Pressure Driven Oxygen Separation via Mixed Conducting Dual Phase Technology

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Richland, WA

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2019 Annual Project Review

Gasification Systems

Pittsburgh, PA

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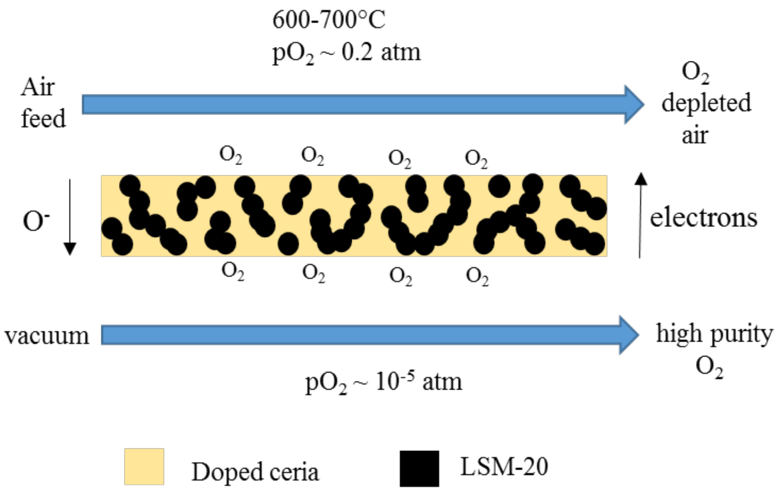
Outline

- **Project Description and Objectives**
- **Project Background**
- **Experimental Procedure and Analysis Methods**
- **Project Update**
  - **Composite Membrane**
  - **Porous Support**
- **Next Steps/Concluding Remarks**

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 MWe gasifier at low cost and high efficiency

  - Mixed conducting two phase material capable of separating oxygen at 600-700°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>



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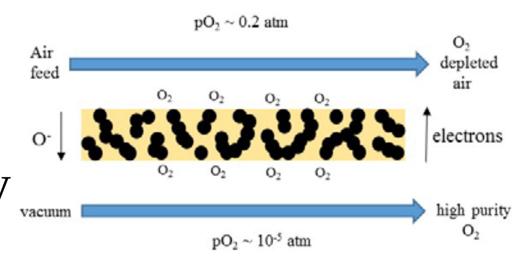
Background – Oxygen Separation

- Cryogenic Air Separation – mature development
  - 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 low capacities (i.e. 300-400 T/day)
  - Purity ~ 95%

- Polymer Membranes – mature
  - Low purity (~ 40%)
- **Ceramic Membranes – R&D**
  - High purity (99+), thermal integration
  - Can be economical depending on oxygen permeability
  - Examples: OTM and ITM

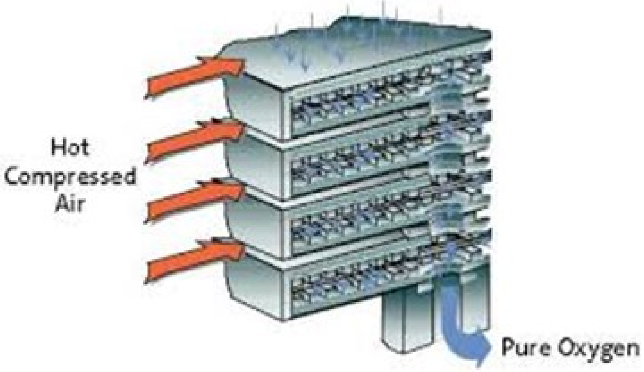


Background – Ceramic Membranes

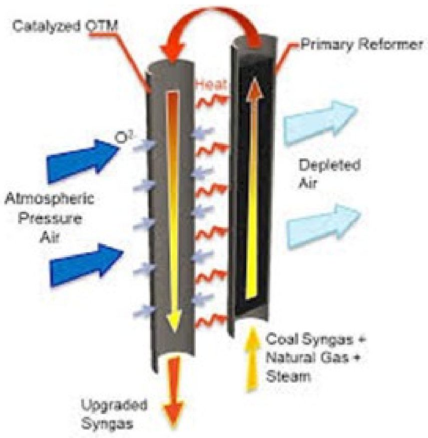
Planar vs Tubular Design

- ***Planar design***
- Ease of manufacturing
- High surface area
- Increased sealing surface area
- Lower/medium temperature (600-700°C)
- Two phase composite membrane (σ_i and σ_e)
- SOFC design experience at PNNL

Planar Design



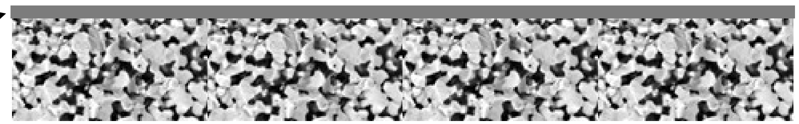
Tubular Design



Background – Bilayer structure

Planar Membrane/Porous Support

Thin composite membrane
(~ 10 µm)



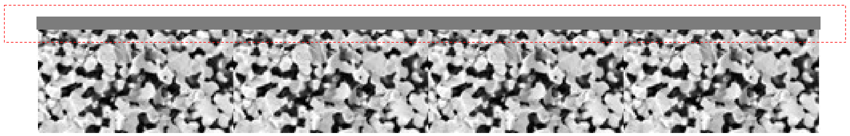
Porous support (~ 0.5-1mm)

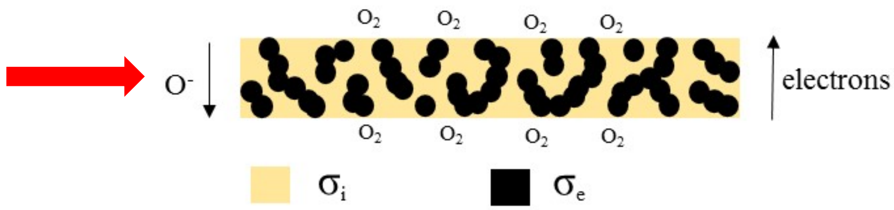
Composite membrane	***Porous Support***
▪ Dense	▪ ~ 50% dense
▪ High σ_i and σ_e	▪ TEC match to membrane
▪ Compatible with glass seal	▪ Mechanical integrity
▪ Inexpensive fabrication	▪ Co-fired w/ membrane
▪ No electrodes	

→ *Design will leverage SOFC stacks developed at PNNL*

Background – Ceramic Membranes

Thin composite membrane (~ 10 μm)





Composite membrane

- Two phase composite
- Similar TEC
- Limited interaction during firing
- High σ_i phase
- Sufficient σ_e phase
- Compatible with glass seal

Material Selection

- <u>*Ionic Conductor*</u>
  - YSZ
  - Doped CeO_2
- <u>*Electronic Conductor*</u>
  - Doped $LaMnO_3$, $LaFeO_3$
  - LSCF
  - $LaCrO_3$

Background – Dense Membrane

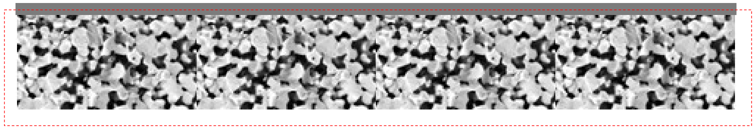
Preliminary Oxygen Flux Calculations

	Doped Ceria	LSM-20
Electrical Conductivity (S/cm)		
600°C	-	100
700°C	-	120
Ionic Conductivity (S/cm)		
600°C	0.018	-
700°C	0.04	-
Thermal Expansion Coefficient (10^{-6})	11.7	11.5

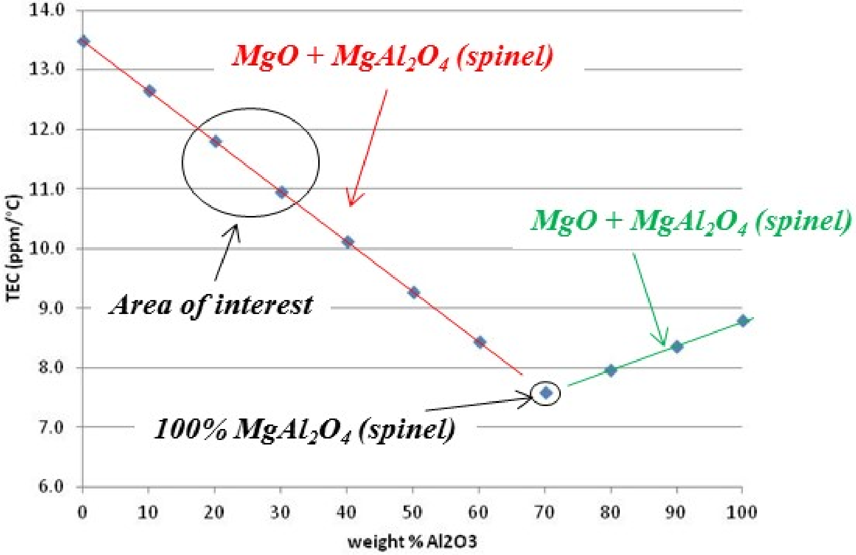
	600°C	700°C
Ionic Conductivity (S/cm)	0.018	0.039
pO2 - air side (atm)	0.2	0.2
pO2 - vacuum side atm	10^{-4}	10^{-4}
Thickness (µm)	10	10
O_2 Flux (A/cm^2)	3.4	8.1
Tons of O_2/day	10	10
Cell area (cm^2)	420	420
Cells/stack	100	100
# stacks required	8.99 (9)	3.72 (4)

→ ***# of stacks is < 10 for both cases which appears to be very reasonable for a 10 ton/day modular ASU***

Background – Porous Support



Porous support (~ 0.5-1mm)



Porous Support

- Two phase composite (Al_2O_3 & MgO)
- Tailor the TEC to match membrane
- Mechanical support
- Use of fugitive phase if necessary
- Sintering aid, Y_2O_3
- Match shrinkage profile of membrane

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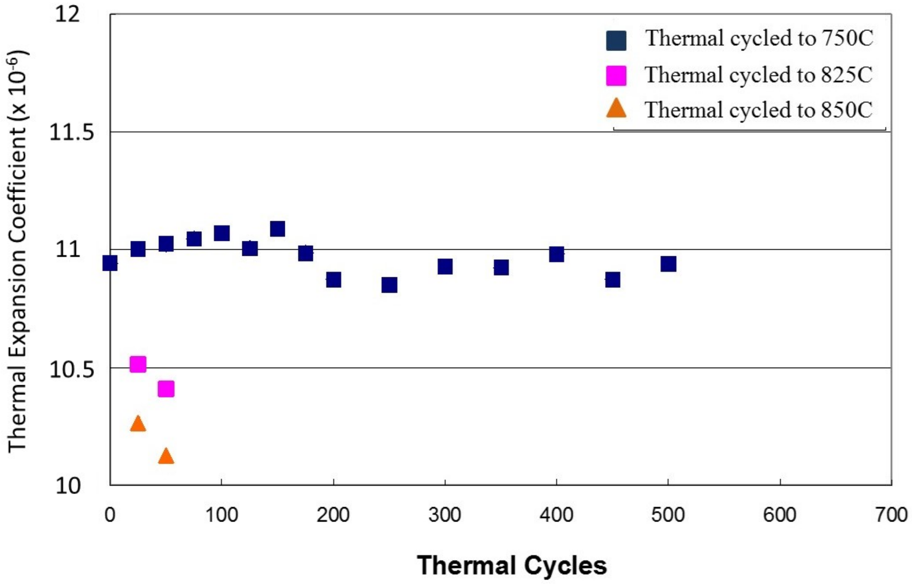
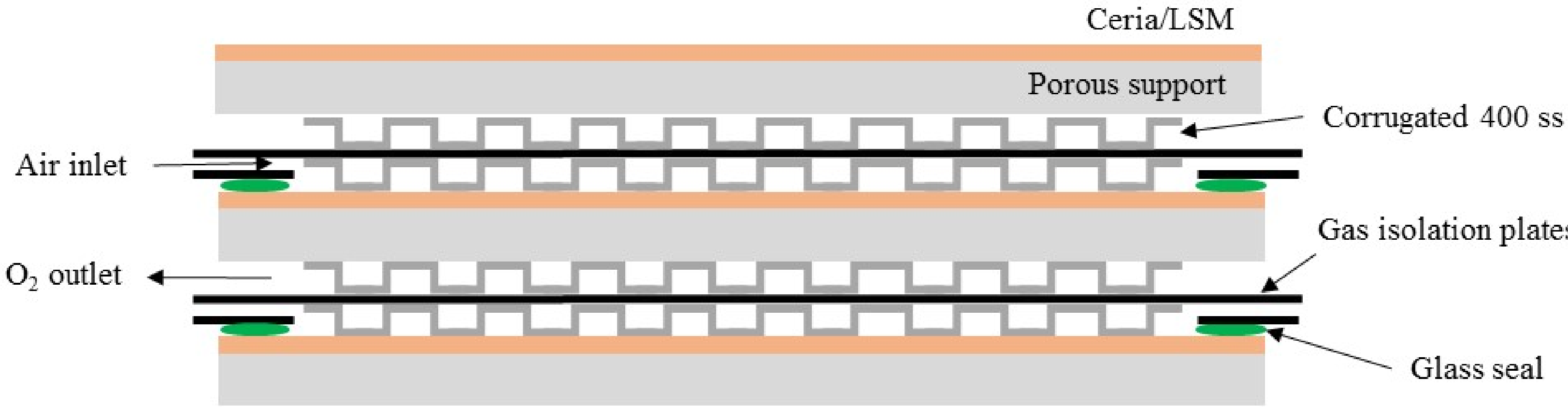
Background – Glass Seals

Proposed Glass-Ceramic Seal

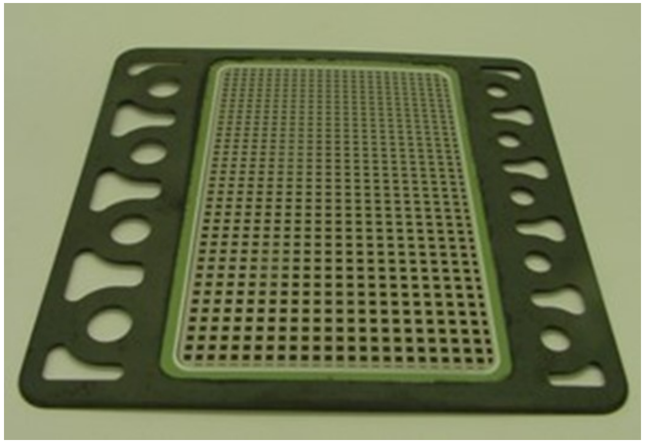
- Barium aluminosilicate glass
- Modified with B_2O_3 and CaO
- Glass-ceramic
- TEC match to membrane
- Minimal interactions
- Extensively studied at PNNL
  - Very stable up to 800°C
    - XRD, SEM,
    - Thermal cycling
    - SOFC tests



Background – Stack Design



- Low cost 400 series stainless punched to net shape & used as manifold
- 400 stainless also used as gas isolation plate
- Barium aluminosilicate glass seal
- Low cost manufacturing methods

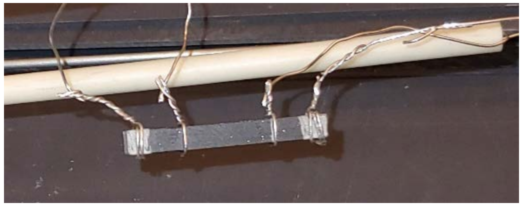


Experimental Procedure & Analysis Methods

Dense Membrane – V_f (ionic conductor)

- σ_{ionic} and $\sigma_{electronic}$
- Chemical and microstructural stability (XRD and SEM w/ EDS and EBSD)
- Dilatometry and sintered shrinkage

4 pt σ measurement



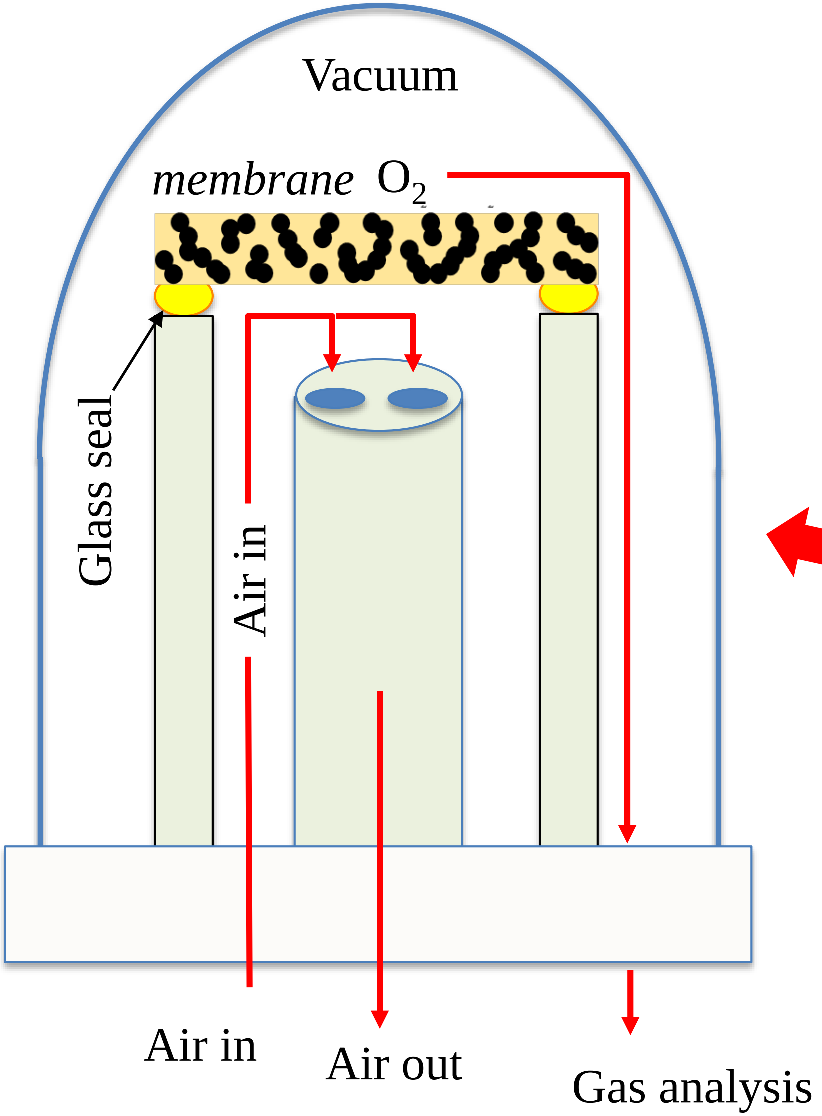
Porous Support – V_f (MgO)

- Mechanical integrity
- Chemical and microstructural stability (XRD and SEM w/ EDS and EBSD)
- Dilatometry and sintered shrinkage

Bilayers (membrane and support)

- Tape casting and lamination process
- Co-sintering for a flat, crack free sample

Experimental Procedure & Analysis Methods



Oxygen Permeability Measurements

- Temperature
- Oxygen partial pressure
- Catalytic surface treatments
  (if needed to improve surface exchange kinetics)

Project Update

Material Selection

Composite Membrane - V_f (ionic conductor)

Electronic conducting phase

$La_{0.9}MnO_3$ (LM90)
$La_{0.75}Sr_{0.2}MnO_3$
$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$*

Ionic conducting phase

$Ce_{0.8}Sm_{0.2}O_2$
$Ce_{0.9}Gd_{0.1}O_2$
$Ce_{0.8}Gd_{0.2}O_2$
$Ce_{0.8}Sm_{0.2}O_2$ w/ 1% Co (SDCC)

Support Structure - V_f (MgO)

Al_2O_3
MgO
Y_2O_3
Carbon black
PMMA spheres

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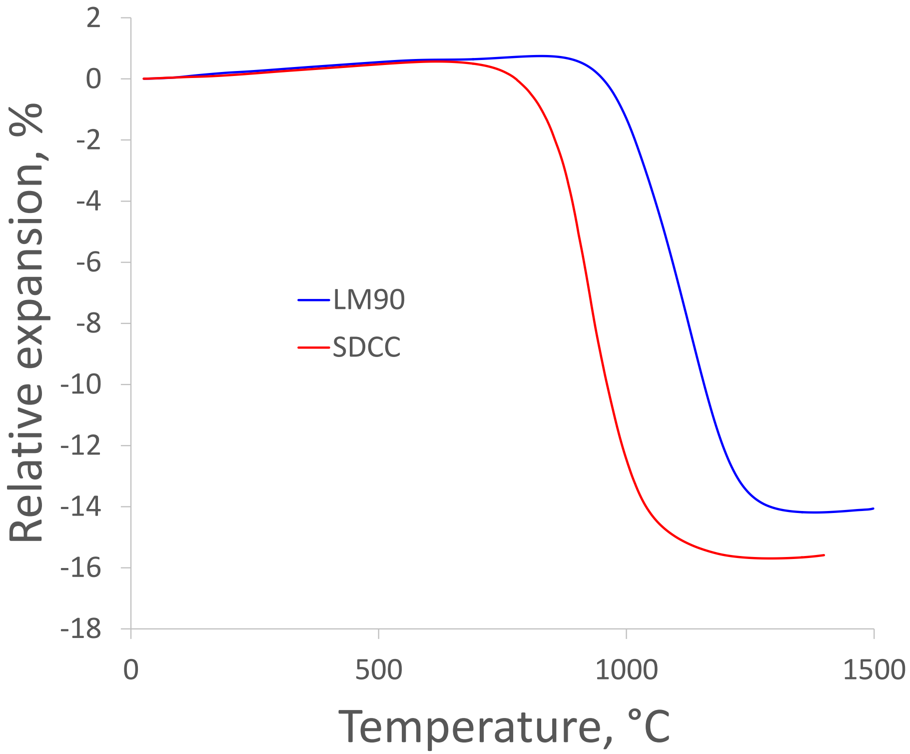
* LSCF is a mixed conductor

Project Update – Sintering SDCC/LM90

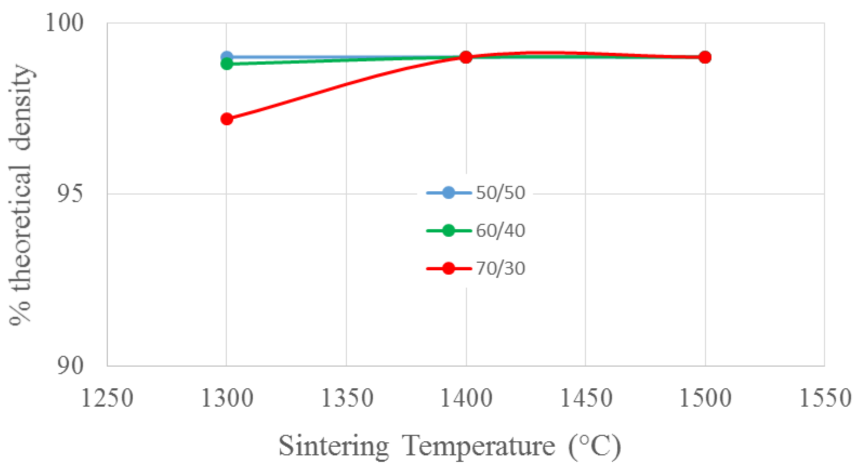
Membrane

End Member Sintering



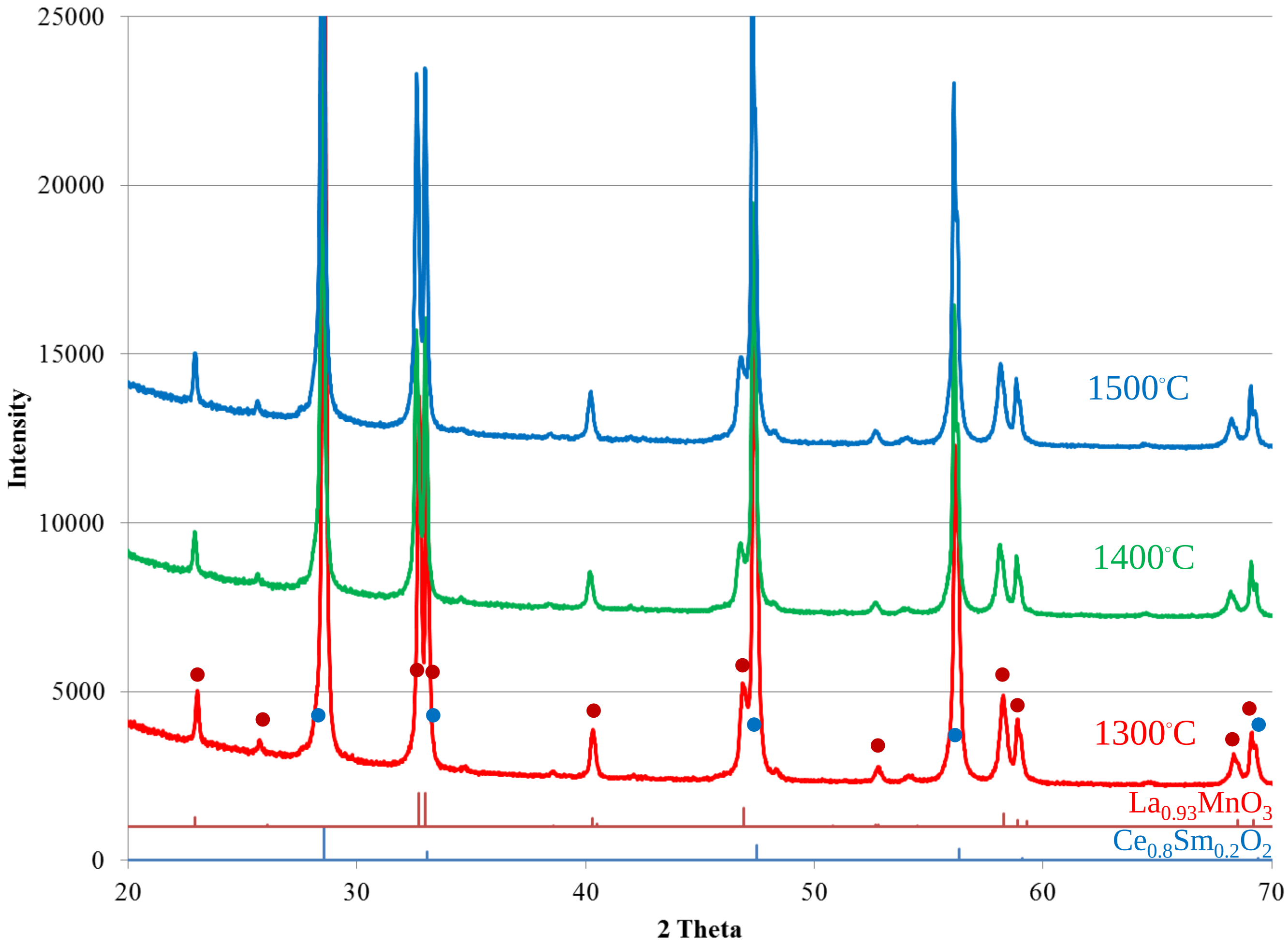
Composite Sintering

	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+



Project Update – Phase Analysis SDCC/LM90 (70/30)

Membrane

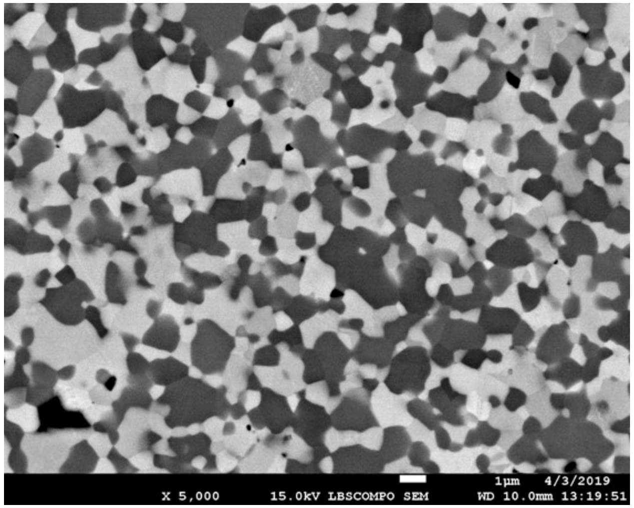


Limited interaction between $LaMnO_3$ and ceria during sintering at 1300-1500°C.

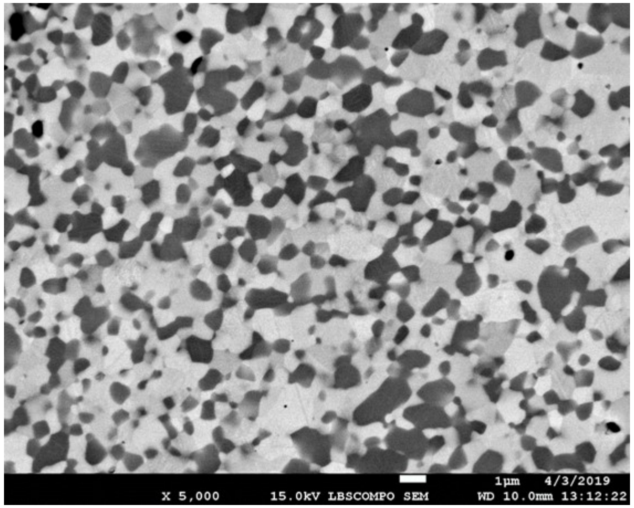
Project Update – Sintering SDCC/LM90 (SEM)

Membrane **Composites sintered at 1400°C**

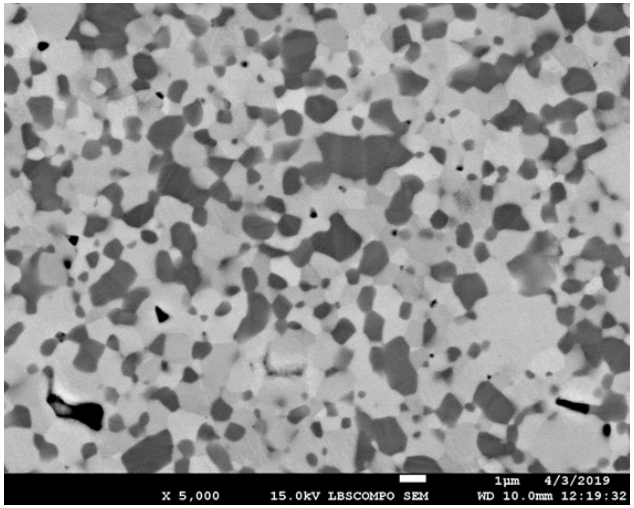
50/50



60/40



70/30



SDCC

LM90

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Project Update – Expansion, conductivity, and O_2 flux

Membrane

		700◦C		
Membrane Component	α	$\sigma_{electronic}$	σ_{ionic}	j
	(10^{-6})	*S/cm*		*A/cm^2*
$La_{0.9}MnO_3$ (LM90)	*	*	-	-
$La_{0.75}Sr_{0.2}MnO_3$	11.5	120	-	-
$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$	14.3	400	0.05	
$Ce_{0.8}Sm_{0.2}O_2$	11.7	-	0.04	-
$Ce_{0.9}Gd_{0.1}O_2$	11.6	-	0.035	-
$Ce_{0.8}Gd_{0.2}O_2$	11.7	-	0.04	-
$Ce_{0.8}Sm_{0.2}O_2$ w/ 1% Co (SDCC)	*	-	*	-
Composites				
SDCC/LM90 (70/30)	11.7		*	*

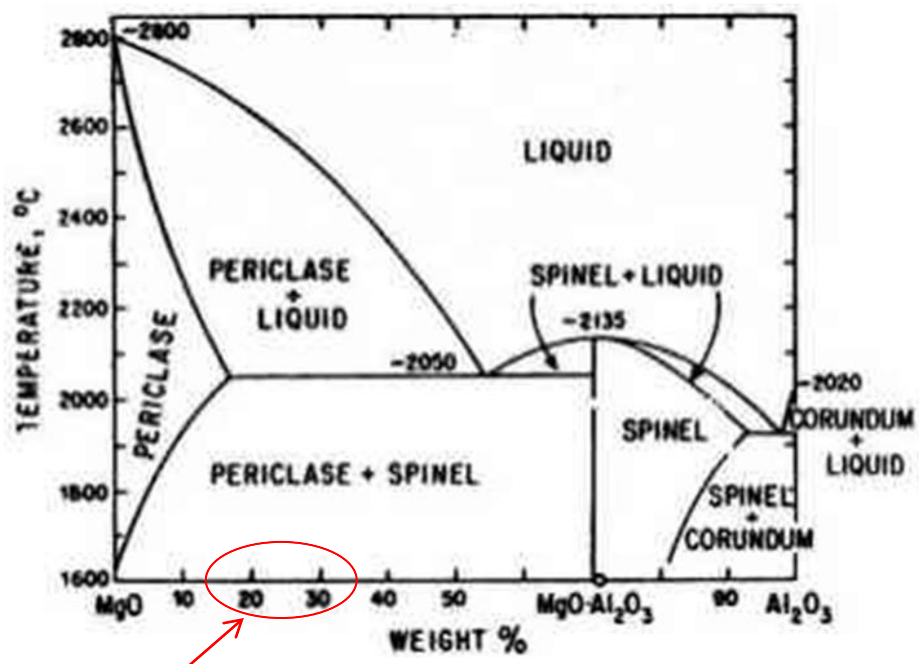
Project Update –MgO/Al_2O_3 Porous support

Support

Material Selection and of Interest

	density (g/cc)	TEC (/°C)	Melting Point (°C)
MgO	3.58	13.5	~2800
Al_2O3	3.99	8.8	~2200
$MgAl_2O_4$	3.58	7.6	~2150
$YAlO_3$	5.35		~2150
Y_2O_3	sintering aid (~ 1-3 %)		~2650

MgO – Al_2O_3 Phase Diagram



Composition of interest ($MgO + MgAl_2O_4$)

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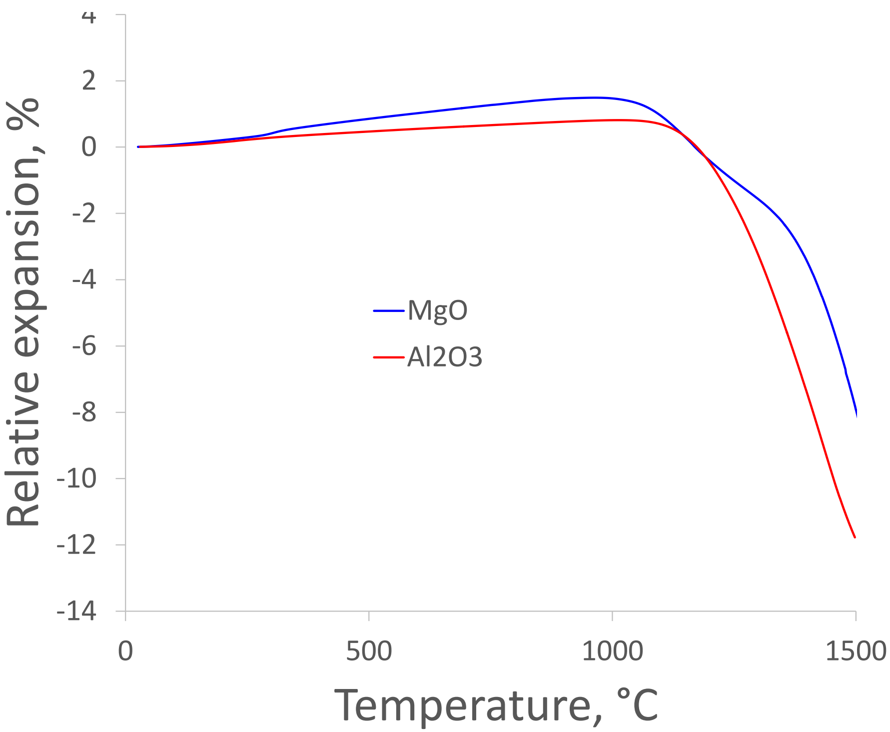
Project Update – Sintering MgO/Al_2O_3

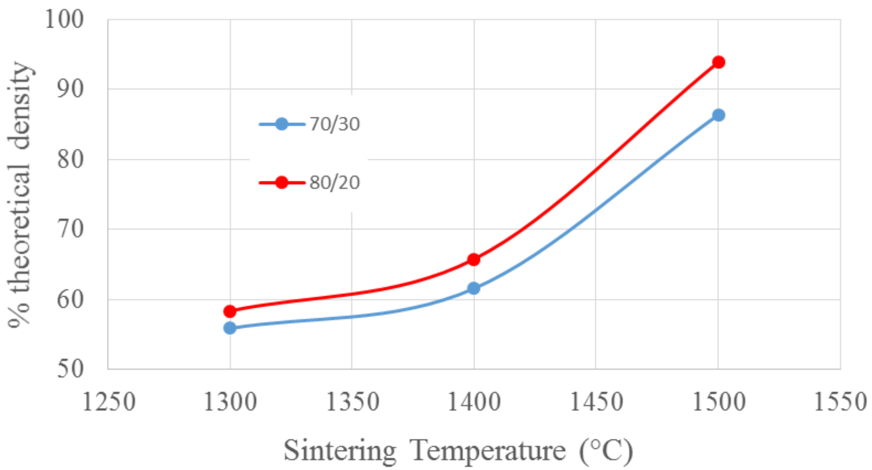
Support

End Member Sintering



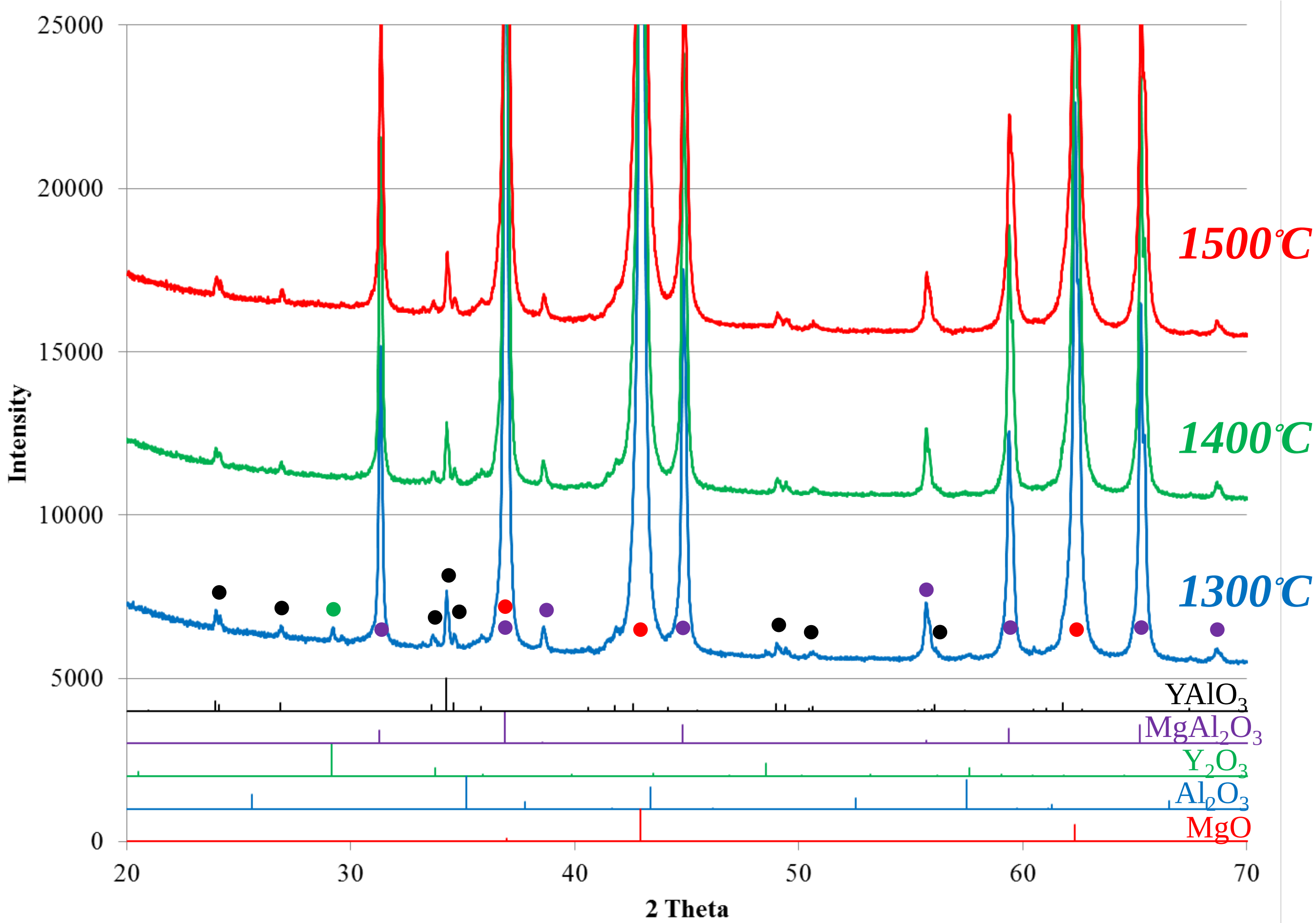
Composite Sintering

	MgO/Al_2O_3 (vol%)	
Sintering Temperature (°C)	70/30	80/20
1300	55.9	58.4
1400	61.6	65.8
1500	86.4	93.9



Project Update - Phase Analysis MgO/Al_2O_3 (70/30)

Support



- MgO and Alumina react to form spinel $MgAl_2O_4$ during sintering between 1300-1500℃.
- Alumina consumed in reaction, sintering aid (Y_2O_3) forms $YAlO_3$.

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Project Update – Expansion and conductivity

Porous Support

		700°C	
Support	α	$\sigma_{electronic}$	σ_{ionic}
	(10^{-6})	*S/cm*	
Al_2O_3	8.8	-	-
MgO	13.4	-	-
$MgAl_2O_4$ (spinel)	7.8	-	-
Composites			
MgO/Al_2O_3 (70/30)	11	-	-
MgO/Al_2O_3 (80/20)	11.8	-	-

Next Steps/Concluding Remarks

Next Steps

- Complete physical, microstructural, electrical, and thermal property evaluations of compositions of interest (membrane and support)
- Analyze oxygen permeability measurements ↔ surface treatments
- Tape cast and laminate bilayers (flat and crack free)

Concluding Remarks

- Preliminary results are encouraging and follow early predictions
- Oxygen permeability measurements and results are critical to minimize number of stacks required to produce 10 tons/day of oxygen

Acknowledgements

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