Pacific Northwest NATIONAL LABORATORY

# Pressure Driven Oxygen Separation

FWP-73130

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Pacific Northwest National Laboratory
Richland, WA

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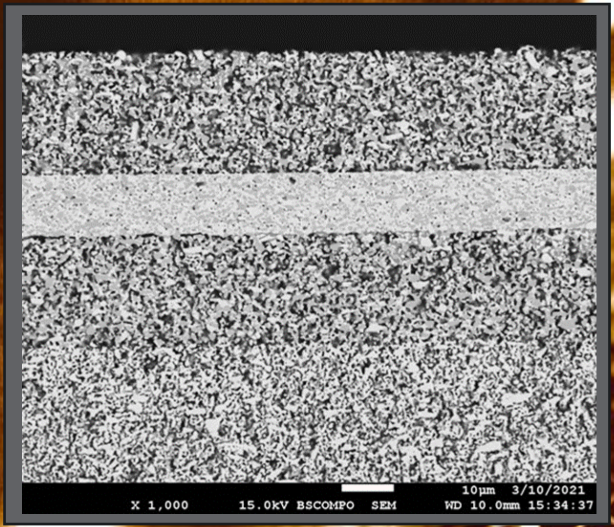


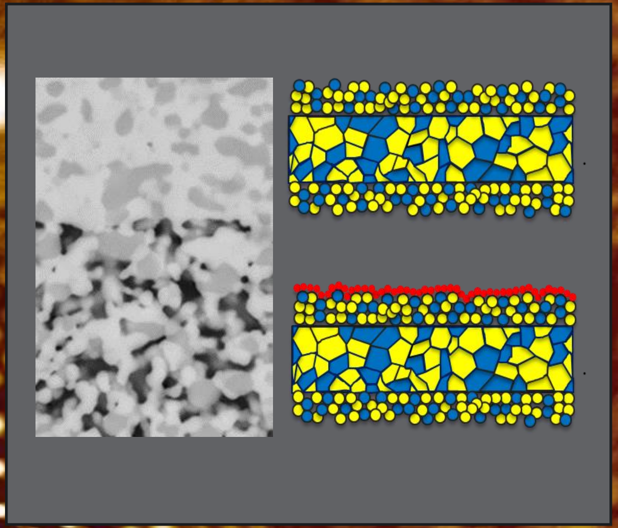

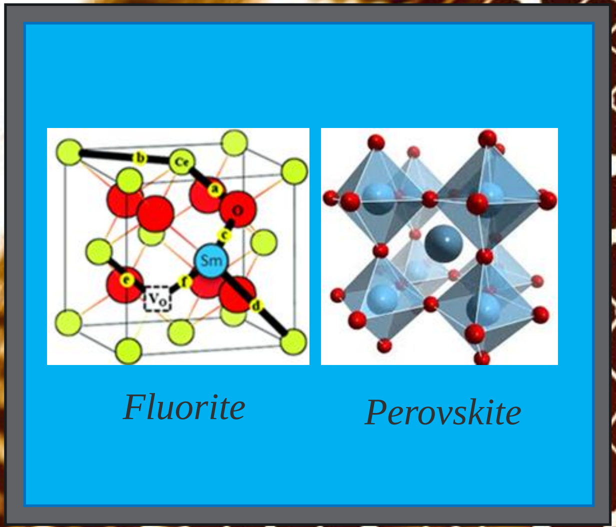


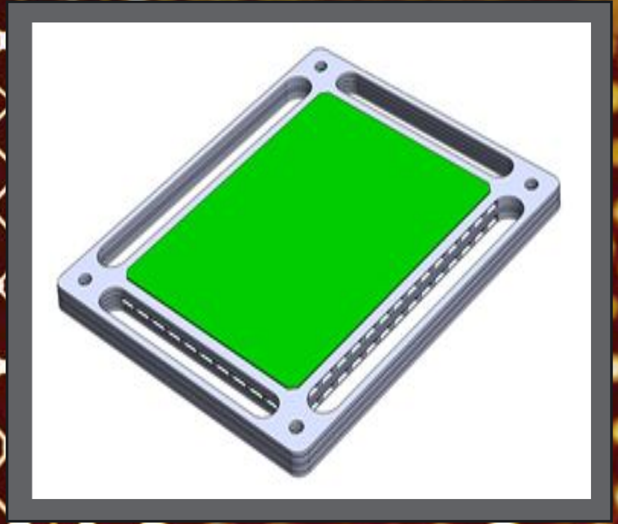

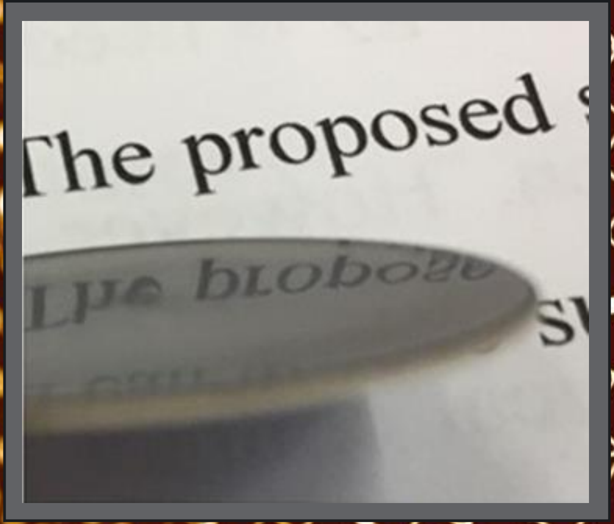


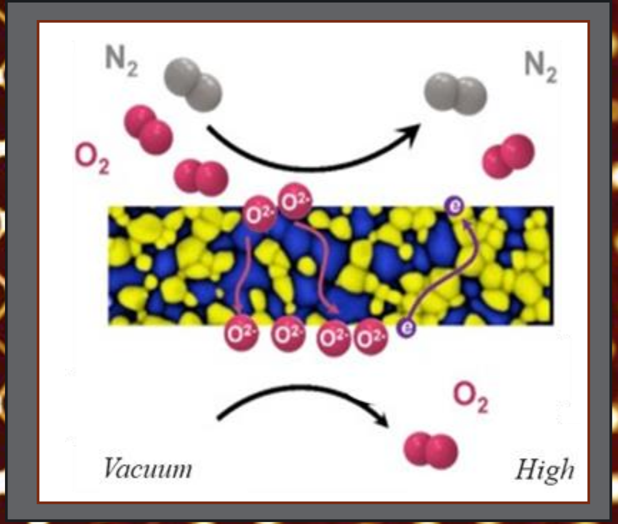


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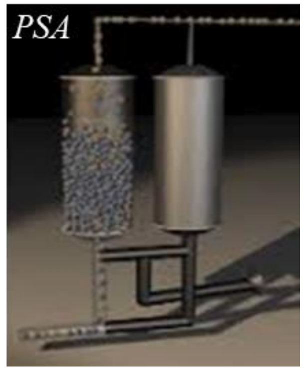
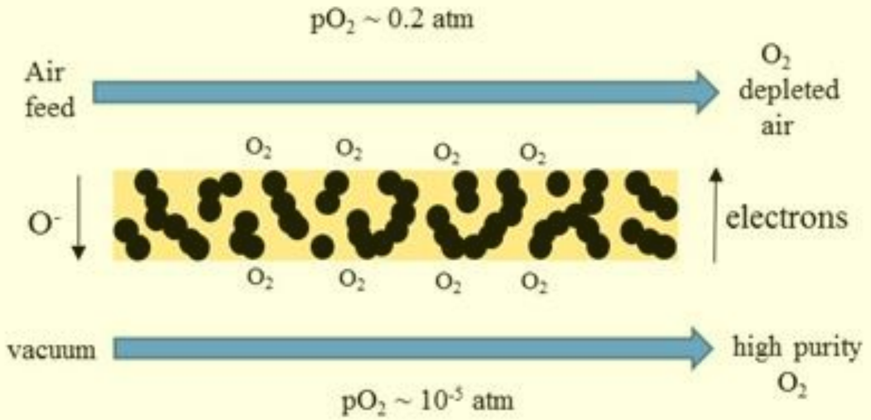
# Oxygen Separation Techniques

- **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%)

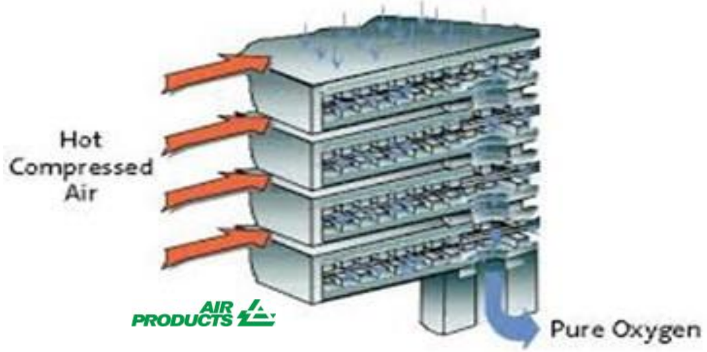

- **Pressure Driven Oxygen Separation with Ceramic Membranes** – R&D
  - High purity (99+), ~10 T/day
  - Thermal integration
  - Can be economical depending on oxygen permeability
  - Examples: OTM (Oxygen Transport Membrane) Linde
    ITM (Ion Transport Membrane) AIR PRODUCTS

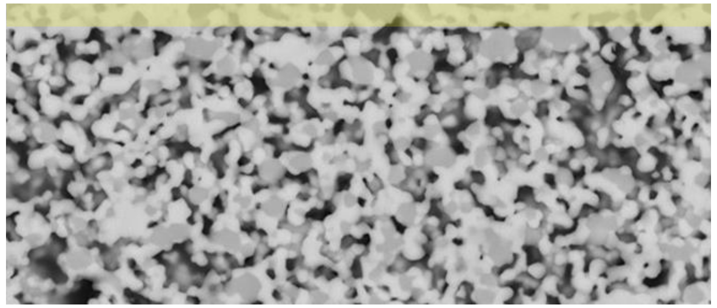


# Project Description and Objectives

***The overall goal is to 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)



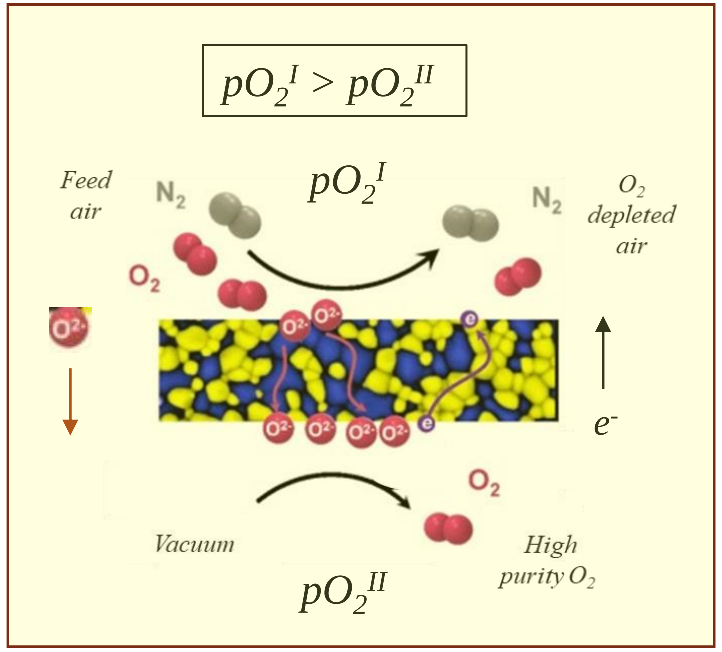



← Thin composite membrane (~ 10 μm)

← Porous support (~ 0.5 -1mm)

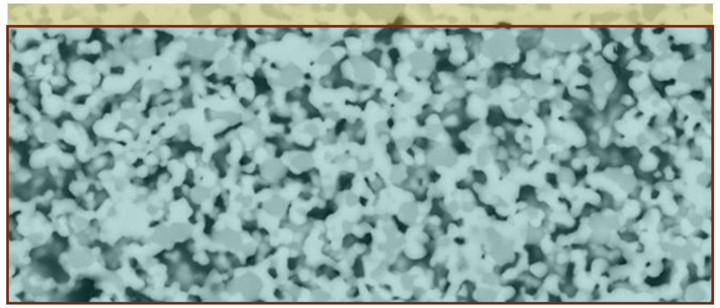
- Composite membrane made of mixed conducting two phase material capable of separating oxygen at 700-800°C

- 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***

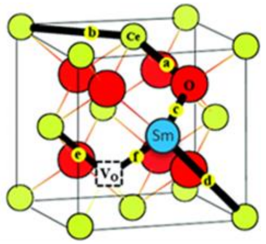
- Dense
- Two phase composite
  - High $\sigma_i$
  - Sufficient $\sigma_e$
- Similar TEC
- Limited interaction during firing
- Compatible with glass seal
- Inexpensive fabrication
- No electrodes

***Porous Support***

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

*Ionic Conductor*

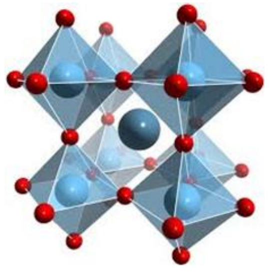
- Doped $CeO_2$



*Fluorite structure*

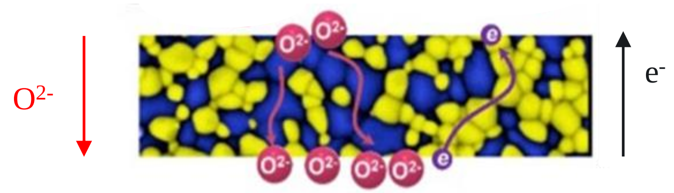
*Electronic Conductor*

- Doped $LaMnO_3$
- Doped $LaFeO_3$



*Perovskite*

$pO_2^I$




$pO_2^{II}$

# Proposed Ceramic Membrane Technology

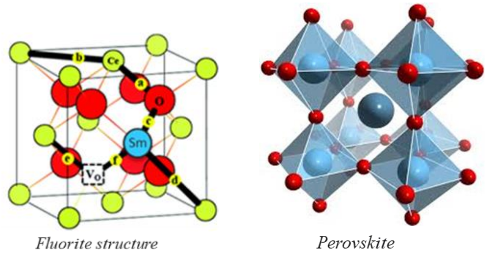
## *Factors Critical for Project Success*

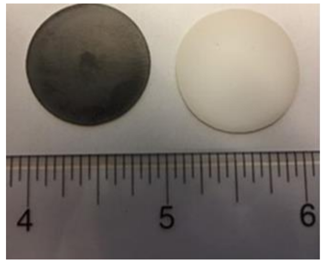
- **Low-cost materials** to enable market penetration and maximize energy efficiency
- **Minimize interactions** between ionic and electronic conducting phases
- **Co-sinter thin composite membrane on low-cost porous supports** without warping and cracking
- Design a planar stack architecture with **low-cost fabrication processes**

# Proposed Ceramic Membrane Technology

**Year 1**

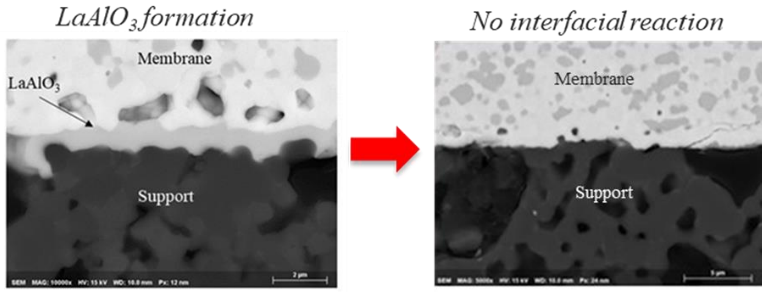
Membrane and Support Characterization
Bilayer Characterization
Membrane Oxygen Permeability

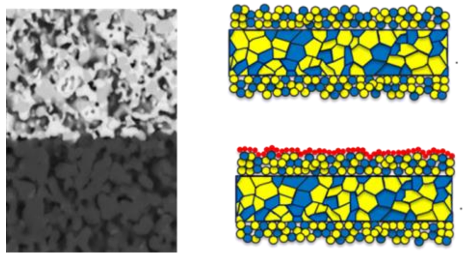


**Year 2**

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



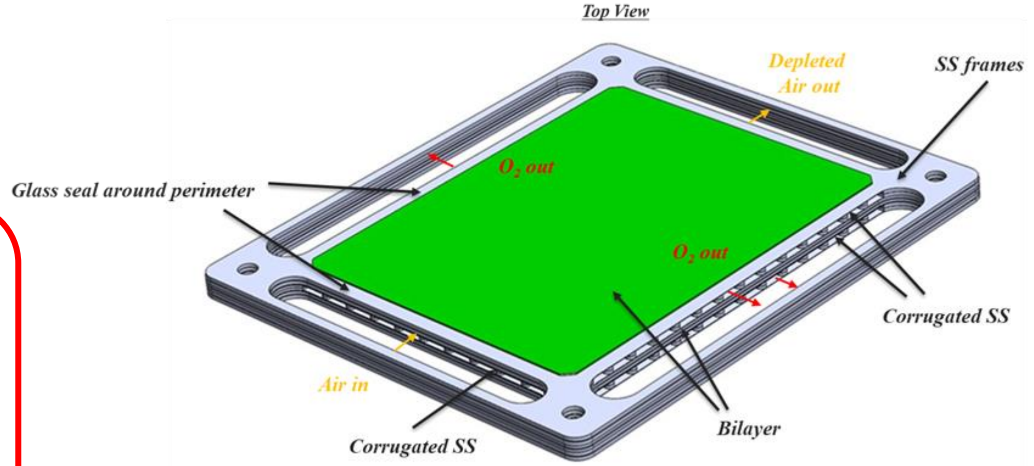



**Year 3**

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

**Year 4**

Scale up/show path to 400 $cm^2$
Cell assembly w/ stainless frames & glass seals
Oxygen Permeability Optimization
Prototype testing – 50 $cm^2$
Cost Analysis

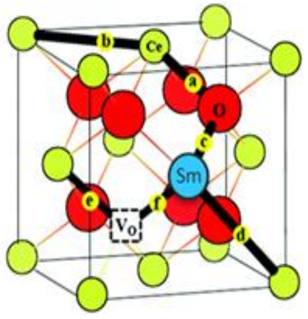


# *Composite Membrane*

## - Microstructure Control/Conductivity -

*Ionic Conductor*

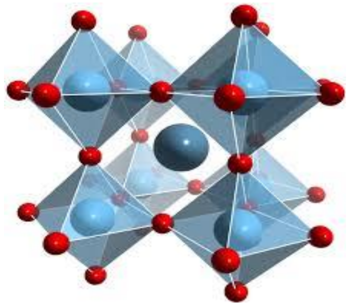
- Doped $CeO_2$
- $Sm_{Ce}' \rightarrow 2[V_O^{\circ\circ}]$




*Fluorite structure*

*Electronic Conductor*

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



*Perovskite*

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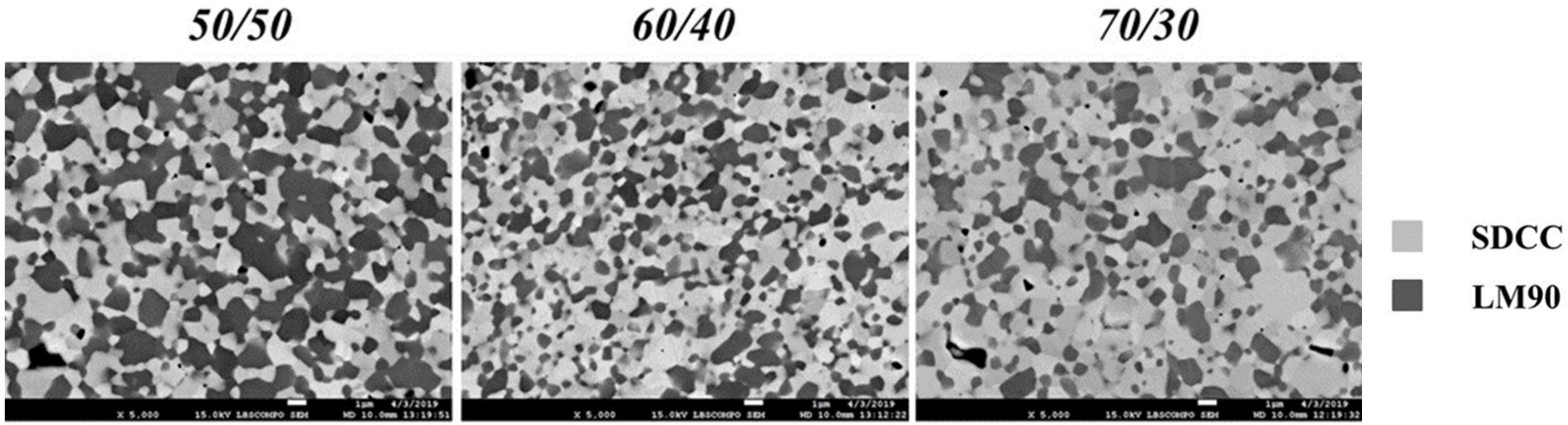
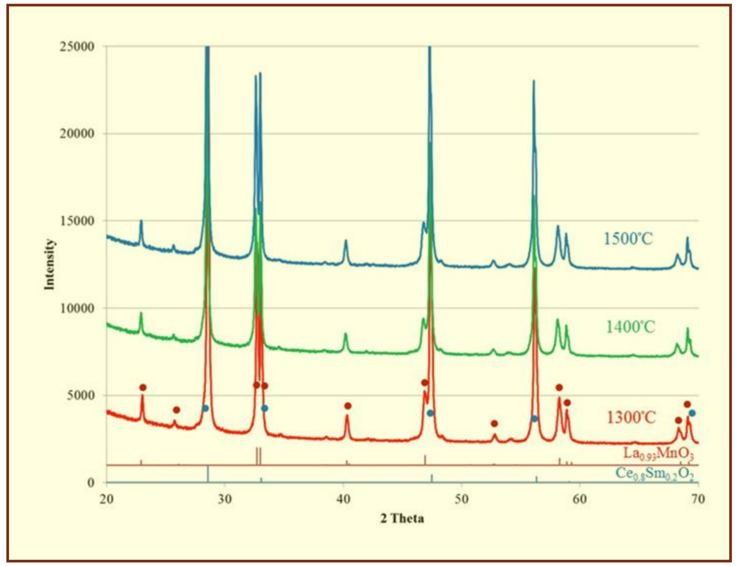
➢ Minimize stress during sintering, hermetically sealed, controlled thermal expansion limited interaction during sintering to maximize oxygen permeability



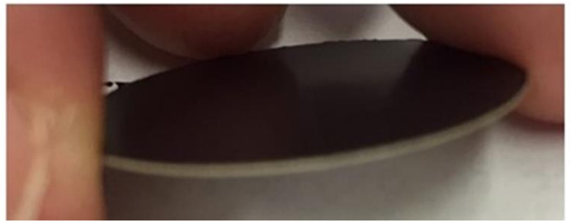




➢ Electrical conductivity ($\sigma_e$) controlled by perovskite phase, $\sigma_e$ ~ 4 orders of magnitude greater than ionic conductivity ($\sigma_i$)
 - $\sigma_i$ for pure ceria phase ~0.07 S/cm at 800°C and 0.03 S/cm at 700°C

➢ ~ 2/3 $\sigma_i$ value used in composite calculations

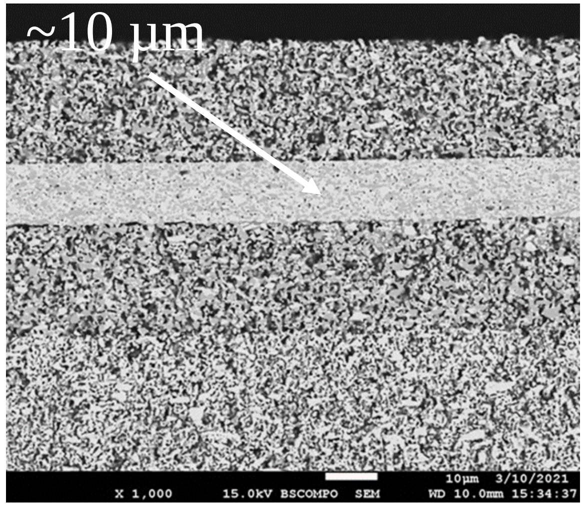
➢ Percolation in both phases

# *Bilayers with Controlled Microstructures*



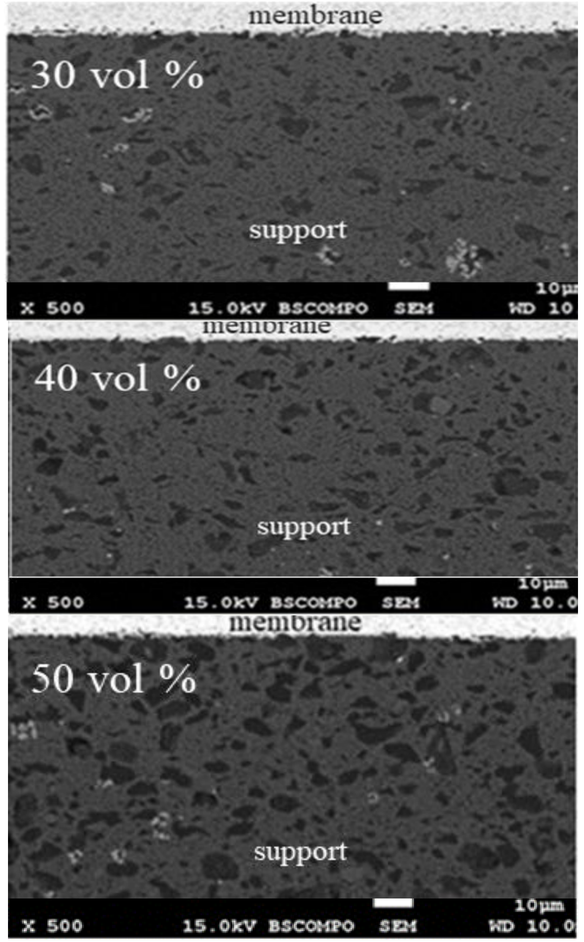
Tailor the **membrane thickness** by controlling the casting thickness

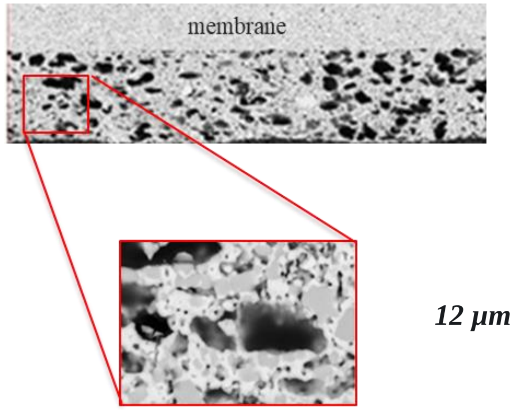
- Dense and thin membrane to maximize the oxygen permeability



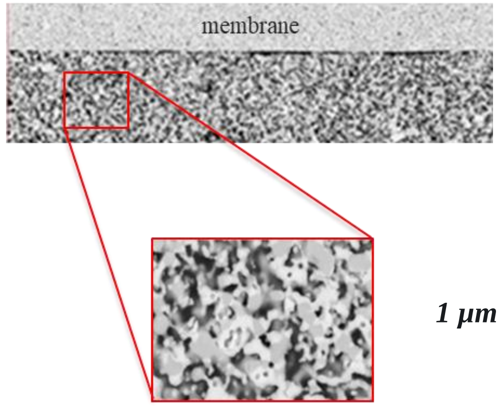

Tailor **amount of porosity** and the **size/distribution of pores** in the **support** by controlling the amount and particle size of fugitive phase used in tape cast suspension

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




*12 µm fugitive phase*




*1 µm fugitive phase*

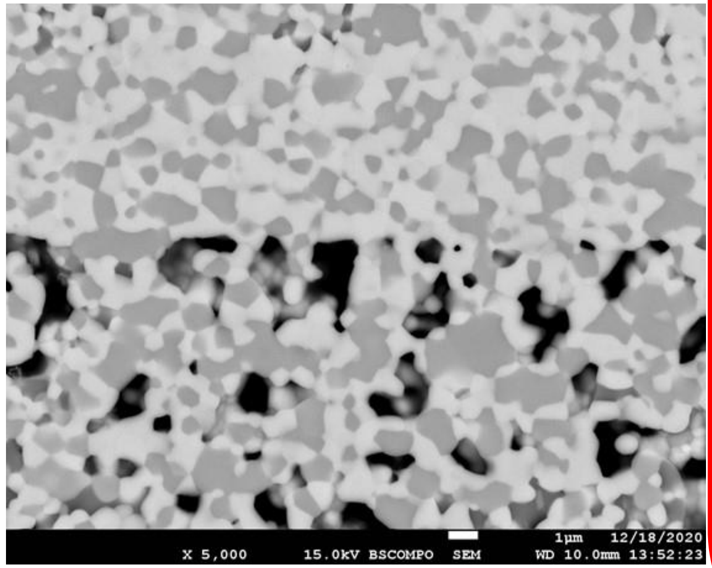
- **Limited interaction during co-sintering**
- **Match sintering shrinkage**

# *Densification of Membrane During Co-firing*

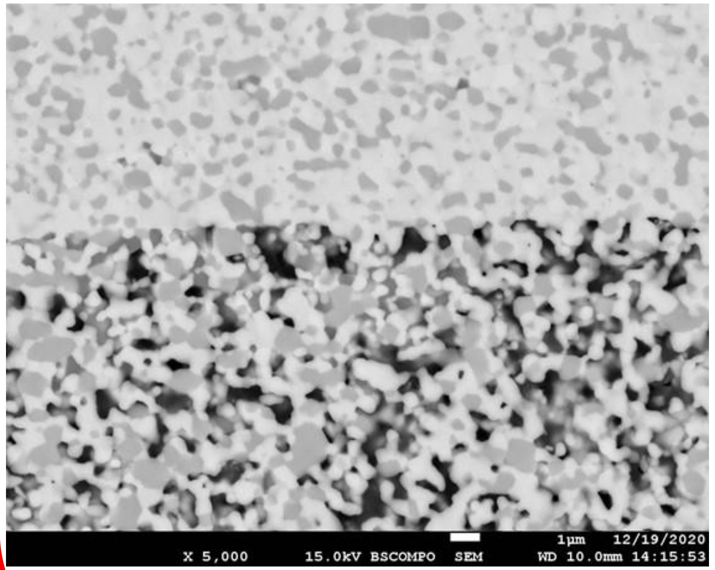
*Gd doped $CeO_2$ w/ $La_{0.75}Sr_{0.2}MnO_3$*

**Sintering Temperature**

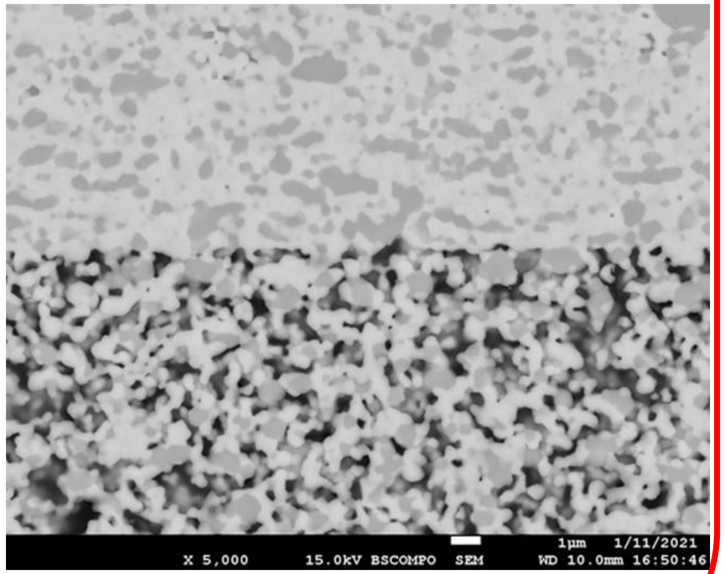
**1375°C**



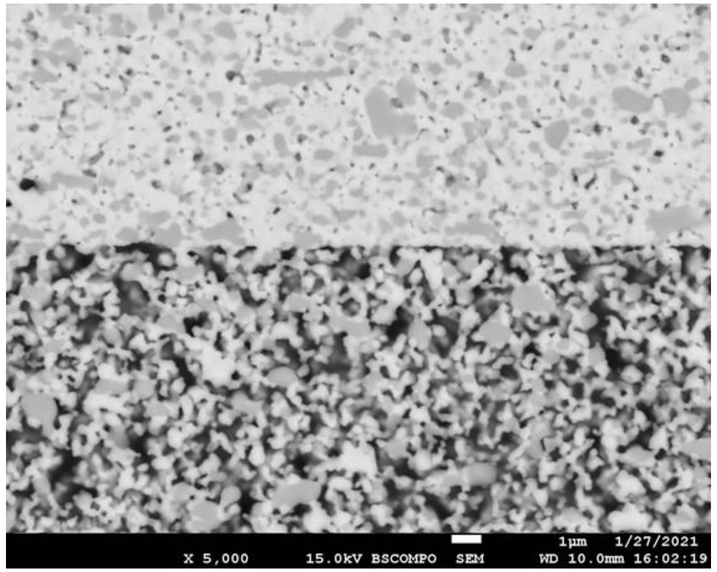

**1325°C**




**1300°C**




**1275°C**




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

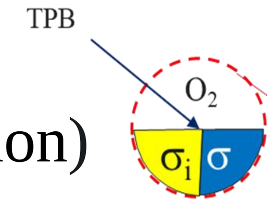
- Dense Membrane
- Finer grains
- Increased number of TPBs
- Less interaction/ diffusion of ions

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

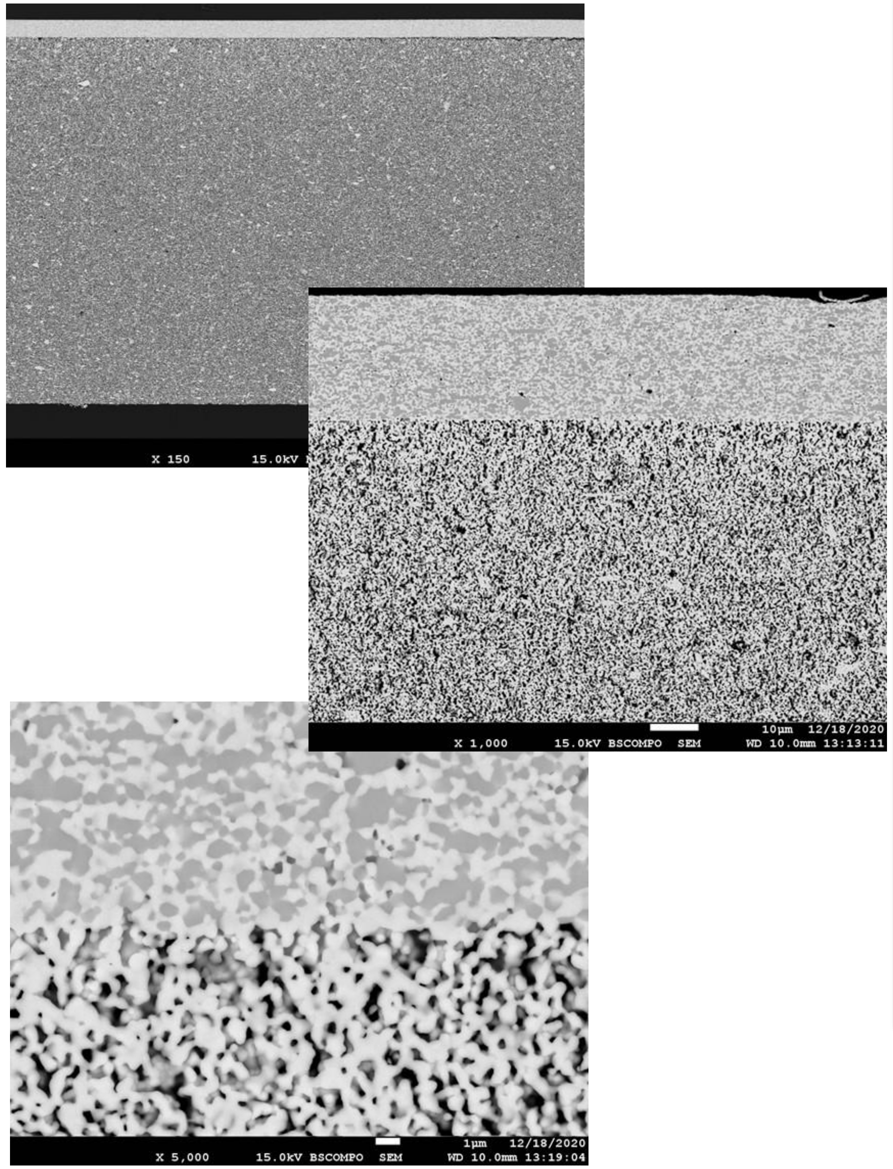
# *Bilayer Microstructures*

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

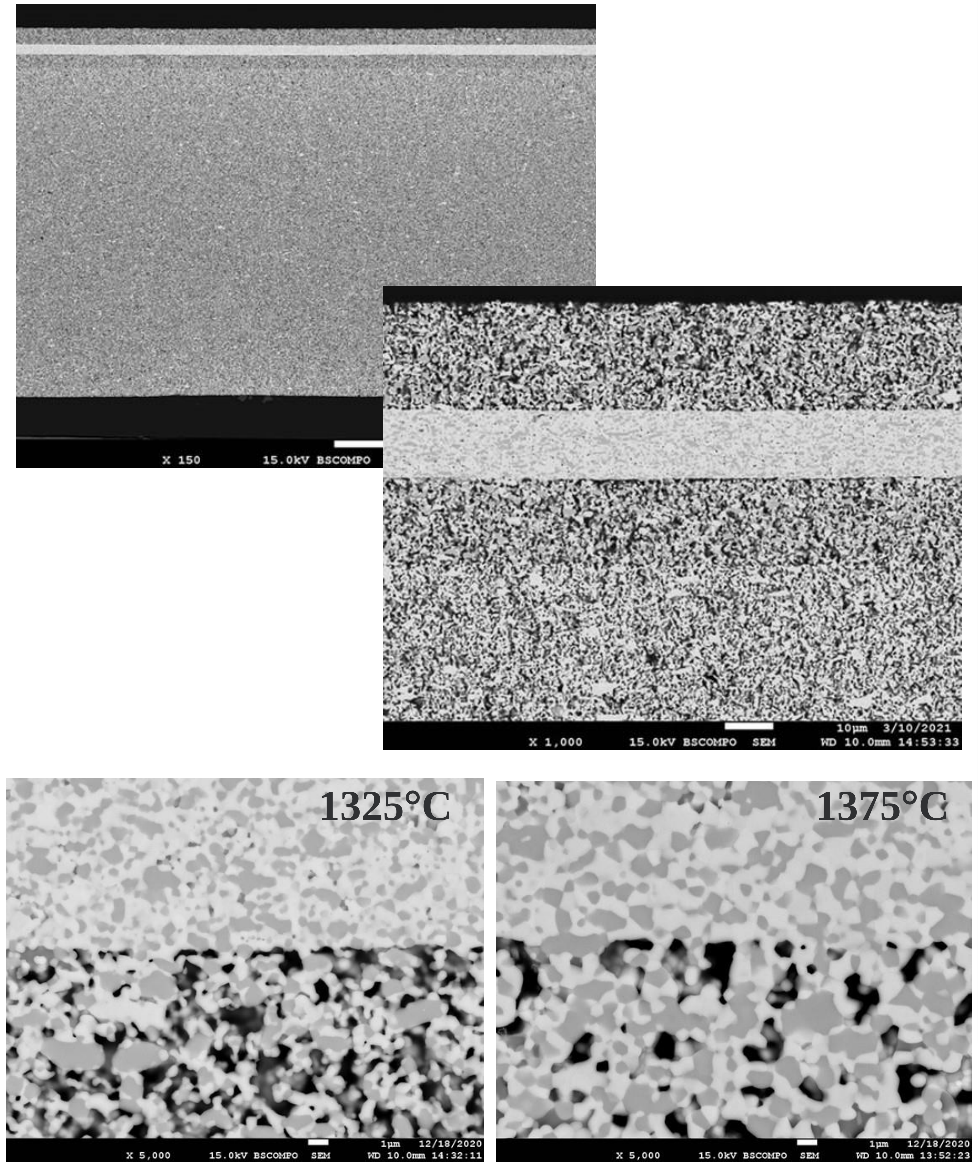
➡ Expanded reaction area improves reaction kinetics ($O_2$ dissociation/recombination)



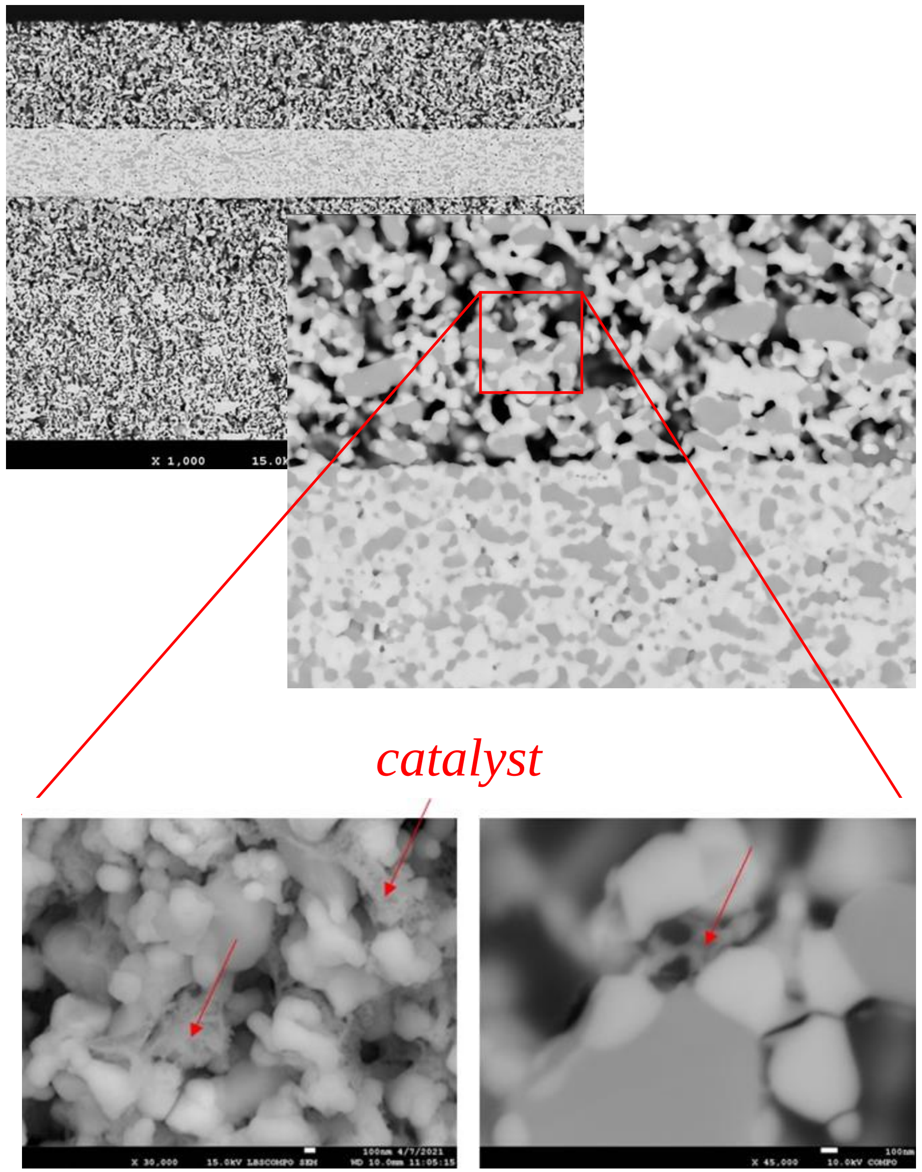

*Planar Membrane*



*w/ Barrier Layers*



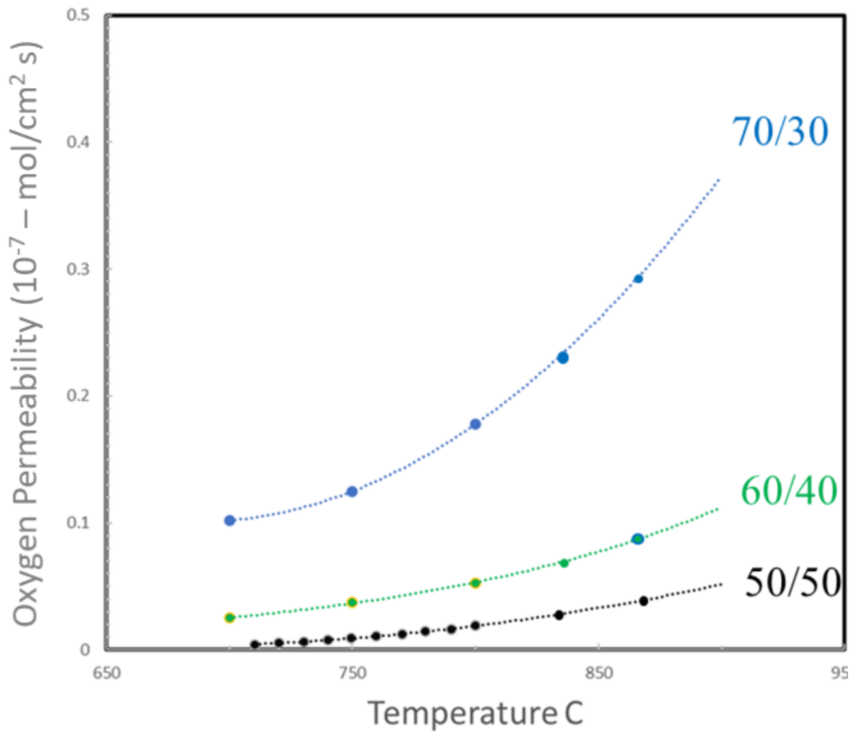

*w/ Barrier Layers & Catalyst*



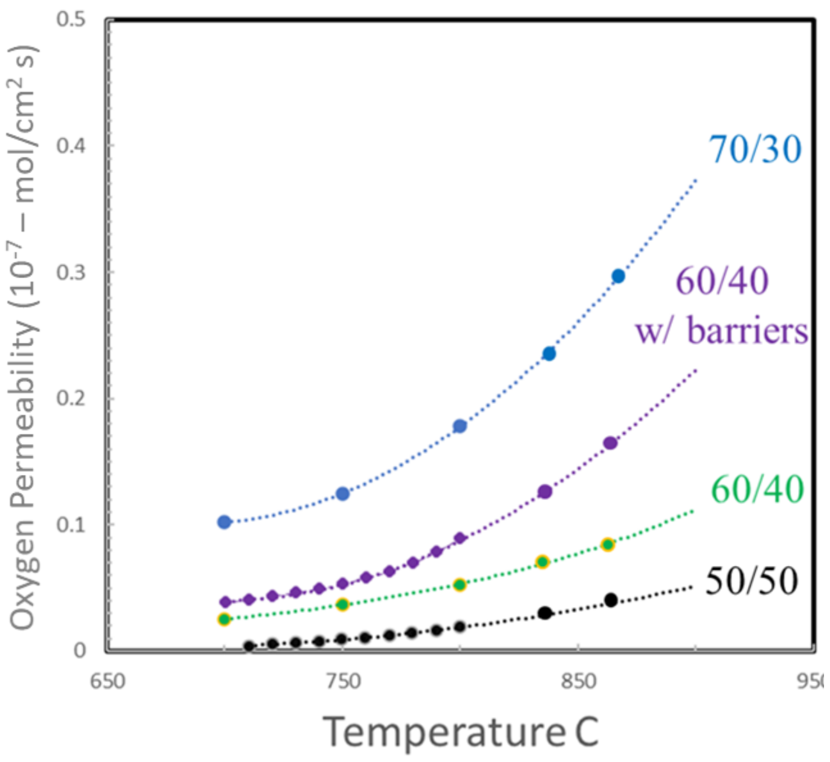
# *Bilayer Permeability*

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

### *Planar Membrane*

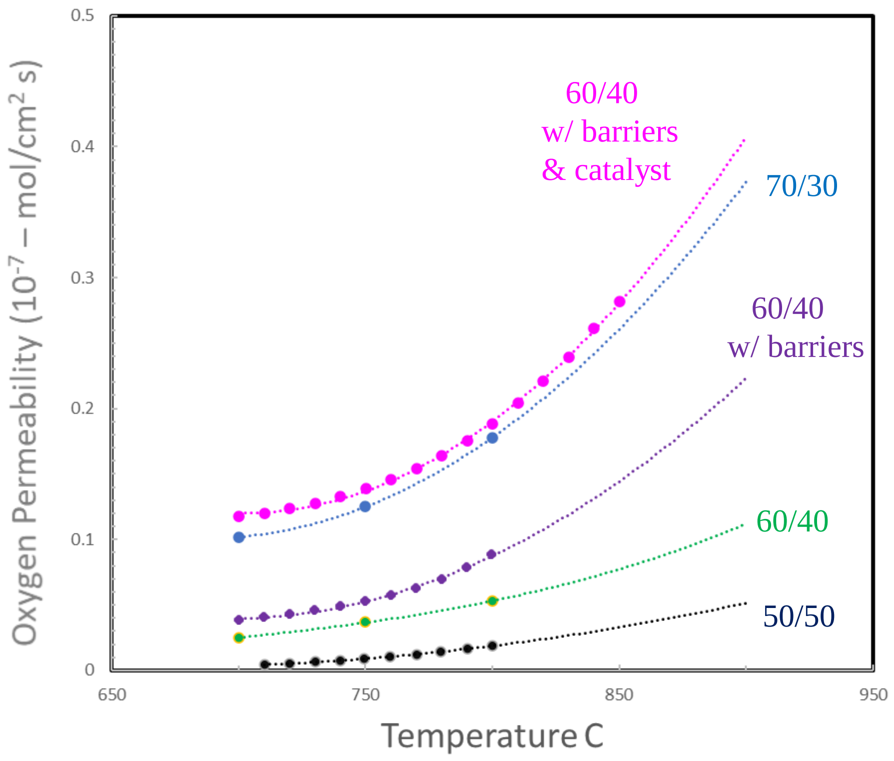



### *w/ Barrier Layers*



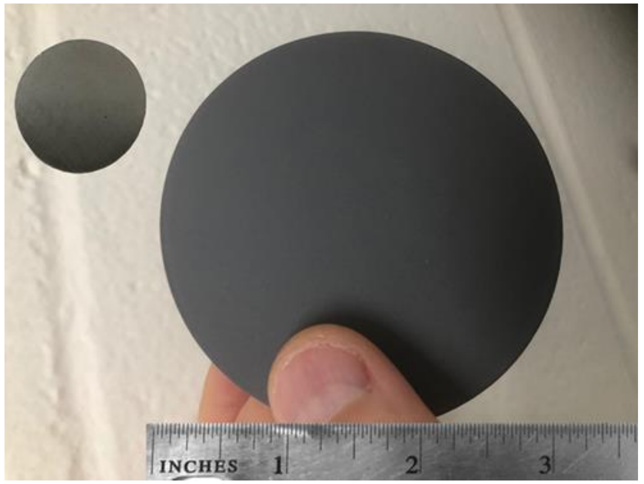

### *w/ Barrier Layers & Catalyst*

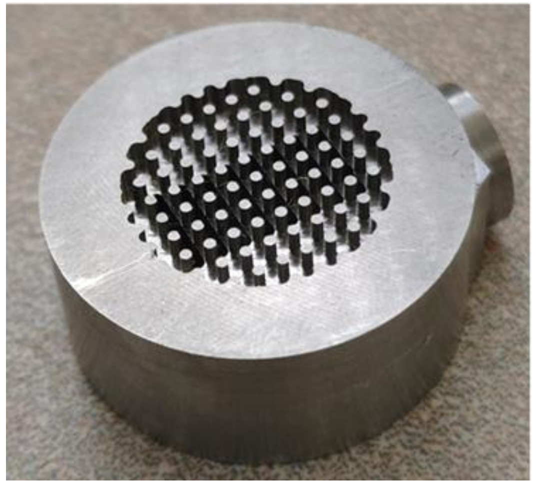
**Catalyst is $CeO_2$**

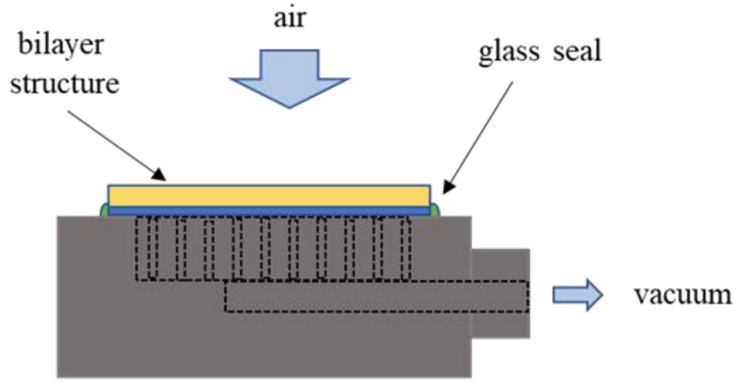


# Bilayer Scale Up and Membrane Composition

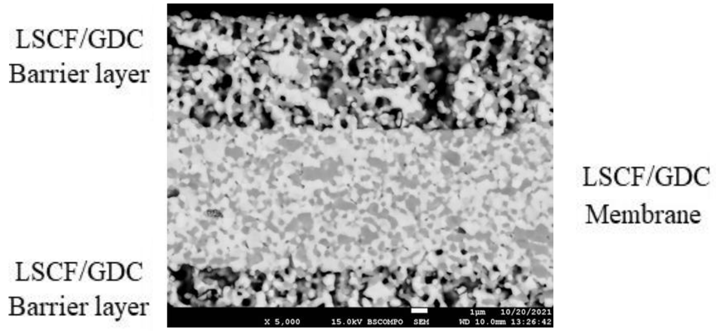
- Fabricated 3” diameter bilayers that are flat and crack free capable of measuring the $O_2$ permeability






- Membrane – additional 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
  - Under development




- Sintered at 1150°C
- Porous barrier layer, dense membrane

→ $O_2$ permeability test in progress

# Catalyst Nanoparticle Infiltration

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*Catalyst Composition*

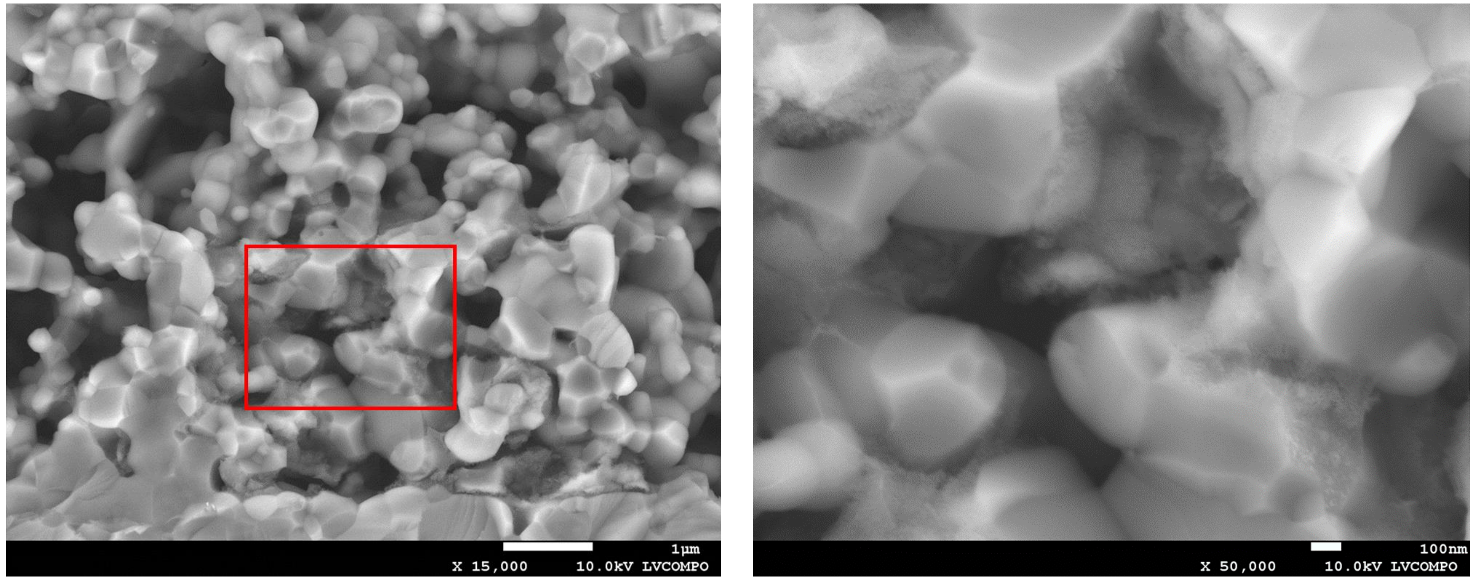
- Doped $CeO_2$
- $LaCoO_3$ based

*Catalyst Optimization*

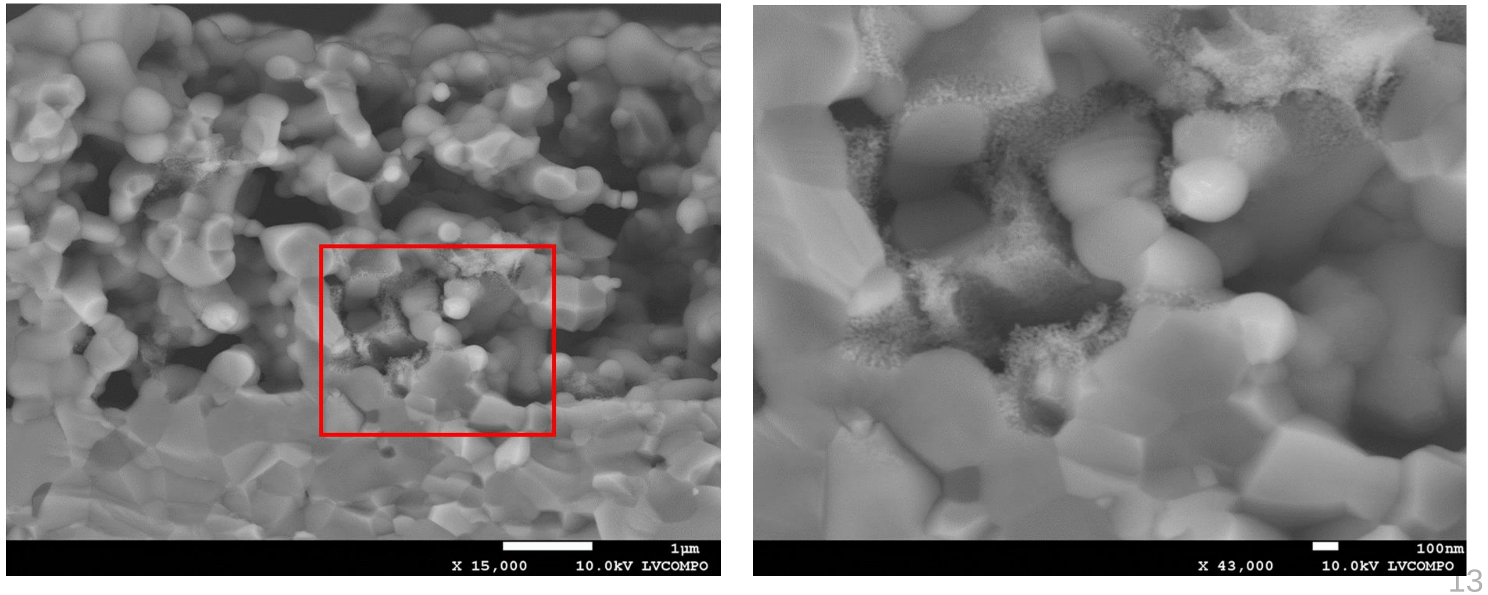
- Concentration and size/distribution of particles
- Coverage
- Deposition technique
- Heat treatment temperature
- Fabrication Temp
- LSM and LSCF based

***Catalyst ↔ $O_2$ Permeability Relations***

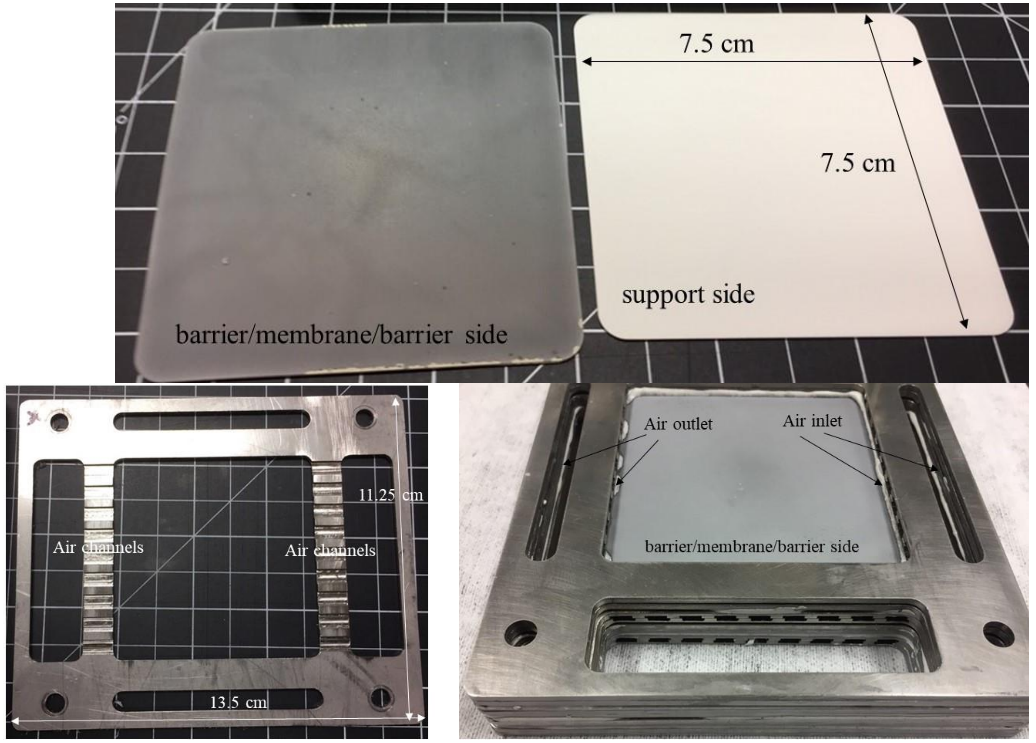
*$CeO_2$ – lower heat treatment temp*



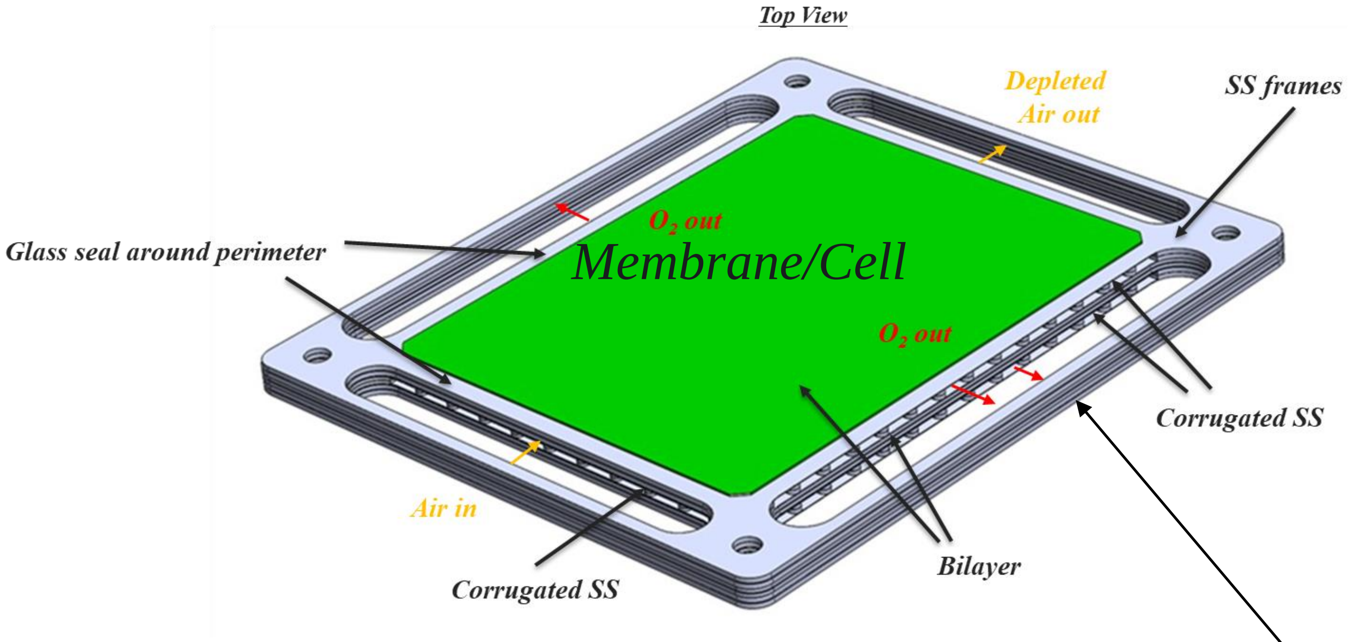

*$CeO_2$ – higher heat treatment temp*

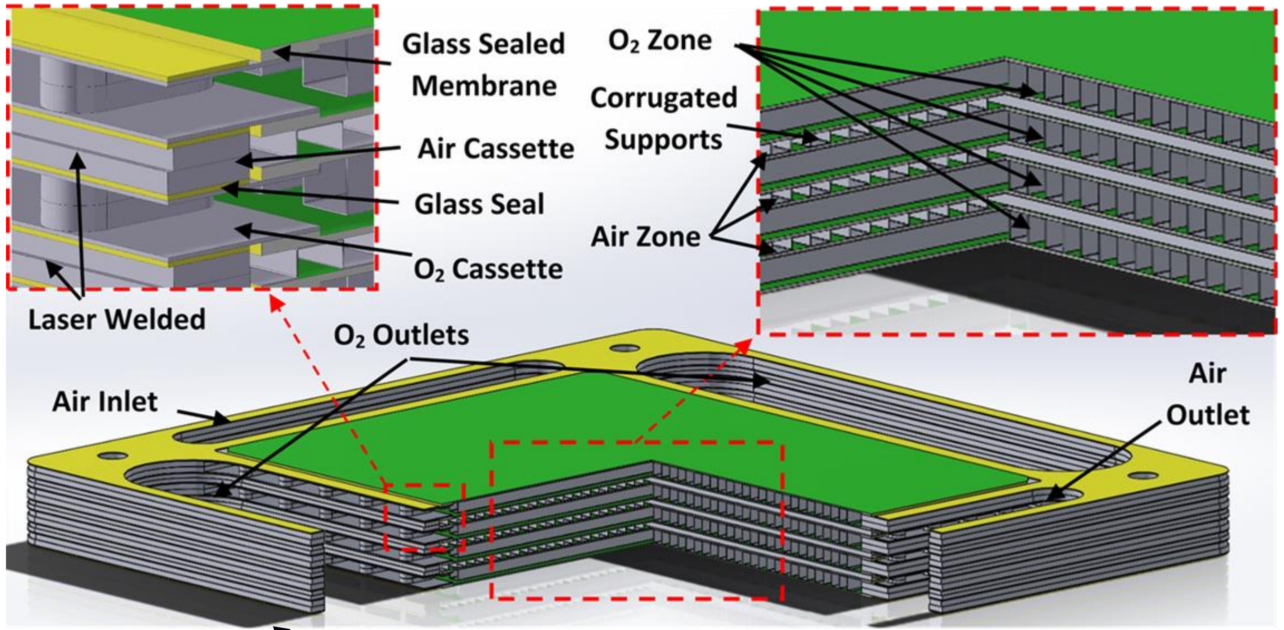


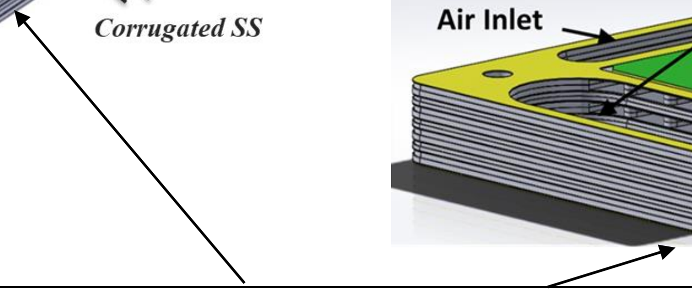
# 3 Cell Demonstration Stack Build




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



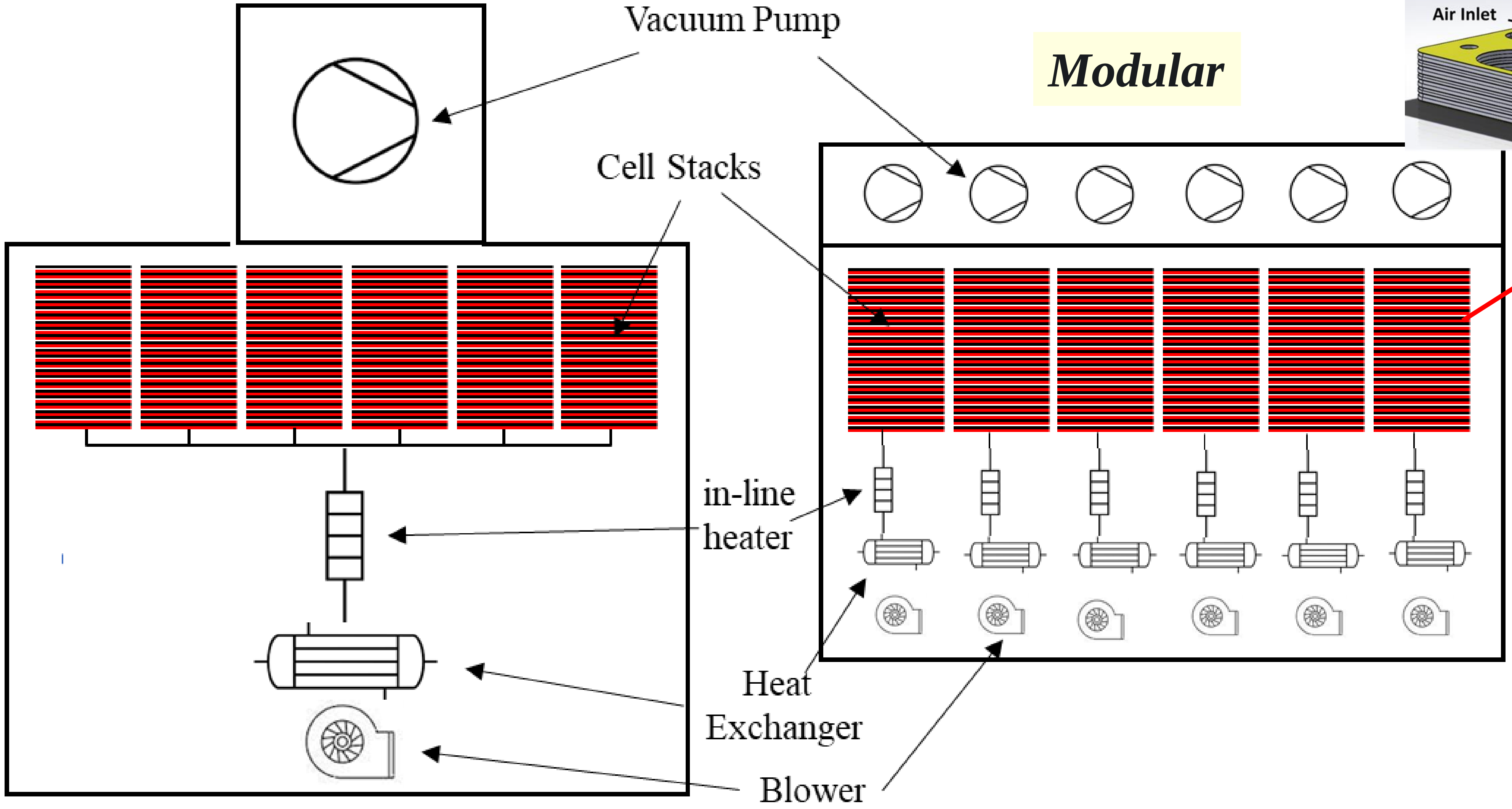
*CFD Optimization on Stack Design*

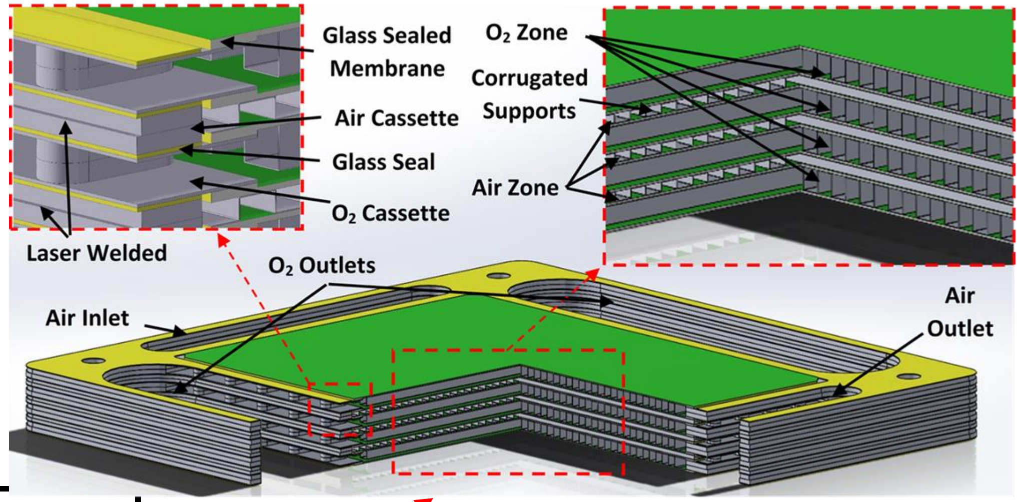
- Higher $O_2$ permeability
- Efficient operation of pumps
- Reduced stress on gaskets and membrane

# System Design

## Single

## Modular



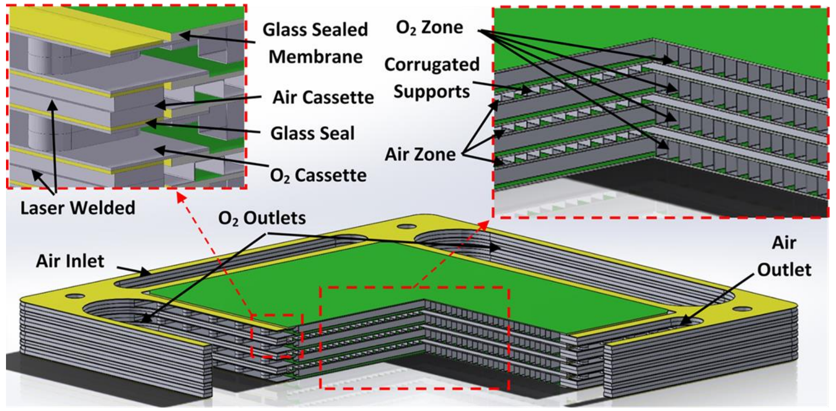

- Simple design
- Equipment limitations
- Single point for system failure
- System downtime

- Improved reliability
- Higher capital costs?
- Equipment options

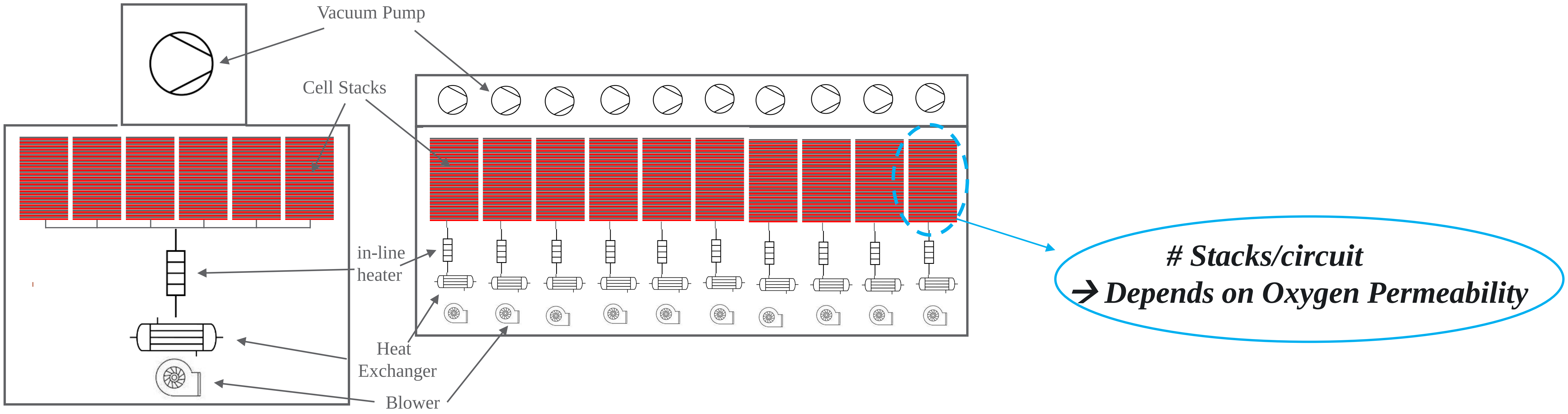
# Techno Economic Analysis

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cost to manufacture stacks (depend on permeability) | | | | | | | | **100 cm2** | | | **400 cm2** |
| | | | | | | | | | | material + labor | |
| • Cassette | 60/40 | | | | 8ft | 8ft | | cell dimensions | | 100 cells | |
| Membrane GDC w/ LSM/LSCF (5 microns) | | | $/kg | density | 50 g batch | | $/cell | 4" x 4" fired (100cm2) | | | (400 cm2) |
| | Material costs | GDC | 1200 | 6 | 30 g | | 0.75 | | | | |
| | | LSM | 1200 | 6 | 20 g | | 0.5 | | | | |
| | | LSCF | 1200 | 6 | | | | | | | |
| | | solvent/bind/etc | 65 | | 25 | | 0.033854 | | | | |
| | | | | | | 48 cells | 1.283854 | 1.283854167 | | 128.3854167 | 513.5416667 |
| | Labor | 96" length | batching, mixing, and casting | | | | 3hr @$30/hr | | | 90 | 135 |
| | | | | | | | | | | | |
| | 60/40 | | | | 32ft | 32ft | | cell dimensions | | | |
| Barrier layer (X2) GDC w/ LSM/LSCF (5 microns) | | | $/kg | density | 50 g batch | | $/cell | 4" x 4" fired (100cm2) | | | |
| | | GDC | 1200 | 6 | 12 g | | 0.1875 | | | | |
| | | LSM | 1200 | 6 | 8 g | | 0.125 | | | | |
| | | LSCF | 1200 | 6 | | | | | | | |
| | | solvent/bind/etc | 65 | | 25 | | 0.008464 | | | | |
| | | carbon | 200 | | 30 | | 0.03125 | | | | |
| | | | | | | 192 cells | 0.320964 | 0.641927083 | | 64.19270833 | 256.7708333 |
| | Labor | 96" length | batching, mixing, and casting | | | | 4hr @$30/hr | | | 120 | 180 |
| | | | | | | | | | | | |
| | | | $/kg | | 16 ft (15 mil) | | | | | | |
| support MgO | | $17.40/lb (450 g) | | | | $/24 cells | $/cell | 4" x 4" fired (100cm2) | | | |
| | | MgO | 38 | | 200g | 7.6 | 0.316667 | 0.316666667 | | 31.66666667 | 126.6666667 |
| | Labor | 96" length | batching, mixing, and casting | | | | 3hr @$30/hr | | | 90 | 135 |
| | | | | | | | | | | | |
| | | | $/kg | amount | $/cell | | | | | | |
| glass seal | | glass | 100 | 1 g/cell | 0.1 | | | | | $114.14 | $456.54 |
| | | solvent/bind/etc | 65 | 3 g/cell | 0.195 | | | | | 19.5 | 78 |
| | Labor | | | | | | 1hr @$30/hr | | | 30 | 45 |
| | | | | | | | | | | | |
| | | | | 100 cells | | | | | | | |
| Laminating, laser cut and sinter | | | laminate | laser cut | sinter | | | 4" x 4" fired (100cm2) | | | |
| | | BL/mem/BL/support | 1 hr | 1 hr | 1 hr | | 1hr @$30/hr | | | 90 | 135 |
| | | | 250 | 250 | 1500 W | | | | | | |
| | $0.1 /kWh | electricity costs ($/hr) | 2.5 | 2.5 | 15 | | | | | 20 | 30 |
| | | | | | | | | | | | |
| assembly labor - glass sealing | | | | 100 cells | | | | 4" x 4" fired (100cm2) | | | |
| | | | robotic dispenser | | 0.5hr | 100 W | | | | | |
| | $0.1 /kWh | electricity costs ($/hr) | | | 1 | | | | | 1 | 1.5 |
| | | | | | | | | | | | |
| assembly labor - welding | | | | 100 cells | | | | 4" x 4" fired (100cm2) | | | |
| | | | fully automated | | | | | | | | |
| | | | 3000W | | | | | | | | |
| | $0.1 /kWh | electricity costs ($/hr) | 30 | | | | | | | 30 | 45 |
| | | | | | | | | | | | |
| Picture frame (430 SS) + aluminization | | | | 100 cells | | | | 4" x 4" fired (100cm2) | | | |
| | | purchase roll 400 series w/ Al2O3 | | | $50,000/x cells | | | | | 100 | 400 |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| Cassette | | | | 100 cells | | | | 4" x 4" fired (100cm2) | | | |
| | | | fully automated | | | | | | | | |
| | | | 3000W | | | | | | | | |
| | $0.1 /kWh | electricity costs ($/hr) | 30 | | | | | | | 30 | 45 |
| | | | | | | | | | | | |
| Material & labor costs - 100 cell stack | | | | | | | | | | 958.88 | 2583.02 |
| | | | | | | | | | | | |
| equipment costs including depriciation | | | | | | | | | | 57.14285714 | 57.14285714 |
| | | | | | | | | | | | |
| | | | | | | | | | total | 1219.228259 | 3168.198752 |
| Yield (80 %) | | | | | | | | | | | |
| | | | | | | | | | | 100 cell stack | 100 cell stack |
| system cost - 10 stacks (building stack including equipment) | | | | | | | | | | 100 cm2 | 400 cm2 |
| | | | | | | | | | | 1219 | 3168 |
| | | | | | | | | | | | |
| | | | | | | | | | | ~1200 | ~3200 |

***Cost to manufacture 100 cell stack at different cell dimensions***



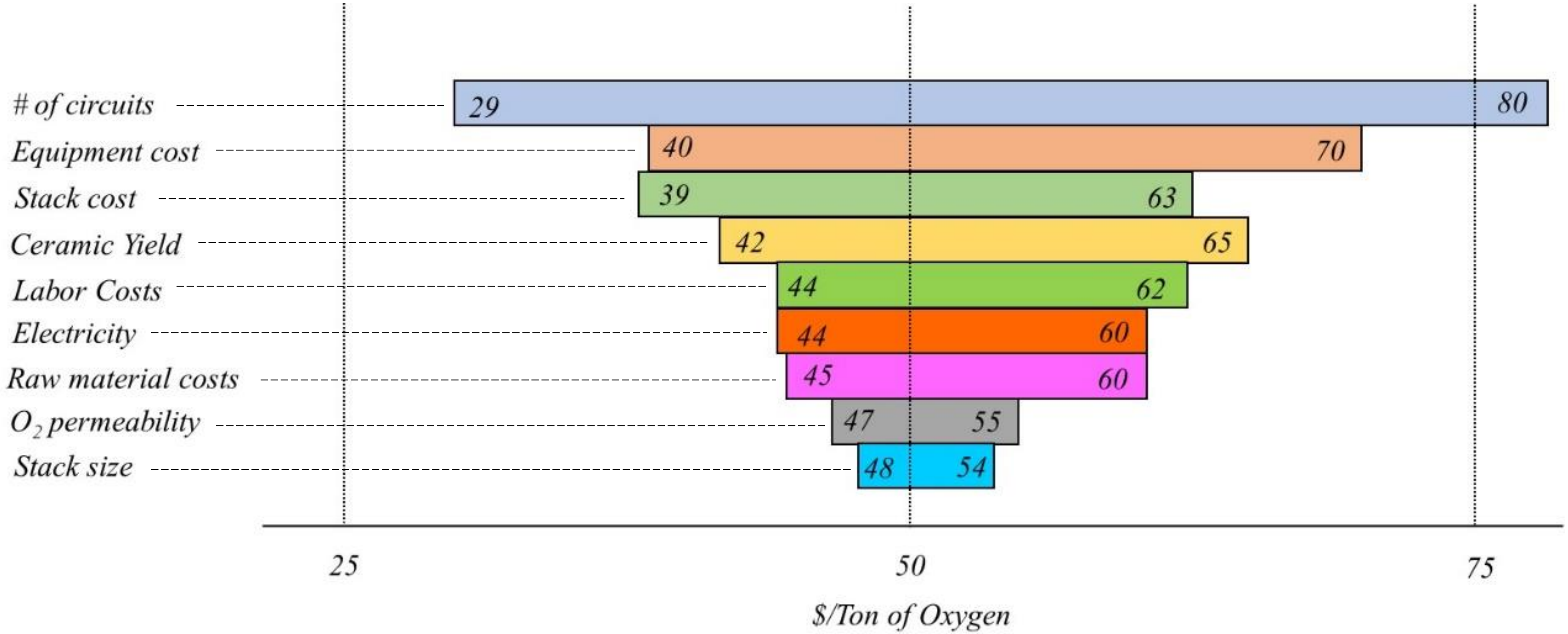
# Techno Economic Analysis




**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.

# Next Steps – Year 4

| Fiscal Year | ID | Description | Date |
|---|---|---|---|
| 4 | M1 | Submit Tech Maturation Plan (TMP). | 6/15/2023 |
| 4 | M2 | Perform single cell tests on a 50 $cm^2$ cell with aluminized frames and glass seals. | 7/31/2023 |
| 4 | M3 | Perform cost analysis based on optimized oxygen permeability. | 10/31/2023 |
| 4 | M4 | Construct system capable of testing cells and stacks with areas of 50 $cm^2$ to 400 $cm^2$. | 10/31/2023 |
| 4 | M5 | Demonstrate ability to sinter larger area bilayers, i.e. 200 and 400 $cm^2$. | 1/31/2024 |
| 4 | M6 | Demonstrate a 5-10 cell stack based on either LSM or LSCF membranes using 50 $cm^2$ cells with aluminized frames and glass seals. | 1/31/2024 |

# 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
- The initial techno economic analysis shows that the cost is competitive with other available $O_2$ production technologies.

# Acknowledgements

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# 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.

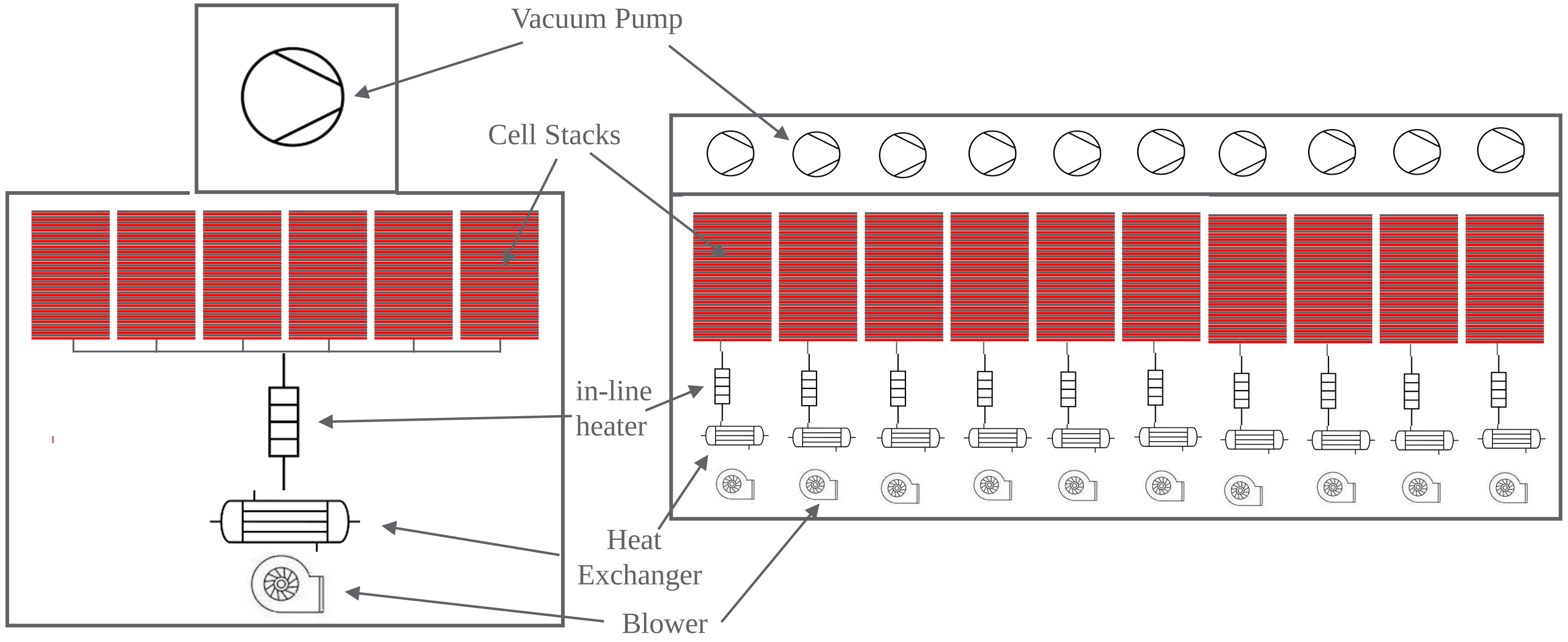
- ***What performance metrics are most important for technical and economic success (at component and system levels)?***
- ***Identify R&D gaps and critical components that are lagging in maturity?***

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?***

<u>Techno Economic Analysis/System Cost</u>

- 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 ($mol/cm^2 \cdot s$)** | $4.0 \times 10^{-8}$ | $1.2 \times 10^{-7}$ | $4.0 \times 10^{-7}$ |
| **# 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