Membrane Development for Hybrid Sulfur Electrolysis and Oxygen Separation

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.
The Nuclear Hydrogen Initiative is investigating thermochemical cycles as one of the promising methods for hydrogen production using Generation IV reactors.

The Sulfur-based cycles –
- Sulfur-Iodine
- Hybrid Sulfur
are the focus of the current NHI research program.

These cycles are the most technically developed of the more than 200 cycles reviewed and have the potential for high efficiencies.

Figure 2  Schematic of nuclear reactor heat source with a water/thermochemical hydrogen production system.

Sulfur-Iodine versus Hybrid Sulfur Cycle

Hybrid-Sulfur (thermal and electrochemical reactors)

advantages
- fewer reactions
- no HI or I₂

disadvantages
- electrochemical reactor cost
- electricity needed (efficiency??)

Sulfur Iodine
(1) \( \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2 \)
(2) \( 2\text{HI} \rightarrow \text{I}_2 + \text{H}_2 \)
(3) \( 2\text{H}_2\text{O} + \text{SO}_2 + \text{I}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI} \)

Hybrid-Sulfur
(1) \( \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2 \)
(2) \( 2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2 \)
SNL Membrane Approach for Efficiency and Process Improvements

**High temperature thermal reactor**

Synthesize new oxygen anion conducting ceramic membranes for high temperature oxygen separation.

Sandia has proven capability in novel ceramic materials and a wide-ranging program in membrane separations.

Oxygen anion conducting ceramics are being tested for their stability in the high temperature reactor environment and their separation characteristics.

**Proton exchange membrane electrochemical reactor**

Develop new high-temperature (120-150°C) proton exchange membranes with high conductivity and low SO₂ crossover for efficient electrolysis.

Sandia-synthesized polymer membranes have shown promise in high temperature electrochemical processes, e.g. fuel cells.

Sulfonated membranes with high temperature capability are being tested under a variety of conditions in an SO₂ electrolysis cell. Conditions of the process unit are being optimized and efficiency/lifetime is being measured.
Ceramic Oxygen Separation Membranes

**Characteristics:**
- Dense Ceramic Membrane—separates via ion conduction, not size exclusion
- Self-supporting
- Mixed ionic-electronic conductor—ionic component allows for conduction of oxide anion while electronic component eliminates the need for an applied potential
Perovskite $\text{ABO}_3$

- Stable at high temperatures
- Amenable to doping and substitution by a variety of cations on both the A- and B-sites
- Can stabilize oxygen nonstoichiometries
- Mixed ionic-electronic conductivities
- Known membrane materials
**Synthesis and Characterization**

**Nitrate synthesis:**
- Nitrates of starting materials dissolved in DI H₂O
- Citric acid added
- Sol’n heated at 90 ºC to evaporate H₂O
- Resulting gels dried overnight then self-ignited at 400 ºC
- Powder ground up in mortar and pestle
- Sintered at 1250 ºC for 24 hr

**Characterization:**
- Powder x-ray diffraction (PXRD)
- Thermogravimetric analysis (TGA)
- Four-probe conductivity
- Scanning electron microscopy/electron dispersive spectroscopy
- Permeation measurements
PXRD of La$_{0.1}$Sr$_{0.9}$Co$_{0.7}$Mn$_{0.3}$O$_{3-\delta}$

Space group $Pm-3m$

$R_f = 4.78$

$\text{Chi}^2 = 4.44$
The first part of the graph shows the weight change as the temperature is cycled between 50-850 °C, under a constant flow of O₂ gas. This describes an easily reversible temperature-swing adsorption/desorption of oxygen.

The second part of the graph illustrates the reversible weight change as a function of oxygen partial pressure, by cycling the gas between O₂ and Ar at a constant temperature of 850 °C. This implies that the material can transport oxygen across a membrane by pressure differential.

X-ray diffraction of the material after TGA cycles shows little/no change in structure which illustrates the stability of the structure.
Four-Probe Conductivity of LSCM

• Conductivity is several orders of magnitude better than YSZ
• Conductivity ↑ as temperature ↑ and pO₂ ↑
• Large magnitude implies electronic conductivity contribution
• Ionic contribution between 0.2 – 0.4 S/cm at 850 °C

Garino, SNL
Oxygen Permeation Unit

- Constructed of Inconel 600 Ni alloy
- Mass flow controller (air)
- Thermocouple
- Membrane
- To μGC
Permeation Unit - Design

Cu O-ring seal

thermocouple

He

O$_2$

tube furnace

$\frac{3}{4}$"

$\frac{1}{8}$"

$\frac{1}{8}$"

membrane

to micro GC

air out

air in
Permeation of LSCM Membranes

Eltron Research Inc.
Mini $\text{H}_2\text{SO}_4$ Decomposition Reactor

Goal: To test the stability of the membrane under “reactor” conditions

F. Gelbard, SNL
Post-\(\text{H}_2\text{SO}_4\) Decomposition

- Microscopy of cross-section reveals corrosion layer of approx. 5 µm
- XRD (above) shows formation of \(\text{SrSO}_4\) and possibly \(\text{SrS}\)
- Not yet known if corrosion caused by exposure to \(\text{H}_2\text{SO}_4\), \(\text{SO}_2\), or both
- Membrane can be regenerated by heating to 1300 °C under \(\text{O}_2\)
Summary

• The La$_{0.1}$Sr$_{0.9}$Co$_{1-y}$Mn$_y$O$_{3-\delta}$ (LSCM) family shows promise for use as ceramic high-temperature oxygen separation membranes
• The materials are robust under varying pO$_2$ and show reversible oxygen sorption properties at 850 ºC
• Permeation measurements show the membranes are oxygen permeable
• Preliminary stability tests show at least some corrosion occurs upon exposure to the H$_2$SO$_4$ decomposition stream at 850 ºC

Ongoing Work

• Ongoing high temperature permeation studies (SNL)
• Continued structural elucidation
• Determine extent of corrosion during H$_2$SO$_4$ decomposition and possible mitigation steps
• Continue membrane development (density, processing, scale-up)
• Testing on actual decomposition reactor
High Temperature Polymeric Proton Conducting Membranes
Sulfonated Diels-Alder Poly(phenylene) - SDAPP

- Thermal Stability
- Good Chemical Stability
- Chemical Diversity
- Compositional Control
- Ion Conductivity
- Morphology

Polyphenylenes are a chemically, thermally, and mechanically stable backbone upon which to build a library of membranes (with both cation and anion fixed sites) for application to a large array of membrane-based processes such as fuel cells, water desalination, electrodialysis, etc.

Fujimoto, C.H, Hickner, M.A., Cornelius, C.J., Loy, D.A.  
Membrane is critical for:
• low $\text{SO}_2$ crossover
• efficient water transport
• high temperature operation

**SNL Membrane Performance**
Target: 0.5 mA/cm$^2$ at 0.6V
Increased Temperature Promotes Better Performance
High Temperature Enabled by SNL membranes

Cell Conditions:
- 10 cm² cell
- SDAPP 2.2 meq/g membrane batch
- 2 mg Pt/cm² Pt Black anode and cathode
- Dry SO₂ gas anode, 100 sccm constant SO₂ flow rate with 15 psig backpressure
- Preheated liquid water cathode, 3 mL/min constant H₂O flow rate with 15 psig backpressure

Total cell current at 0.7 V cell potential of SDAPP 2.2 meq/g electrolysis cell with time at 100°C, 110°C, and 120°C cell temperature.
Performance increase of SNL Membrane Electrolysis Cell at 0.7 V

Current density at 0.7 V cell potential of SDAPP 2.2 meq/g electrolysis cell as a function of temperature
The average potential of the electrolysis cell for 10 minutes is 0.75 V. The previous best performance of this membrane was 0.83 V at 500 mA/cm² and 80°C as measured by University of South Carolina.

Cell potential at 500 mA/cm² and 120°C for SNL SDAPP 2.2 meq/g electrolysis cell.
Higher current densities are achieved at elevated temperatures with 0.4 mA/cm² at 120°C. Extended stable performance for 16 hours at 0.8V and 120°C is also demonstrated. The SDAAP 2.2 meq/g (4-141-D batch) electrolysis cell was tested with 100 sccm dry SO₂ and 6.4 ml/min H₂O(Ⅰ) flow rates and 15 psig backpressure.
Decreased SO₂ Crossover Using SNL Membranes –
less process loss, higher efficiency

SO₂ crossover
- process loss
- parasitic H₂ consumption
- elemental sulfur buildup on the cathode, block reaction sites

SO₂ flux to cathode is lower for Sandia membranes even though SNL membranes are thinner.

Steady-state SO₂ flux for Sandia membrane SDAAP 2.2 meq/g (4-141-D) and Nafion 212 (Lynntech MEA).
Potential H₂ Losses from SO₂ Crossover

Hydrogen consumption at cell cathode from SO₂ Crossover:

\[ \text{SO}_2 + 2 \text{H}_2 \rightarrow \text{S}_{\text{solid}} + 2 \text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Crossover Flux ( \mu\text{mol SO}_2/\text{cm}^2\text{s} )</th>
<th>Theoretical Maximum H₂ Consumption ( \mu\text{mol H}_2/\text{cm}^2\text{s} )</th>
<th>Cell Hydrogen Production ( \mu\text{mol H}_2/\text{cm}^2\text{s} )</th>
<th>Theoretical Maximum %H₂ Loss</th>
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</thead>
<tbody>
<tr>
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<td>26.9</td>
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<tr>
<td>120</td>
<td>0.176</td>
<td>0.352</td>
<td>2.10</td>
<td>16.8</td>
</tr>
</tbody>
</table>

More efficient hydrogen production is achieved at 120°C cell operating temperature.

The number noted above are the maximum amount of H₂ lost. In reality, ~ 5% penalty is observed due to counter water flux at high currents.
**Summary**

- SNL membranes have shown promise in SO$_2$ electrolyzer tests.
- High temperature, up to 120°C, and long run-time performance has been demonstrated with SNL membranes.
- SNL membranes have approximately 50% less SO$_2$ permeability than Nafion membranes.
- Batch-to-batch repeatability needs improvement.

**Ongoing Work**

- Repeated scaled-up synthesis of the polymer.
- Large film casting.
- Higher temperature variants of SNL polymers being tested.
- Additional SO$_2$ crossover measurements.
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