-Scale Oxygen Permeation Testing

Ceramic bilayer

MBSB



Porous Barrier
GDC10-HP/LSCF 60/40
Thickness: 8.8-10 µm

Screen-printed
Sintered at 1000°C

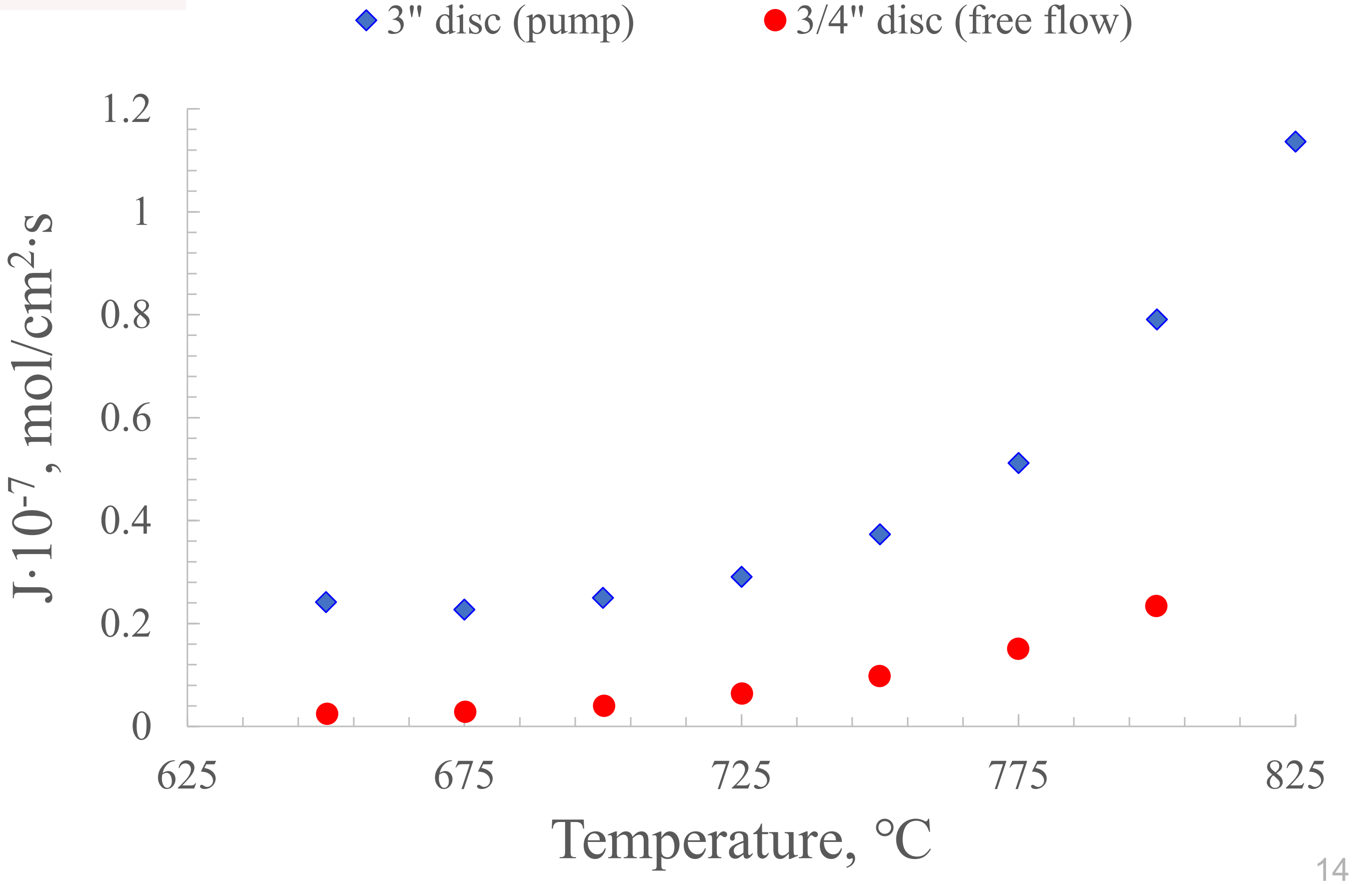
Dense Membrane
GDC10-HP/LSM20-HP 60/40
Thickness: 23.6 µm

Porous Barrier
GDC10-HP/LSM20-HP 60/40
Thickness: 6.5 µm

Laminated
sintered at 1325°C

Porous Support
GDC10-HP
Thickness: 0.6 mm

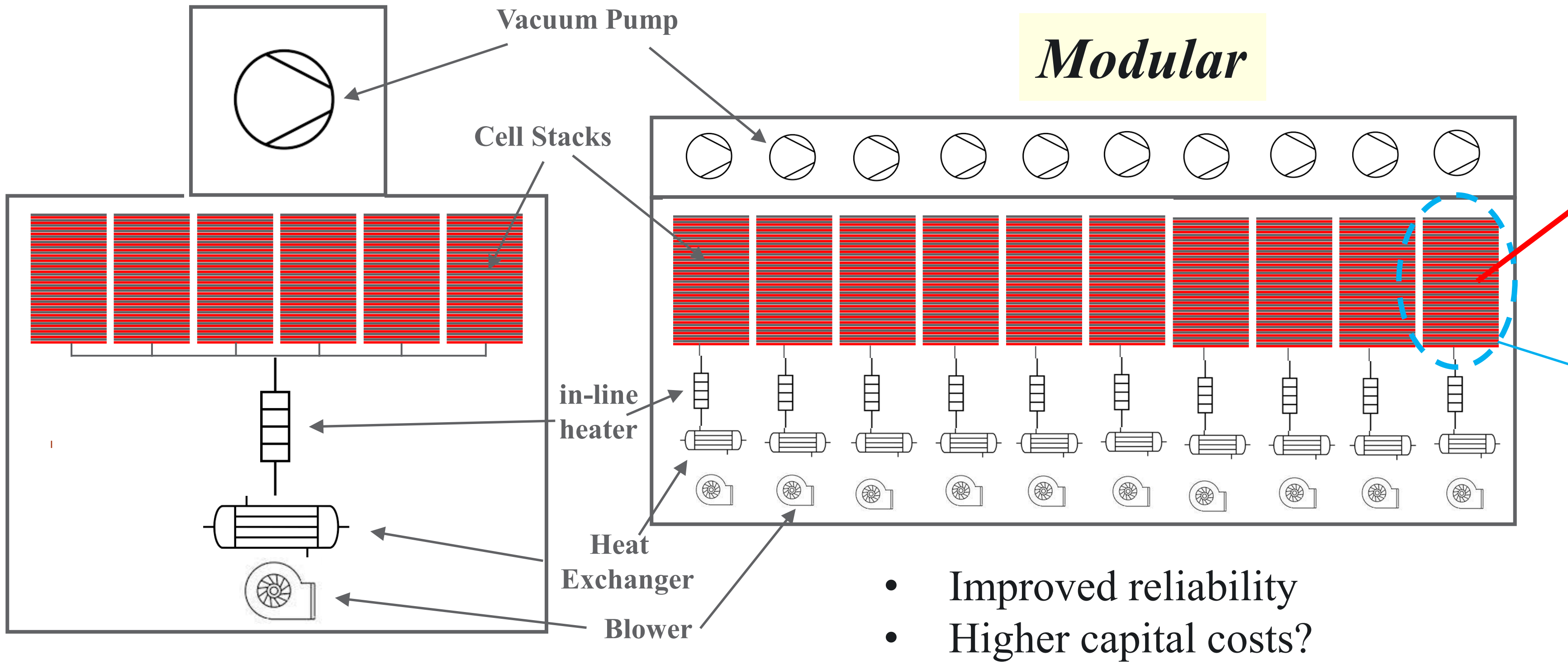
Oxygen flux



Techno Economic Analysis for System Design

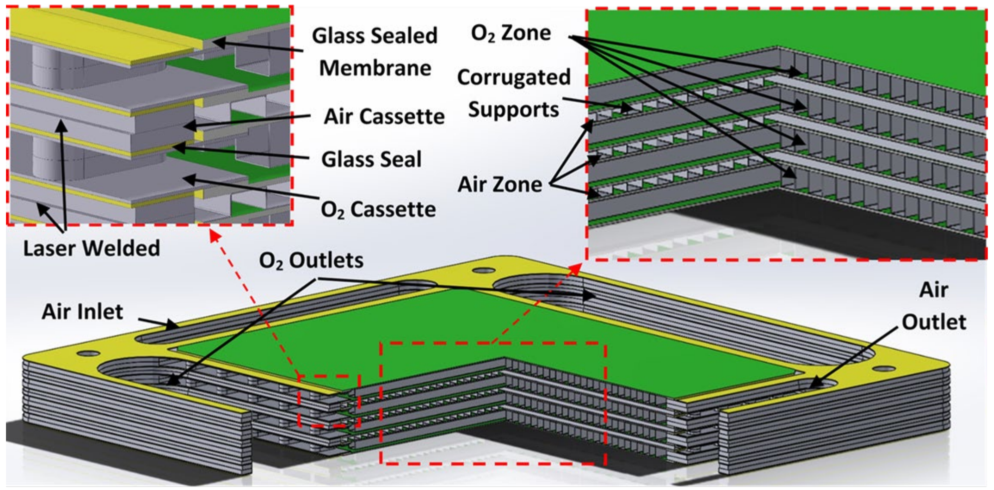
Single

Modular



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

- Improved reliability
- Higher capital costs?
- Equipment options

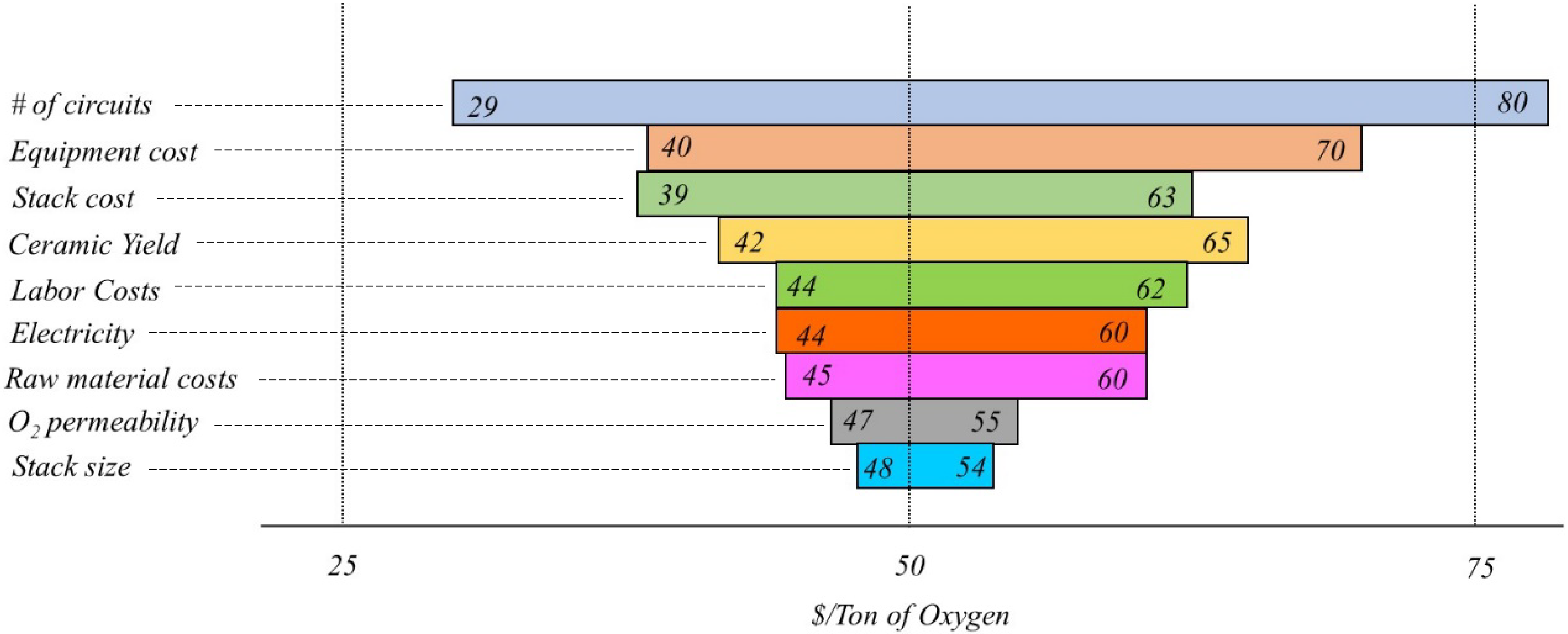


 # Stacks/circuit
→ Depends on Oxygen Permeability

Techno Economic Analysis/System Cost

- Stack cost as a f(cell dimension) – material, labor, equipment, yield, etc.
- System cost – capital costs, # of stacks, depreciation, etc.
- Oxygen Cost largely dependent on stack costs/oxygen permeability

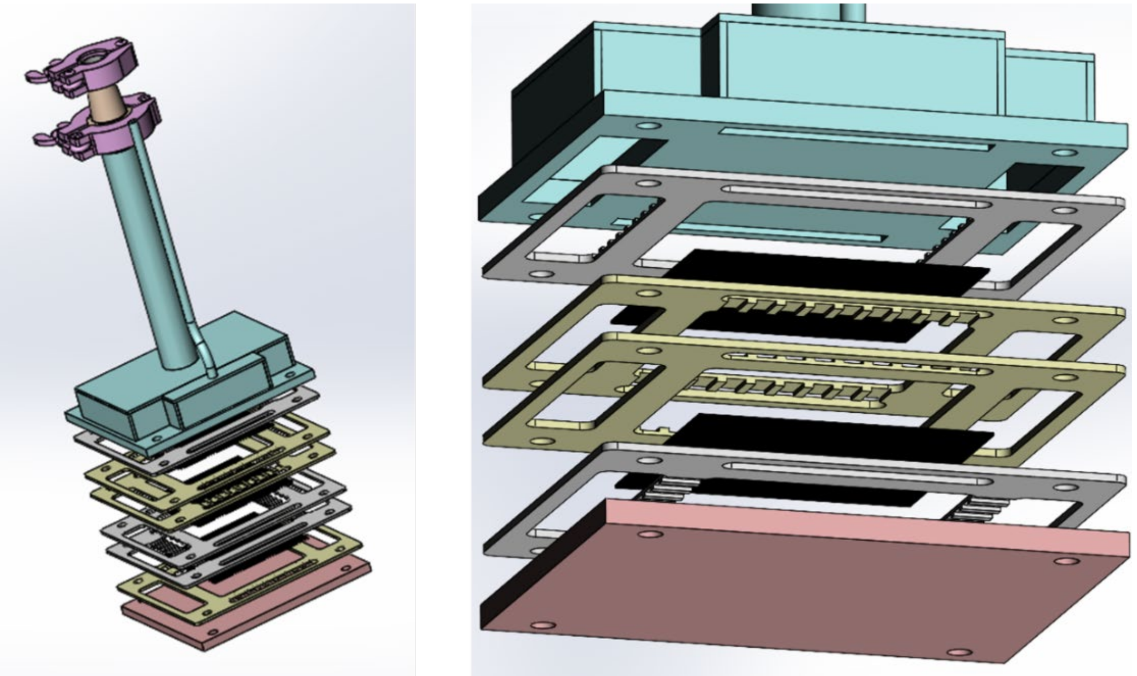
Tornado plot showing sensitivity of various items to the overall oxygen production cost



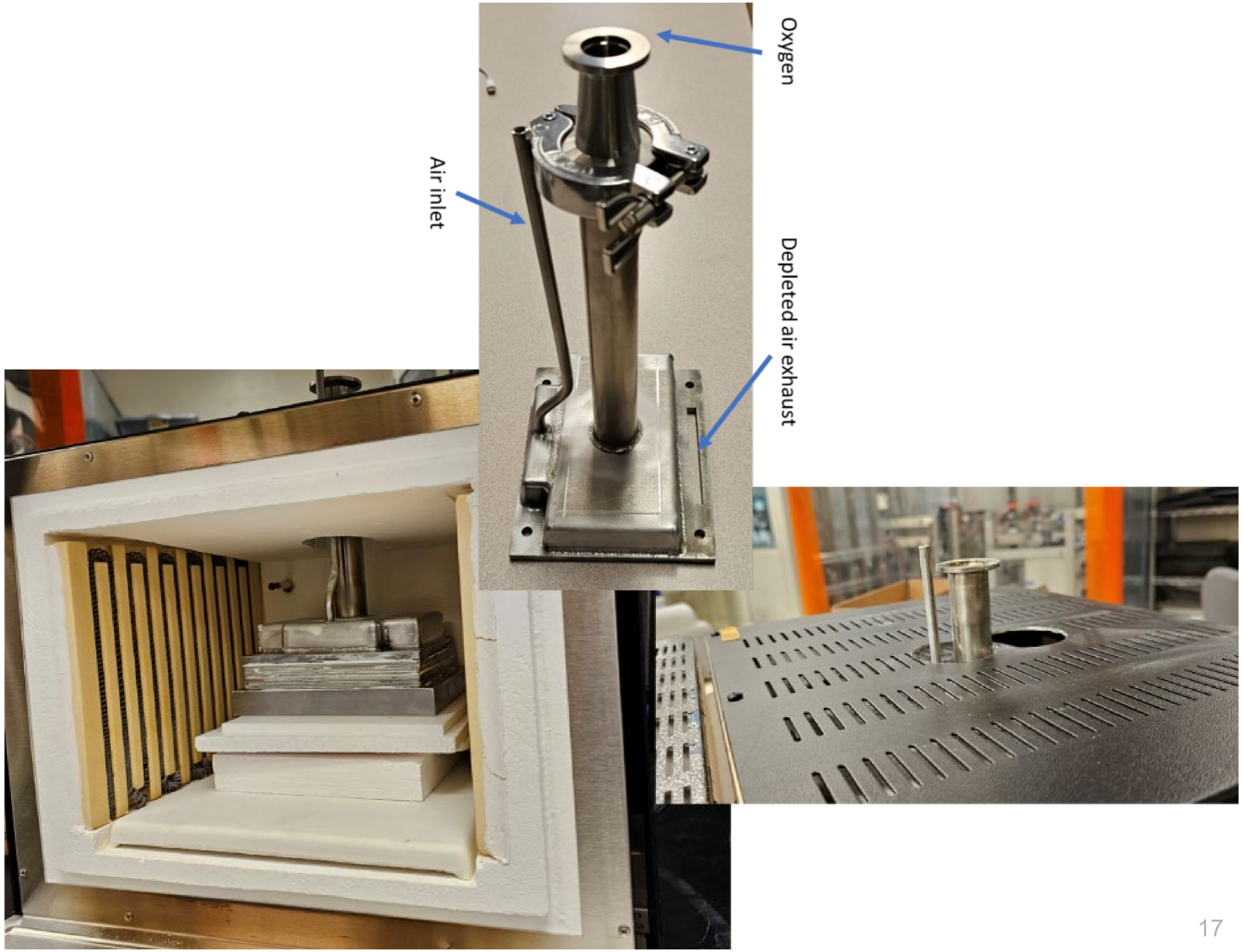
- The case of 10 circuits with 80 stacks is the center line at $50/Ton of O_2
  - If the number of circuits decreases to 5 by various methods, the O_2 cost would drop to $29/Ton.
  - Several items are connected and would have a cumulative effect on the overall cost. They will be constantly evaluated as the project continues.
  - The initial evaluation shows that the cost is competitive with other available O_2 production technologies.

System Capable of Testing Multiple Cells and Stacks with Active Area of 50 cm^2

Schematic of System

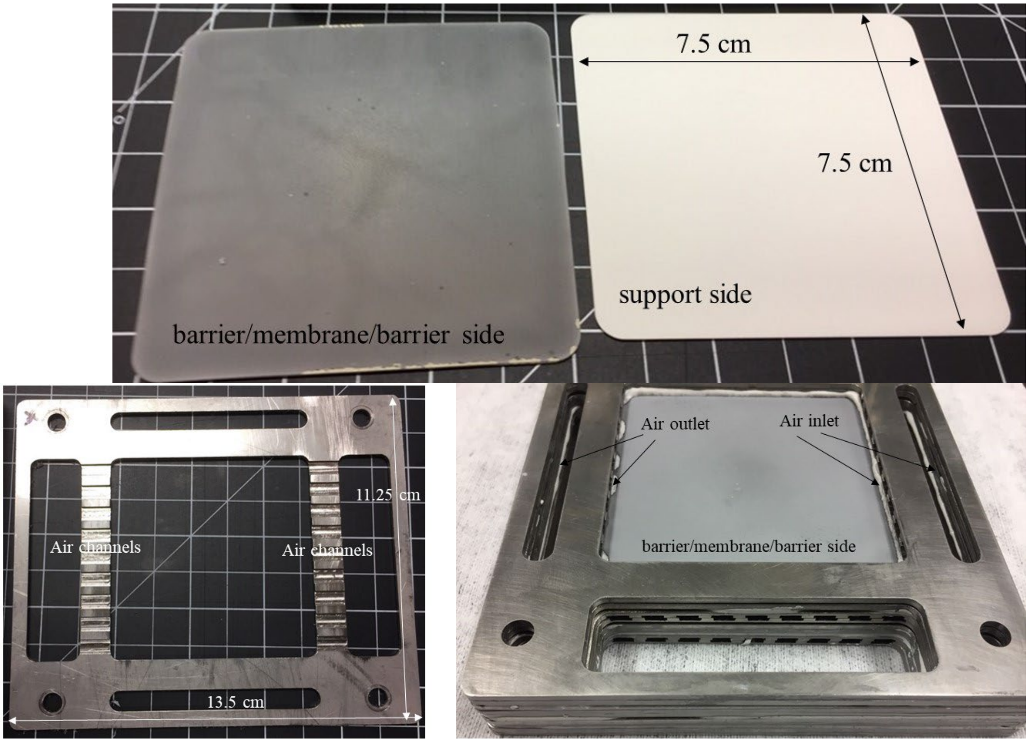


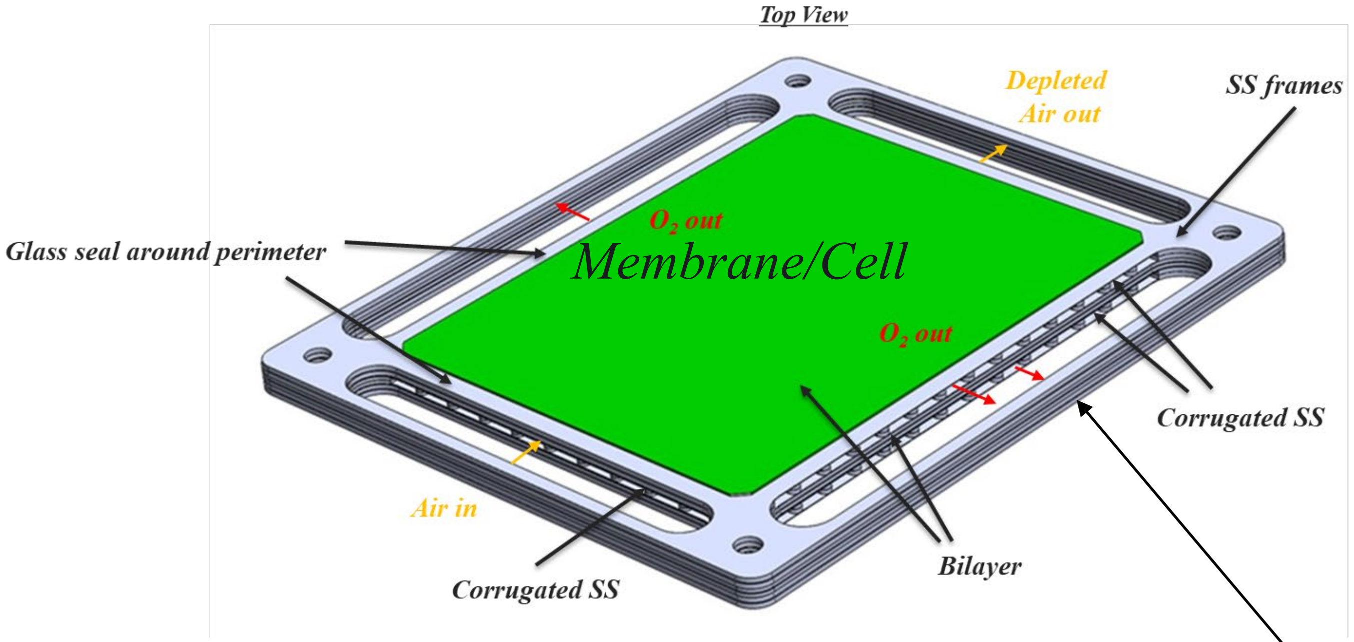
Constructed

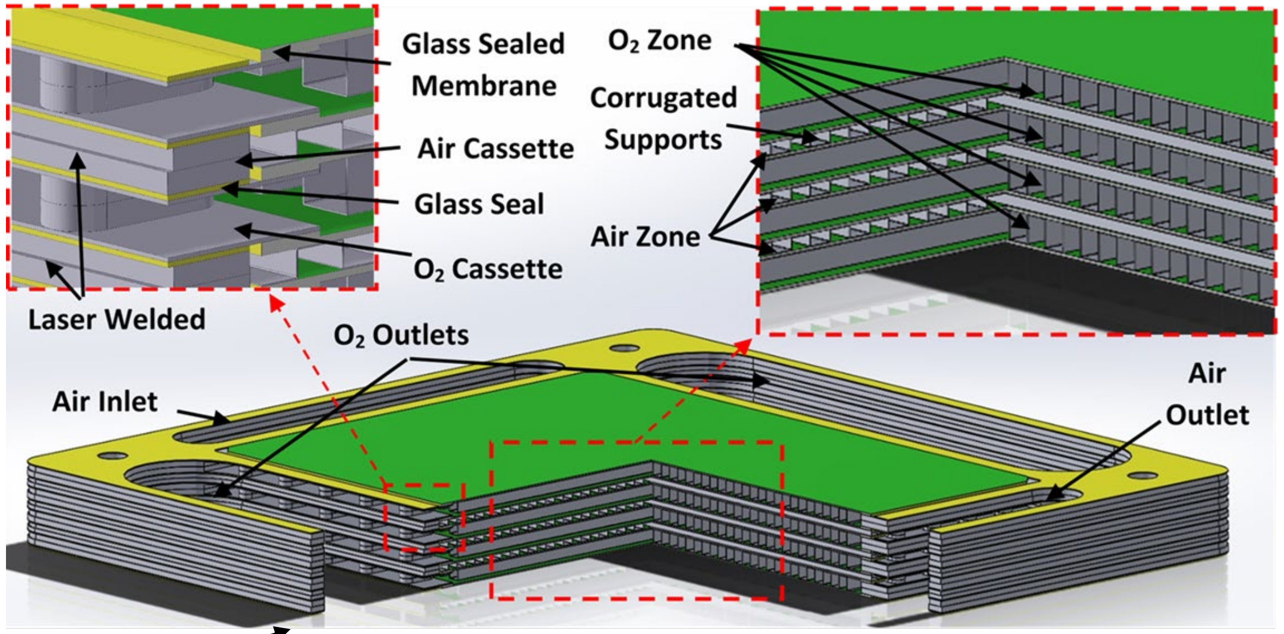


Three Cell Stack is Being Built and Tested

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





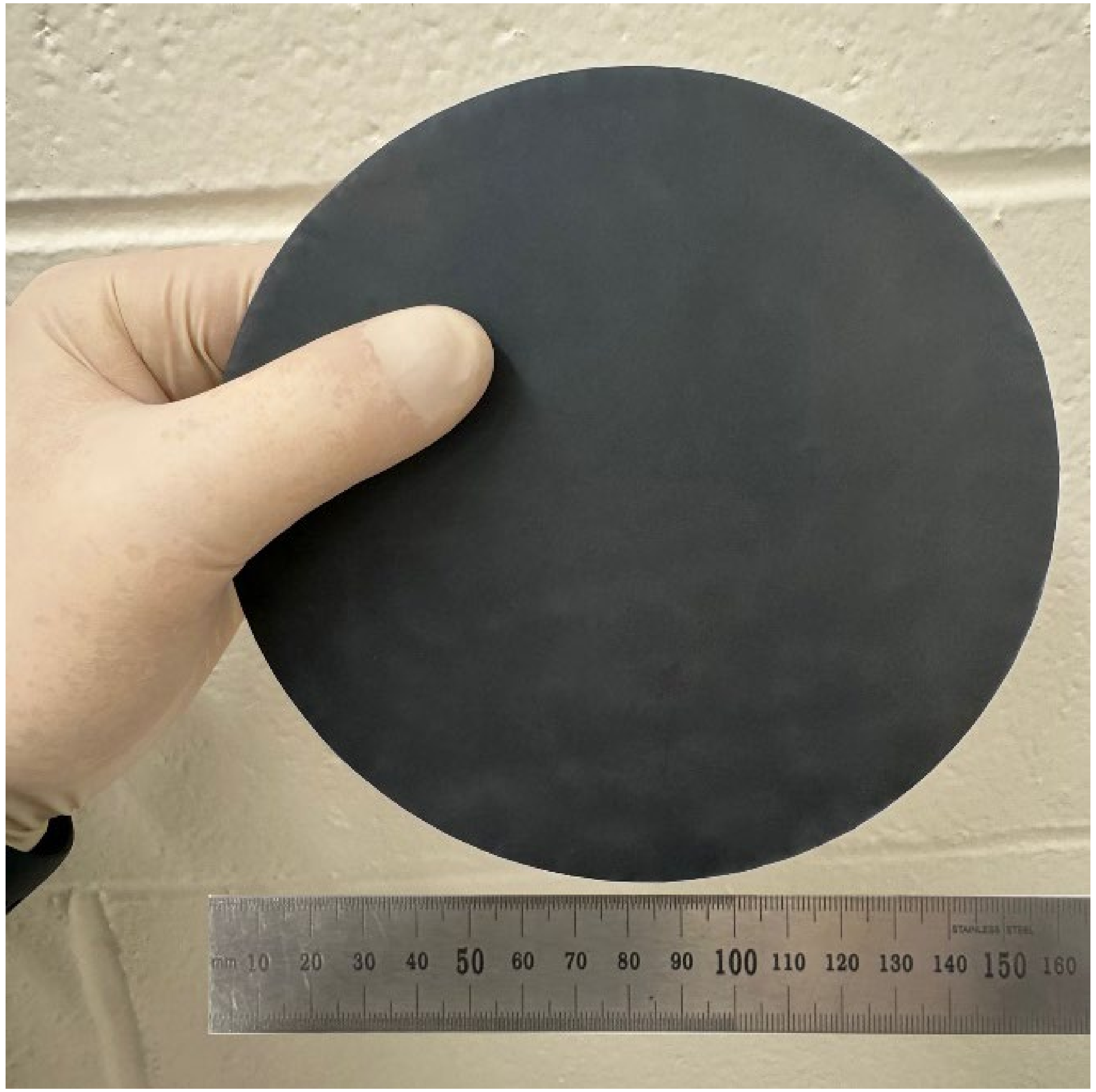


CFD Optimization on Stack Design

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

Demonstrate Ability to Sinter Larger Area Bilayers of 200 cm^2

Ceramic Bilayer Disc - ⌀ 6.3″, 0.6 mm thick



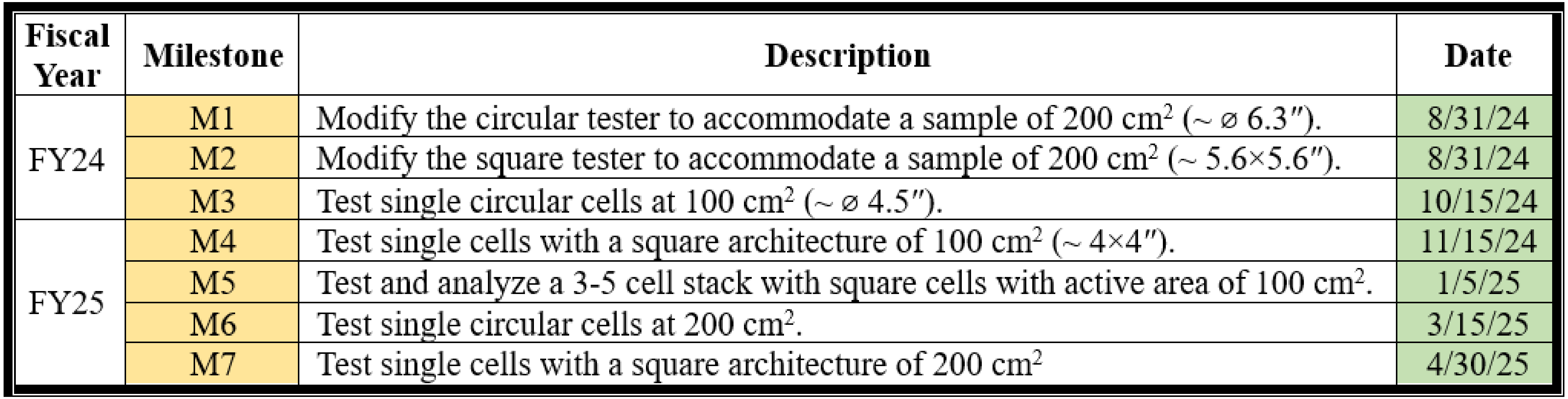
Manufactured by a two-step process

1. Lamination of the 9x9″ tapes of support (GDC10-HP + 60% C composition), barrier (GDC10-HP/LSM20-HP 60/40 + 60% C composition), and membrane (GDC10-HP/LSM20-HP 60/40 composition) at 275°F under a pressure of 60 psi.
2. The 7-inch disc was cut out by laser, sandwiched between a thin MgO film (deposited on a dense alumina plate) and an in-house-made MgO porous plate with a ZAL porous plate on top as weight, and fired at 1325 °C.

Project Accomplishments

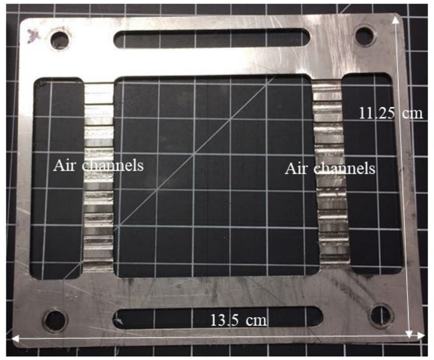
- Utilization of inexpensive materials of construction.
- Ability to fabricate a thin dense membranes (10-20 µm) on flat and crack free porous supports.
- Ability to control porosity and pore size in the support and barriers.
- Good mechanical strength/flexibility of porous support.
- Ability to scale up bilayers to different sizes and shapes using traditional inexpensive techniques.
- Efficient infiltration of catalysts into porous barriers with an ultrasonic dispenser.
- Ability to measure oxygen permeation rates under realistic conditions for bilayers of different sizes, single cells and multiple cells.
- Significant oxygen flux can be achieved 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).
- Modular system approach with improved reliability.
- The techno-economic analysis shows that the cost is competitive with other available O_2 production technologies.

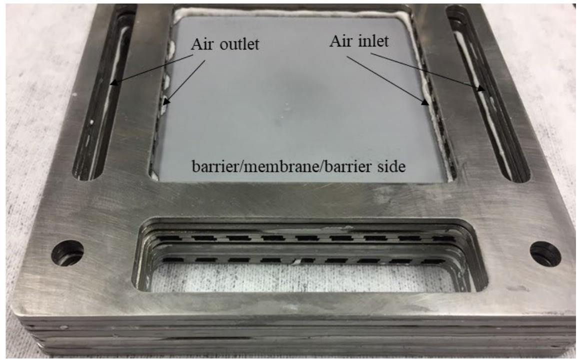
Next Steps – Year 5



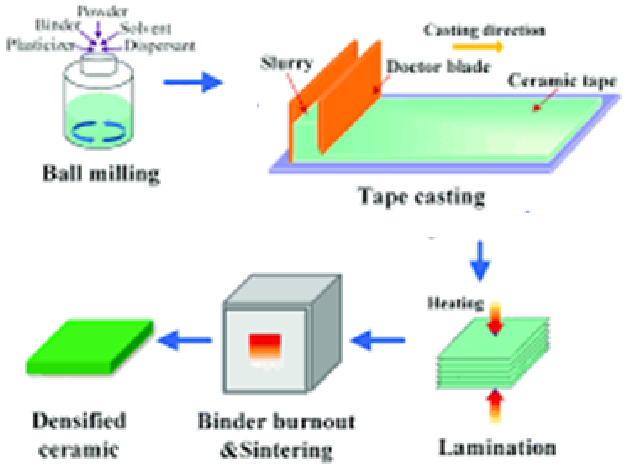
Fiscal Year	Milestone	Description	Date
FY24	M1	Modify the circular tester to accommodate a sample of 200 cm^2 (~ ⌀ 6.3″).	8/31/24
	M2	Modify the square tester to accommodate a sample of 200 cm^2 (~ 5.6×5.6″).	8/31/24
	M3	Test single circular cells at 100 cm^2 (~ ⌀ 4.5″).	10/15/24
FY25	M4	Test single cells with a square architecture of 100 cm^2 (~ 4×4″).	11/15/24
	M5	Test and analyze a 3-5 cell stack with square cells with active area of 100 cm^2.	1/5/25
	M6	Test single circular cells at 200 cm^2.	3/15/25
	M7	Test single cells with a square architecture of 200 cm^2	4/30/25

Future Work





- Demonstrate a 5-10 cell stack (50 cm^2) operated at 750-800°C utilizing bilayer structures, stainless frames, and a glass seal in a laboratory setting.



- Demonstrate ability to sinter larger bilayer structures (200-400 cm^2) that are flat and defect free using traditional low cost thick film manufacturing processes for commercial scale up (i.e., tape casting, screen printing, stamping)

- Economic analysis to assess sensitivities, stack costs, impact of capital costs, operating and maintenance costs, and life in a commercial environment

- Team with industrial partner to scale up and commercialize technology with additional funding through a TCF (Technology Commercialization Fund) or a traditional funding process.

Acknowledgements

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Questions?

Extra slides

Technology Maturation Plan

- Critical Questions from TMP Template
- Technology TRL
- Steps for Commercialization

Critical Questions

- ***What is required for integration into higher-level systems?***
- ***What is the critical decision point at moving the technology from a laboratory project to a larger-scale pilot project?***

Demonstrate a 50 cm^2 stack composed of aluminized stainless frames that are sealed to cells using a glass seals (i.e., 5-10 cell stack). Testing performance of the stack will dramatically reduce risk in scaling up the process and enhance potential commercialization with industrial partners. In addition, the ability to sinter bilayers structures up to 200 cm^2 and 400 cm^2 would also significantly reduce scale up risks.

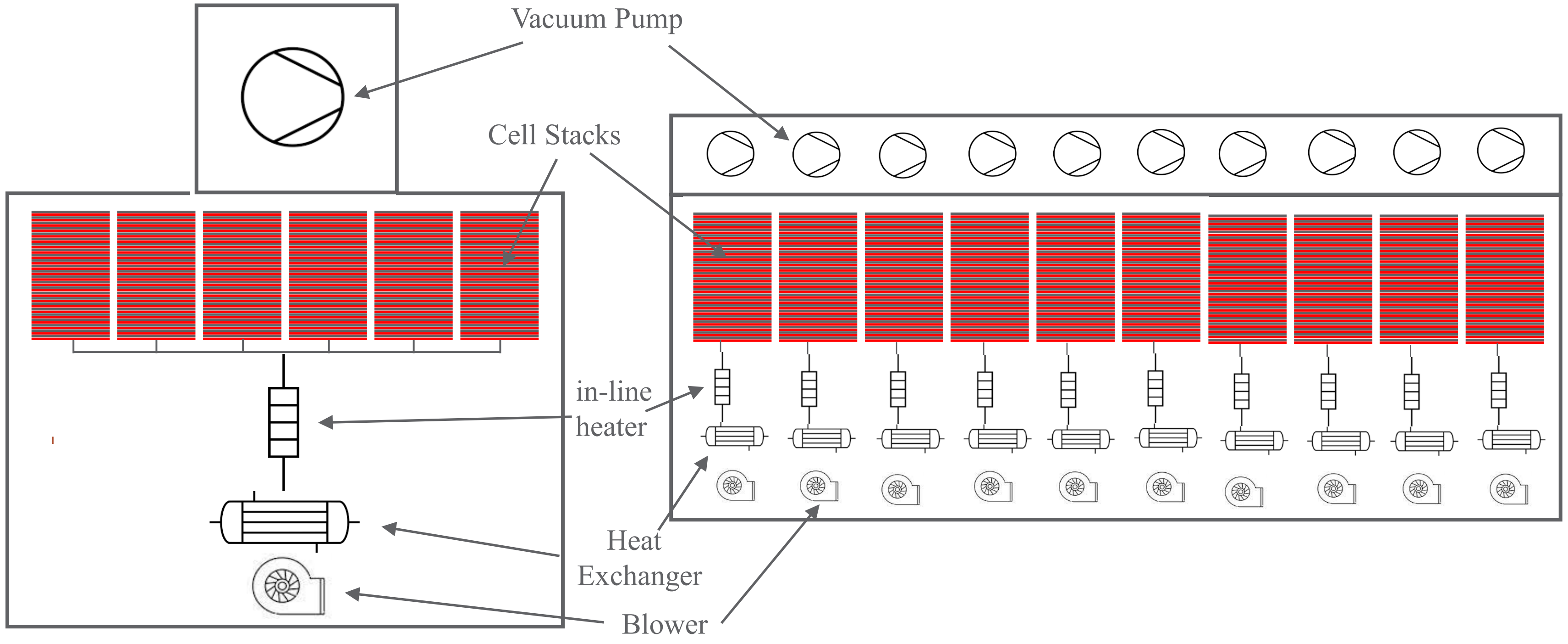
- ***What performance metrics are most important for technical and economic success (at component and system levels)?***
- ***Identify R&D gaps and critical components that are lagging in maturity?***

Continue oxygen permeability optimization on LSM and LSCF based membranes. Attaining a high oxygen permeability will enable less stacks to be used, and therefore improve reliability and costs of the system.

Critical Questions

- ***How can one improve the balance of the project to mitigate risks and increase the likelihood of R&D success?***

A single system with one large vacuum pump, heat exchanger, blower and in-line heater would be simpler to design, but a modular approach would dramatically improve reliability by eliminating a single point failure mechanism.



- Modular approach will improve reliability by increasing redundancy
- Reduce probability of system failure (i.e. ceramic components)

Critical Questions

- ***What does the forecast of the cost and duration of technology development look like through demonstration and commercialization?***

Techno Economic Analysis/System Cost

- Stack cost as a f(cell dimension) – material, labor, equipment, yield, etc.
- System cost – capital costs, # of stacks, depreciation, etc.
- Oxygen Cost largely dependent on stack costs/oxygen permeability

	LSM Based (barriers & catalyst) *60/40*	**LSM Based (barriers & catalyst)** *70/30*	**LSCF Based* (barriers & catalyst)**
O_2 Permeability (mol/cm^2·s)	4.0×10^{-8}	1.2×10^{-7}	4.0×10^{-7}
# Stacks 400 cm^2	205	68	20
Oxygen Cost ($/T)	62-86	49-74	45-70

- Operating cost – and compare to existing technologies

Technology Maturation Plan

Beginning Technology Readiness Level (TRL) (Pre- Project Award – 01/2018)

- TRL 1 – White paper study that provided details on how to drive oxygen through an oxygen conducting ceramic without an electric potential. Details provided a potential technology that would provide oxygen on a ton/day level that would operate at elevated temperatures with a chemical potential as the driving force.

Proposed Research to Mature the TRA System (Year 1-3)

- TRL 2 – 4 Experimental work started to verify material phase, purity, and compatibility with other components. Preliminary oxygen permeability experiments started with some material interactions observed. Verified that individual components meet specifications needed for the system, very thin membranes on porous support structures are need to have the appropriate oxygen flux for the mixed conducting membrane. Preliminary integration of components (membrane, support, glass seals, stainless frames) will be performed on 50 cm^2 bilayer structures. Initial economic analysis

Technology Maturation Plan

Proposed Research to Mature the TRA System (Year 4)

- TRL 4-5 The focus will move from testing components to a system which integrates all components into an operating system. Components will be integrated sealed into an operating stack such that the system will be similar to the final design. The dimension will be smaller that the final design but will provide insight into operation of the system. Potential IP developed on operating system. Provide economic analysis refinement based on Year 4 results.

Post Year 4

- TRL 6 – Prototype construction, demonstration, and cost validation (commercialization partner – SOFC, SOEC developers, industrial gas suppliers, ceramic manufacturers)

- TRL7-9 – Full scale demonstration and qualification