Pressure Driven Oxygen Separation

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Richland, WA

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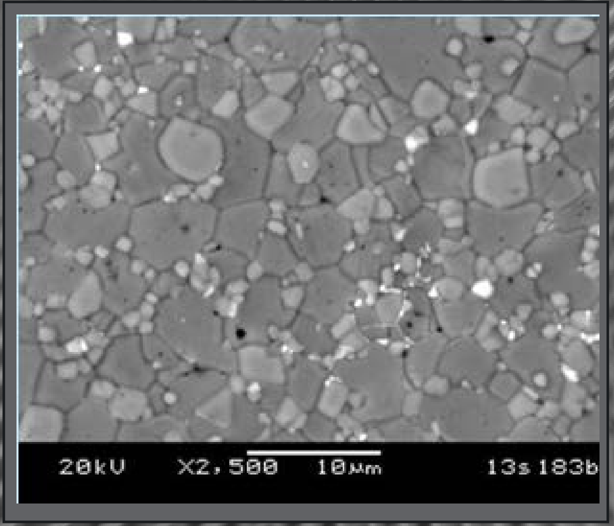
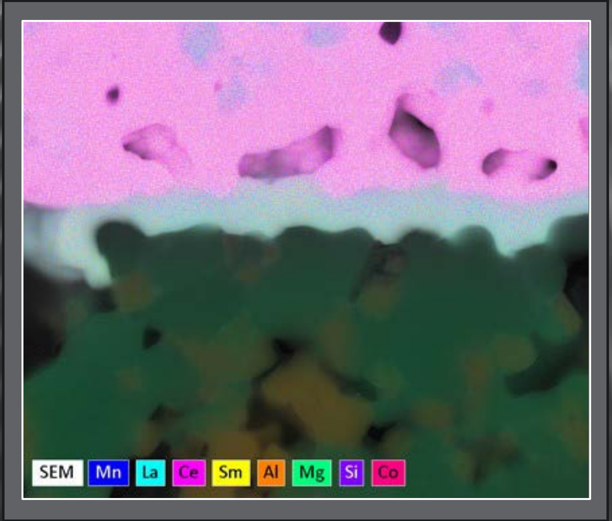
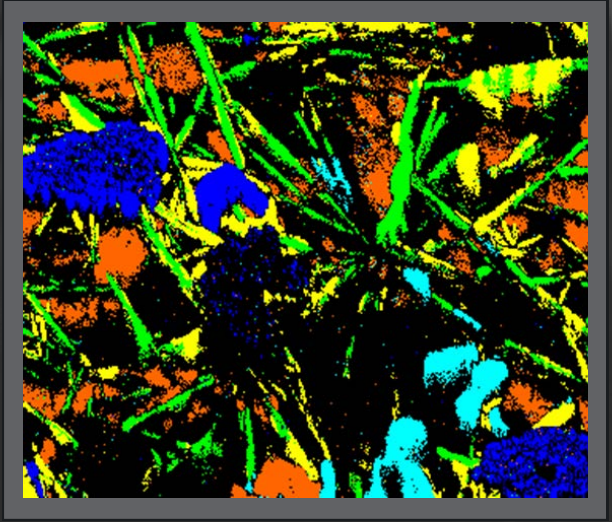






Pressure Driven Oxygen Separation

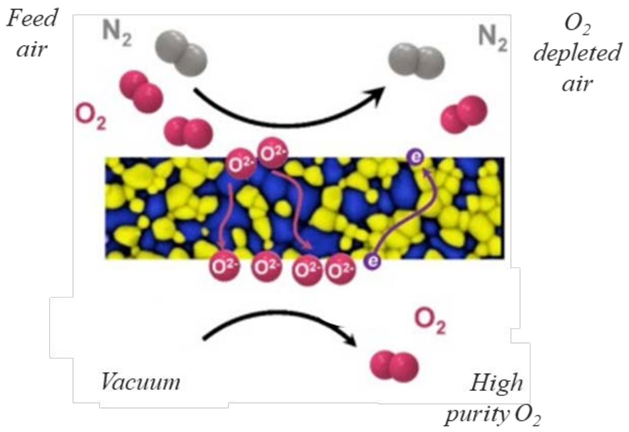
Outline

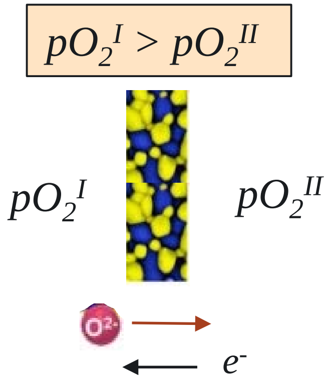
- Project Description and Objectives
- Project Background
- Critical Factors for Project Success
- Project Update
- Next Steps

Project Description and Objectives

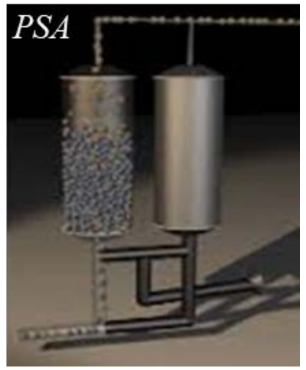
The overall goal of the proposed effort is to develop a small scale, modular air separation unit providing 10-40 tons/day of high purity oxygen to a 1-5 MW gasifier at low cost and high efficiency

- 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>



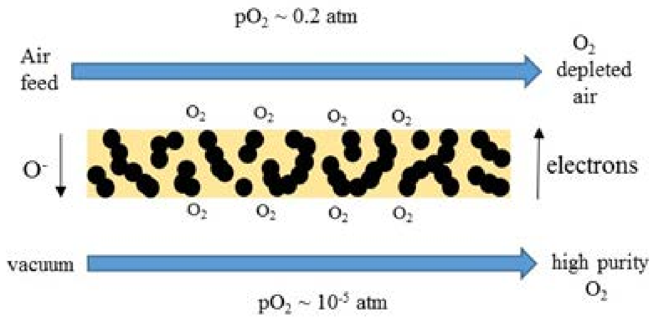


Oxygen Separation Techniques



- **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)

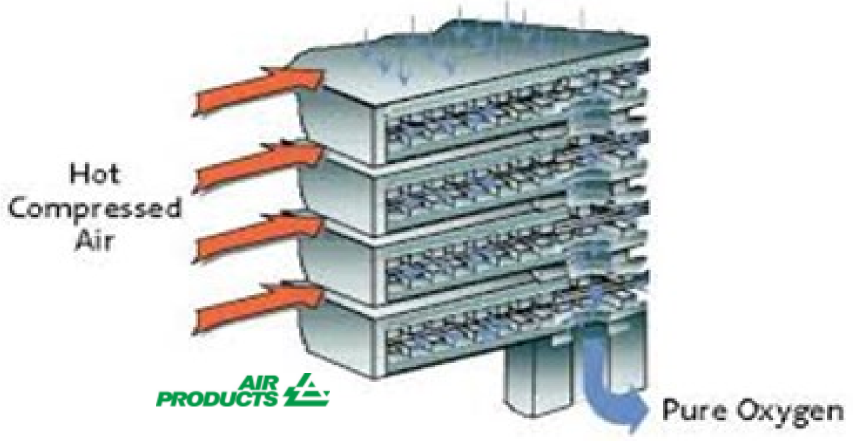


Proposed Ceramic Membrane Technologies

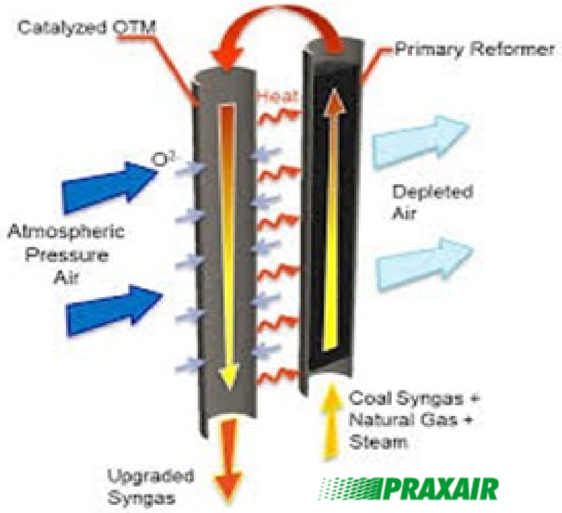
Planar vs Tubular Design

- Ease of manufacturing
- High surface area
- Increased sealing surface area
- Lower/medium temperature (700-800°C)
- Two phase composite membrane (σ_i and σ_e)
- SOFC design experience at PNNL

Planar Design

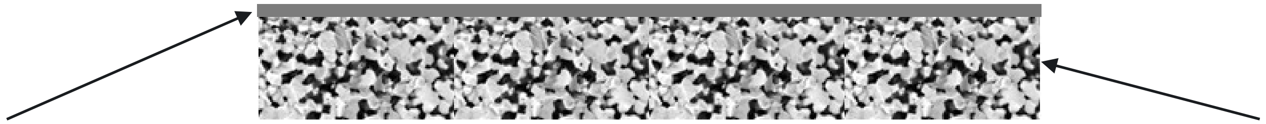


Tubular Design



Proposed Ceramic Membrane Technologies

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

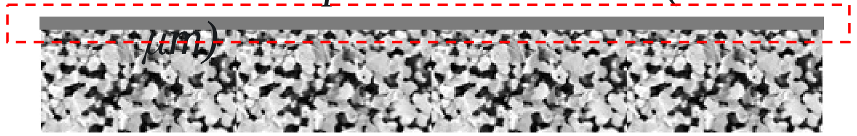
- ~ 50% dense
- TEC match to membrane
- Mechanical integrity
- Co-fired w/ membrane

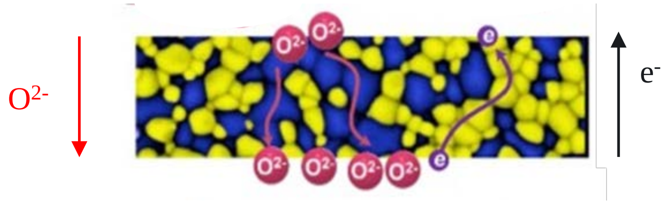
Design will leverage SOFC stacks developed at PNNL

Proposed Ceramic Membrane Technologies

Composite Membrane

Thin composite membrane (~ 10 μm)



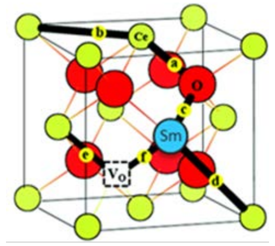


- Two phase composite (σ_i & σ_e)
- Similar TEC
- <u>Limited interaction during firing</u>
- High σ_i phase
- Sufficient σ_e phase
- Compatible with glass seal

Material Selection

Ionic Conductor

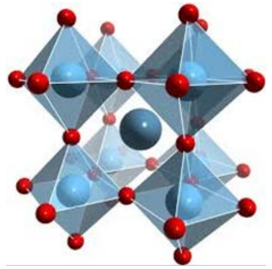
- Doped CeO_2



Fluorite structure

Electronic Conductor

- Doped $LaMnO_3$
- Doped $LaFeO_3$



Perovskite

Proposed Ceramic Membrane Technologies

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 Technologies

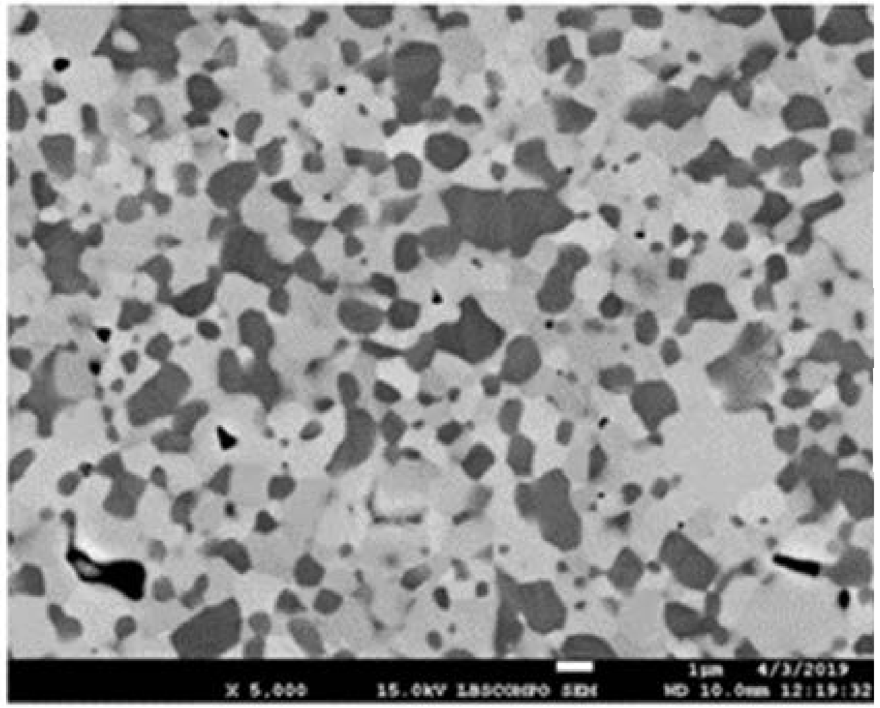
Factors Critical for Project Success

- **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**

Minimal Interaction within Membrane

70/30 vol%
Ionic/Electronic phase

SEM micrograph



Ionic Conductor

Electronic Conductor

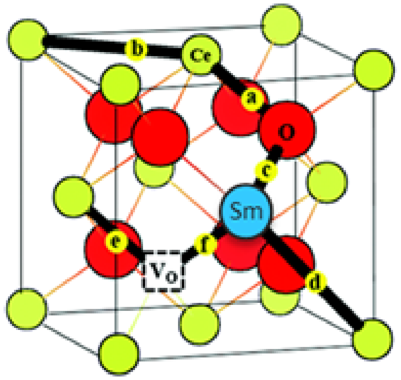
Doped CeO_2

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

<u>*Examples*</u>

$Ce_{0.8}Sm_{0.2}O_{2-x}$ w/1% Co (SDCC)
$Ce_{0.8}Gd_{0.2}O_{2-x}$ (GDC)
$Ce_{0.8}Sm_{0.2}O_{2-x}$ (SDC)

- TC grade (5-8 m^2/g), T_s~1400°C
- HP grade (10-14 m^2/g), T_s~1300°C



Fluorite structure

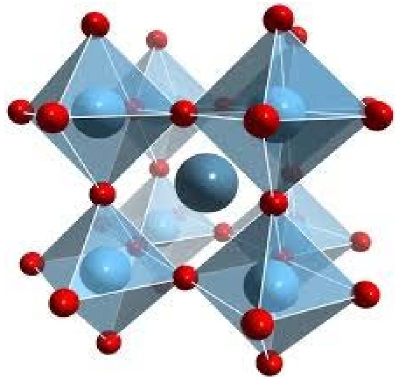
Doped $LaMnO_3$

Acceptor doped p-type

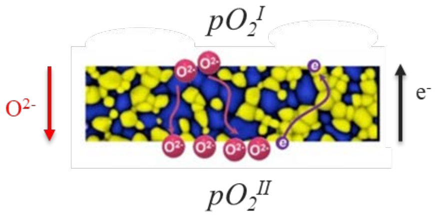
<u>*Examples*</u>

$La_{0.9}MnO_{3-x}$ (LM90)
$La_{0.75}Sr_{0.2}MnO_{3-x}$ (LSM-20)

- TC grade (4-8 m^2/g)
- HP grade (10-14 m^2/g)

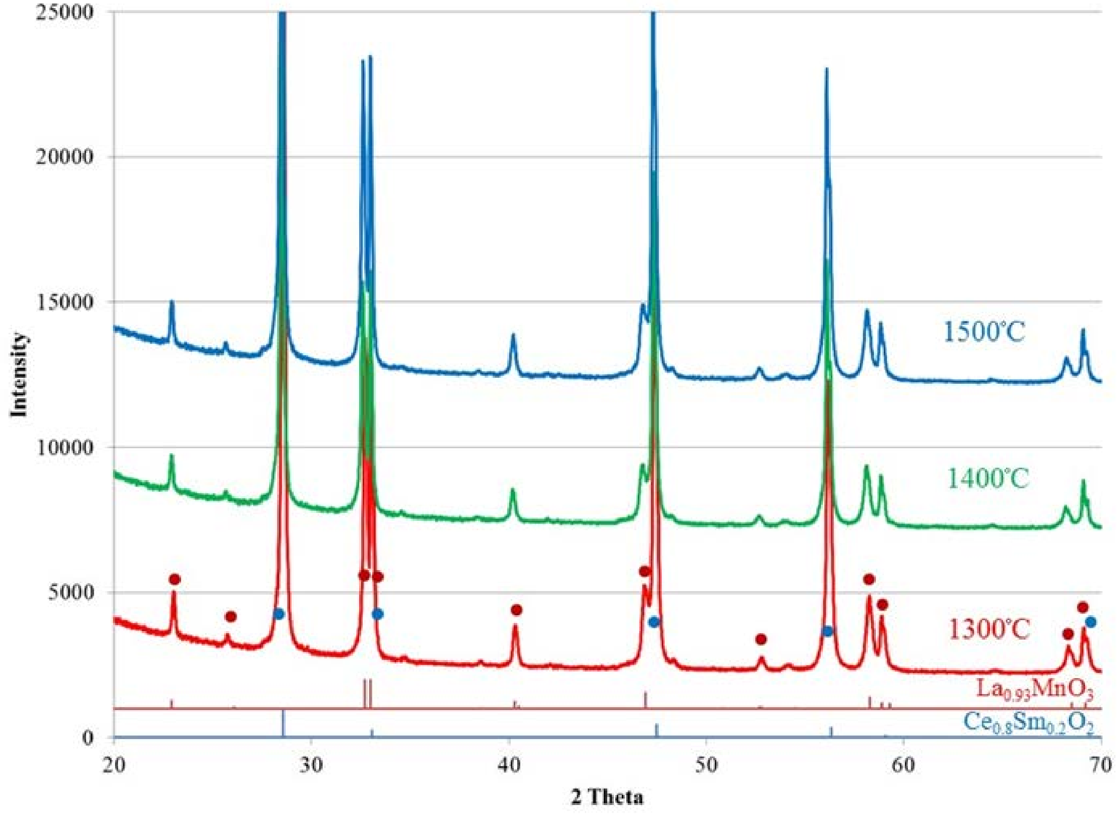


Perovskite



Composite Membrane Characterization

Interaction Studies



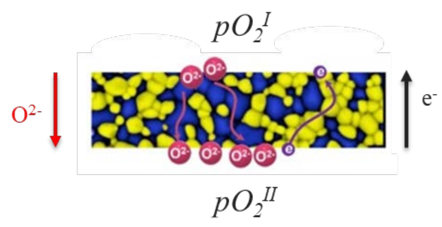
- Limited interaction, no 2nd phase formation
- Potential interdiffusion, Mn & Sr into fluorite structure

Composite Dilatometry

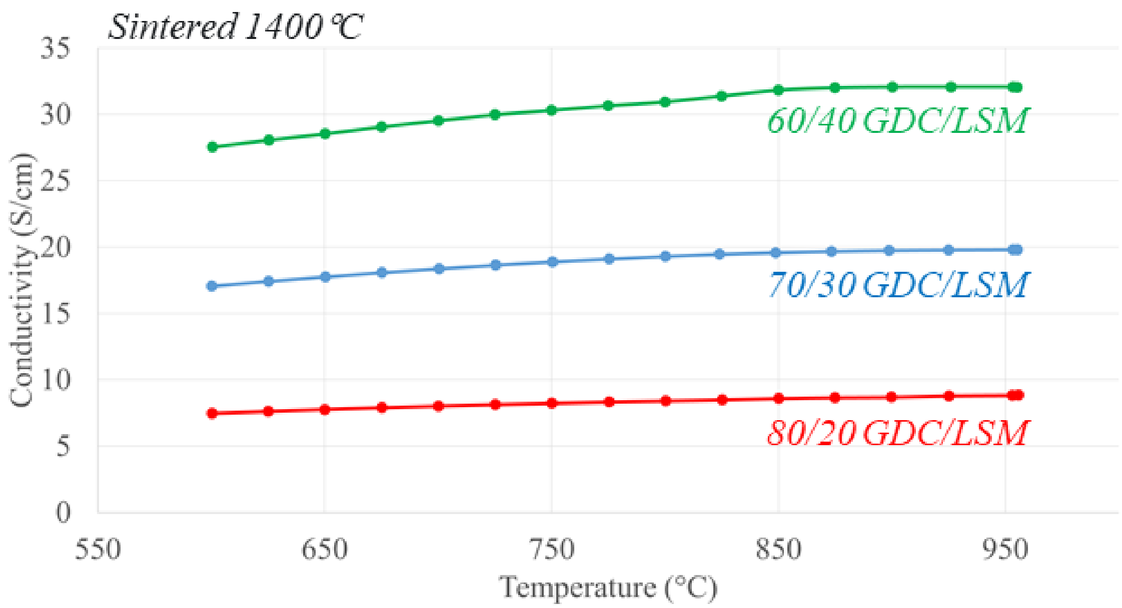
Material	α (x 10^{-6})
SDCC-LM90 50/50	11.11
SDCC-LM90 60/40	11.57
SDCC-LM90 70/30	12.02
GDC20-LSM20 50/50	11.83
GDC20-LSM20 60/40	11.89
GDC20-LSM20 70/30	12.09
SDCC-LSM20 60/40	11.93
SDCC-LSM20 70/30	11.91

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

Composite Membrane Characterization

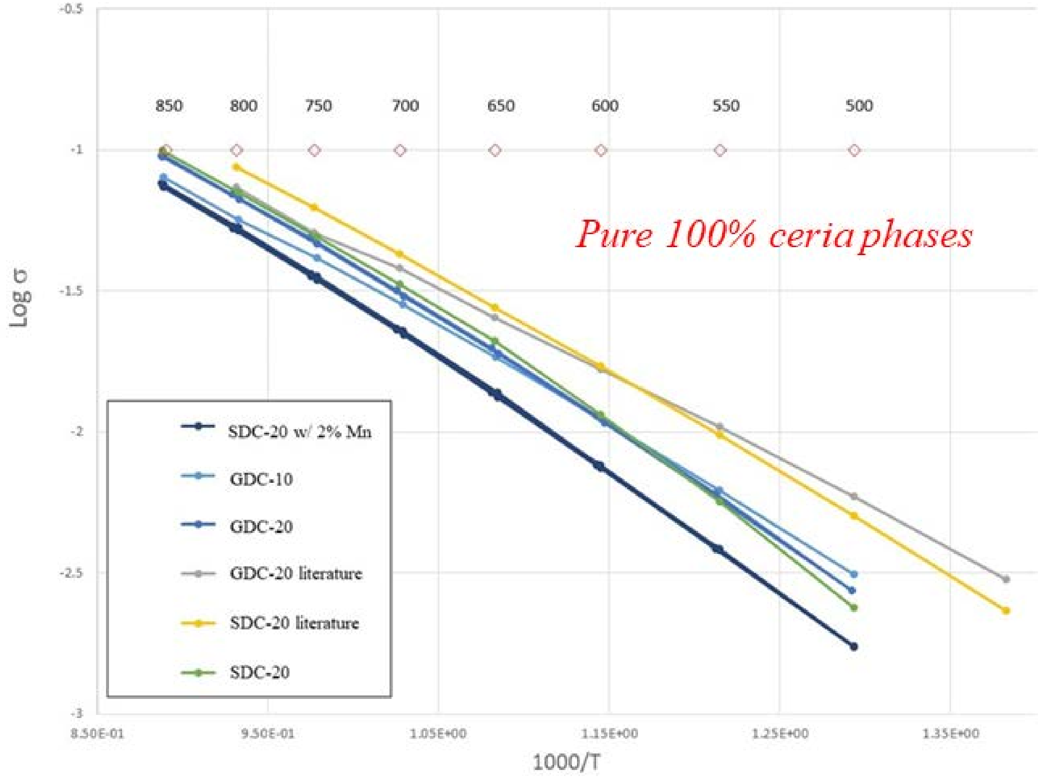


Electrical Conductivity



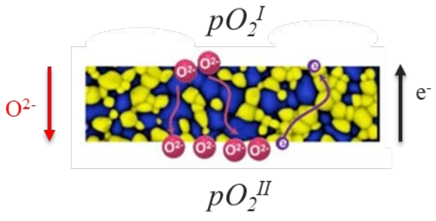
- Electrical conductivity (σ_e) controlled by perovskite phase
- σ_e ~ 3 orders of magnitude greater than ionic conductivity (σ_i)
- Percolation in perovskite phase

Ionic Conductivity

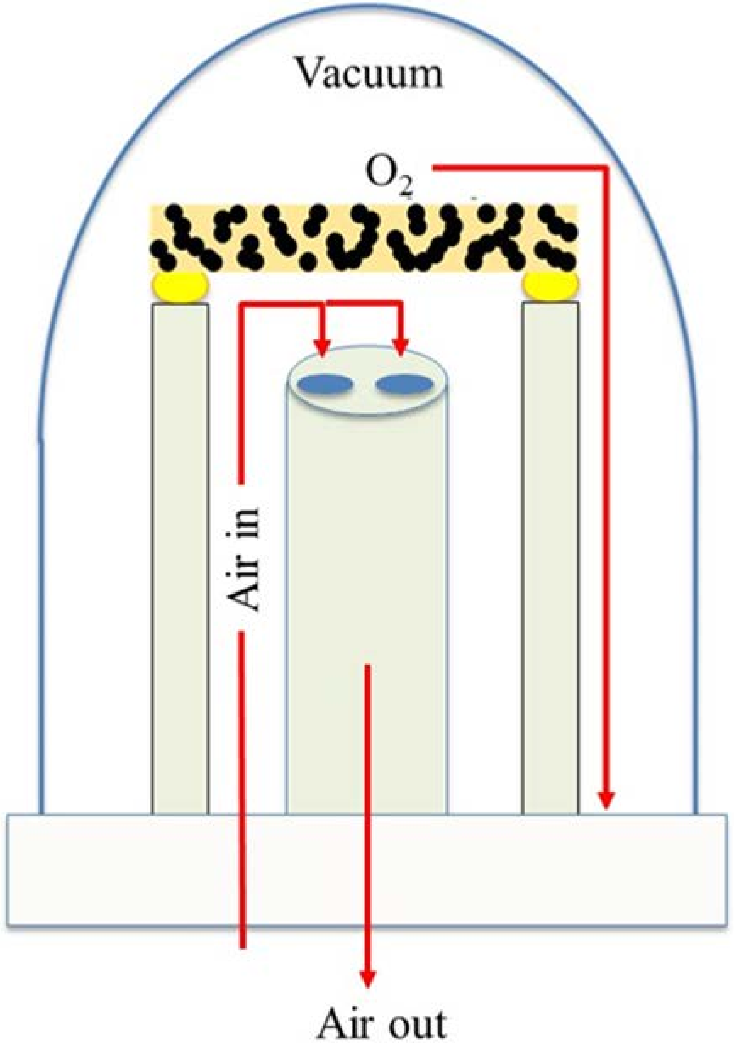


- σ_i ~ 0.07 at 800°C and 0.03 at 700°C
- ~ 2/3 σ_i value used in composite calculations
- Percolation in both phases

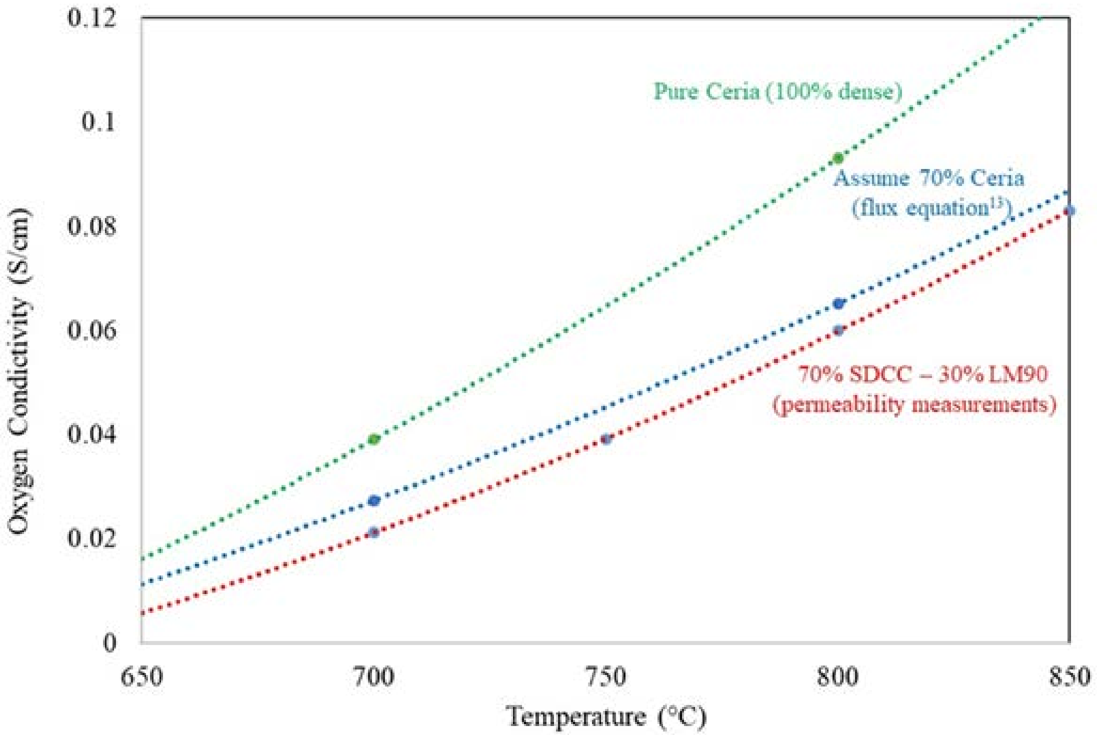
Composite Membrane Characterization



Permeability Measurements

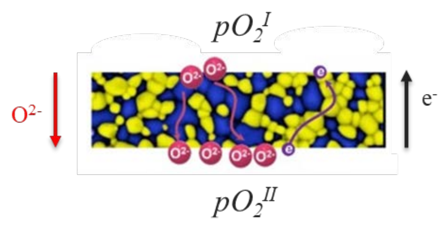


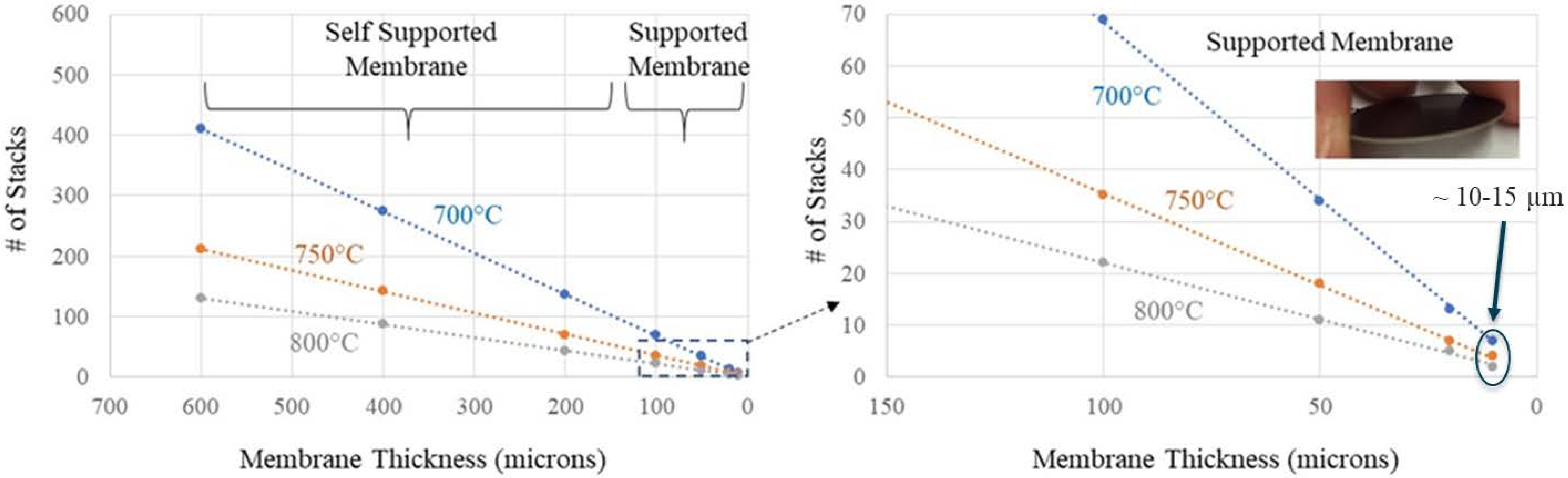
Self-supporting composite membranes
(~ 600 µm)



- σ_i calculated from oxygen permeability measurements
- Similar to predicted value

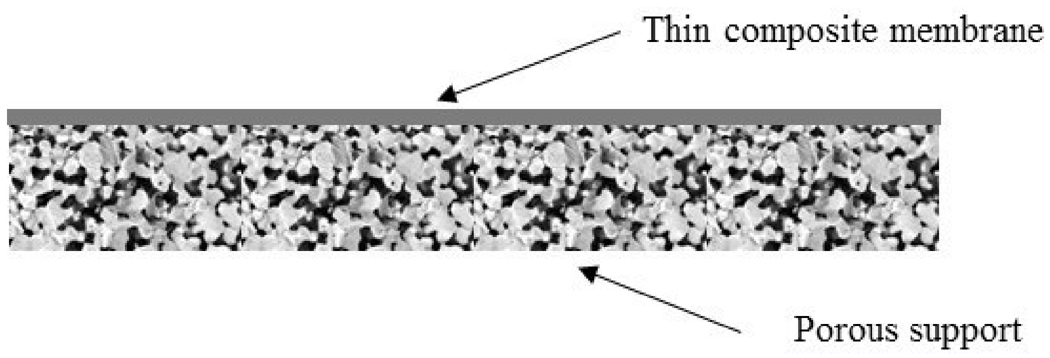
Composite Membrane Characterization

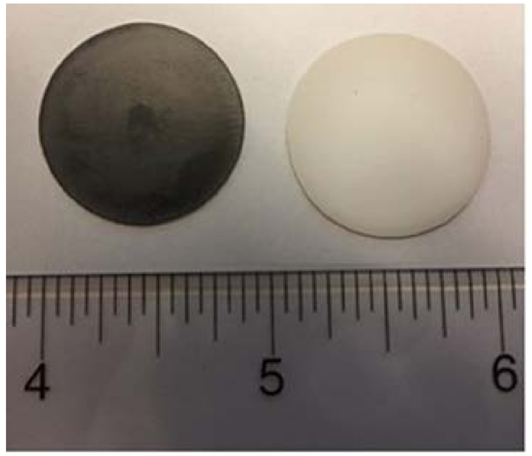


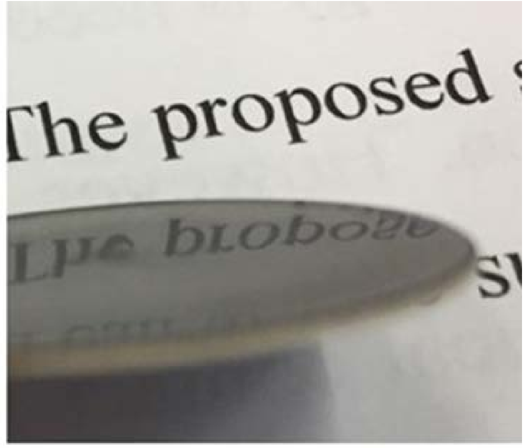


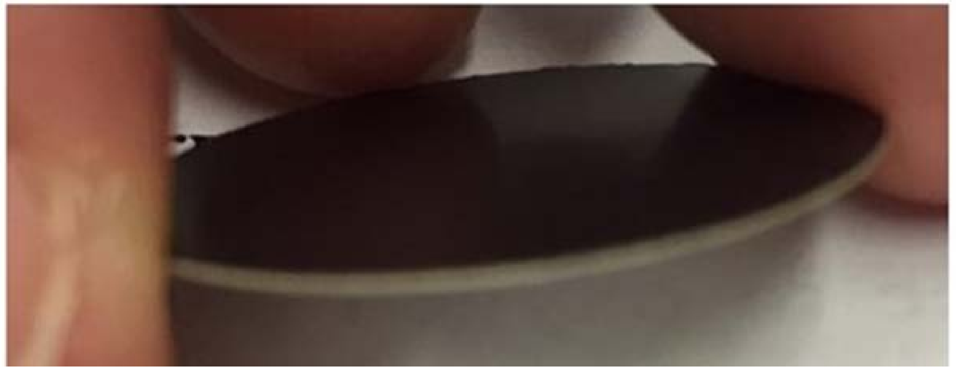
- To have a realistic number of stacks for producing 10 T/day of O_2 → the membrane thickness needs to be on the order of 10-15 µm.
- Membrane will need to be supported → Bilayer Structure

Co-sintered bilayers



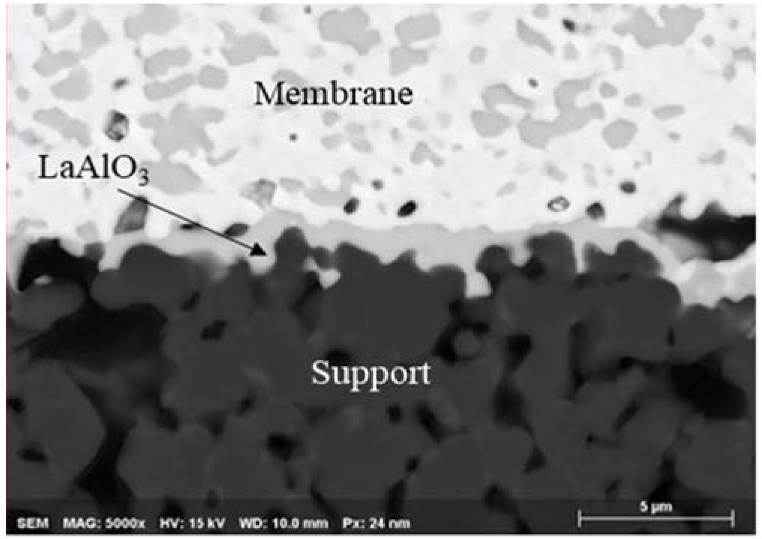


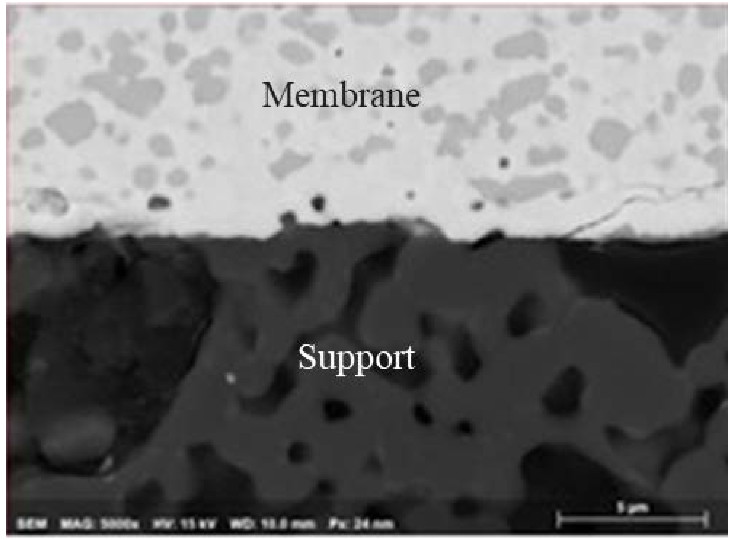


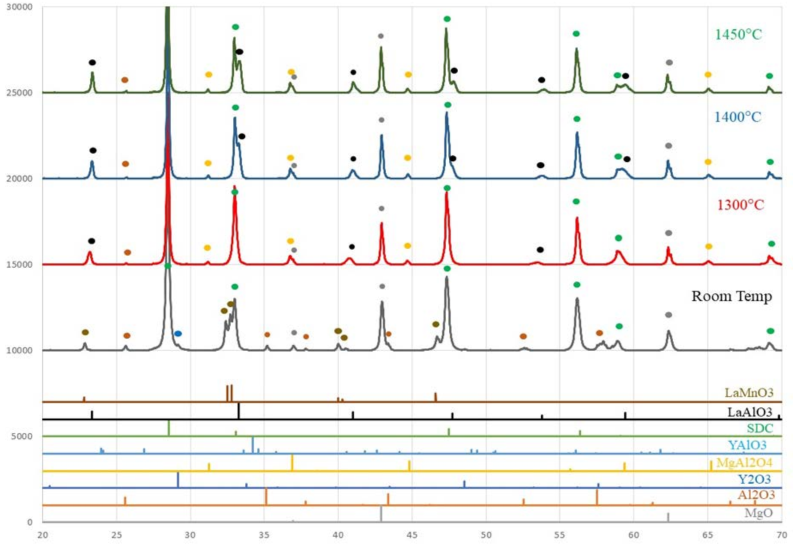


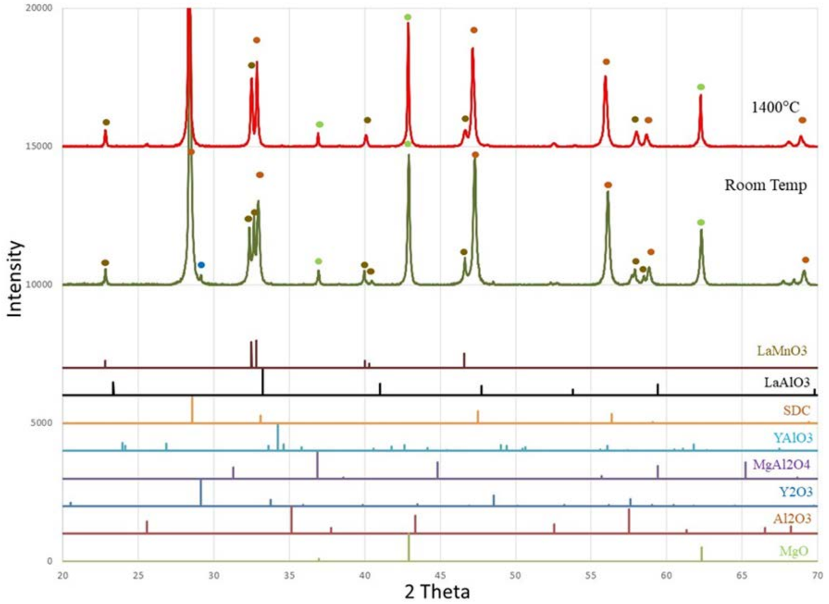
- Dense and thin membrane to maximize the oxygen permeability
- Thick and porous support to provide mechanical integrity and maximize gas diffusion
- Limited interaction during co-sintering

Co-sintered bilayers







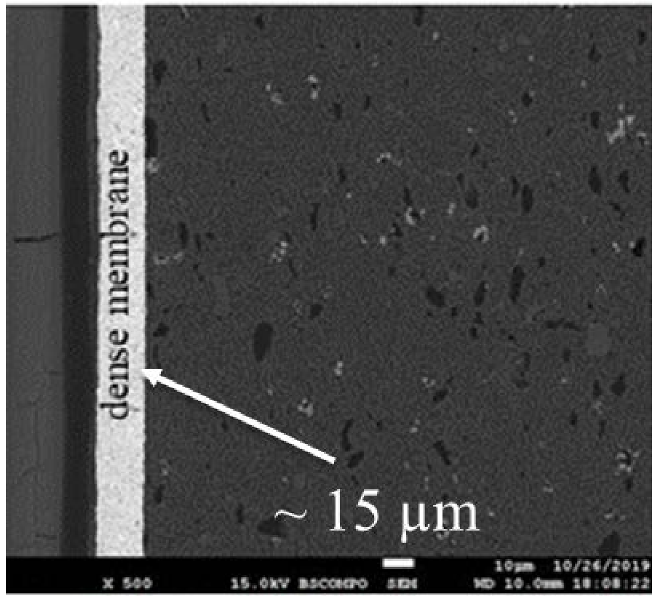


Insulating $LaAlO_3$ formation at membrane/support interface – extremely low oxygen flux

No interfacial reaction w/ compositional change – future direction

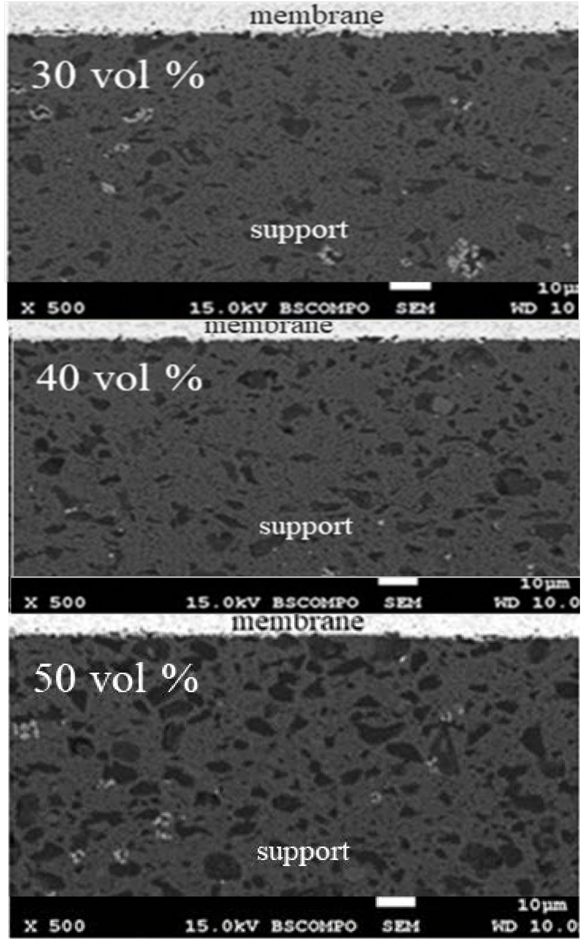
Bilayers with Controlled Microstructures

Membrane Thickness



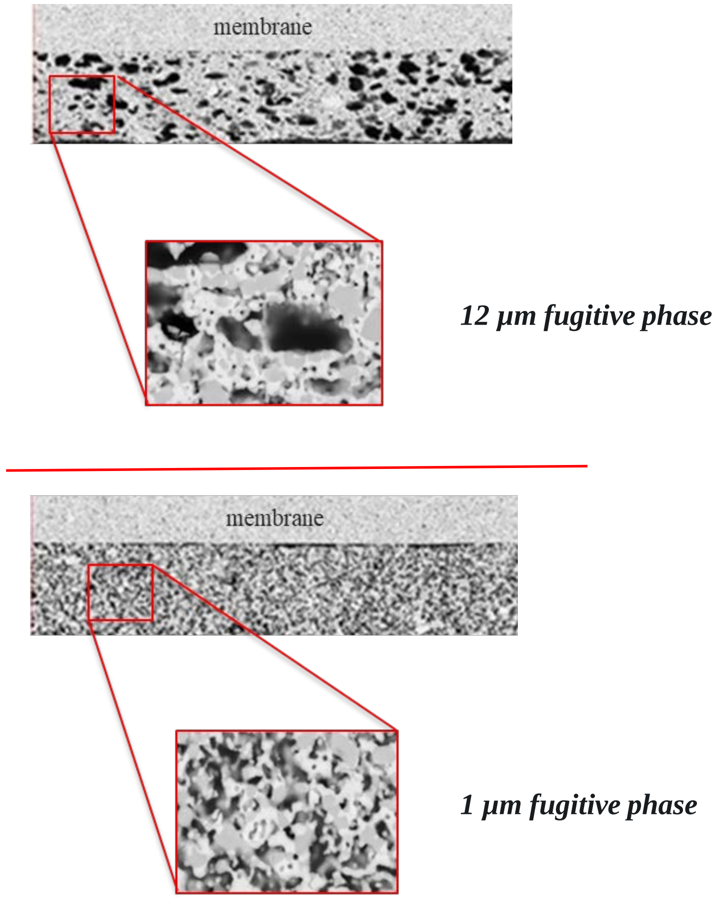
Tailor the membrane thickness by controlling the casting thickness

Vol % Porosity



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

Size of Porosity



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

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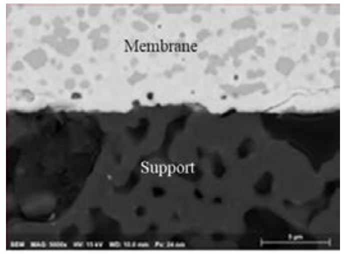
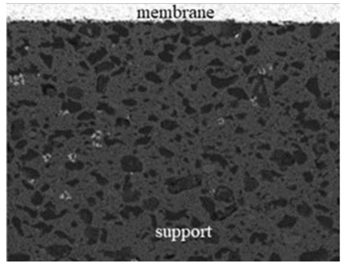
Bilayers with Maximum Oxygen Permeability

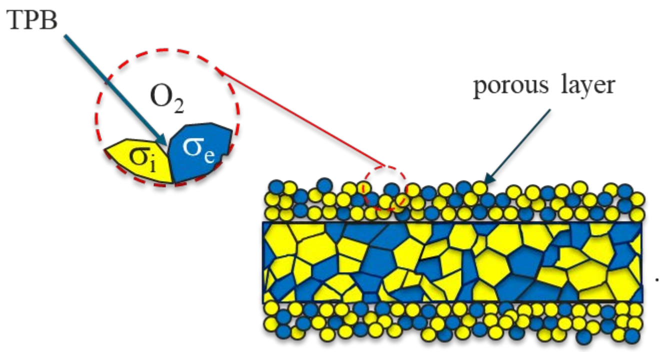
- Limited interaction during sintering of membrane and support (no 2nd phase formation)
- Thin, dense, crack-free membrane
- Porous support with controlled microstructure

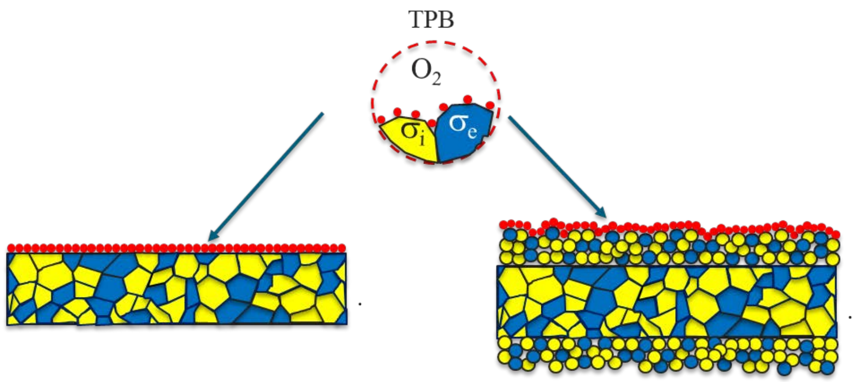
- Expansion of the reaction area into three dimension → improve the reaction kinetics by increasing the effective area of the three-phase boundary (TPB) at both reaction sites

- Increase the reaction kinetics by utilizing a known catalysts at the three phase boundaries

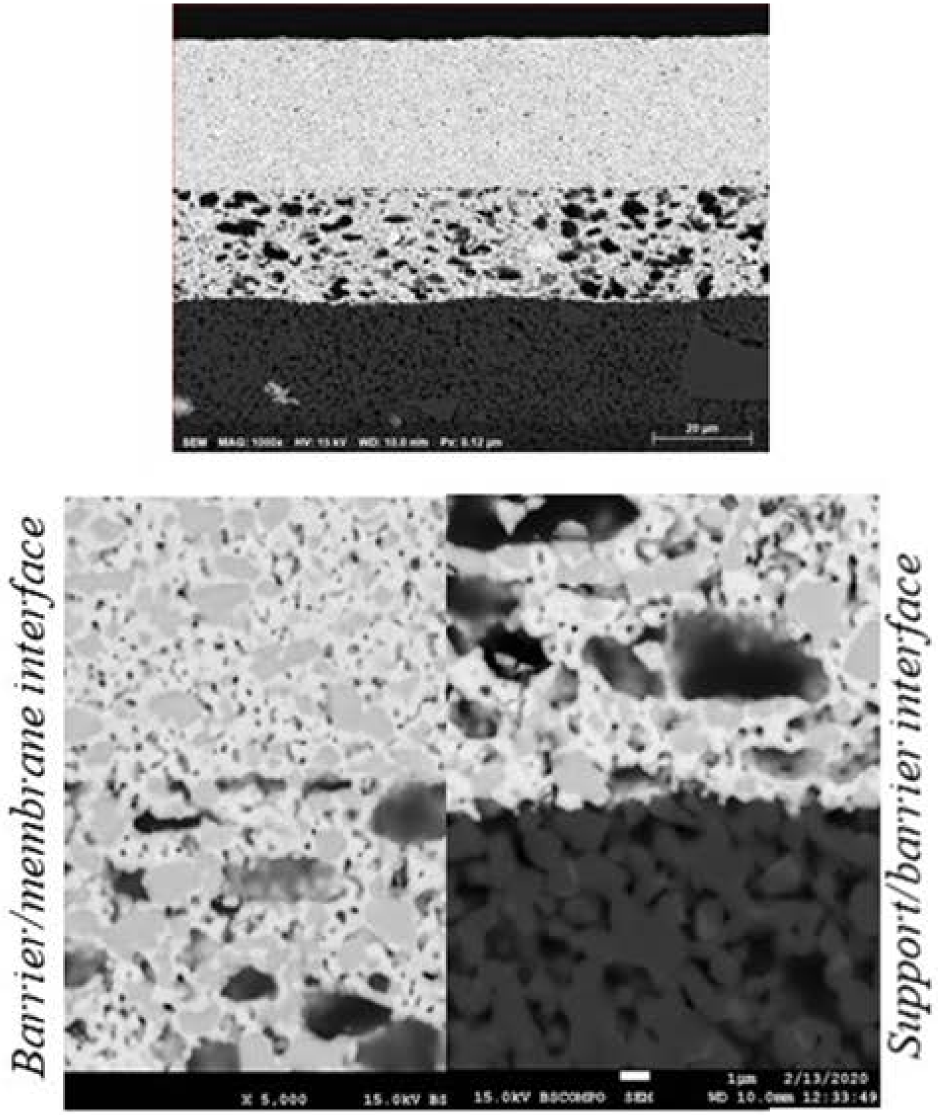


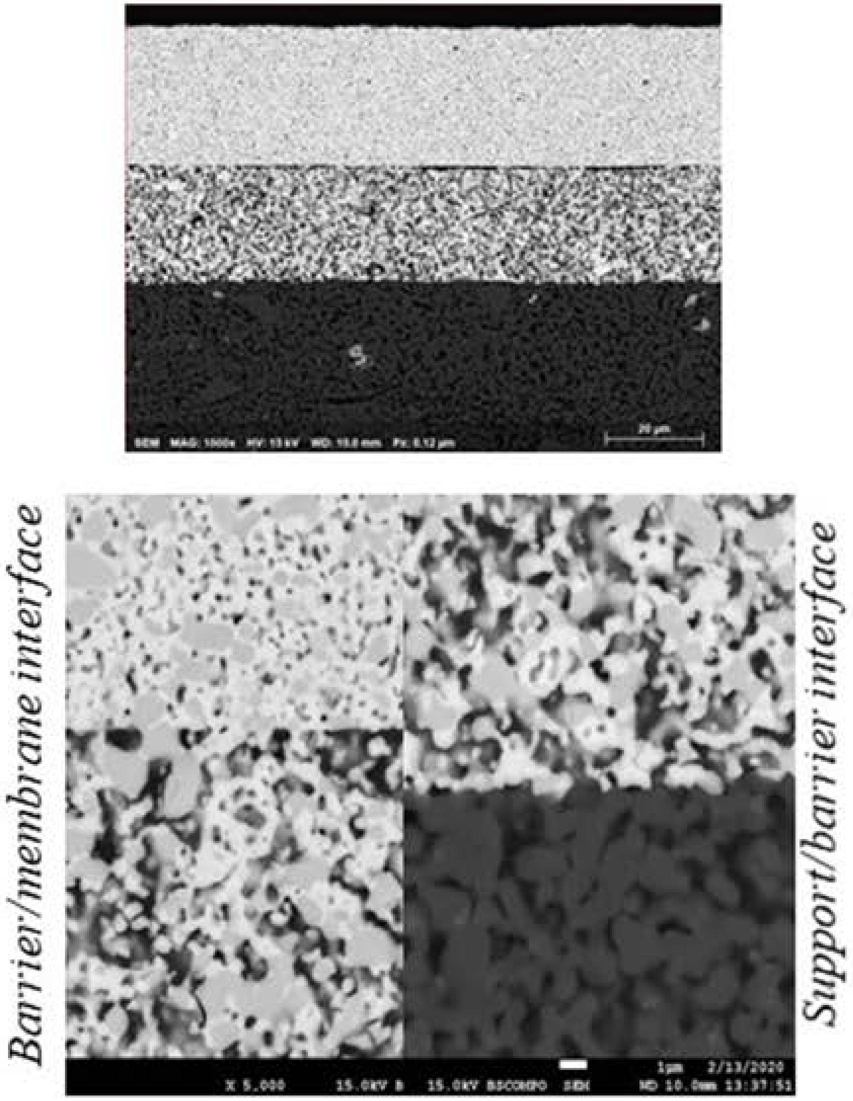






Barrier Layer for Maximum Oxygen Permeability

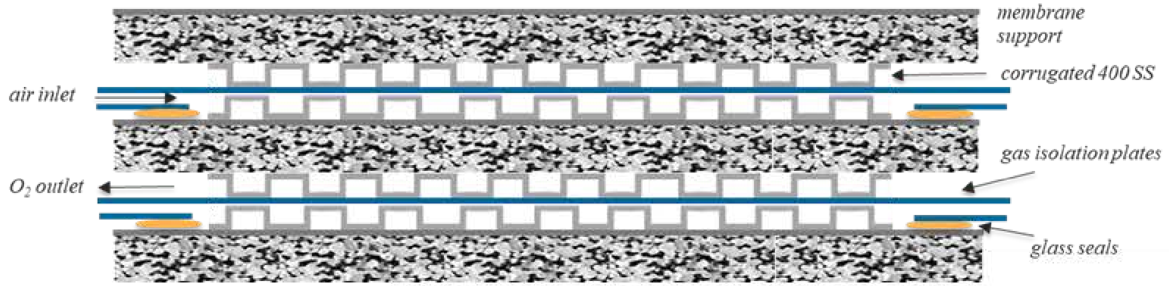




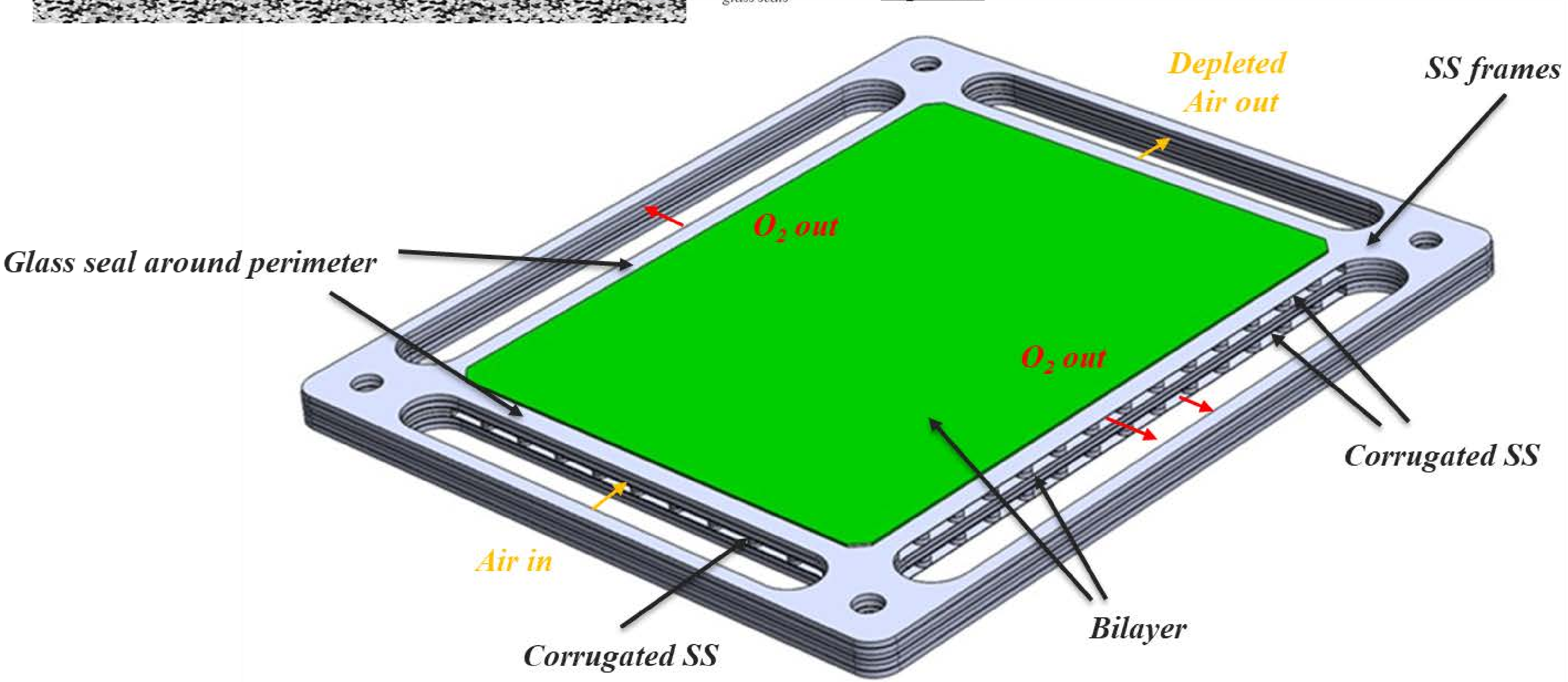
- Barrier layer provides 3-D surface to improve reaction kinetics

Stack Design

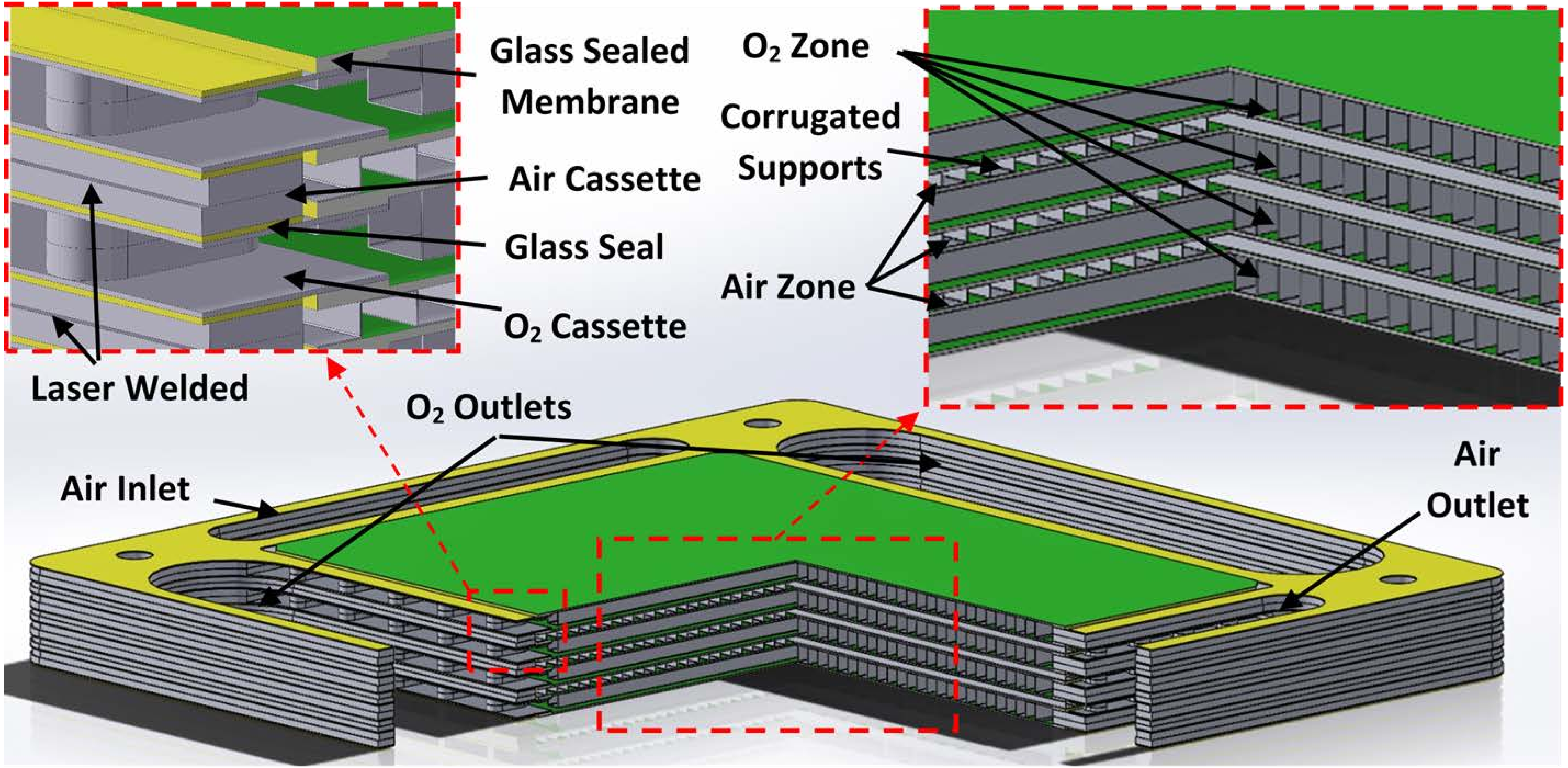
Side View



Top View



Stack Design



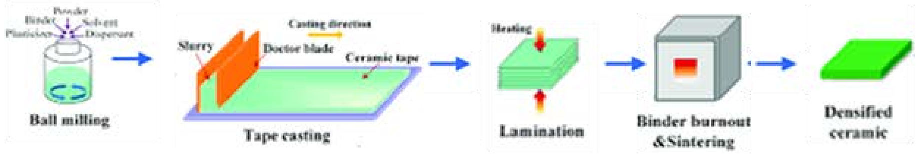
Low Cost Materials and Processes

Materials

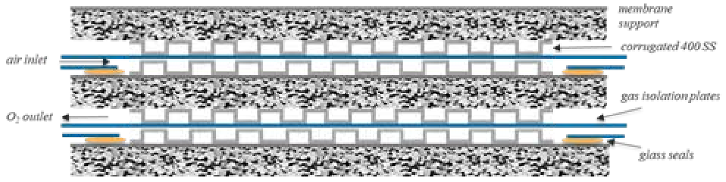
- Membrane (least amount of material used ~ 10-15 µm thick)
  - Ionic conductor - $Ce_{1-x}Gd_xO_{2-x}$
  - Electronic conductor – $La_{0.75}Sr_{0.2}O_{3-x}$
- Support – MgO
- Glass seal (BaO-Al_2O_3-SiO_2)
- Frames, gas isolation plates and corrugated supports
  - 400 series stainless steel

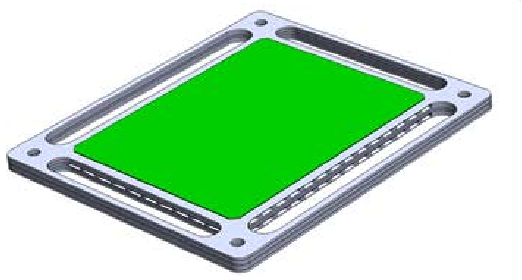
Fabrication processes

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



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



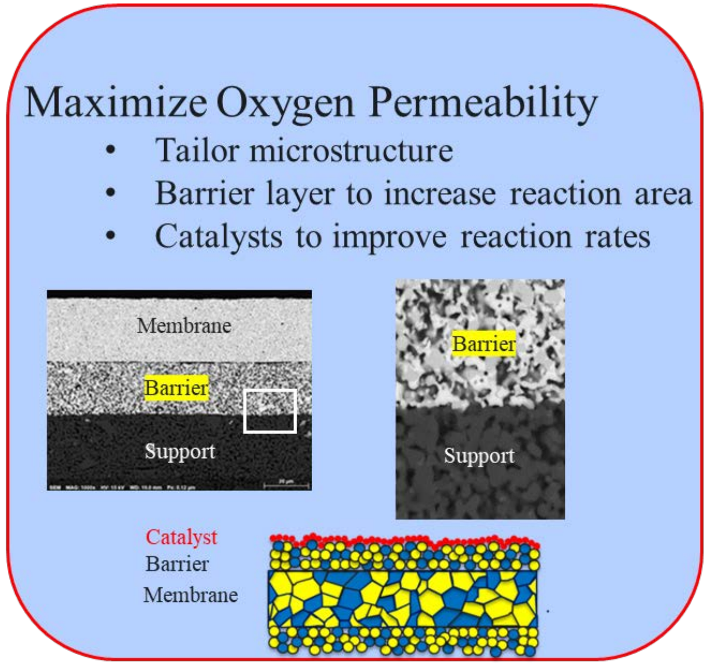


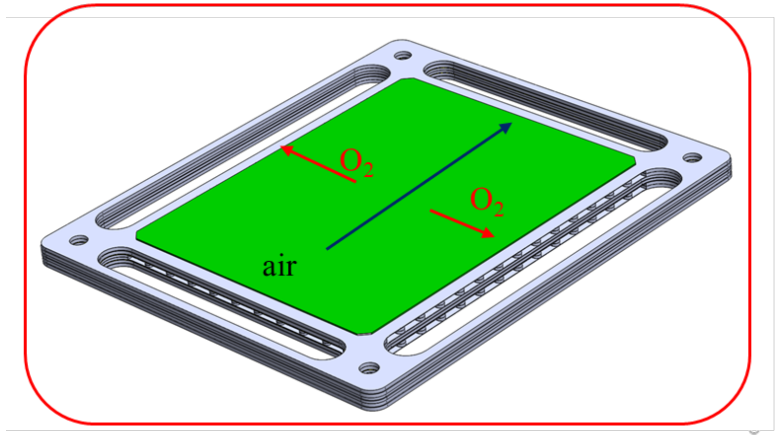
Accomplishments

- Reduced sintering temperature during co-firing to reduce interactions (~1300°C)
- Limited interactions at the membrane/support interface
- 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
- Good mechanical strength 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 such as density, % porosity, size of porosity, shrinkage, etc.
- Ability to scale technology using traditional inexpensive thick film techniques

Project Milestones

Fiscal Year	ID	Description	Planned/ Expected Completion Date	Actual Completion Date	Verification Method
2	M1	Reduce interfacial reactions at membrane-support interface	5/31/2020	3/31/2020	Reduce interfacial interactions via sintering temperature and/or alternative materials to improve the oxygen permeability in the bilayer structure
2	M2	Optimize oxygen flux for 1-2" diameter bilayer structures using barrier layers and catalysts	11/30/2020		Oxygen flux values will be compared to theoretical values calculated at various temperatures on bilayer structures
2	M3	Demonstrate scale up of bilayer structure (10 cm x 10 cm)	2/28/2021		Bilayer structure will be flat and crack free with a dense membrane co-sintered on a porous support using bilayer structures in M2
2	M4	Propose stack Design capable of producing 10 tons/day of oxygen	2/28/2021		Design will use oxygen flux values found on bilayer structures in M2 utilizing low cost frames and glass seals.





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