Pressure Driven Oxygen Separation

David Reed, Kerry Meinhardt, Jon Helgeland, Greg Coffey, and Pepa Matyas

Pacific Northwest National Laboratory
Richland, WA

2020 Gasification Project Review Meeting

September 2, 2020
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, no electrical energy needed for oxygen separation
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 ($\sigma_i$ and $\sigma_e$)
- SOFC design experience at PNNL
Proposed Ceramic Membrane Technologies

**Bilayer Structure**

Thin composite membrane
(~ 10 μm)

Porous support (~ 0.5-1mm)

**Composite membrane**
- Dense
- High $\sigma_i$ and $\sigma_e$
- 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 (σ₁ & σₑ)
- Similar TEC
- Limited interaction during firing
- High σ₁ phase
- Sufficient σₑ phase
- Compatible with glass seal

**Material Selection**

*Ionic Conductor*
- Doped CeO₂

*Electronic Conductor*
- Doped LaMnO₃
- Doped LaFeO₃
Proposed Ceramic Membrane Technologies

Composite Membrane $O_2$ Permeability/Flux Calculations

<table>
<thead>
<tr>
<th>Case 1</th>
<th>Case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic conductivity:</td>
<td>0.0233</td>
</tr>
<tr>
<td>$P(O_2)_{\text{I}}$:</td>
<td>0.2 atm</td>
</tr>
<tr>
<td>$P(O_2)_{\text{II}}$:</td>
<td>1.00E-04 atm</td>
</tr>
<tr>
<td>Temp (°C):</td>
<td>700</td>
</tr>
<tr>
<td>Temp (K):</td>
<td>973</td>
</tr>
<tr>
<td>Thickness (um):</td>
<td>10</td>
</tr>
<tr>
<td>Thickness (cm):</td>
<td>0.001</td>
</tr>
<tr>
<td>Flux (A/cm²):</td>
<td>3.71</td>
</tr>
<tr>
<td>Flux (moles O₂/cm²-s):</td>
<td>9.62E-06</td>
</tr>
<tr>
<td>Flux (grams O₂/cm²-s):</td>
<td>3.08E-04</td>
</tr>
<tr>
<td>Flux (grams O₂/cm²-h):</td>
<td>1.11</td>
</tr>
<tr>
<td>Flux (grams O₂/cm²-day):</td>
<td>26.59</td>
</tr>
<tr>
<td>Flux (lbs O₂/cm²-day):</td>
<td>5.86E-02</td>
</tr>
<tr>
<td>Pounds of oxygen required/day:</td>
<td>20000</td>
</tr>
<tr>
<td>Total cell area required (cm²):</td>
<td>341155.97</td>
</tr>
<tr>
<td>Cell area(cm²):</td>
<td>420</td>
</tr>
<tr>
<td># of cells required:</td>
<td>812.28</td>
</tr>
<tr>
<td>Cells/stack:</td>
<td>100</td>
</tr>
<tr>
<td># of stacks required:</td>
<td>8.12</td>
</tr>
</tbody>
</table>

**Input Parameters**
- $\sigma_i$
- $pO_2^I$ and $pO_2^{II}$
- Temperature
- Membrane thickness
- lbs. of oxygen/day
- Cell area
- Cells/stack

**Output Value**
$\Rightarrow$ # 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

Doped CeO$_2$
Sm$_{Ce}$' → $2[V_{O}^{\ddagger\ddagger}]$

Examples
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

Doped LaMnO$_3$
Acceptor doped p-type

Examples
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)
Composite Membrane Characterization

Interaction Studies

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

Composite Dilatometry

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha \times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDCC-LM90 50/50</td>
<td>11.11</td>
</tr>
<tr>
<td>SDCC-LM90 60/40</td>
<td>11.57</td>
</tr>
<tr>
<td>SDCC-LM90 70/30</td>
<td>12.02</td>
</tr>
<tr>
<td>GDC20-LSM20 50/50</td>
<td>11.83</td>
</tr>
<tr>
<td>GDC20-LSM20 60/40</td>
<td>11.89</td>
</tr>
<tr>
<td>GDC20-LSM20 70/30</td>
<td>12.09</td>
</tr>
<tr>
<td>SDCC-LSM20 60/40</td>
<td>11.93</td>
</tr>
<tr>
<td>SDCC-LSM20 70/30</td>
<td>11.91</td>
</tr>
</tbody>
</table>

• Typical values of $\alpha$ are $\sim 12 \times 10^{-6}/°\text{C}$
Composite Membrane Characterization

**Electrical Conductivity**

- Electrical conductivity ($\sigma_e$) controlled by perovskite phase
- $\sigma_e \sim 3$ orders of magnitude greater than ionic conductivity ($\sigma_i$)
- Percolation in perovskite phase

**Ionic Conductivity**

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

Permeability Measurements

Self-supporting composite membranes (~ 600 µm)

- $\sigma_1$ 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\textsubscript{2} \rightarrow the membrane thickness needs to be on the order of 10-15 µm.
- Membrane will need to be supported \rightarrow 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

Results
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
Results

- 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

Glass seal around perimeter

SS frames

Corrugated SS

Depleted Air out

O₂ out

O₂ out

Air in

Corrugated SS

Bilayer

Corrugated 406/SS

Gas isolation plates
Stack Design
Low Cost Materials and Processes

**Materials**
- Membrane (least amount of material used ~ 10-15 μm thick)
  - Ionic conductor - Ce_{1-x}Gd_{x}O_{2-x}
  - Electronic conductor – La_{0.75}Sr_{0.2}O_{3-x}
- Support – MgO
- Glass seal (BaO-Al_{2}O_{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

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

### Maximize Oxygen Permeability
- Tailor microstructure
- Barrier layer to increase reaction area
- Catalysts to improve reaction rates
The authors wish to thank Venkat Venkataraman, David Lyons, and Jai-Woh Kim from DOE Office of Fossil Energy for their support of this project.