Pressure Driven Oxygen Separation

FWP-73130

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Richland, WA

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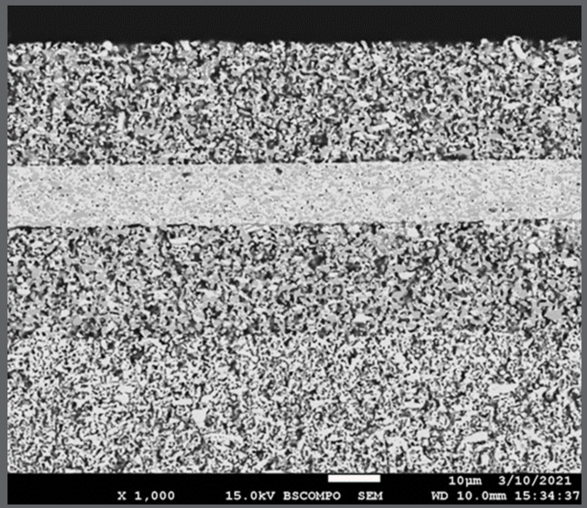
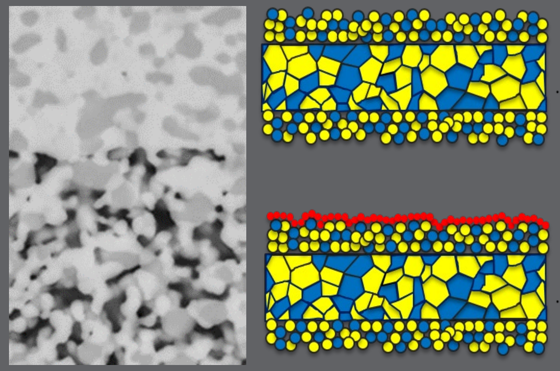
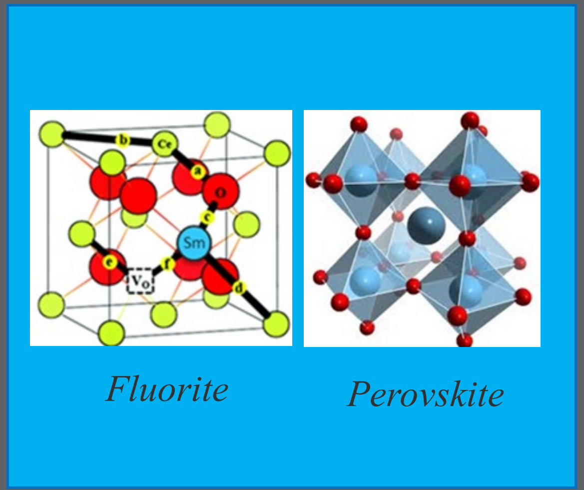
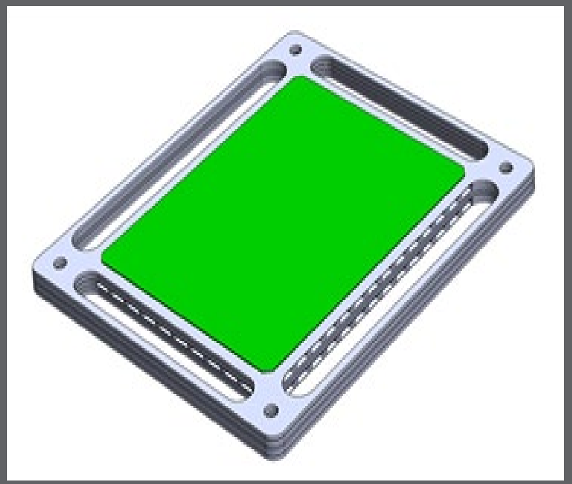
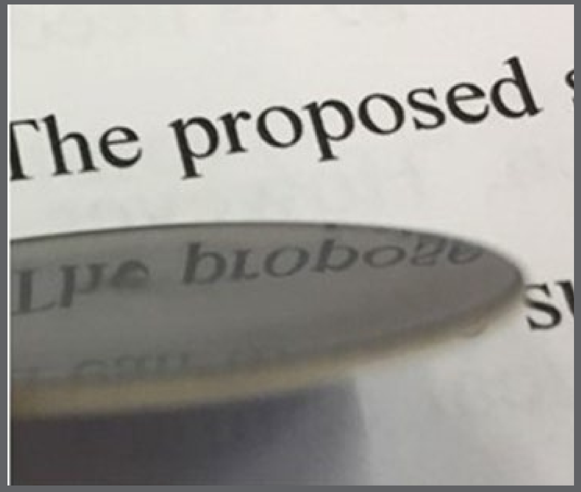
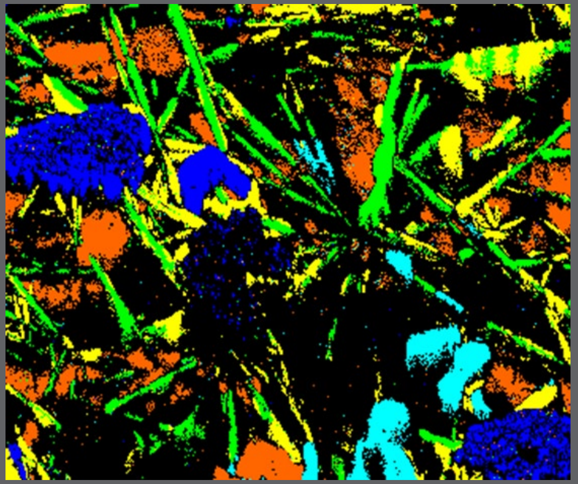












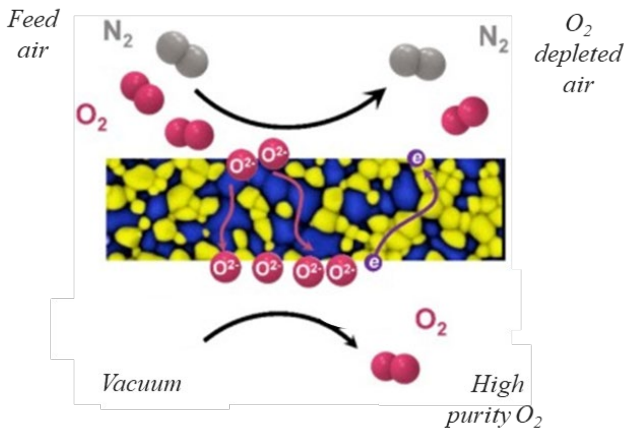
Pressure Driven Oxygen Separation

Outline

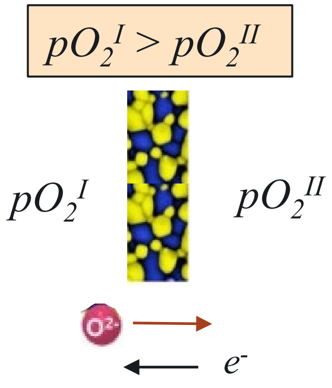
- Project Description and Objectives
- Project Background
- Critical Factors for Project Success
- Project Update
- Next Steps

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

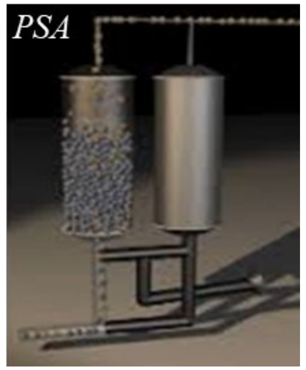


- Mixed conducting two phase material capable of separating oxygen at 700-800°C.
- Planar membrane/support structure
- Utilize the difference in oxygen partial pressure across the membrane to drive oxygen from air, <u>no electrical energy needed for oxygen separation</u>



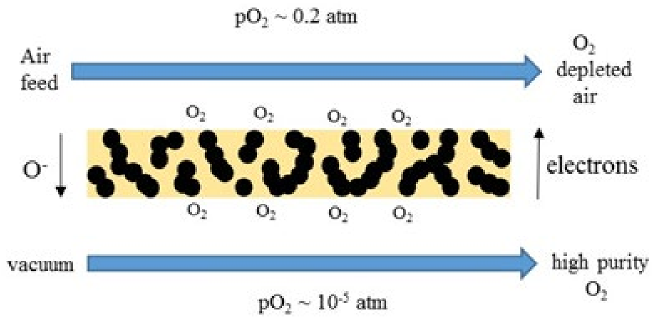
Oxygen Separation Techniques

- **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)

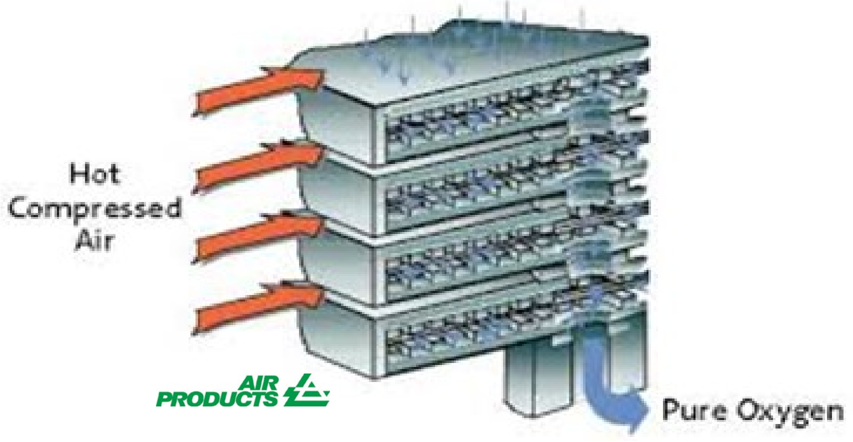


Proposed Ceramic Membrane Technology

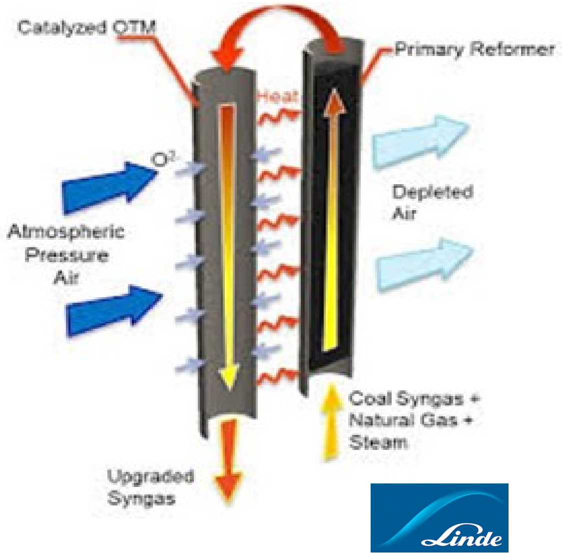
<u>Planar</u> vs Tubular Design

- 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

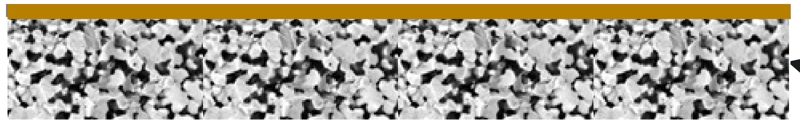


Tubular Design



Proposed Ceramic Membrane Technology

Bilayer Structure



Thin composite membrane
(~ 10 µm)

Porous support (~ 0.5-1mm)

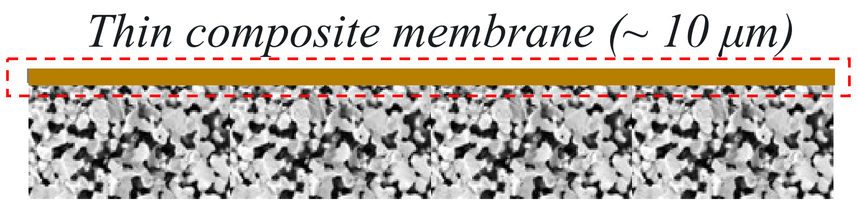
Composite membrane
- Dense
- High σ_i and σ_e
- Compatible with glass seal
- Inexpensive fabrication
- No electrodes

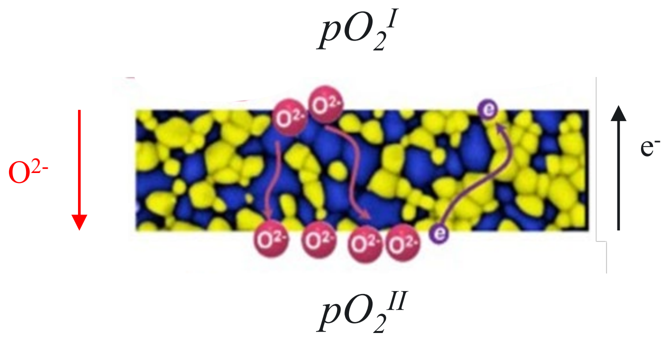
Porous Support
- ~ 50% dense
- TEC match to membrane
- Mechanical integrity
- Co-fired w/ membrane

Design will leverage SOFC stacks developed at PNNL

Proposed Ceramic Membrane Technology

Composite Membrane





- <u>Two phase composite</u> (σ_i & σ_e)
- Similar TEC
- <u>Limited interaction during firing</u>
- High σ_i phase
- Sufficient σ_e phase
- Compatible with glass seal

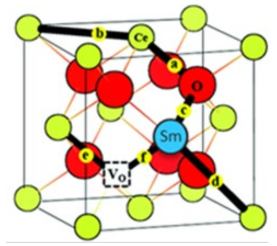
Material Selection

Ionic Conductor

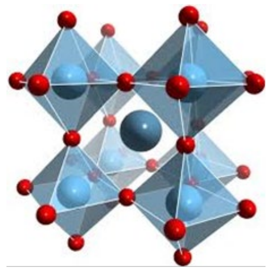
- Doped CeO_2

Electronic Conductor

- Doped $LaMnO_3$
- Doped $LaFeO_3$



Fluorite structure



Perovskite

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Proposed Ceramic Membrane Technology

Composite Membrane O_2 Permeability/Flux Calculations

	Case 1	Case 2	
Ionic conductivity:	0.0233	0.05	S/cm
P(O2)1:	0.2	0.2	atm
P(O2)2:	1.00E-04	1.00E-04	atm
Temp (°C):	700	800	
Temp (K):	973	1073	
Thickness (um):	10	10	
Thickness (cm):	0.001	0.001	
Flux (A/cm2):	3.71	8.78	
Flux (moles O2/cm2-s):	9.62E-06	2.28E-05	
Flux (grams O2/cm2-s):	3.08E-04	7.28E-04	
Flux (grams O2/cm2-h):	1.11	2.62	
Flux (grams O2/cm2-day):	26.59	62.93	
Flux (lbs O2/cm2-day):	5.86E-02	1.39E-01	
Pounds of oxygen required/day:	20000	20000	
Total cell area required (cm2):	341155.97	144162.40	
Cell area(cm2):	420	420	
# of cells required:	812.28	343.24	
Cells/stack:	100	100	
# of stacks required:	8.12	3.43	

Input Parameters

- σ_i
- pO_2^{I} and pO_2^{II}
- Temperature
- Membrane thickness
- lbs. of oxygen/day
- Cell area
- Cells/stack

Output Value

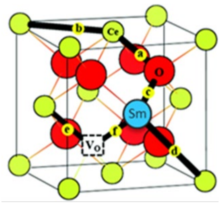
→ # of stacks required

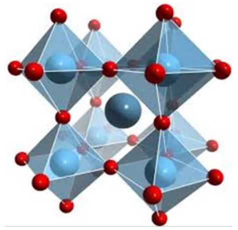
# of stacks appears to be very reasonable for a 10 ton/day modular ASU

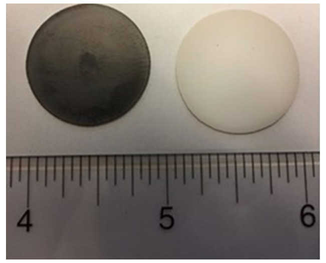
Proposed Ceramic Membrane Technology

Year 1

Membrane and Support Characterization
Bilayer Characterization
Membrane Oxygen Permeability

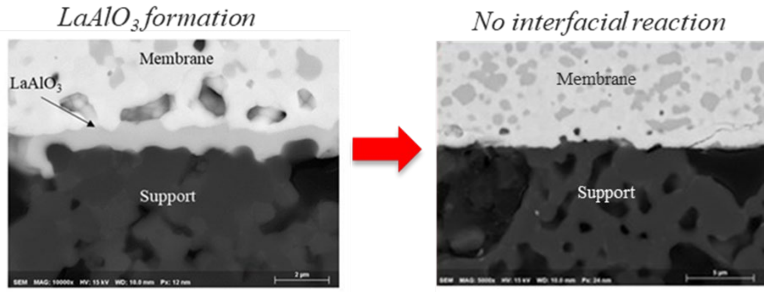

Fluorite structure

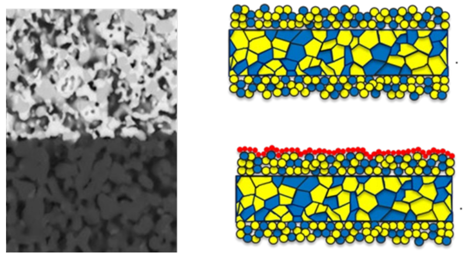

Perovskite



Year 2

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



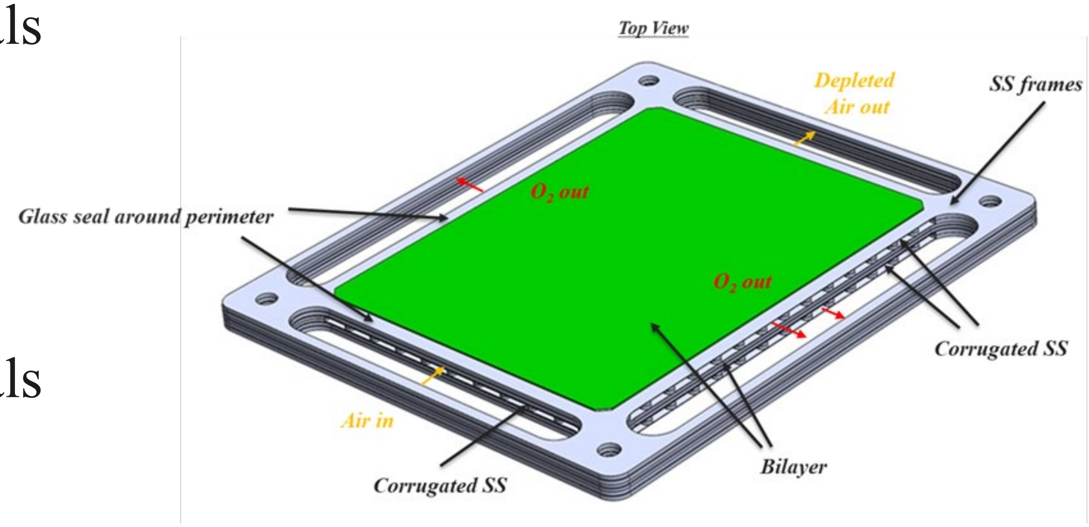


Year 3

Scale up 100 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
Cost Analysis



Proposed Ceramic Membrane Technology

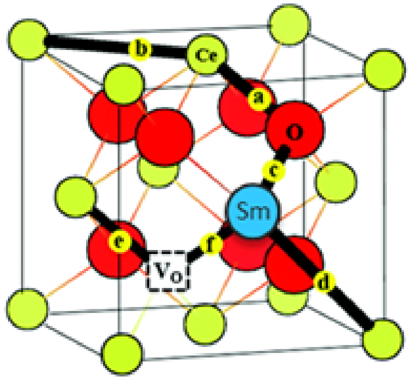
Factors Critical for Project Success

- **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**

Composite Membrane Characterization

Ionic Conductor

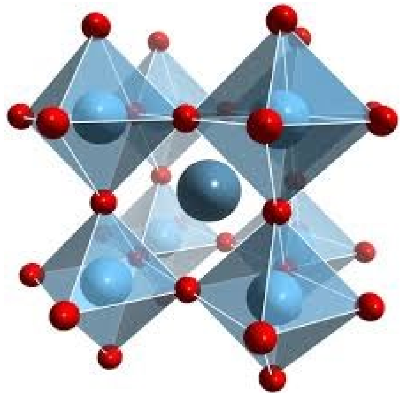
- Doped CeO_2
- $Sm_{Ce}' \rightarrow 2[V_O^{\circ\circ}]$



Fluorite structure

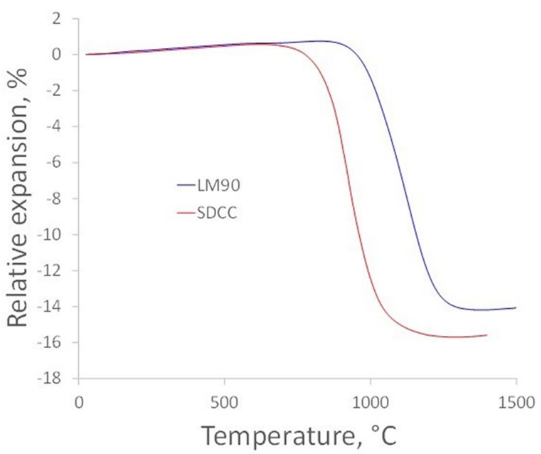
Electronic Conductor

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



Perovskite

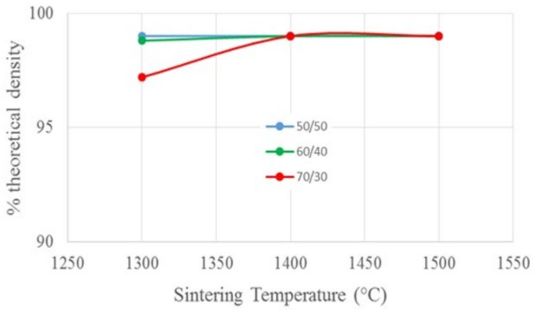
Sintering Shrinkage



- Minimize stress during sintering
- Particle size/surface area, composition

Sintered Density

	SDCC/LM90 (vol%)		
Sintering Temperature (°C)	50/50	60/40	70/30
1300	99+	98.8	97.2
1400	99+	99+	99+
1500	99+	99+	99+



- Membrane needs to be hermetically sealed

Composite Dilatometry

Material	α (x 10^{-6})
SDCC-LM90 50/50	11.11
SDCC-LM90 60/40	11.57
SDCC-LM90 70/30	12.02
GDC20-LSM20 50/50	11.83
GDC20-LSM20 60/40	11.89
GDC20-LSM20 70/30	12.09
SDCC-LSM20 60/40	11.93
SDCC-LSM20 70/30	11.91

- Typical values of α are ~ 12 x 10^{-6}/°C

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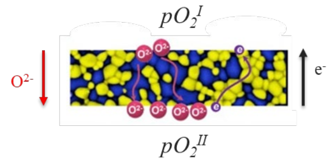
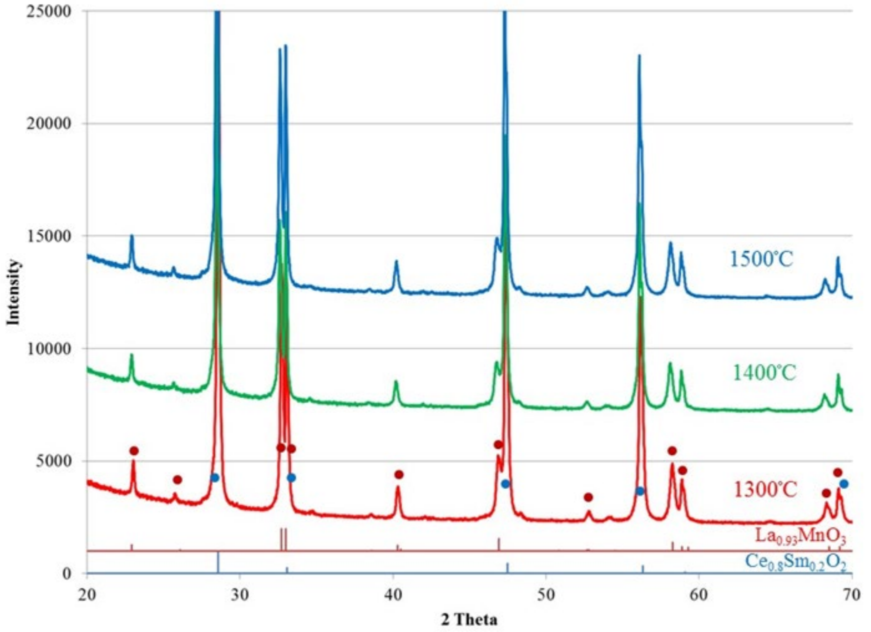
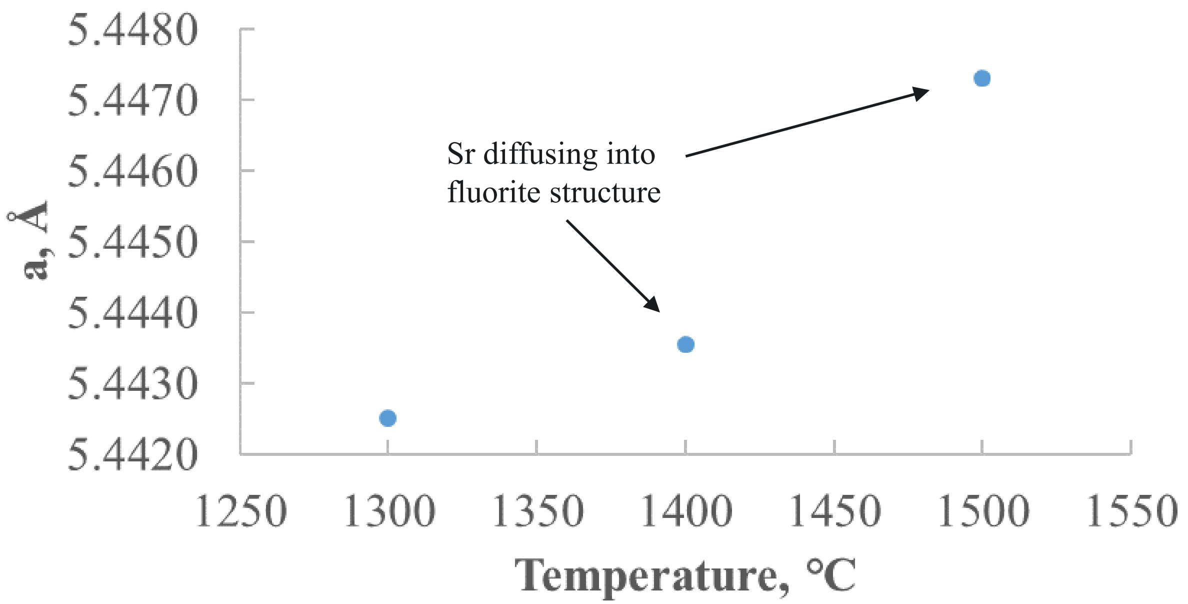
Composite Membrane Characterization



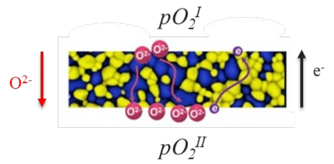
Interaction Studies



$Ce_{0.8}Sm_{0.2}O_{2-x}$ Lattice parameter

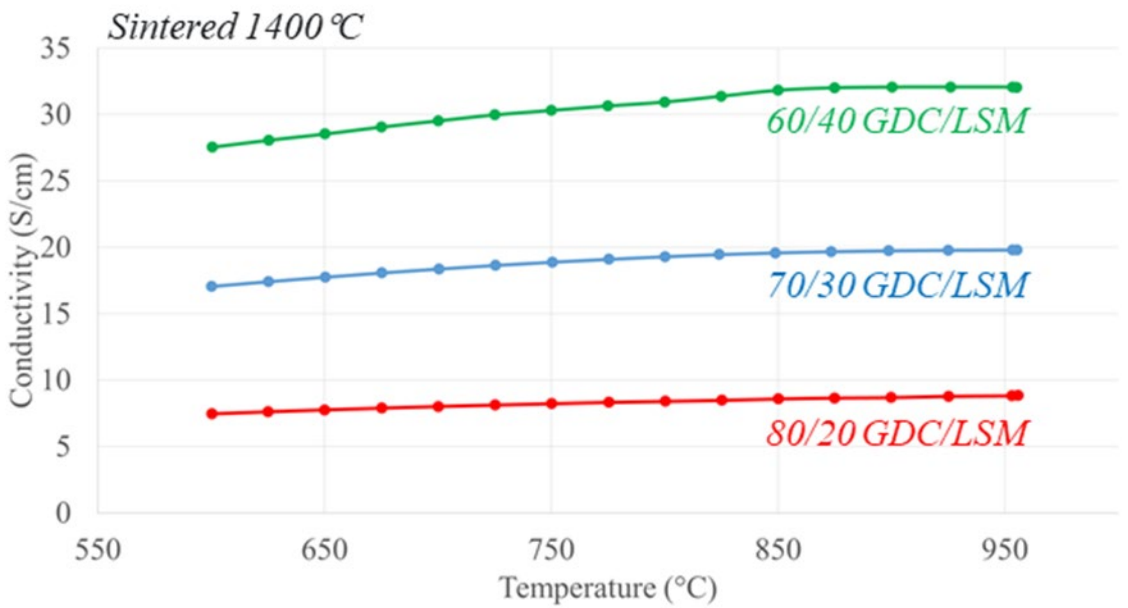


- Limited interaction, no 2nd phase formation
- Diffusion of Sr into ceria fluorite structure at $\geq$ 1400°C
- More formation of $LaMnO_3$ at higher temperatures
- ***<u>Sintering < 1400°C to maximize oxygen permeability</u>***



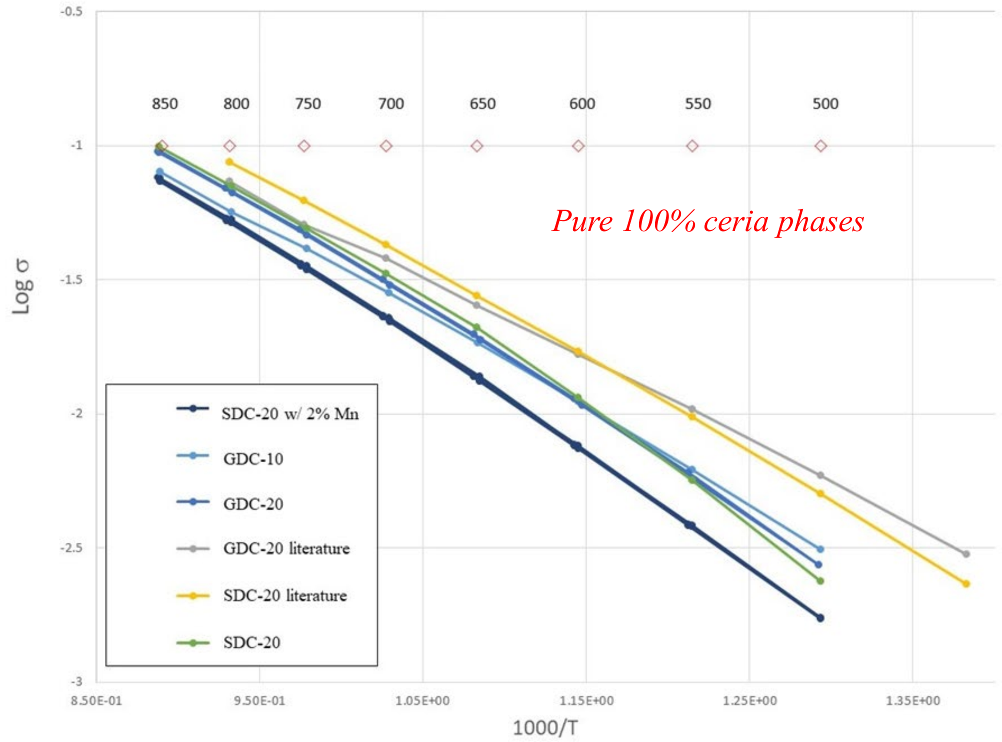
Composite Membrane Characterization

Electrical Conductivity



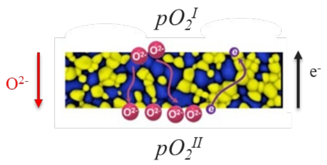
- Electrical conductivity (σ_e) controlled by perovskite phase
- $\sigma_e \sim$ 4 orders of magnitude greater than ionic conductivity (σ_i)
- Percolation in perovskite phase

Ionic Conductivity

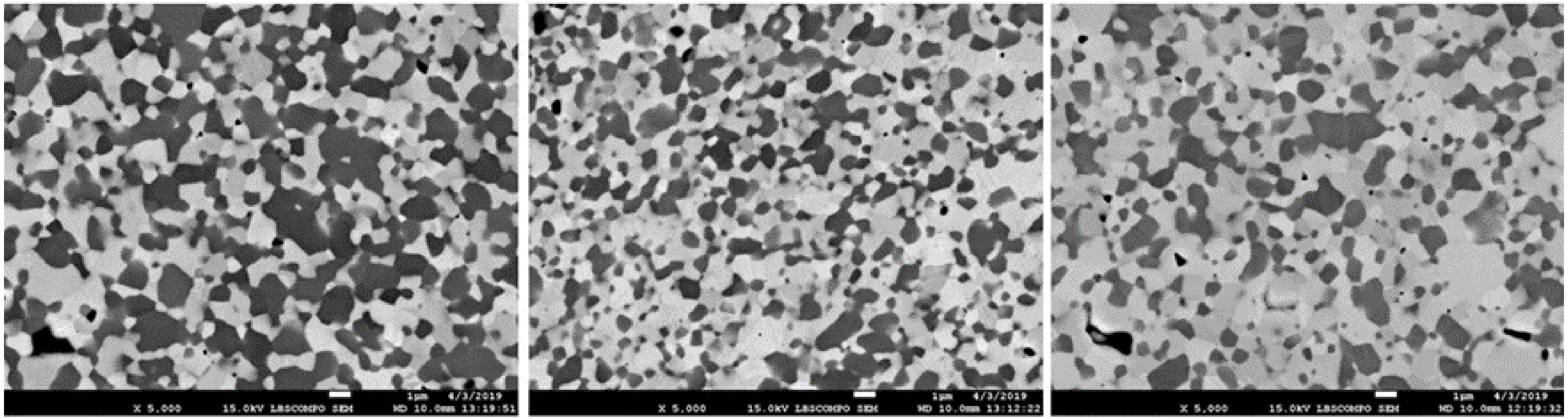


- $\sigma_i \sim$ 0.07 at 800°C and 0.03 at 700°C
- ~ 2/3 σ_i value used in composite calculations
- Percolation in both phases

Composite Membrane Characterization



50/50 60/40 70/30

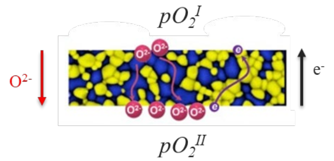


Sintered at 1300°C

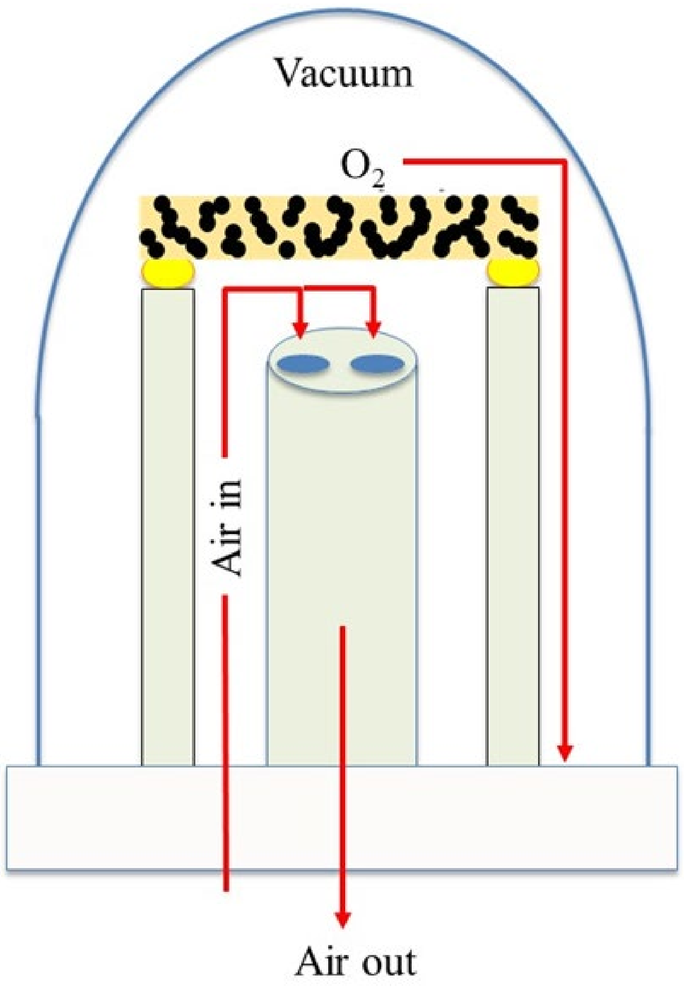
SDCC

LM90

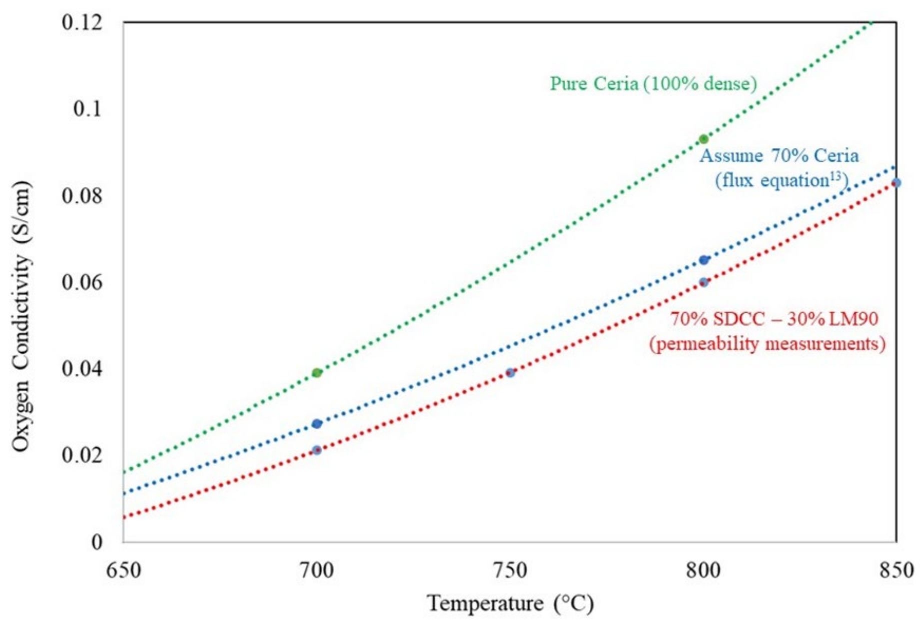
Composite Membrane Characterization



Permeability Measurements

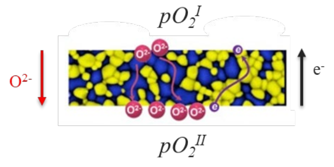


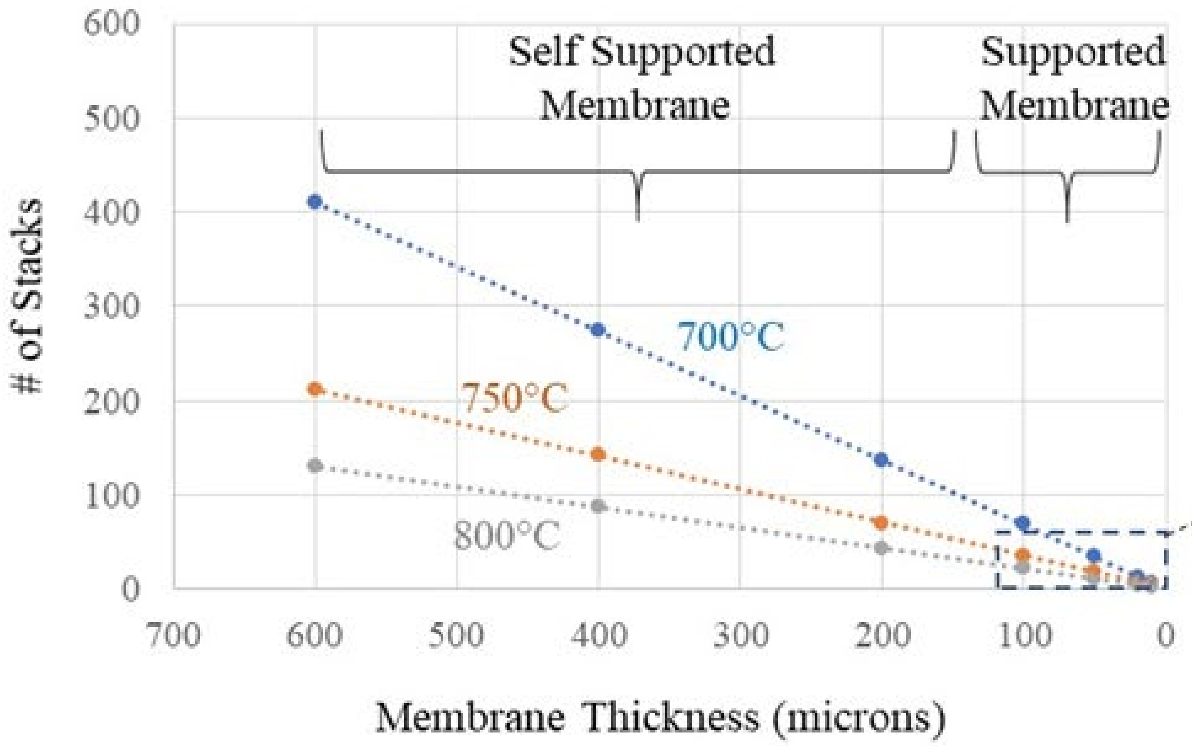
Self-supported composite membranes (~ 600 μm)

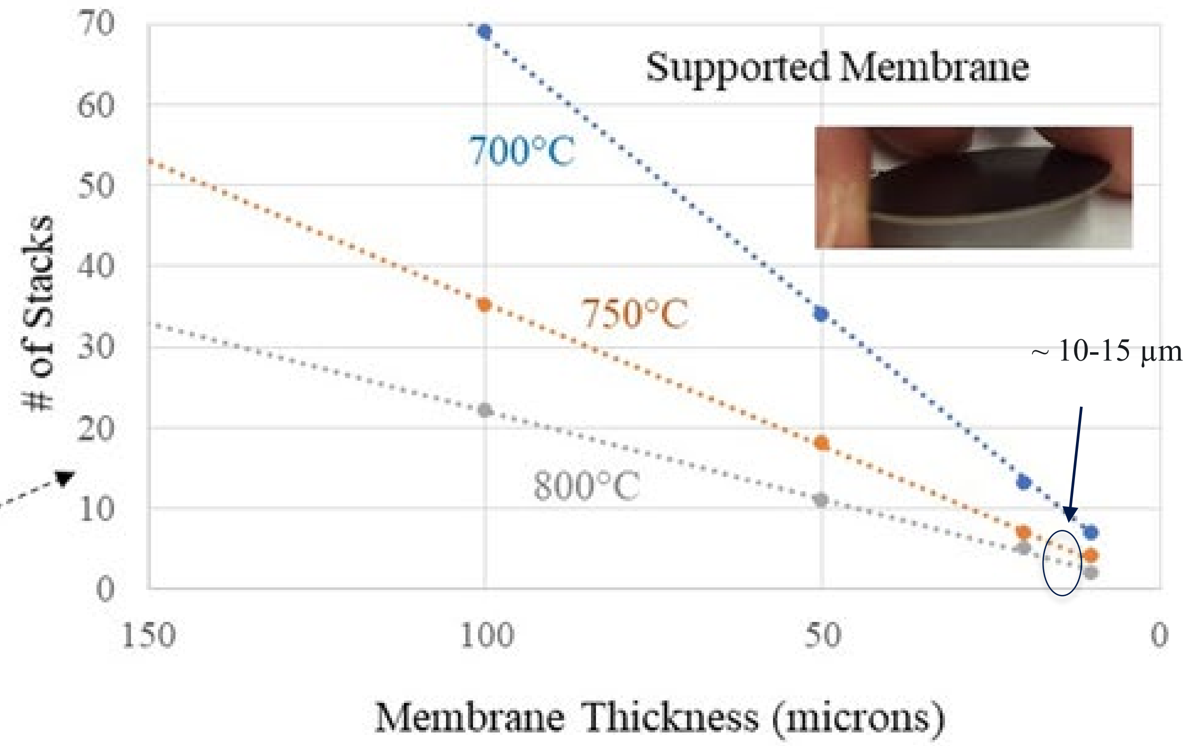


- σ_i calculated from oxygen permeability measurements
- Slightly lower than predicted value (Co doping)

Composite Membrane Characterization

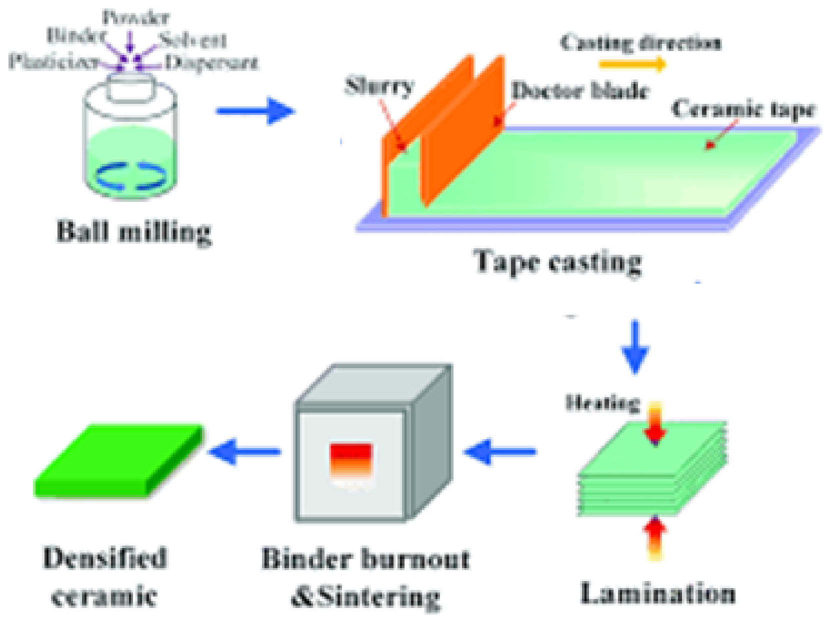


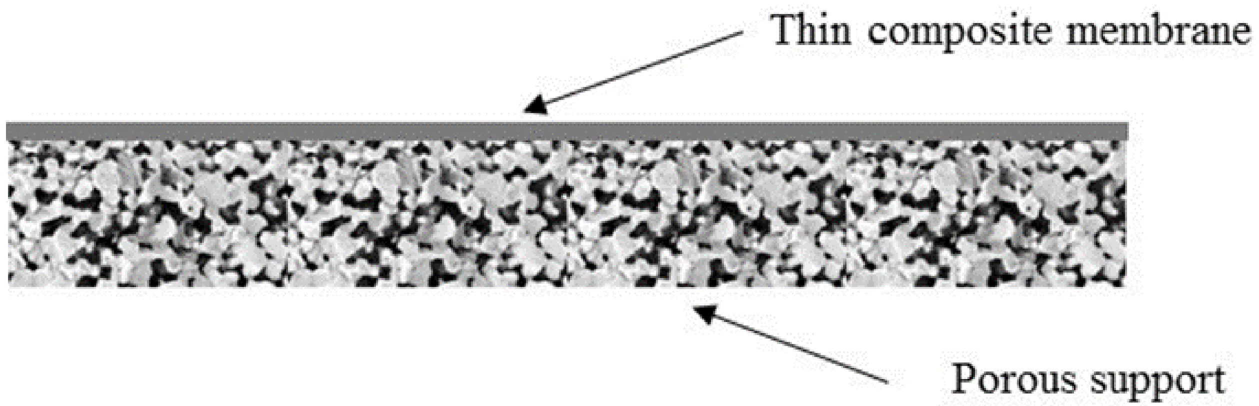


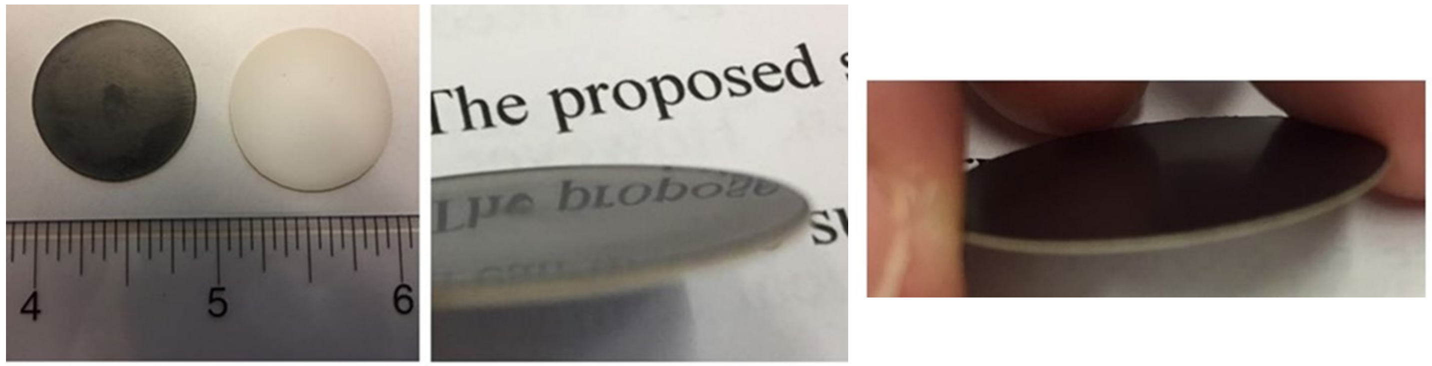


- To have a realistic number of stacks for producing 10 T/day of O_2 → the membrane thickness needs to be on the order of 10-15 μm.
- ***<u>Membrane will need to be supported → Bilayer Structure</u>***

Bilayer Characterization



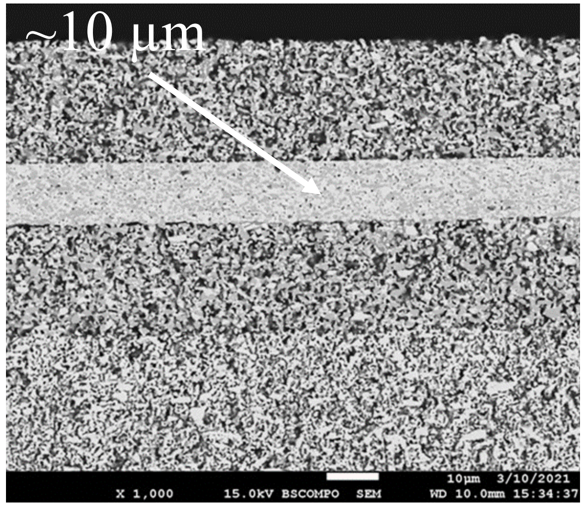




- Dense and thin membrane to maximize the oxygen permeability
- Thick and porous support to provide mechanical integrity and maximize gas diffusion
- Limited interaction during co-sintering
- Match sintering shrinkage
- Control of microstructure (thickness, size and distribution of porosity, etc.)

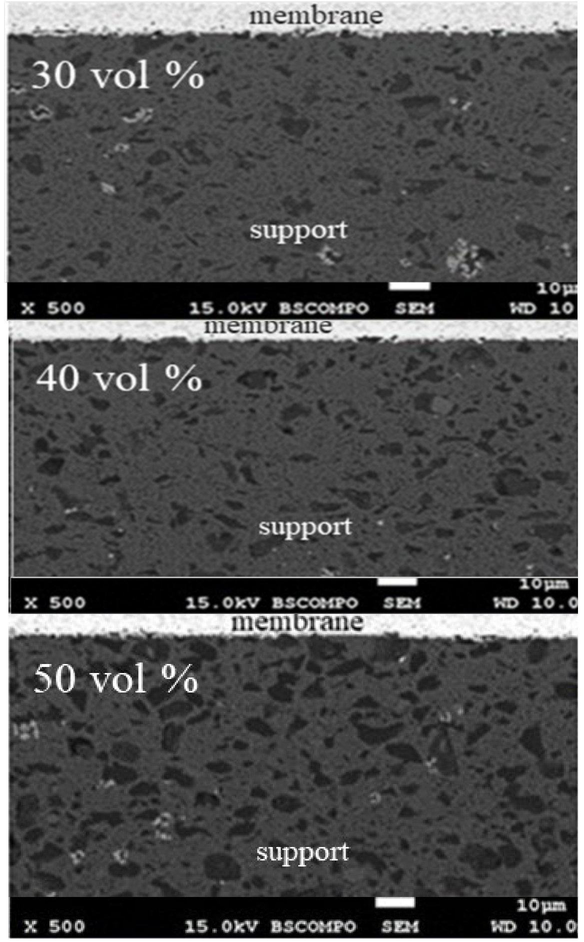
Bilayers with Controlled Microstructures

Membrane Thickness



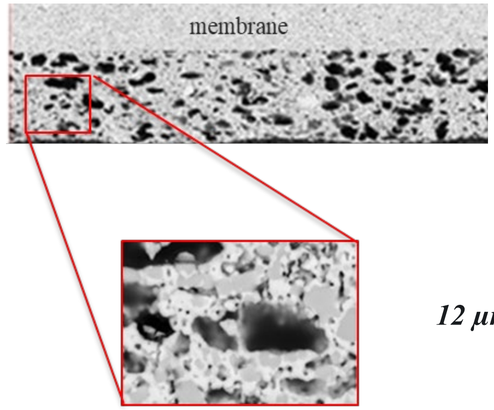
Tailor the membrane thickness by controlling the casting thickness

Vol % Porosity

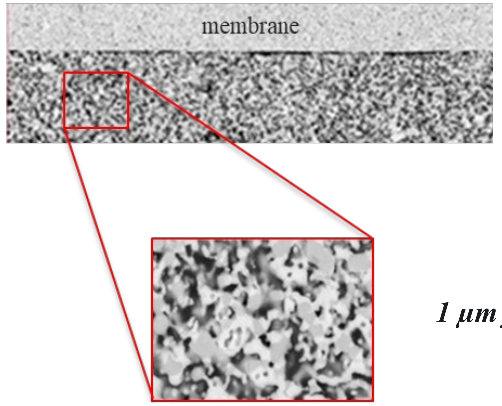


Tailor porosity by controlling the amount of fugitive phase used in tape cast suspension

Size & distribution of Porosity



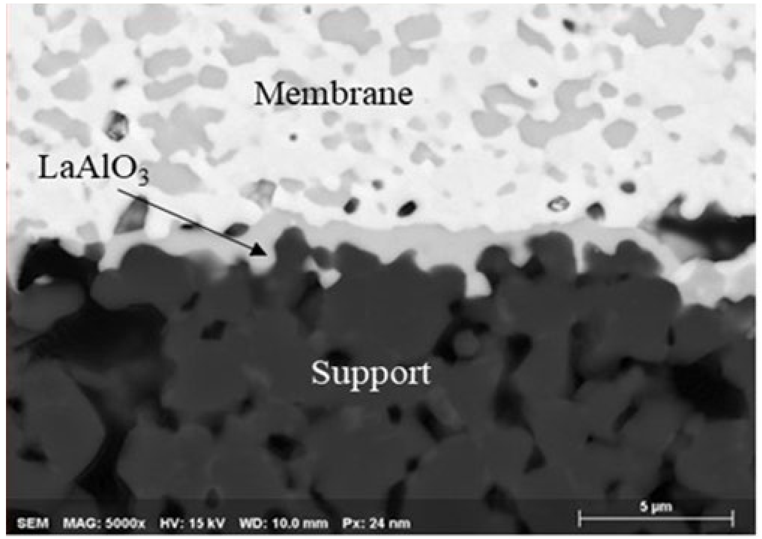
12 µm fugitive phase

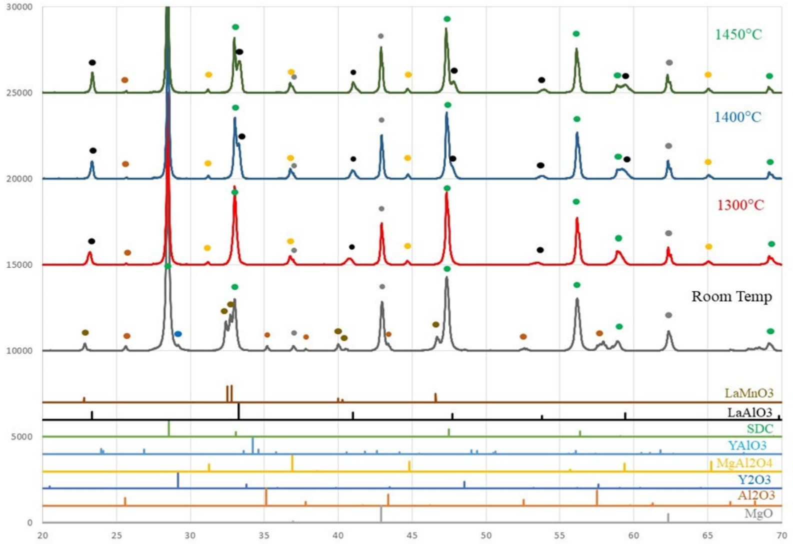


1 µm fugitive phase

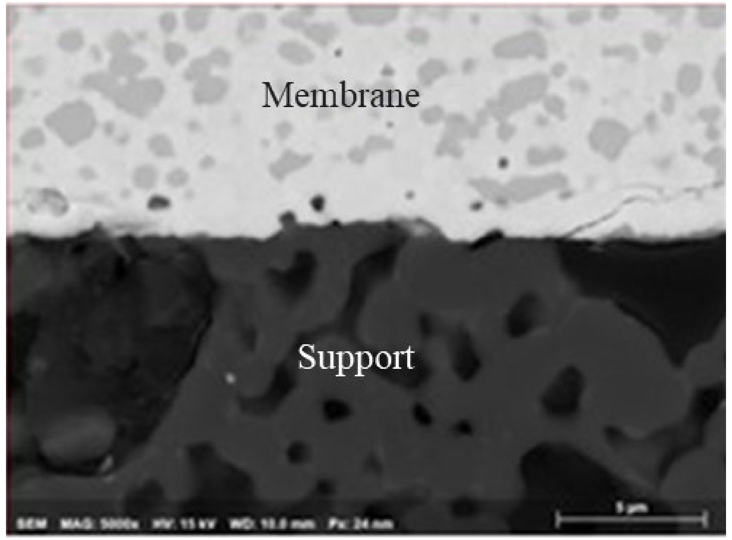
Tailor size & distribution of porosity by controlling size of the fugitive phase

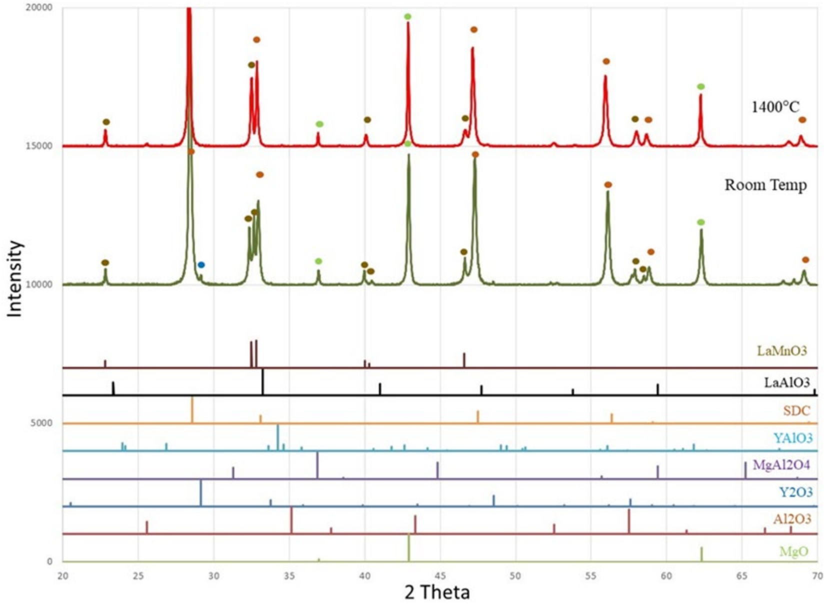
Interaction between Membrane and Support





Insulating $LaAlO_3$ formation at membrane/support interface – extremely low oxygen flux

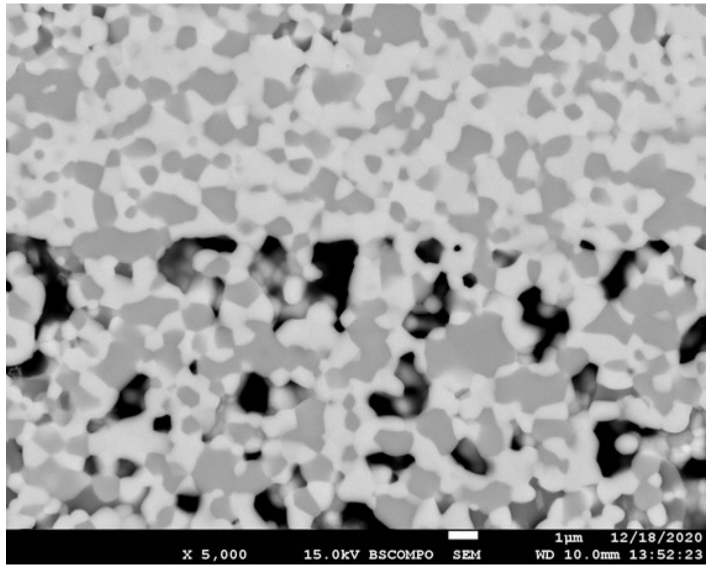




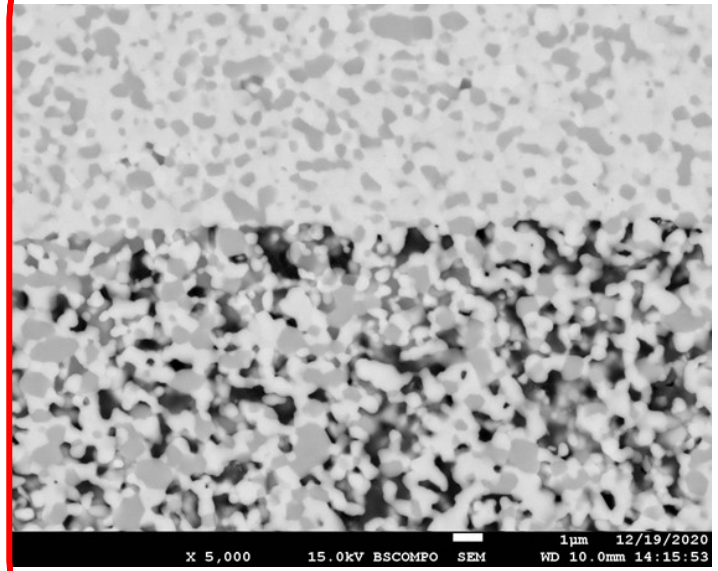
No interfacial reaction w/ compositional change – future direction

Densification of Membrane During Co-firing

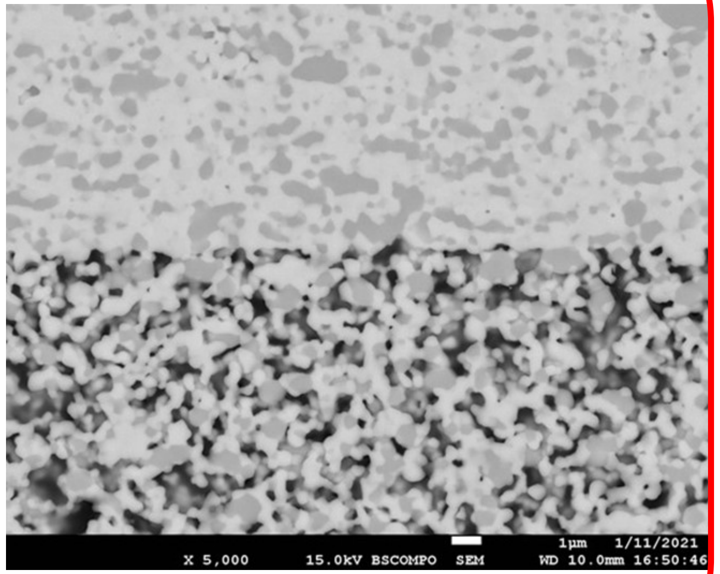
1375°C



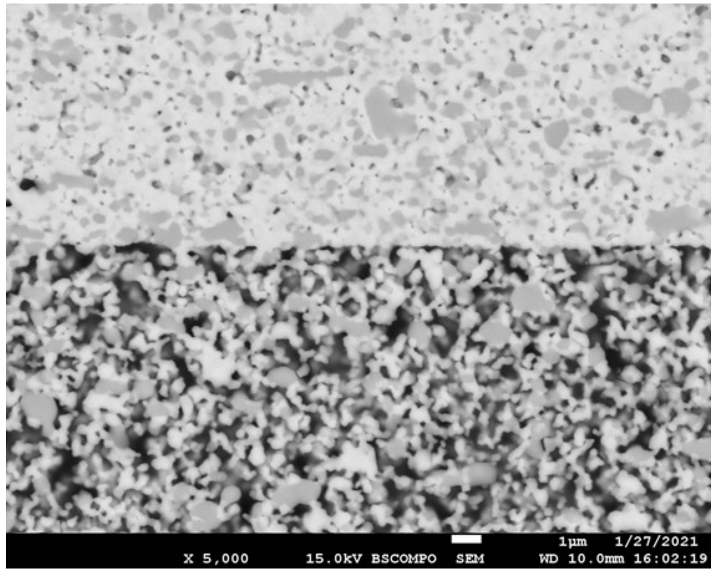
1325°C



1300°C



1275°C



Sintering Temperature

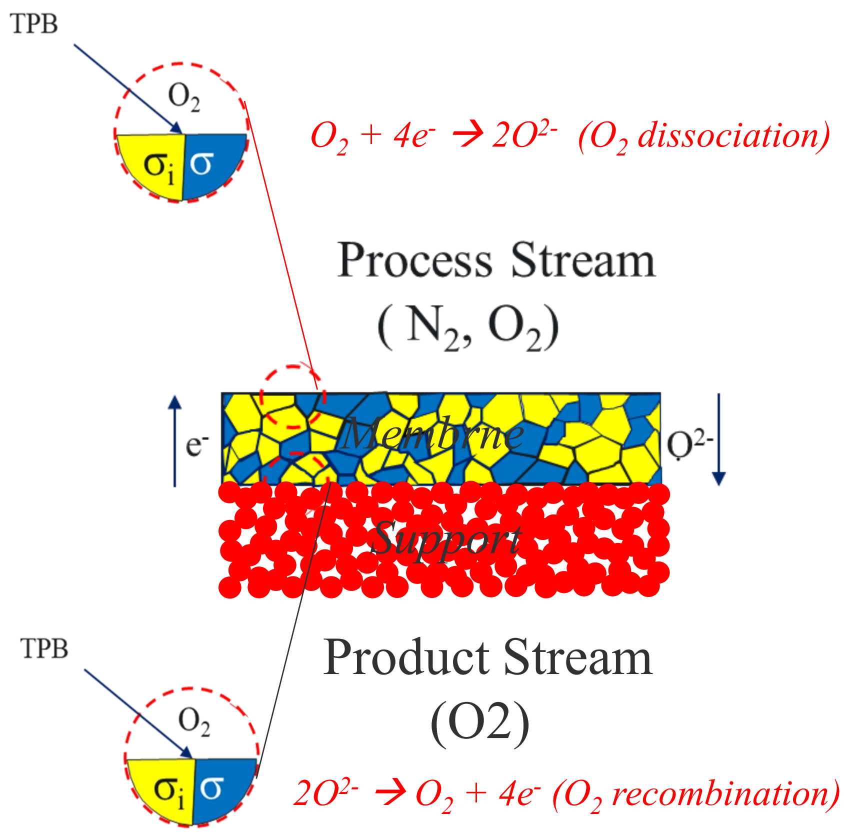
- Dense Membrane
- Larger grains
- Reduced number of TPBs
- Greater interaction/ diffusion of ions

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

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

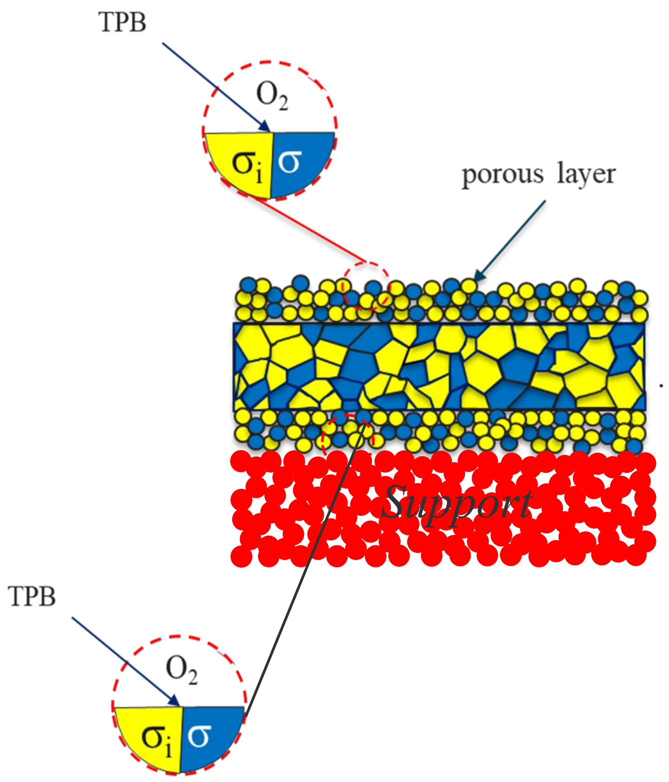
Bilayer Microstructure Designs

Planar Membrane



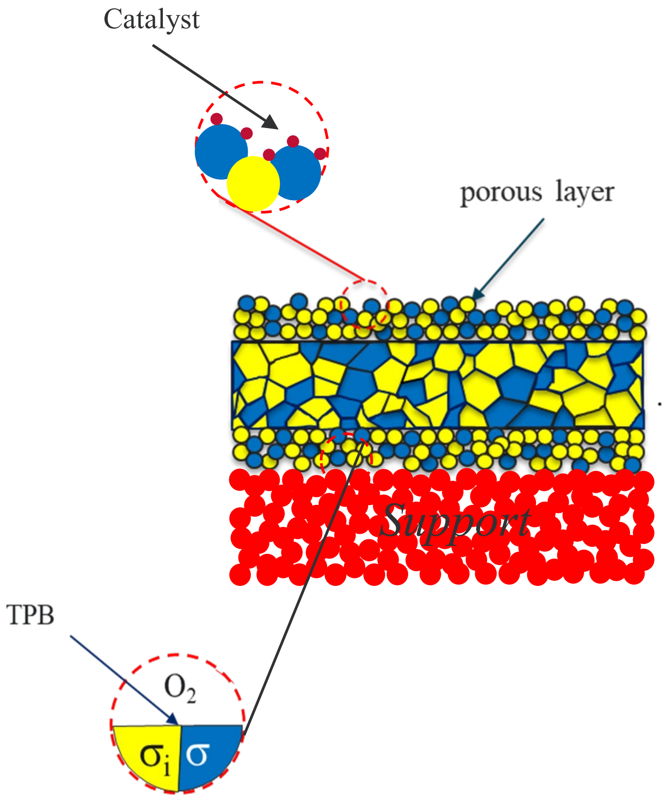
- Reaction area - 2-D surface
- Surface dominated – reduced thickness

w/ Barrier Layers



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

w/ Barrier Layers & Catalyst



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

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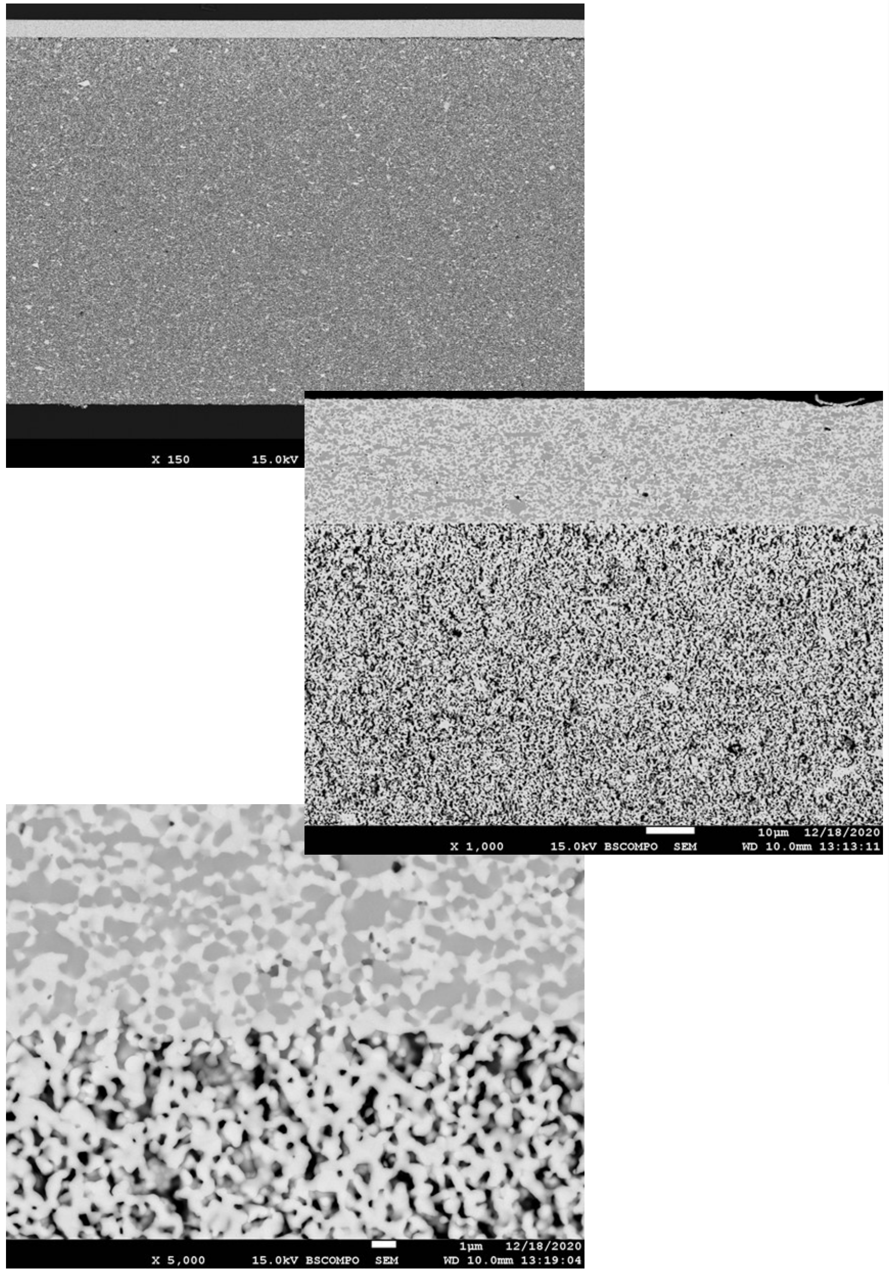
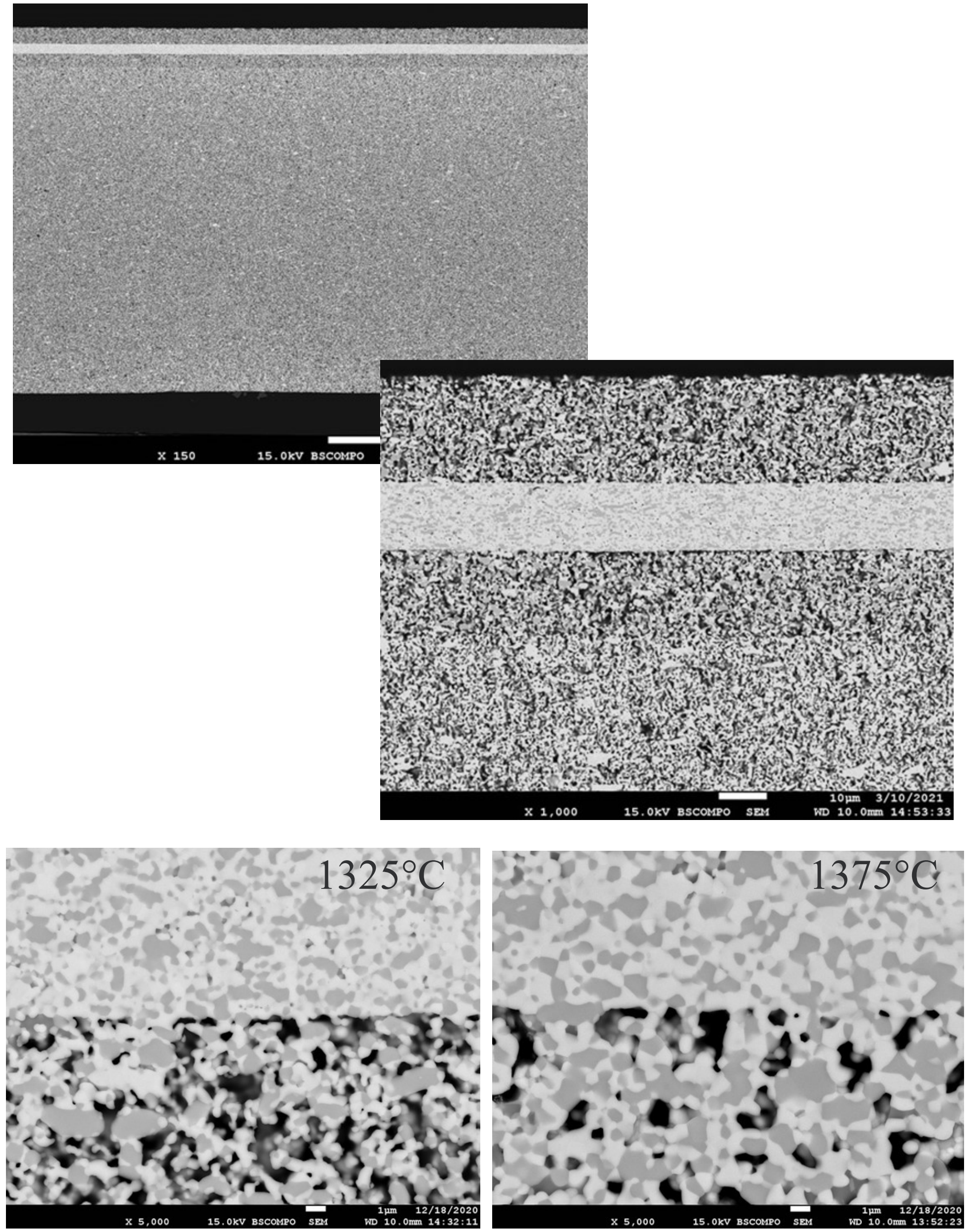
Bilayer Microstructures

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

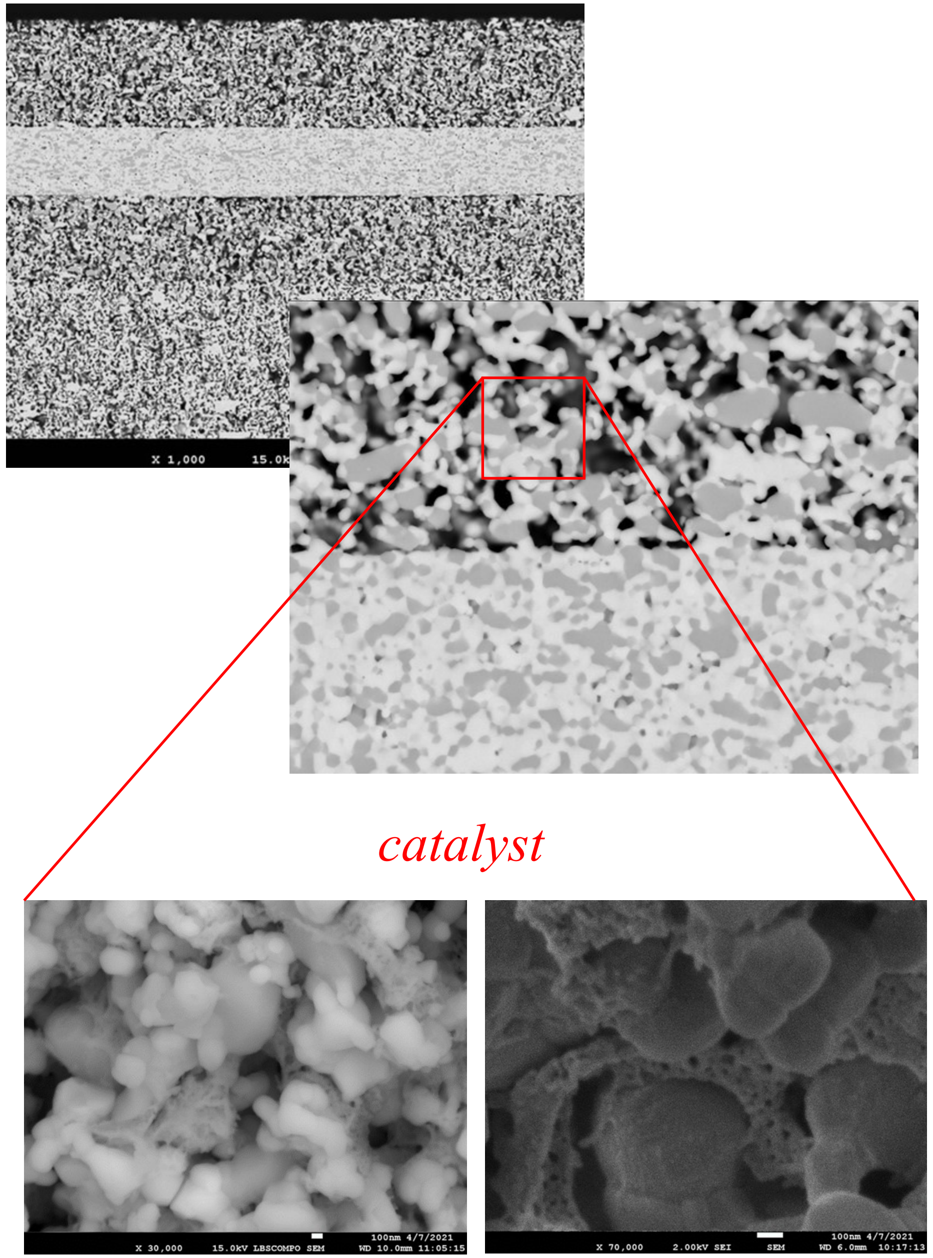
Planar Membrane



w/ Barrier Layers



w/ Barrier Layers & Catalyst



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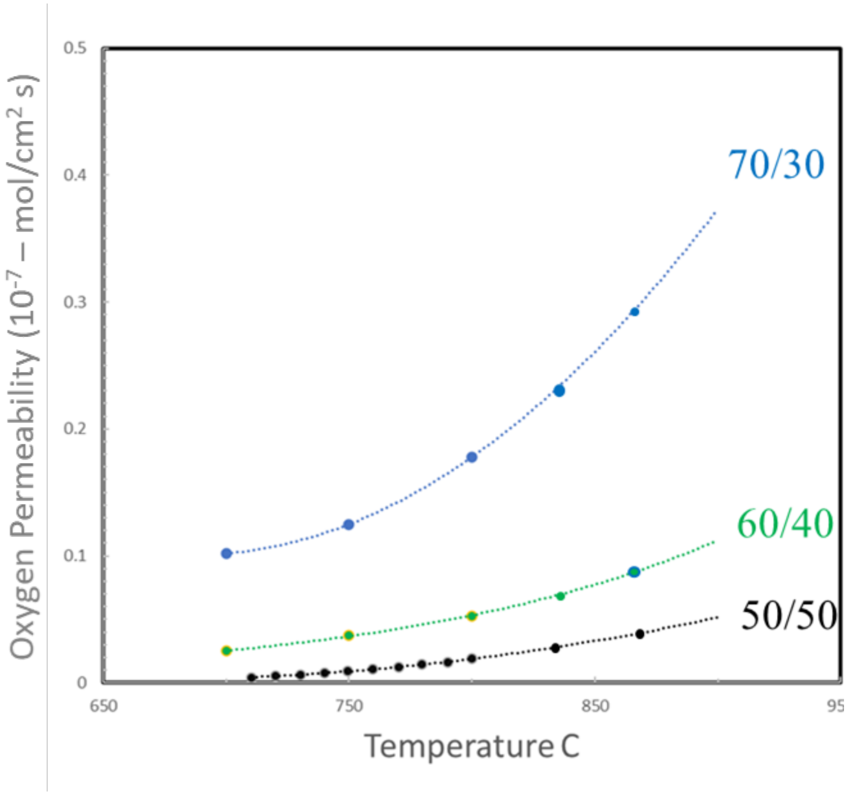
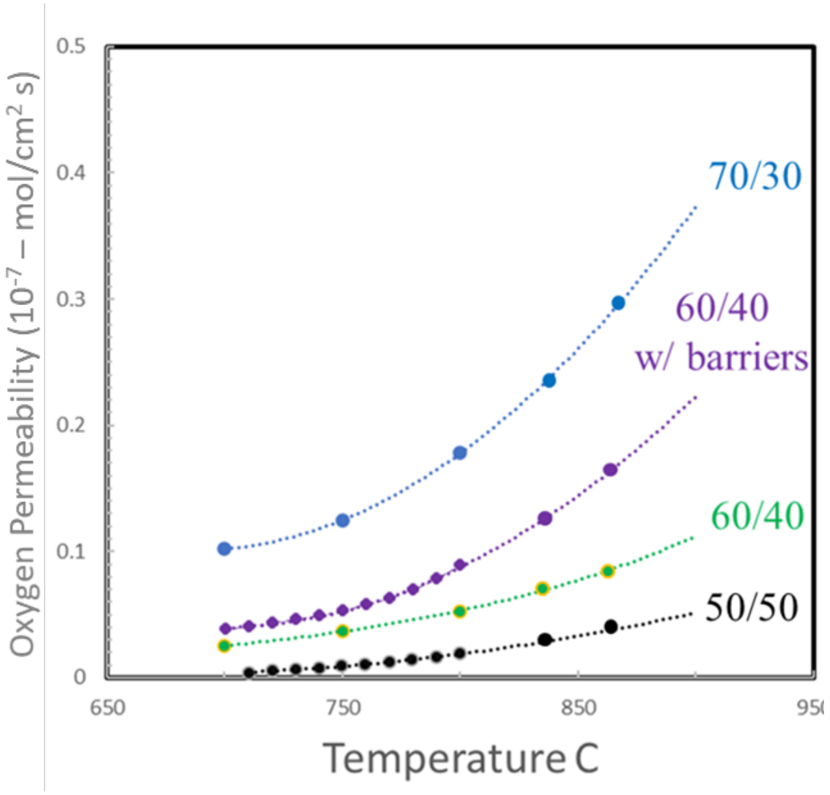
Bilayer Permeability

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

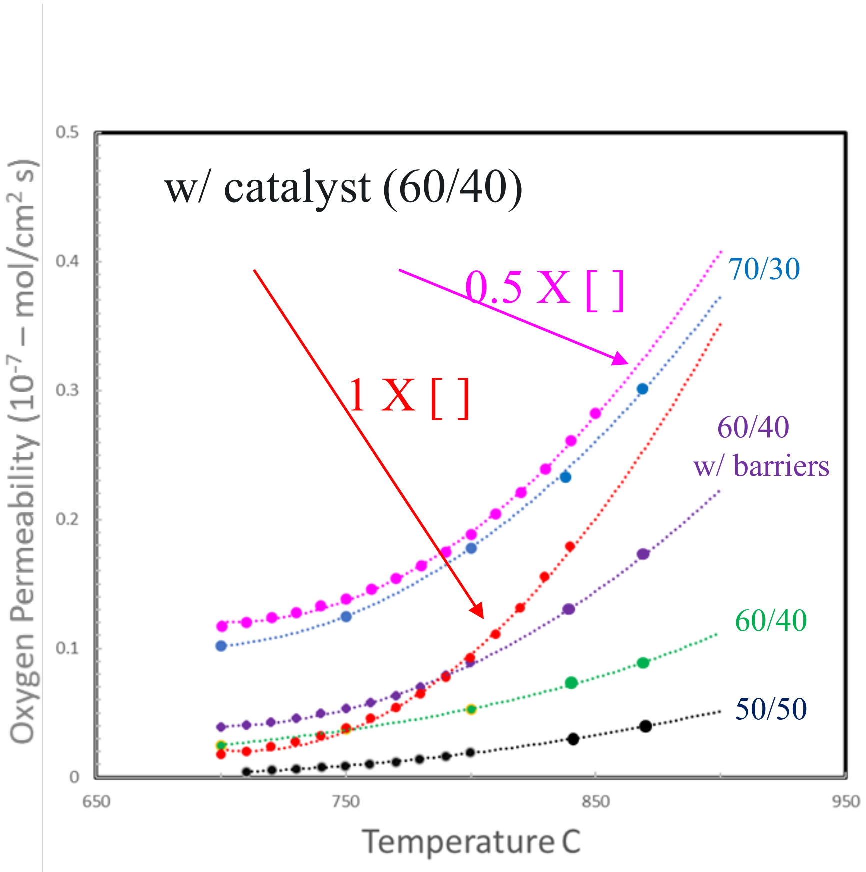
Planar Membrane



w/ Barrier Layers

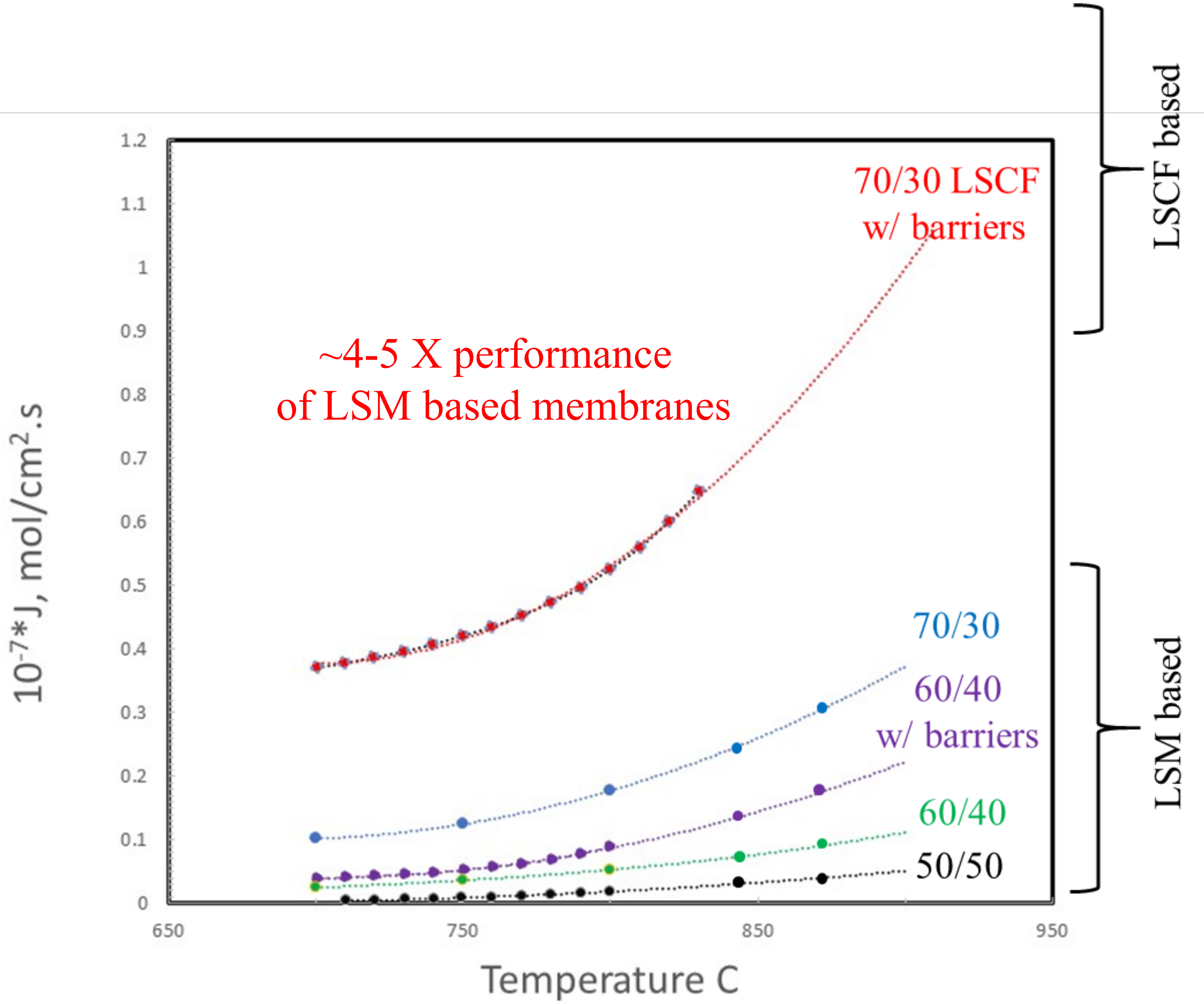


w/ Barrier Layers & Catalyst



Bilayer Permeability

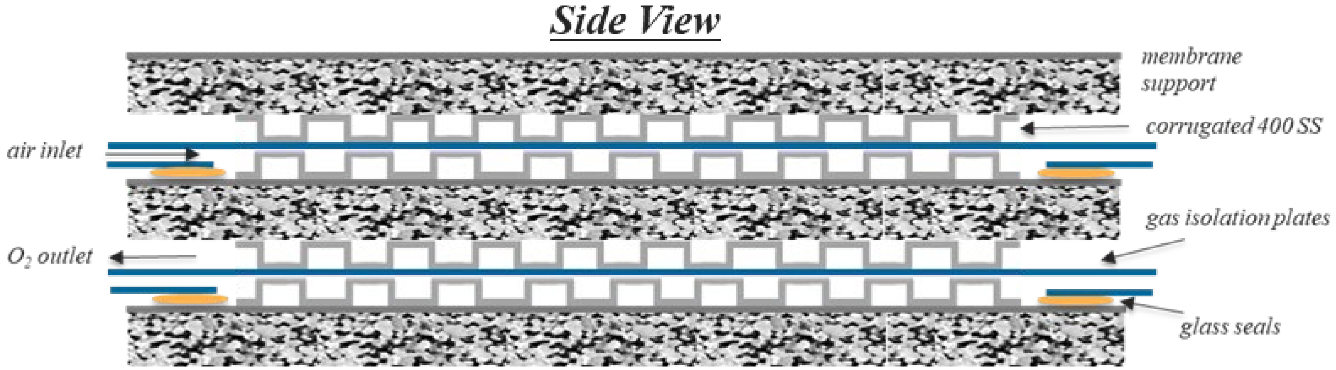
Gd doped CeO_2 w/ $La_{0.75}Sr_{0.2}MnO_3$ (LSM20)
Gd doped CeO_2 w/ $La_{0.6}Sr_{0.4}Fe_{0.8}SCo_{0.2}O_3$ (LSCF)

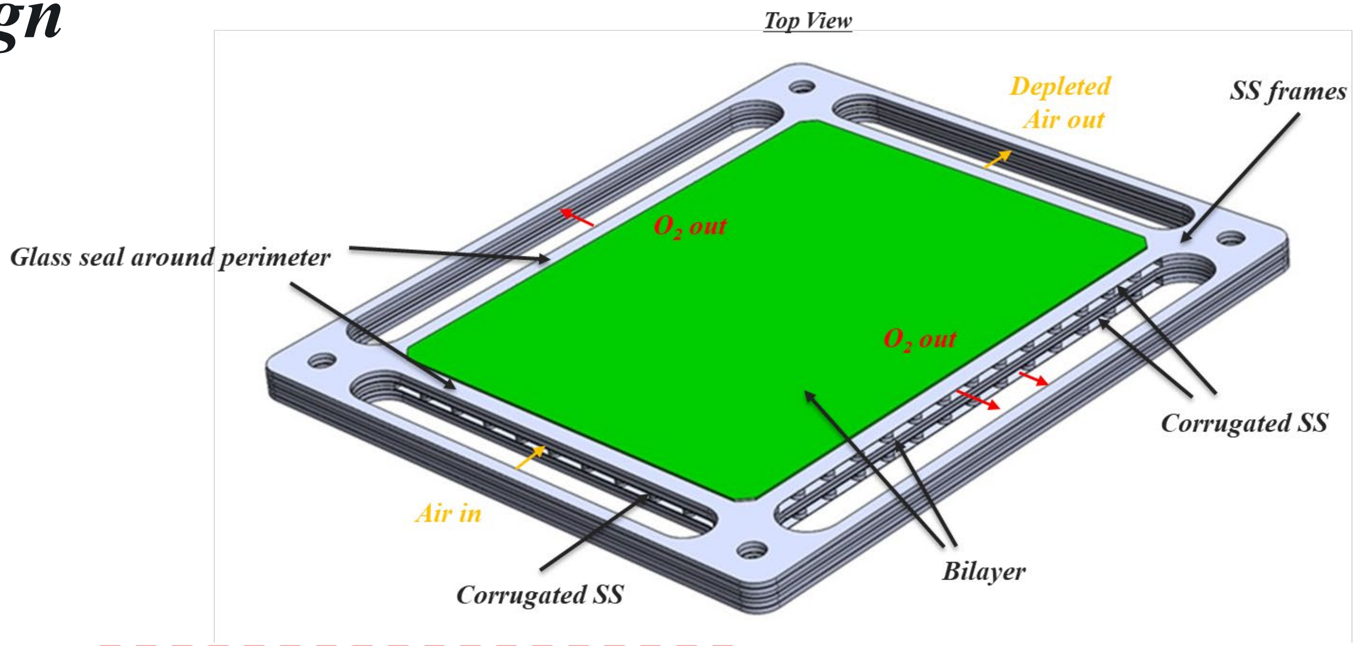


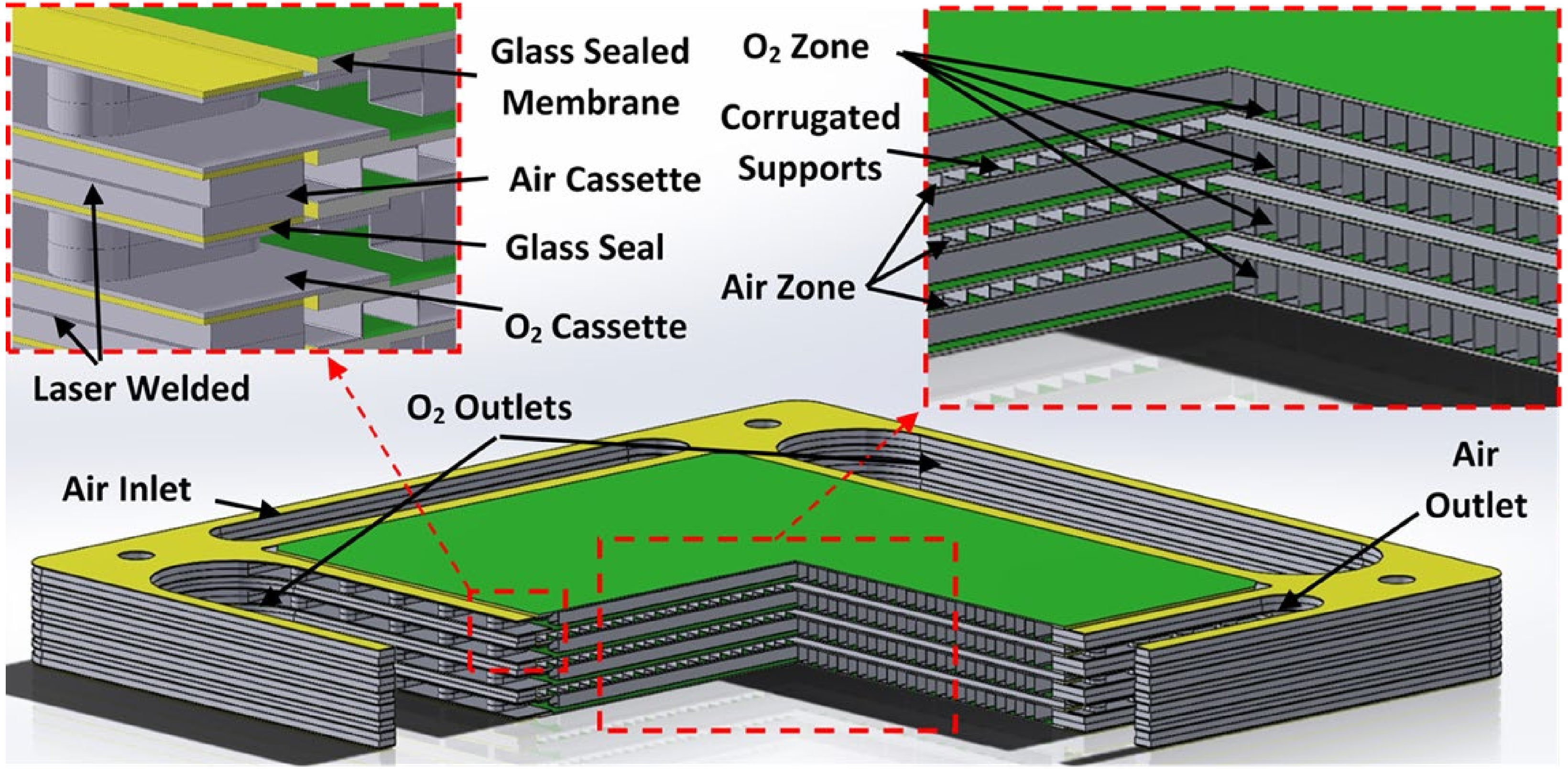
Will also investigate use of catalysts on LSCF based membranes

Ceramic Membrane Technology

Stack Design







Ceramic Membrane Technology

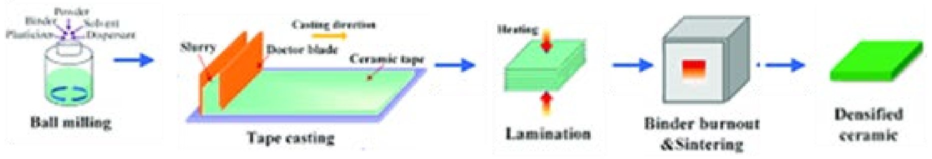
Low-Cost Materials and Processes

Materials

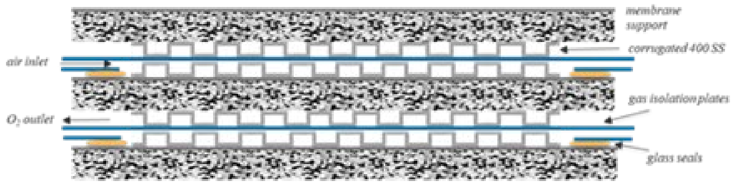
- Membrane (least amount of material used ~ 10-15 μm thick)
  - Ionic conductor - $Ce_{1-x}Gd_xO_{2-x}$
  - Electronic conductor – $La_{0.75}Sr_{0.2}O_{3-x}$
- Support – MgO
- Glass seal (BaO-Al_2O_3-SiO_2)
- Frames, gas isolation plates and corrugated supports
  - 400 series stainless steel

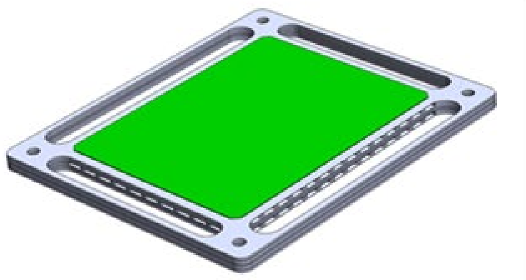
Fabrication processes

- Membrane and support used traditional thick film processing
  - Tape casting
  - Screen printing



- Stainless steel frames, gas isolation plates and corrugated supports will be stamped





Ceramic Membrane Technology

Next Steps

Fiscal Year	ID	Description	Planned/ Expected Completion Date	Complete	Verification Method
3	M1	Demonstrate scale up of bilayer structure (7.5 cm x 7.5 cm)	3/31/2021	✓	Bilayer structure will be flat and crack free with a dense membrane co-sintered on a porous support using bilayer structures in M2
3	M2	Optimize oxygen flux for 1" diameter bilayer structures using barrier layers and catalysts	4/30/2021	✓	Oxygen flux values will be compared to theoretical values calculated at various temperatures on bilayer structures of 5cm^2.
3	M3	O_2 permeation for 3" diameter (~50 cm^2)	11/30/2021		Redesign/reconfigure oxygen permeation measurement set-up to test bilayer structures up to 50 cm^2. Compare permeation values of larger 50 cm^2 bilayers to 5 cm^2 samples.
3	M4	3 cell stack fabrication (56 cm^2)	11/30/2021		Demonstrate a stack build utilizing 7.5 cm x 7.5 cm bilayer structures with low cost frames and glass seals.
3	M5	Techno-economic analysis	11/30/2021		Complete a preliminary techno-economic analysis on the ASU technology baselining the cost and performance

Acknowledgements

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