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DOE Hydrogen Program

# Membrane Development for Hybrid Sulfur Electrolysis and Oxygen Separation

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National Nuclear Security Administration

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Sandia National Laboratories

# Thermochemical Cycles

Joint study by Sandia, General Atomics, U. KY. to define “an economically feasible concept for production of hydrogen, by nuclear means, using an advanced high temperature nuclear reactor as the energy source.”

(L.C. Brown *et al*., High Efficiency Generation of Hydrogen Fuels Using Nuclear Power: Final Technical Report for the period August 1, 1999 through September 30, 2002)

**Metrics included (but not limited to):**

- number of reactions
- degree of demonstration
- temperature
- number of published references
- reaction phases (gas, solid, liquid)
- corrosiveness
- efficiency

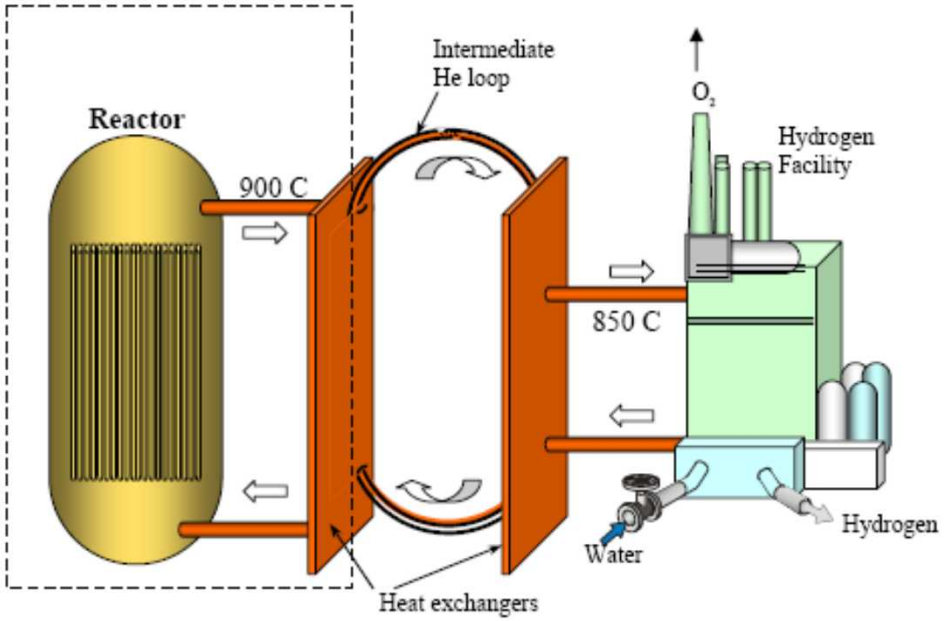


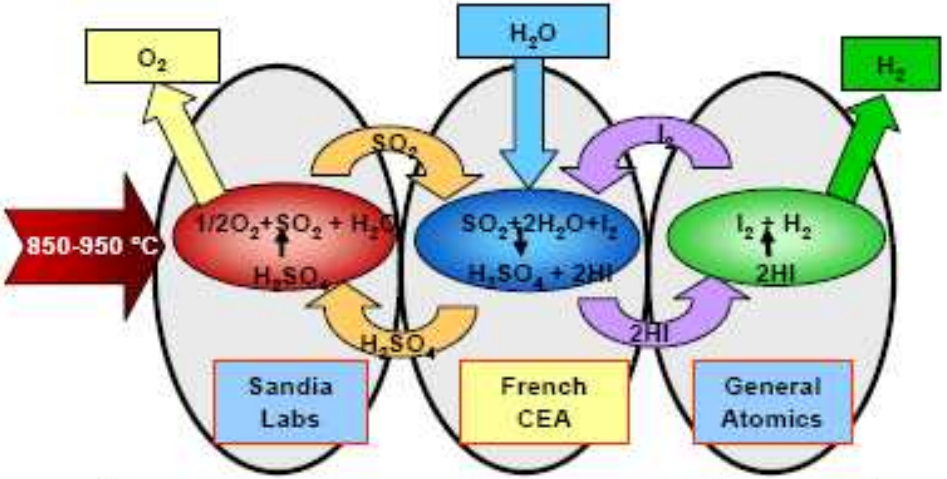

**Figure 2** Schematic of nuclear reactor heat source with a water/thermochemical hydrogen production system.

(Albert C. Marshall SAND2002-0513 February 2002 An Assessment of Reactor Types for Thermochemical Hydrogen Production)

# Sulfur-Iodine versus Hybrid Sulfur Cycle

**Hybrid-Sulfur (thermal and electrochemical reactors)**

| **advantages** | **disadvantages** |
|---|---|
| - fewer reactions | - electrochemical reactor cost |
| - no HI or $I_2$ | - electricity needed (efficiency??) |

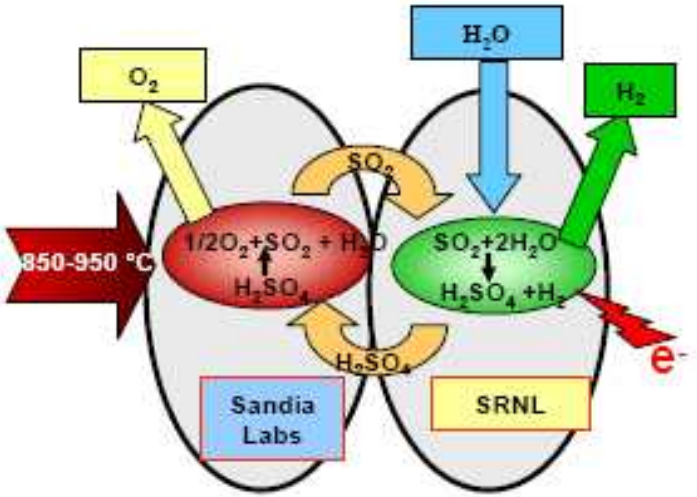



***Sulfur Iodine***

(1) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

(2) $2HI \rightarrow I_2 + H_2$

(3) $2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$




***Hybrid-Sulfur***

(1) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

(2) $2H_2O + SO_2 \rightarrow H_2SO_4 + H_2$

# 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 $SO_2$ crossover for efficient electrolysis**

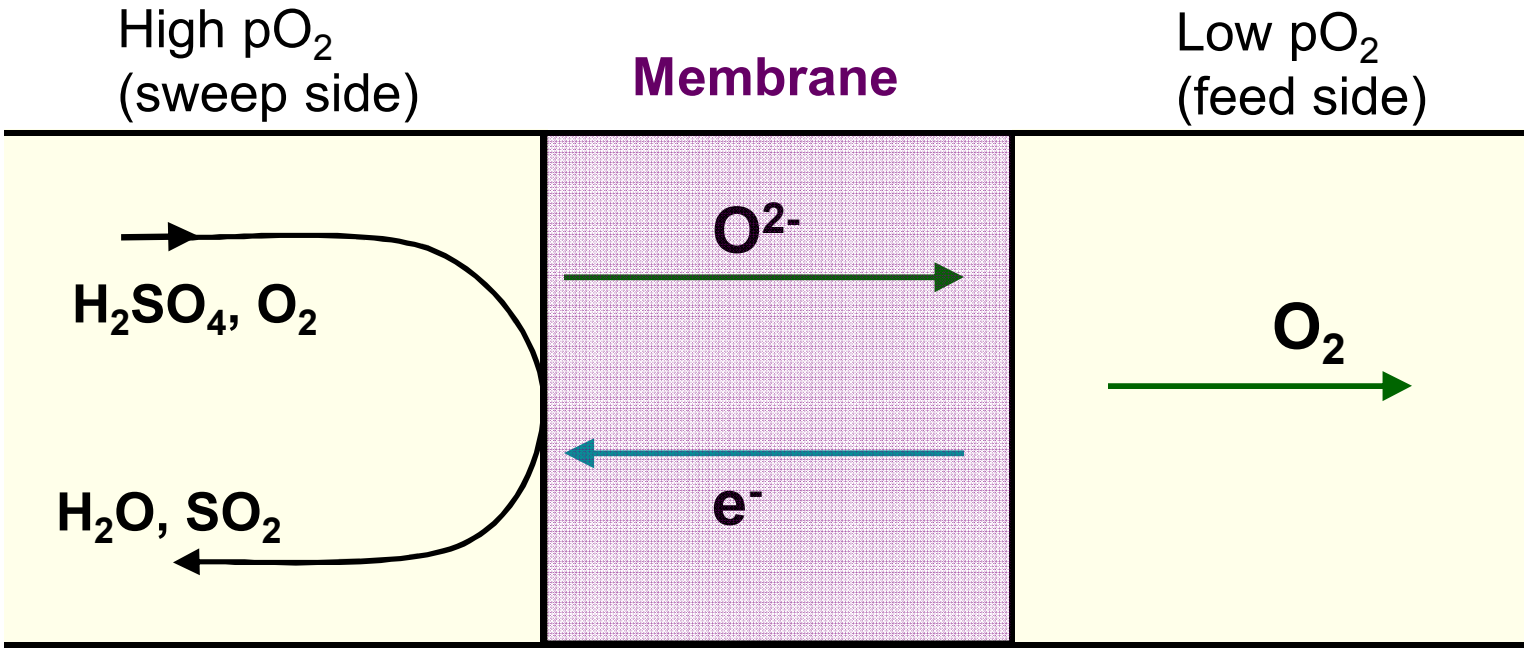
Sandia-synthesized polymer membranes have shown promise in high temperature electrochemical processes, e.g. fuel cells.

Sulfonated membranes with high temperature capability are being tested under a variety of conditions in an $SO_2$ electrolysis cell. Conditions of the process unit are being optimized and efficiency/lifetime is being measured.

# Ceramic Oxygen Separation Membranes

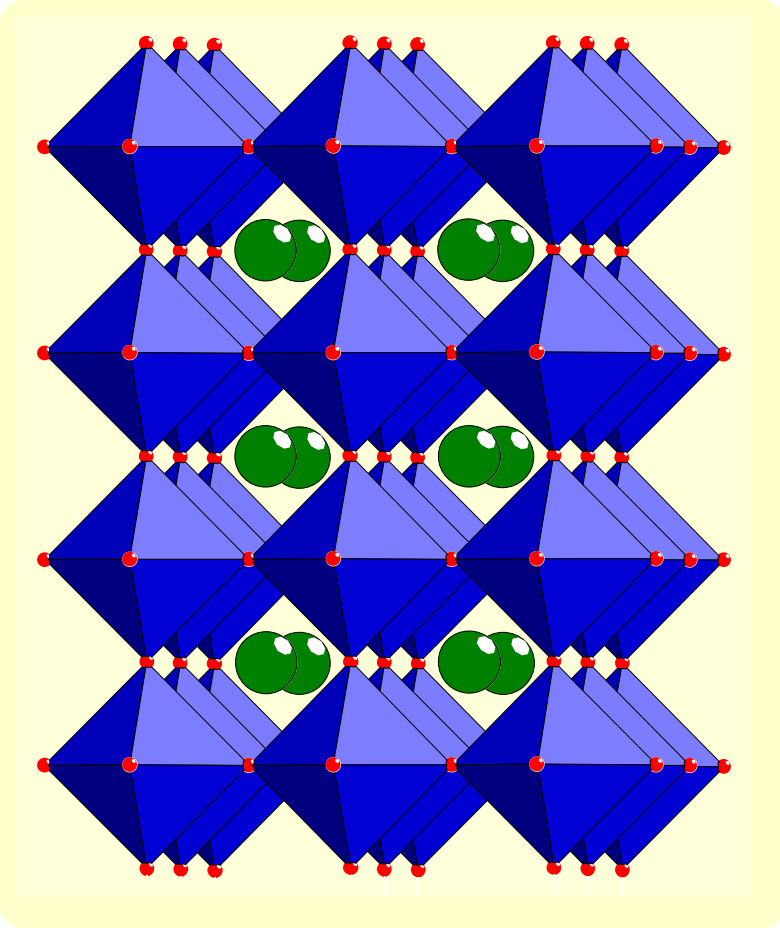
## Characteristics:

- 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 $ABO_3$

- 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

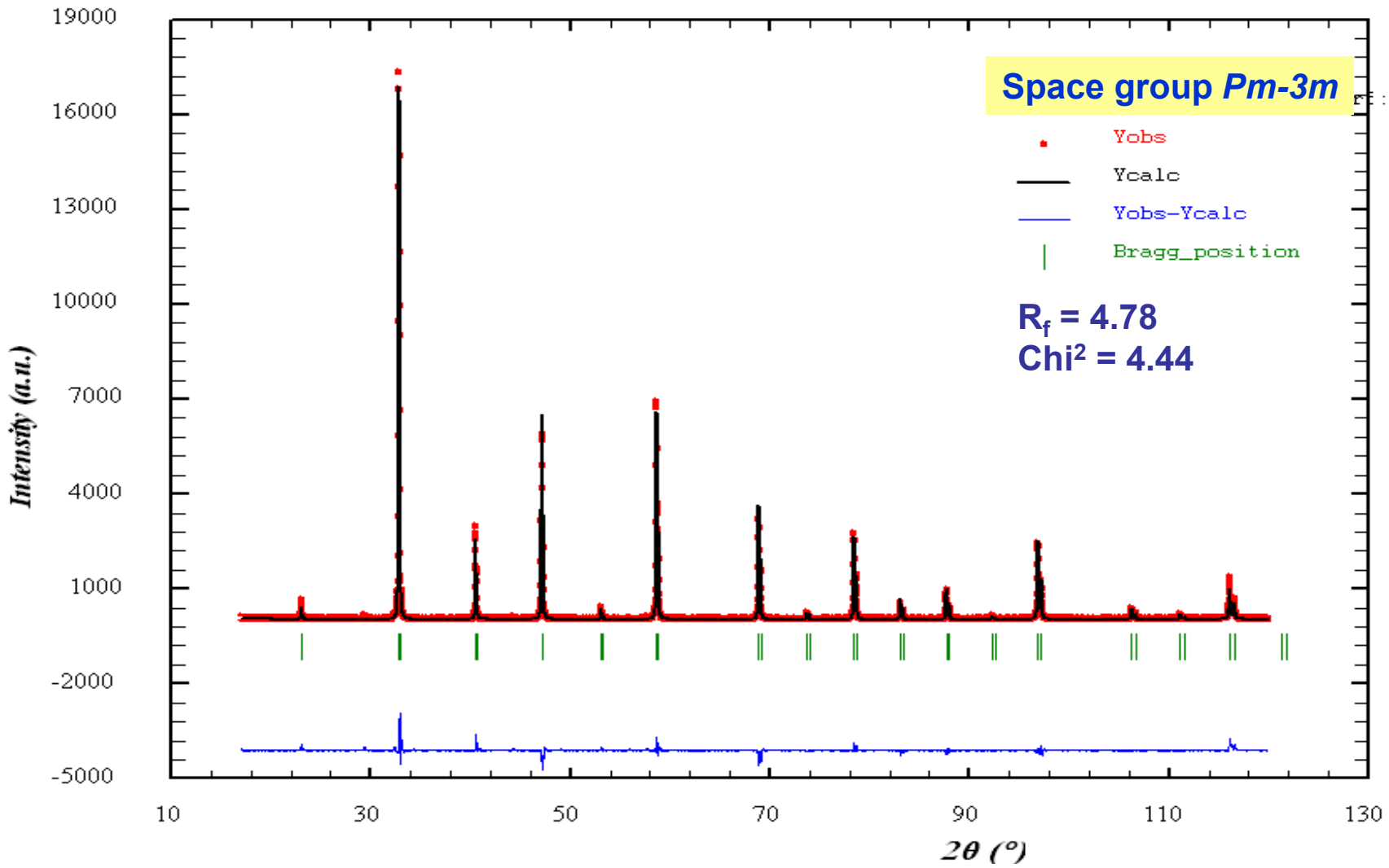
**Nitrate synthesis:**

- Nitrates of starting materials dissolved in DI $H_2O$
- Citric acid added
- Sol'n heated at 90 ºC to evaporate $H_2O$
- Resulting gels dried overnight then self-ignited at 400 ºC
- Powder ground up in mortar and pestle
- Sintered at 1250 ºC for 24 hr

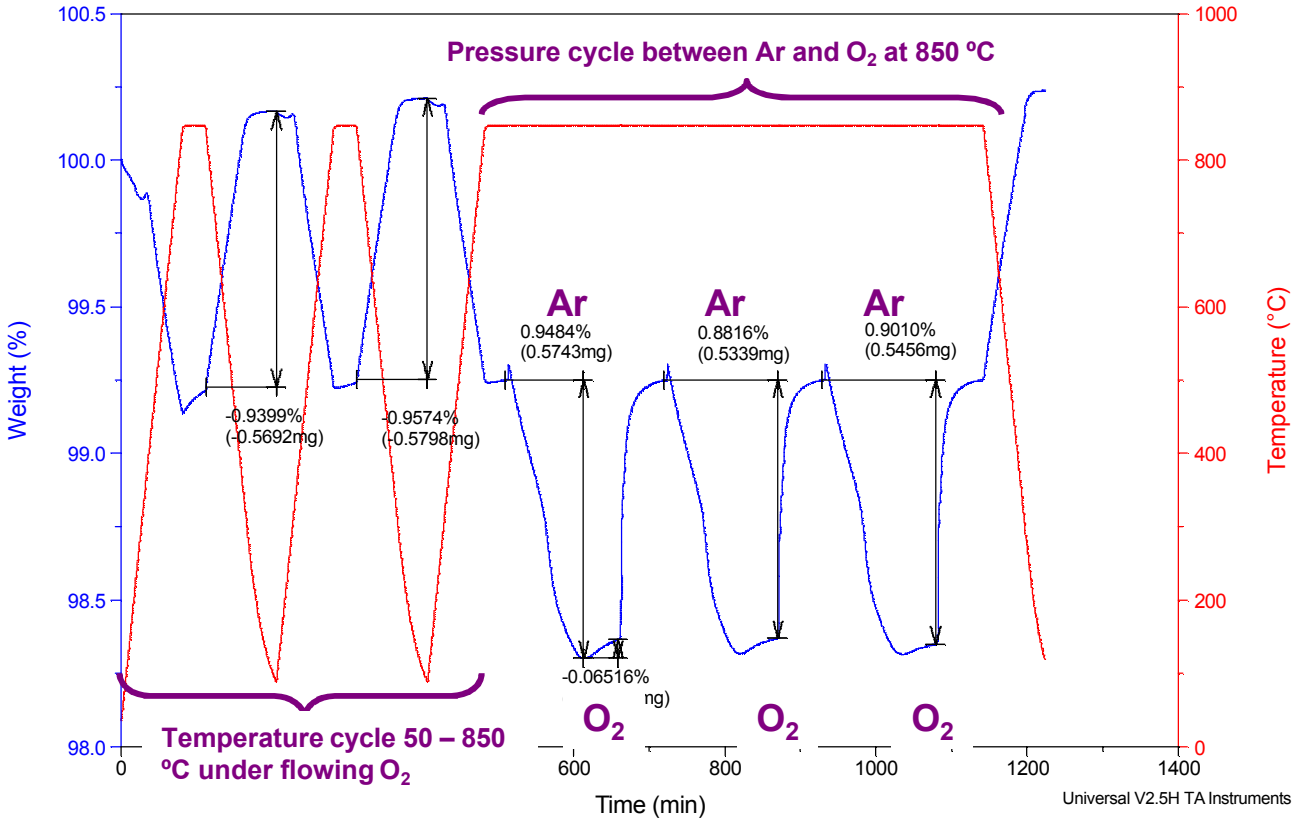
**Characterization:**

- Powder x-ray diffraction (PXRD)
- Thermogravimetric analysis (TGA)
- Four-probe conductivity
- Scanning electron microscopy/electron dispersive spectroscopy
- Permeation measurements

# PXRD of $La_{0.1}Sr_{0.9}Co_{0.7}Mn_{0.3}O_{3-\delta}$



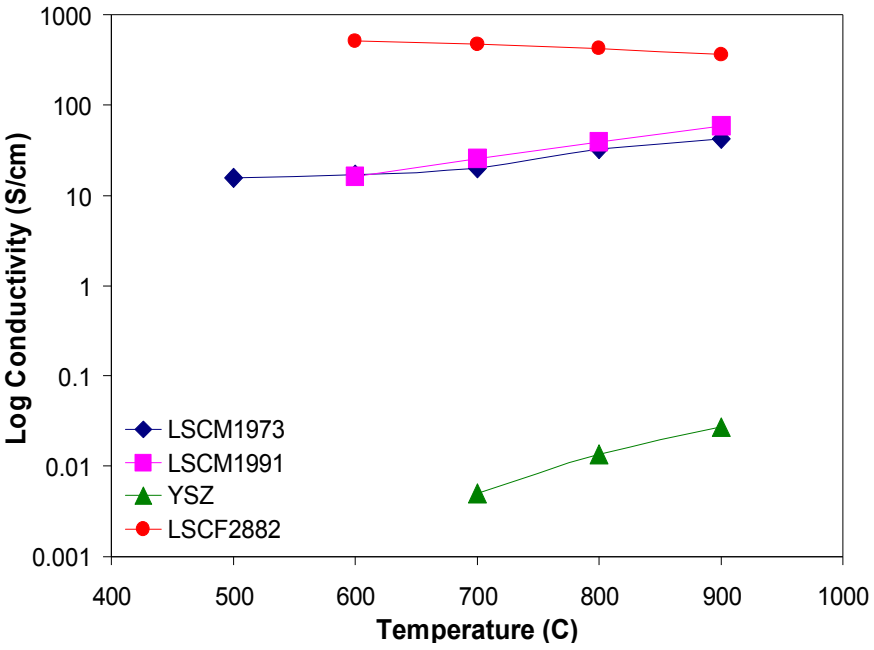
# TGA Cycle of $La_{0.1}Sr_{0.9}Co_{0.7}Mn_{0.3}O_{3-\delta}$



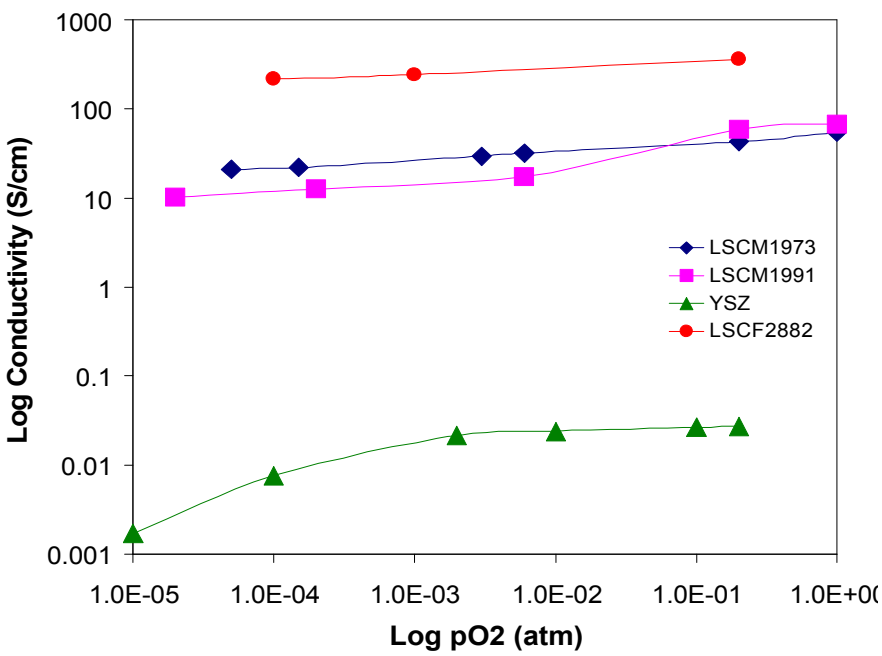

- The first part of the graph shows the weight change as the temperature is cycled between 50-850 °C, under a constant flow of $O_2$ gas. This describes an easily reversible temperature-swing adsorption/desorption of oxygen.
- The second part of the graph illustrates the reversible weight change as a function of oxygen partial pressure, by cycling the gas between $O_2$ 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

## vs. Temperature (in air)




## vs. $pO_2$ (at 900 °C)



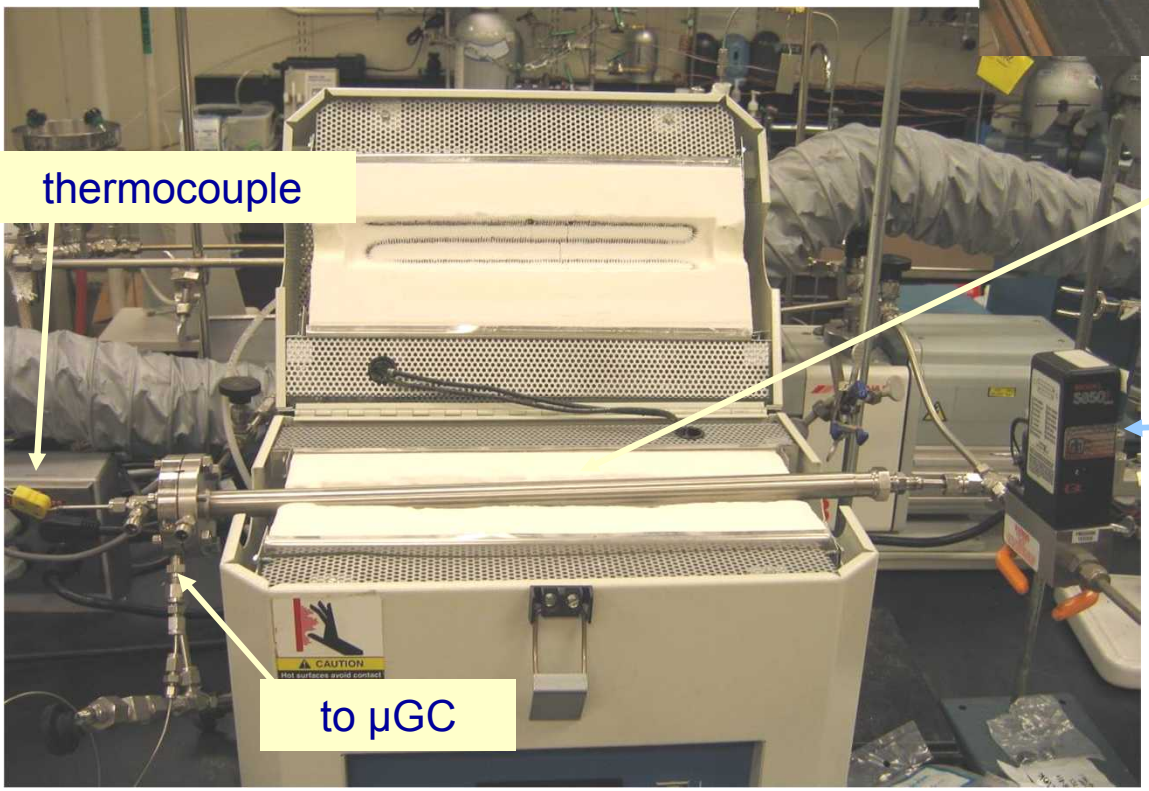

- Conductivity is several orders of magnitude better than YSZ
- Conductivity ↑ as temperature ↑ and $pO_2$ ↑
- Large magnitude implies electronic conductivity contribution
- Ionic contribution between 0.2 – 0.4 S/cm at 850 °C

*Garino, SNL*

# Oxygen Permeation Unit

Constructed of Inconel 600 Ni alloy

membrane

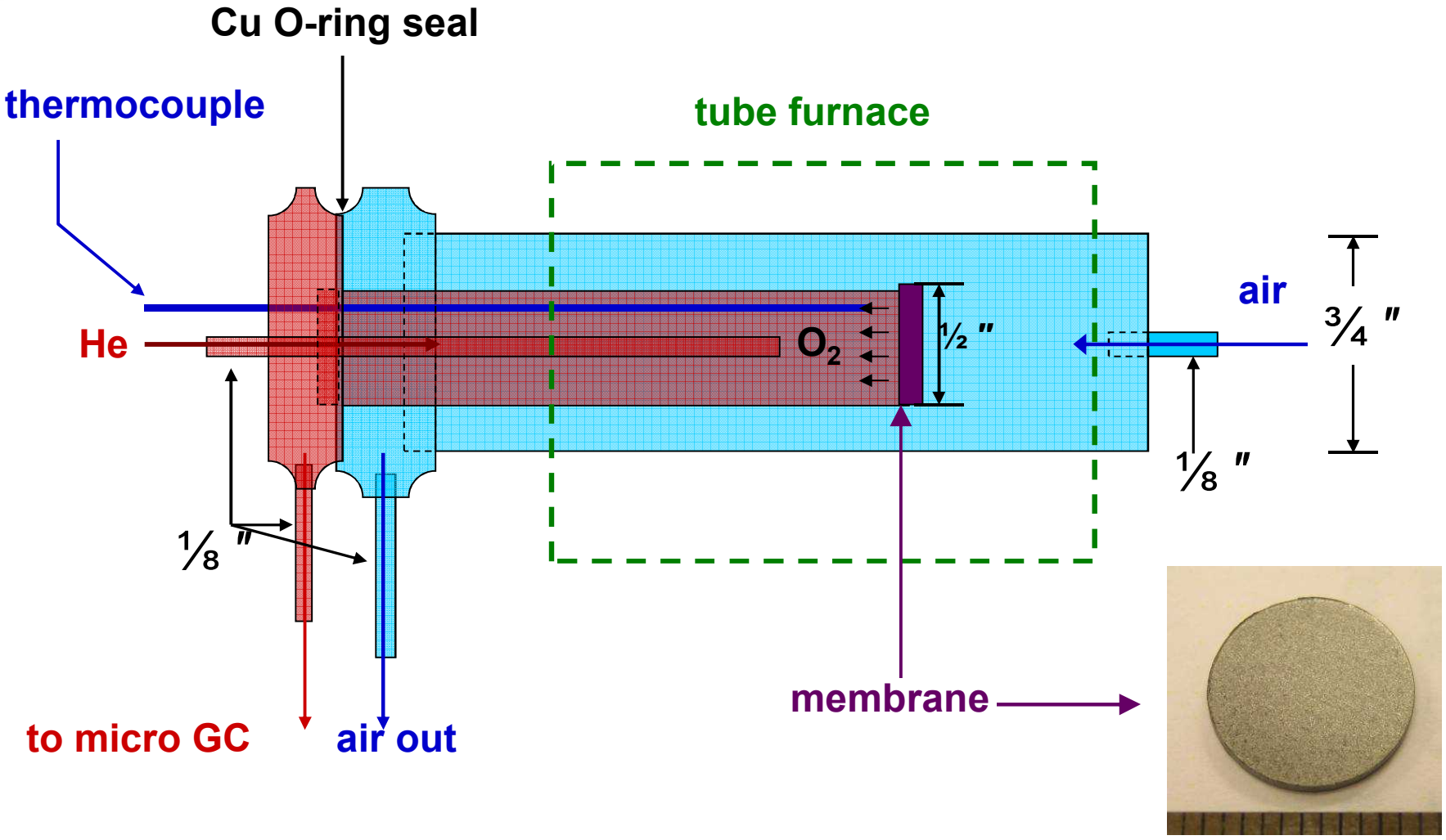



thermocouple

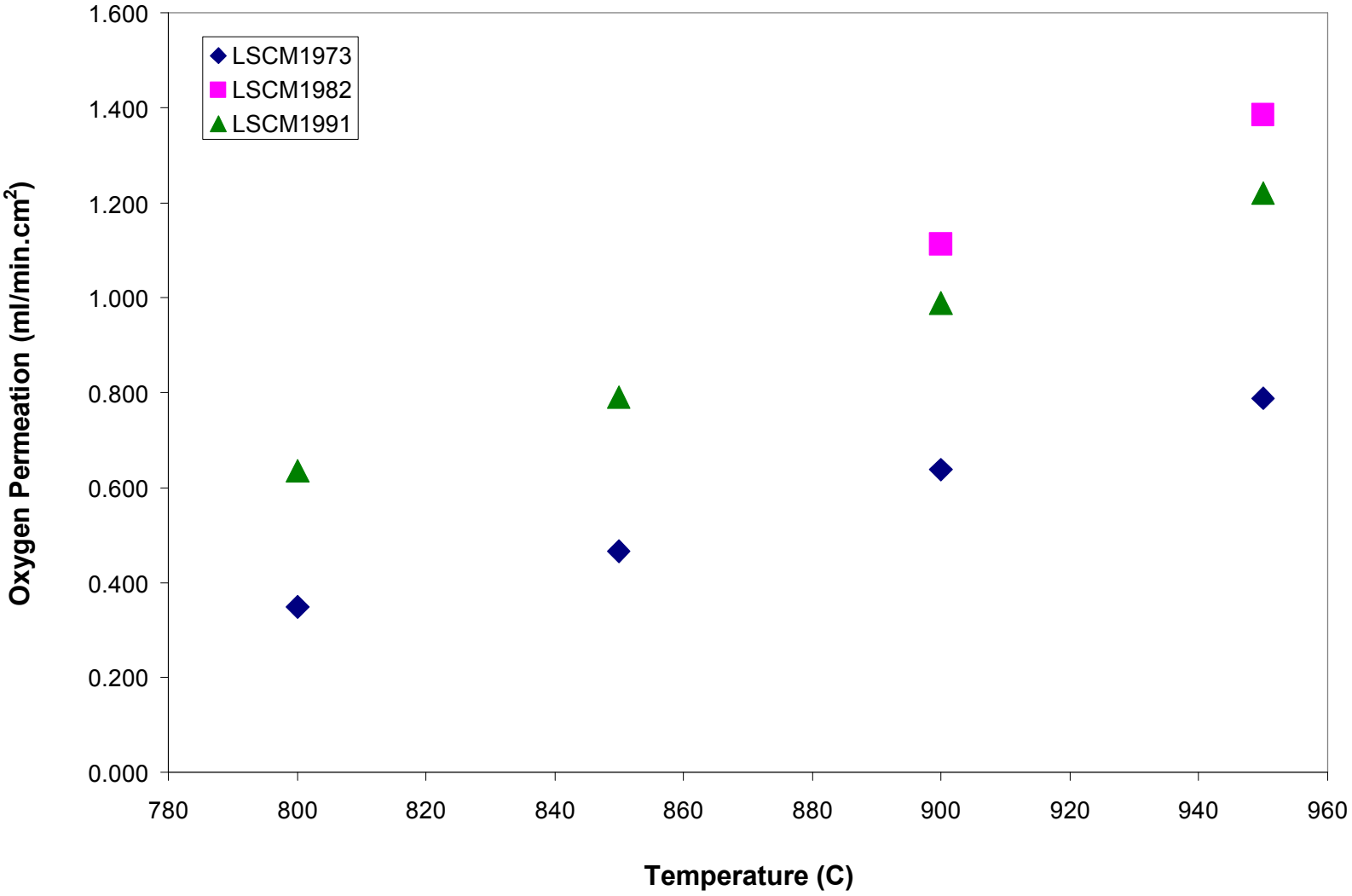
Mass flow controller (air)

to μGC

# Permeation Unit - Design

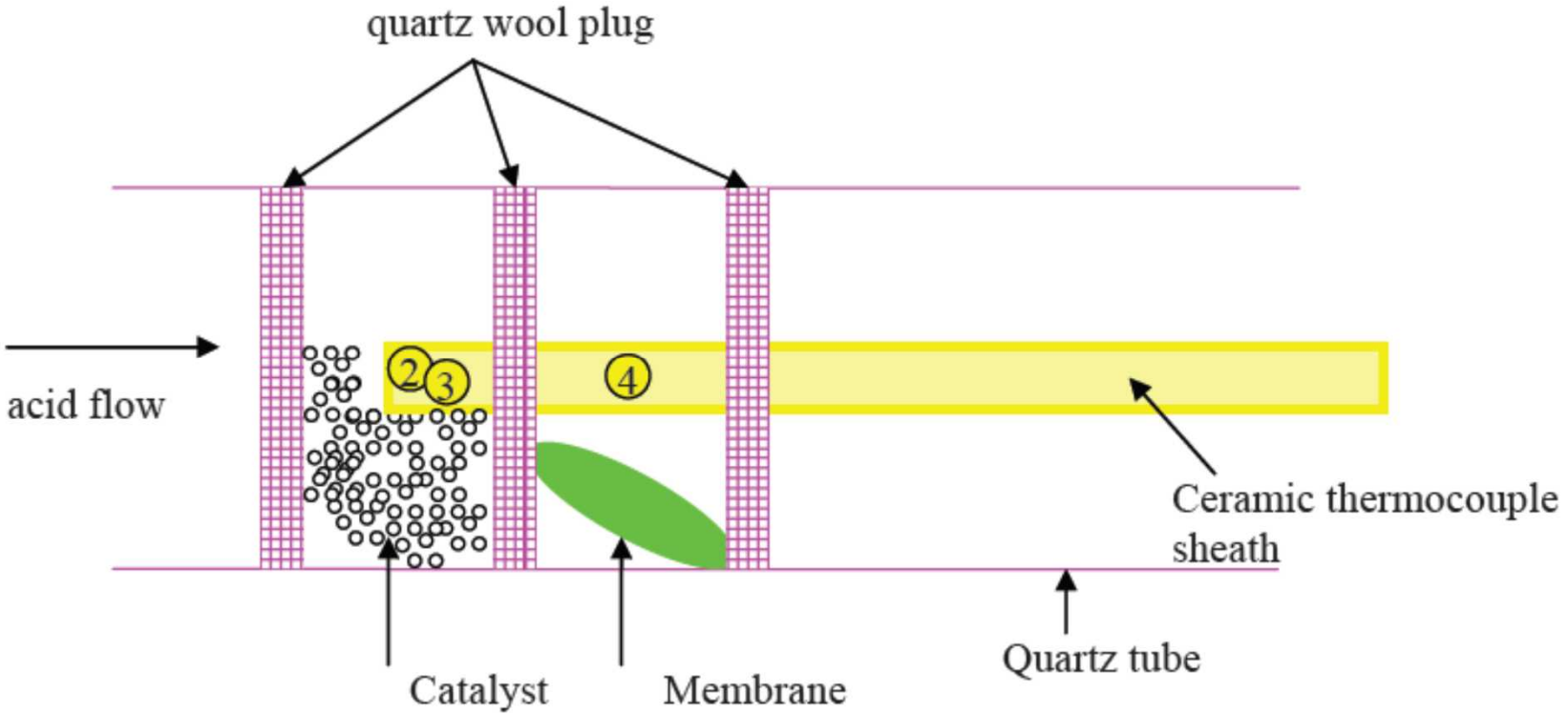


# Permeation of LSCM Membranes



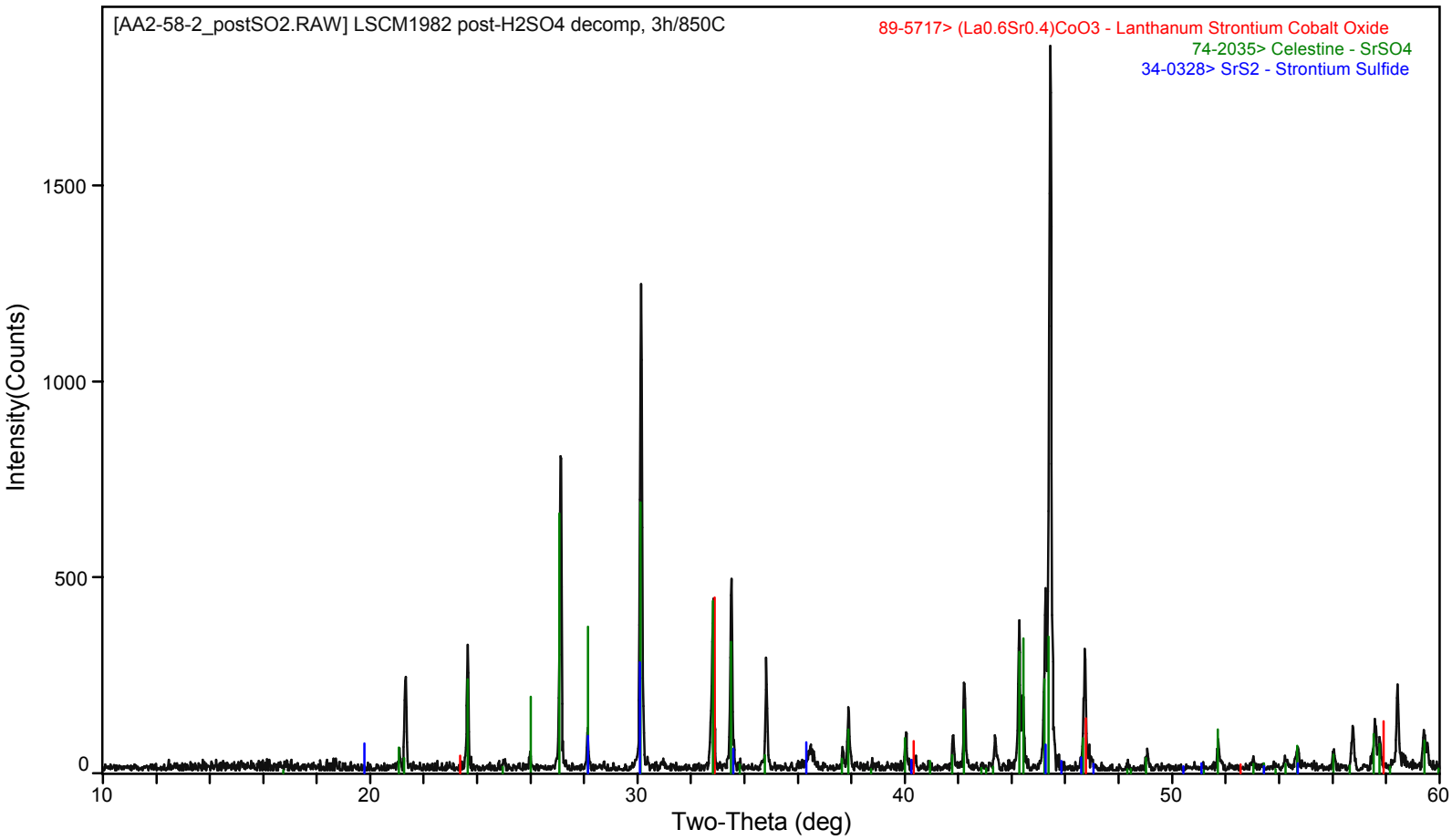
# Mini $H_2SO_4$ Decomposition Reactor

Goal: To test the stability of the membrane under "reactor" conditions




*F. Gelbard, SNL*

# Post-$H_2SO_4$ Decomposition




- Microscopy of cross-section reveals corrosion layer of approx. 5 μm
- XRD (above) shows formation of $SrSO_4$ and possibly SrS
- Not yet known if corrosion caused by exposure to $H_2SO_4$, $SO_2$, or both
- Membrane can be regenerated by heating to 1300 °C under $O_2$

## Summary

- The $La_{0.1}Sr_{0.9}Co_{1-y}Mn_yO_{3-\delta}$ (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 $H_2SO_4$ decomposition stream at 850 ºC

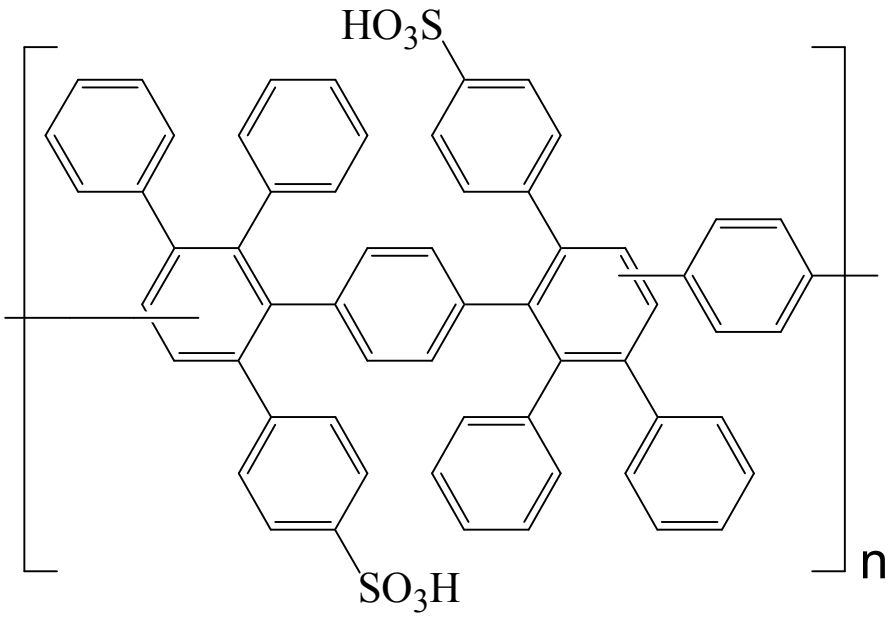
## Ongoing Work

- Ongoing high temperature permeation studies (SNL)
- Continued structural elucidation
- Determine extent of corrosion during $H_2SO_4$ 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.
*Macromolecules* **2005**, 38(12), 5010-5016.

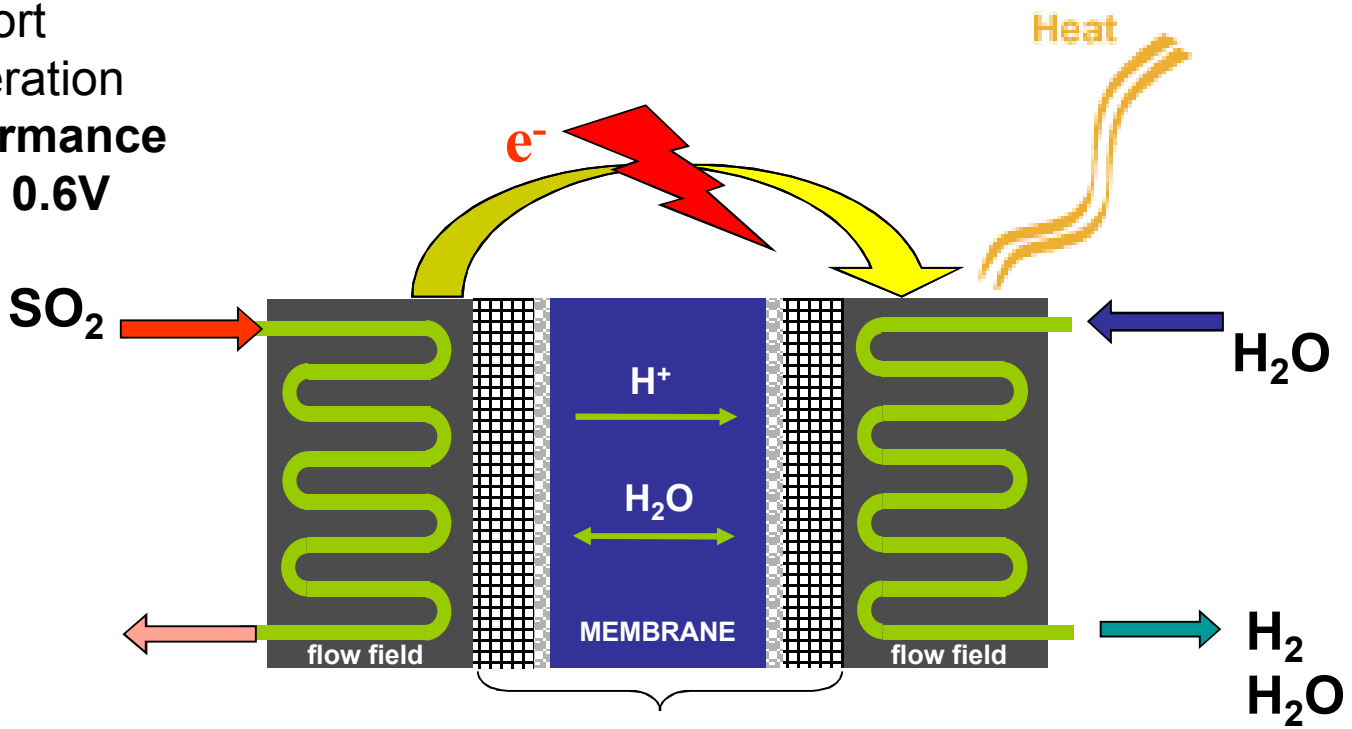
# Electrolyzer Schematic

$SO_2 + 2\ H_2O + \text{electric power} \rightarrow H_2SO_4 + H_2 + \text{heat}$

Membrane is critical for:

- low $SO_2$ crossover
- efficient water transport
- high temperature operation

**SNL Membrane Performance Target: 0.5 mA/cm$^2$ at 0.6V**



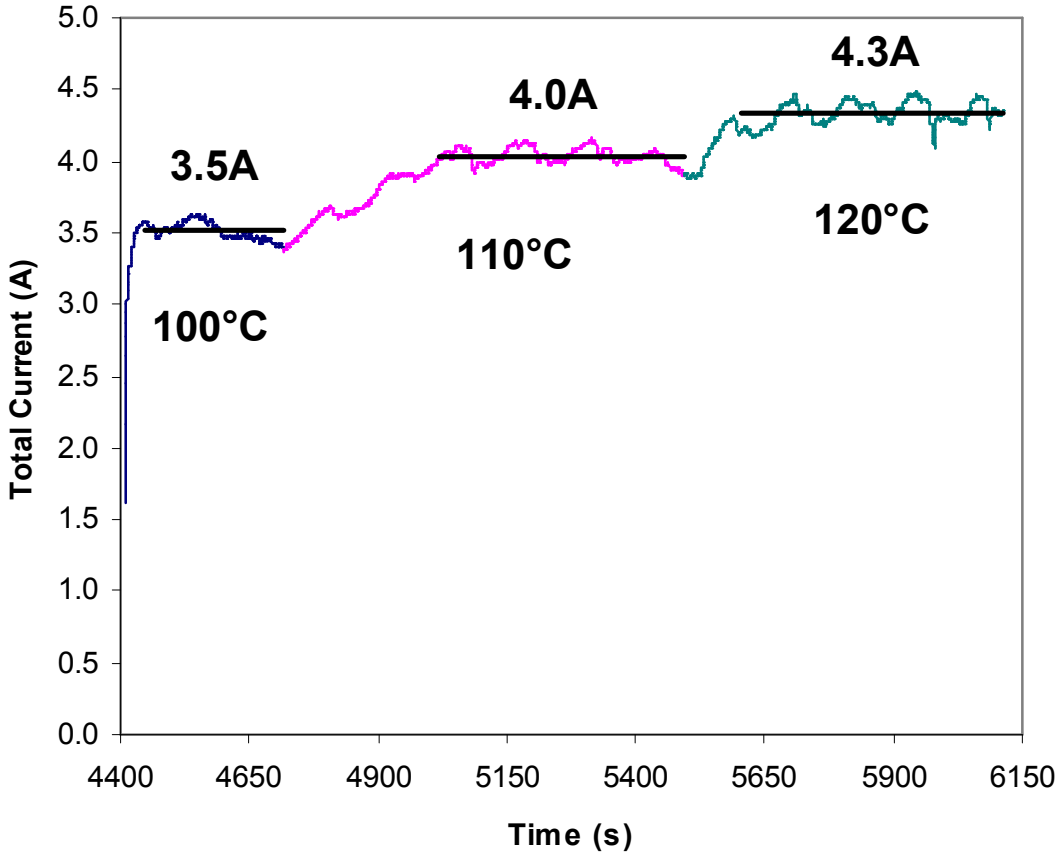

**Membrane Electrode Assembly – MEA**

**Membrane**

**Catalyst layers**

**Gas diffusion layers**

# Increased Temperature Promotes Better Performance
# High Temperature Enabled by SNL membranes

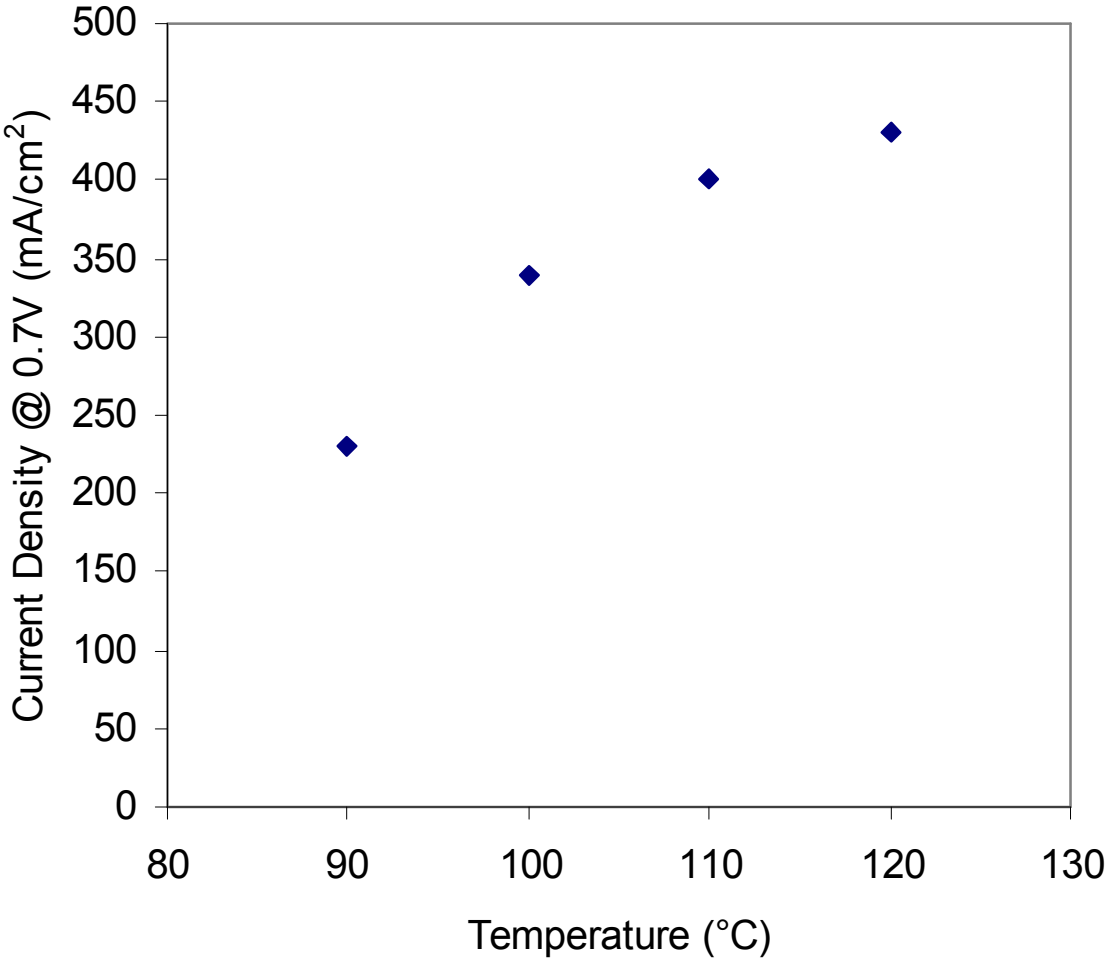



Total cell current at 0.7 V cell potential of SDAPP 2.2 meq/g electrolysis cell with time at 100°C, 110°C, and 120°C cell temperature.

Cell Conditions:

- 10 $cm^2$ cell
- SDAPP 2.2 meq/g membrane batch
- 2 mg Pt/$cm^2$ Pt Black anode and cathode
- Dry $SO_2$ gas anode, 100 sccm constant $SO_2$ flow rate with 15 psig backpressure
- Preheated liquid water cathode, 3 mL/min constant H2O flow rate with 15 psig backpressure

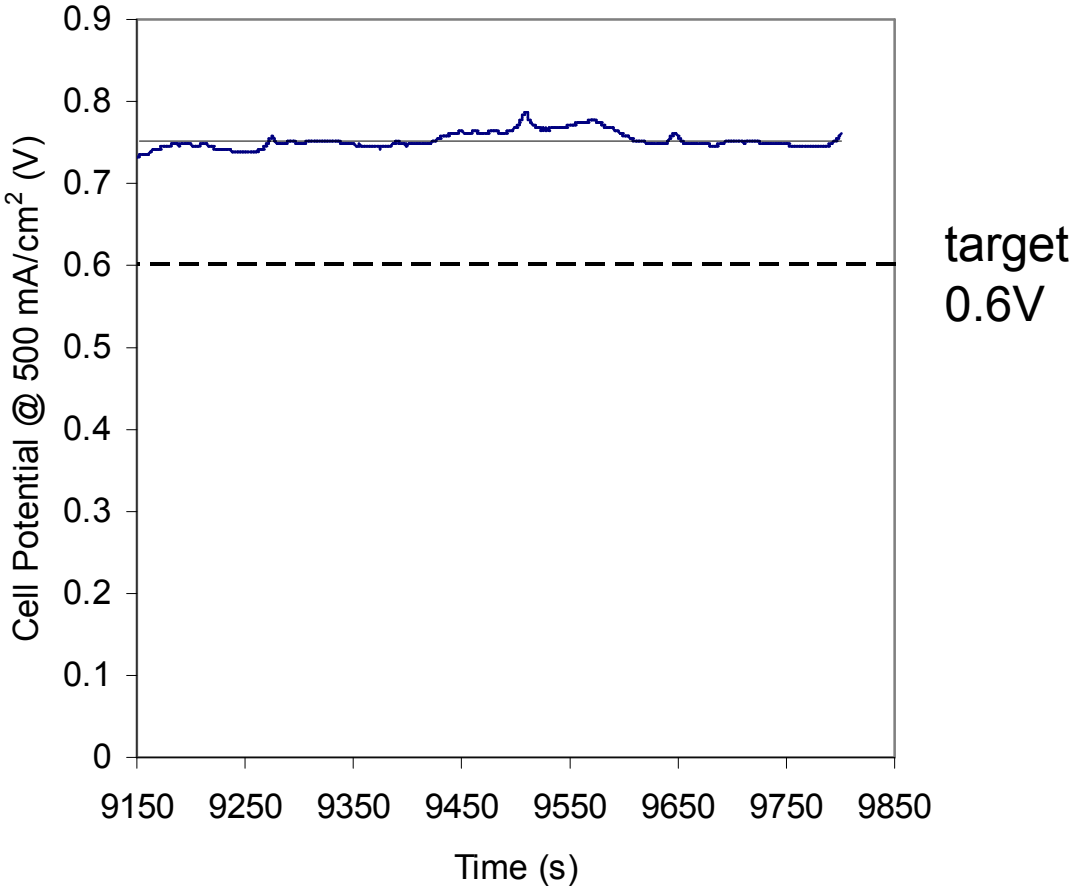
# Performance increase of SNL Membrane Electrolysis Cell at 0.7 V




Current density at 0.7 V cell potential of SDAPP 2.2 meq/g electrolysis cell as a function of temperature

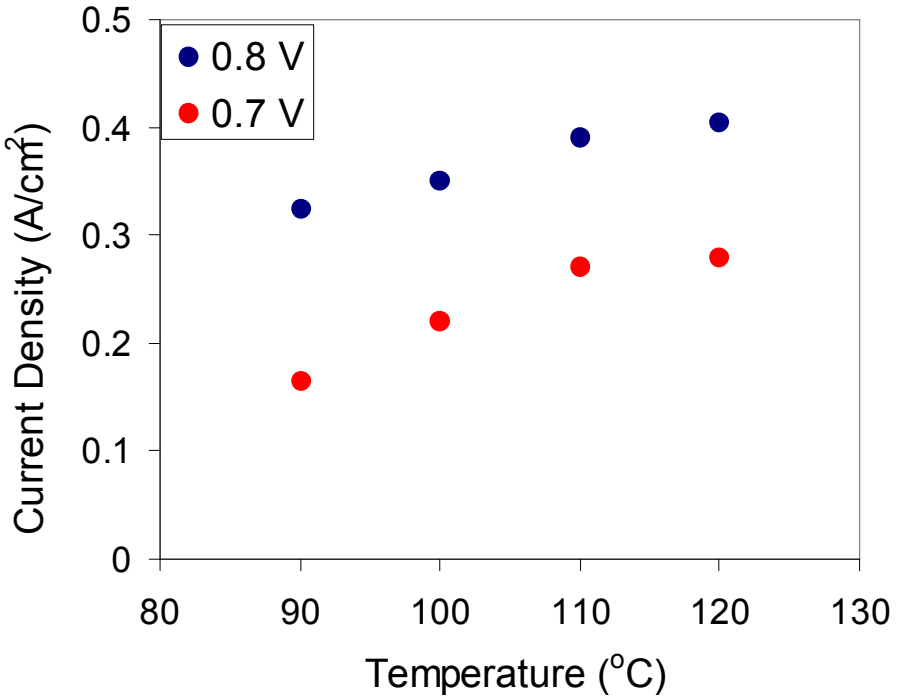
# Galvanostatic Performance of SNL Membrane at 120°C

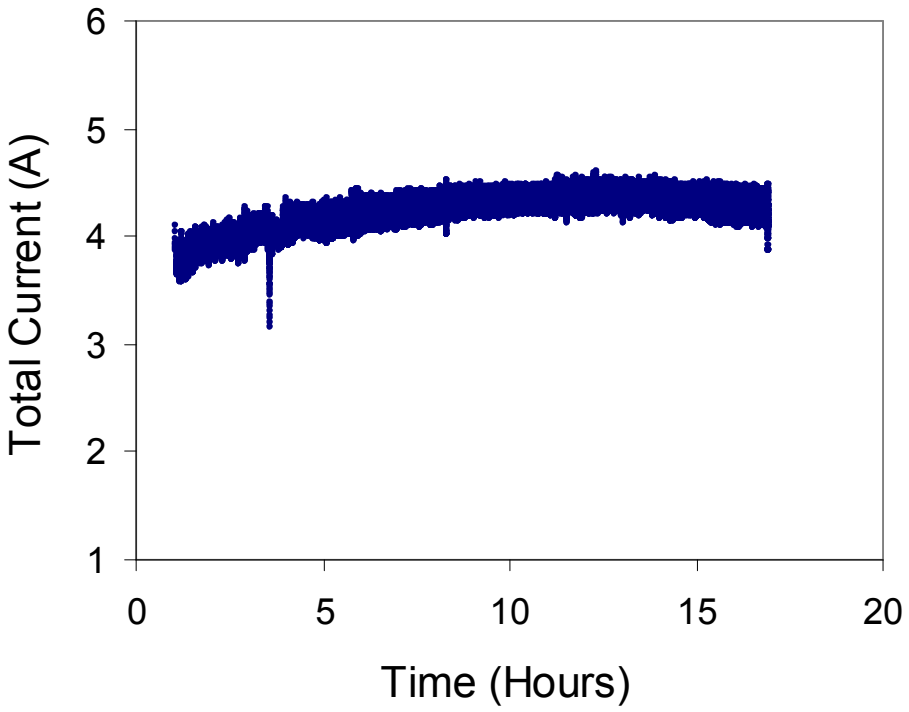
The average potential of the electrolysis cell for 10 minutes is 0.75 V. The previous best performance of this membrane was 0.83 V at 500 mA/cm$^2$ and 80°C as measured by University of South Carolina.




Cell potential at 500 mA/cm$^2$ and 120°C for SNL SDAPP 2.2 meq/g electrolysis cell.

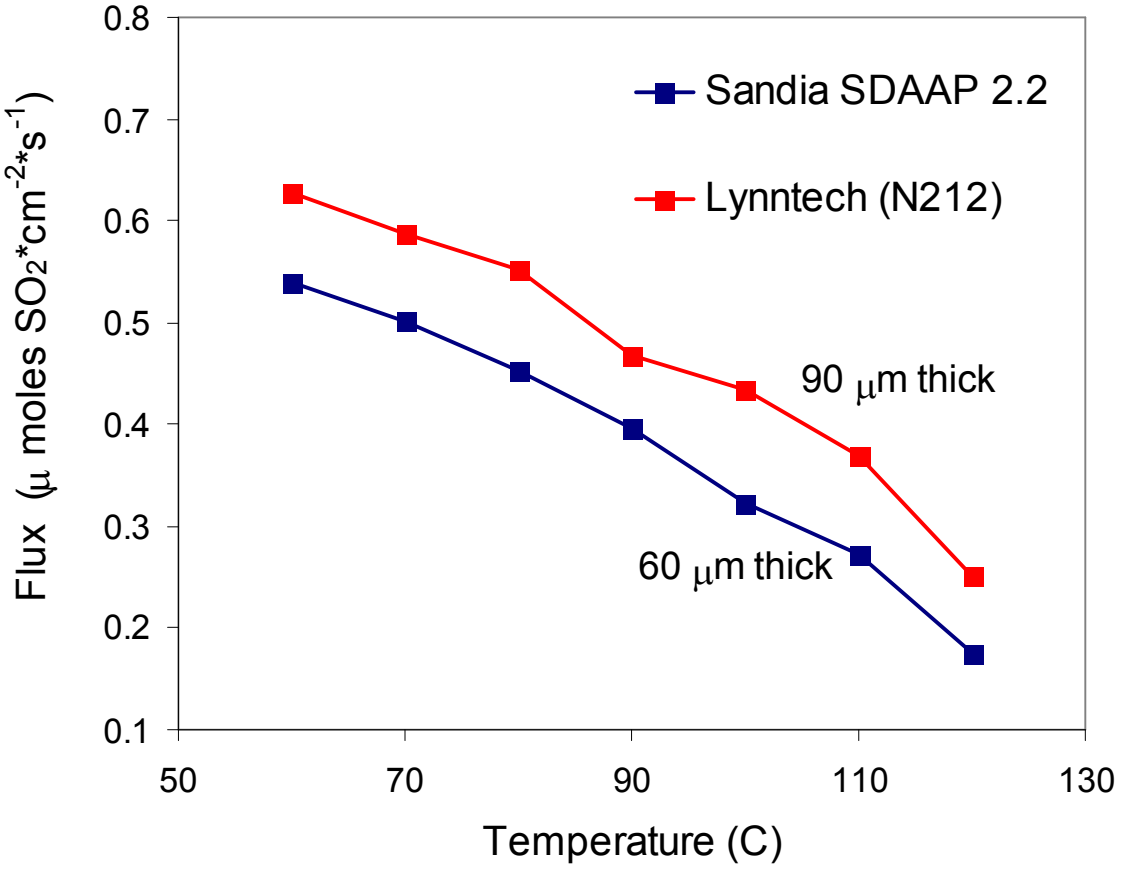
# Performance and Lifetime of SNL (4-141-D) Membranes




Higher current densities are achieved at elevated temperatures with 0.4 mA/cm$^2$ 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 $SO_2$ and and 6.4 ml/min $H_2O_{(l)}$ flow rates and 15 psig backpressure.

# Decreased $SO_2$ Crossover Using SNL Membranes – less process loss, higher efficiency




Steady-state $SO_2$ flux for Sandia membrane SDAAP 2.2 meq/g (4-141-D) and Nafion 212 (Lynntech MEA).

$SO_2$ crossover
- process loss
- parasitic $H_2$ consumption
- elemental sulfur buildup on the cathode, block reaction sites

$SO_2$ flux to cathode is lower for Sandia membranes even though SNL membranes are thinner.

# Potential $H_2$ Losses from $SO_2$ Crossover

Hydrogen consumption at cell cathode from $SO_2$ Crossover:

$$SO_2 + 2\ H_2 \rightarrow S_{(solid)} + 2\ H_2O$$

| Temperature | Crossover Flux | Theoretical Maximum $H_2$ Consumption | Cell Hydrogen Production | Theoretical Maximum $\%H_2$ Loss |
|---|---|---|---|---|
| C | $\mu$mol $SO_2/cm^2*s$ | $\mu$mol $H_2/cm^2*s$ | $\mu$mol $H_2/cm^2*s$ | % |
| 90 | 0.397 | 0.794 | 1.68 | 47.1 |
| 100 | 0.322 | 0.644 | 1.81 | 35.5 |
| 110 | 0.272 | 0.544 | 2.02 | 26.9 |
| 120 | 0.176 | 0.352 | 2.10 | 16.8 |

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

The number noted above are the maximum amount of $H_2$ 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.

# Acknowledgements

Our project partners at:
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Mr. Gary Jones (Permeation unit construction)
Prof. Alexandra Navrotsky & Dr. R.G. Iyer
(UC Davis, Calorimetry)
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