DOE Hydrogen Program

Membrane Development for Hybrid Sulfur Electrolysis and Oxygen Separation

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National Nuclear Security Administration

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Sulfur Based Thermochemical Cycles For Nuclear Hydrogen Production

The Nuclear Hydrogen Initiative is investigating thermochemical cycles as one of the promising method 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 that 200 cycles reviewed and have the potential for high efficiencies.

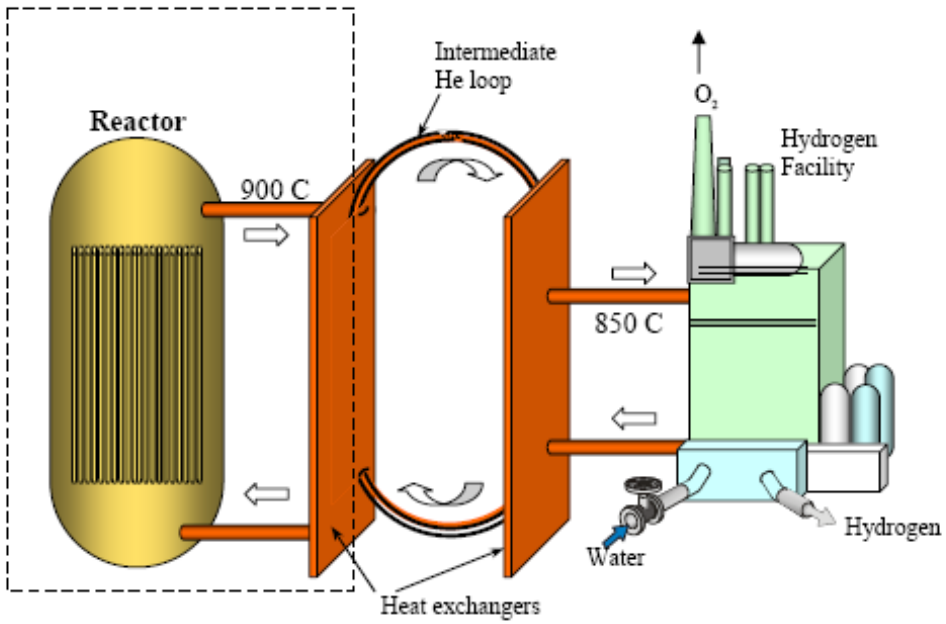


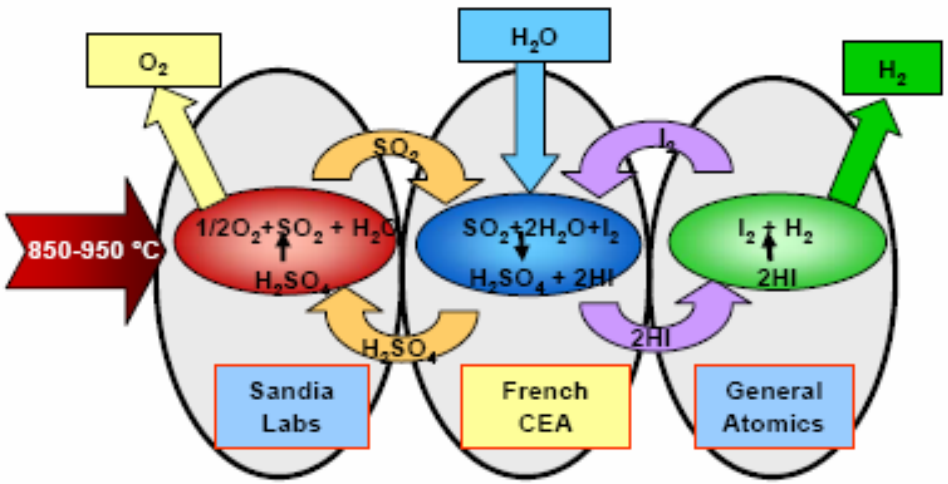
Figure 2 Schematic of nuclear reactor heat source with a water/thermochemical hydrogen production system.

(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??)

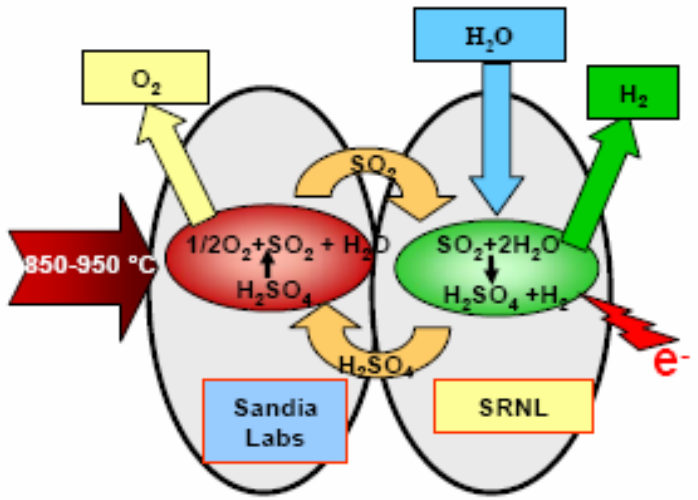


Sulfur Iodine

(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

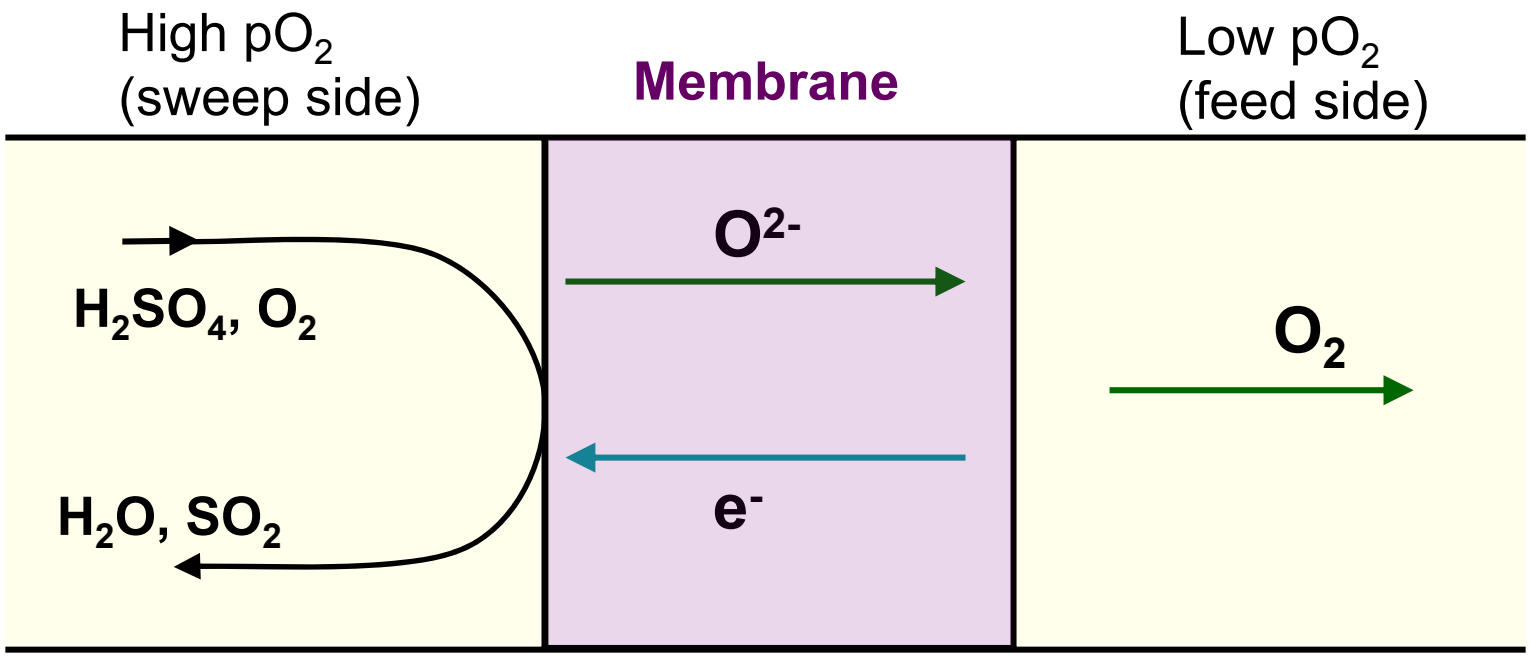
Sandia-synthesized polymer membranes have shown promise in high temperature electrochemical processes, e.g. fuel cells.

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

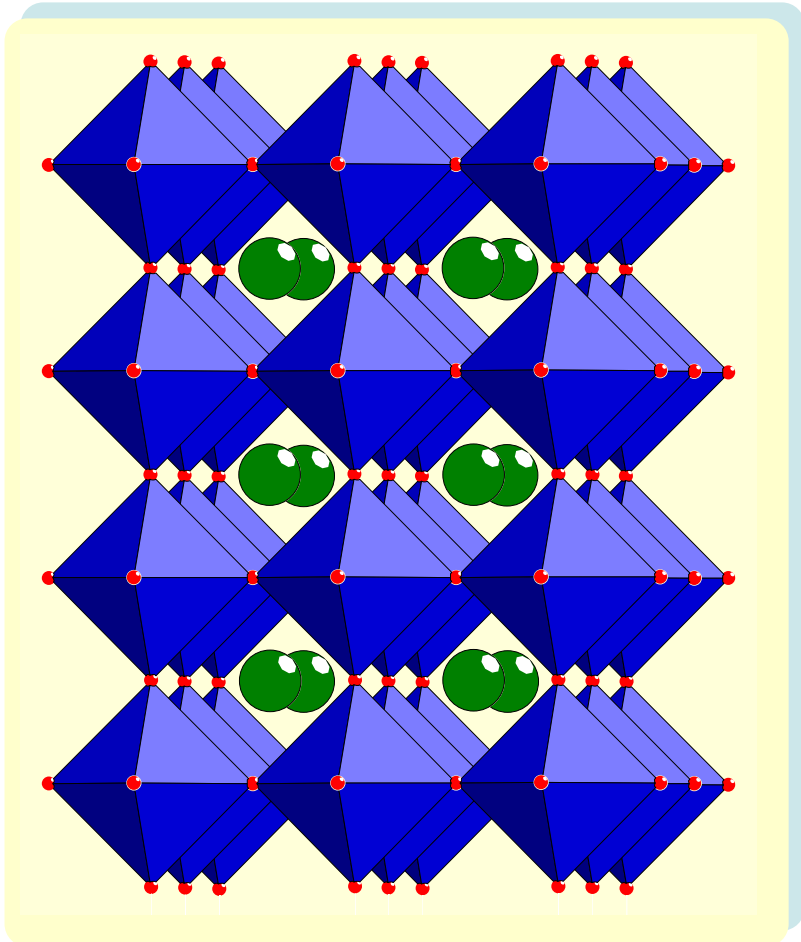
Characteristics:

- 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

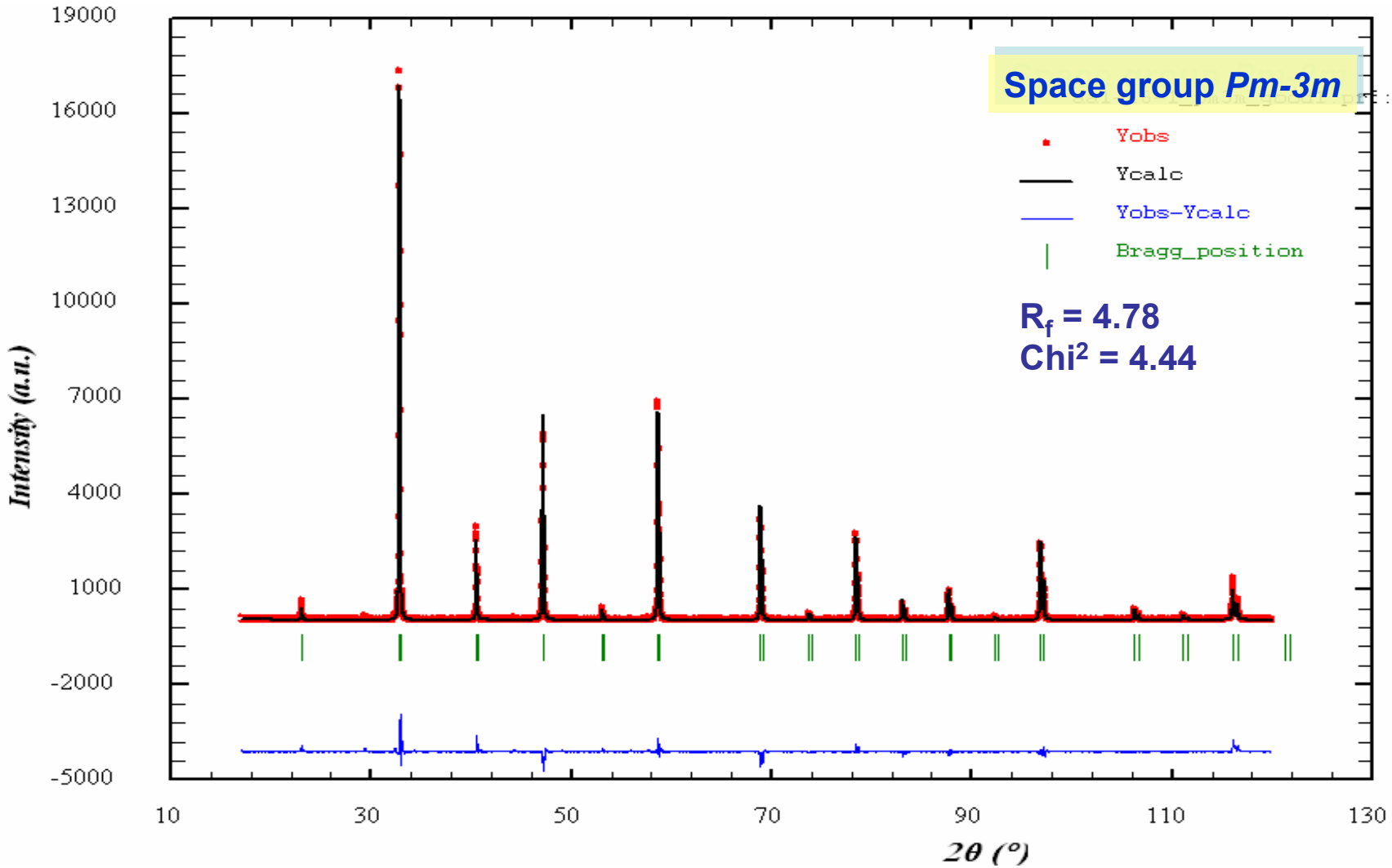
Nitrate synthesis:

- 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

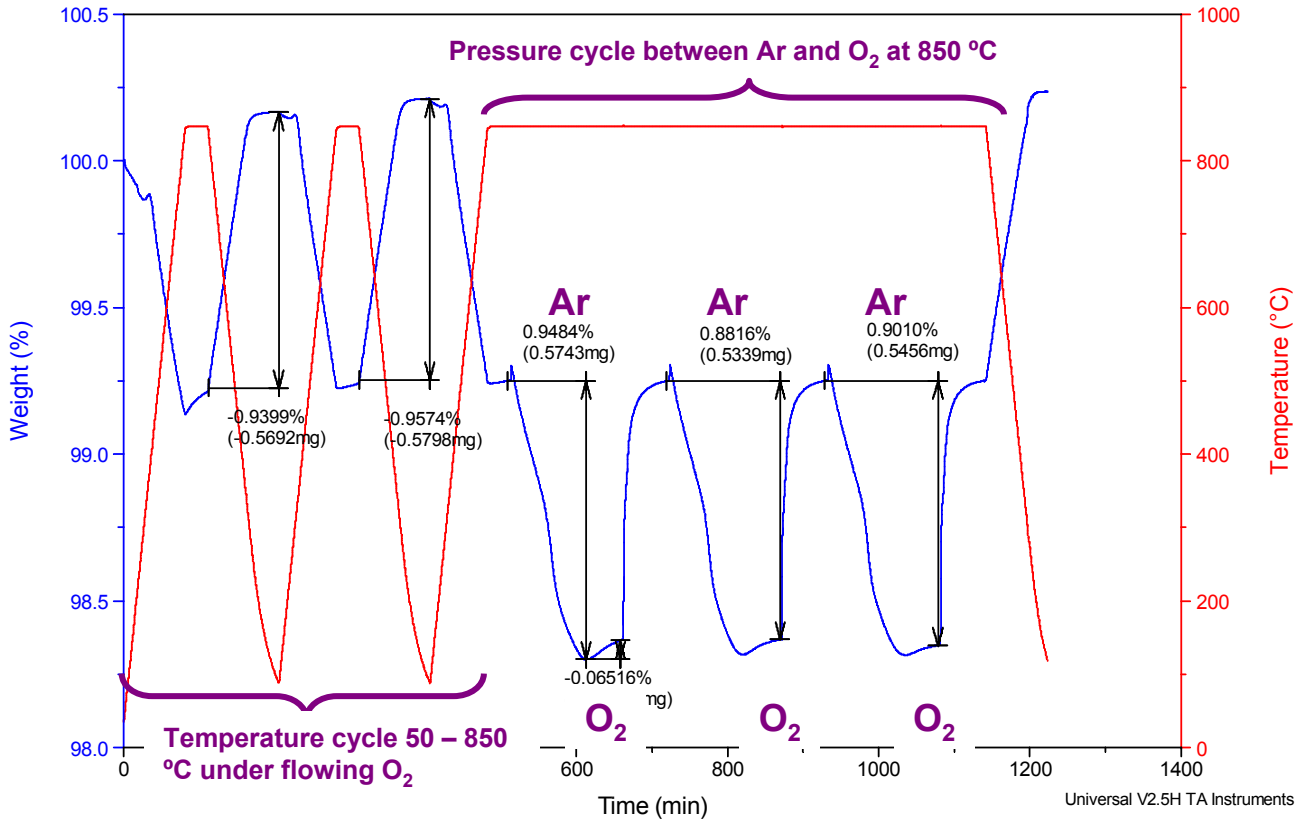
Characterization:

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

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



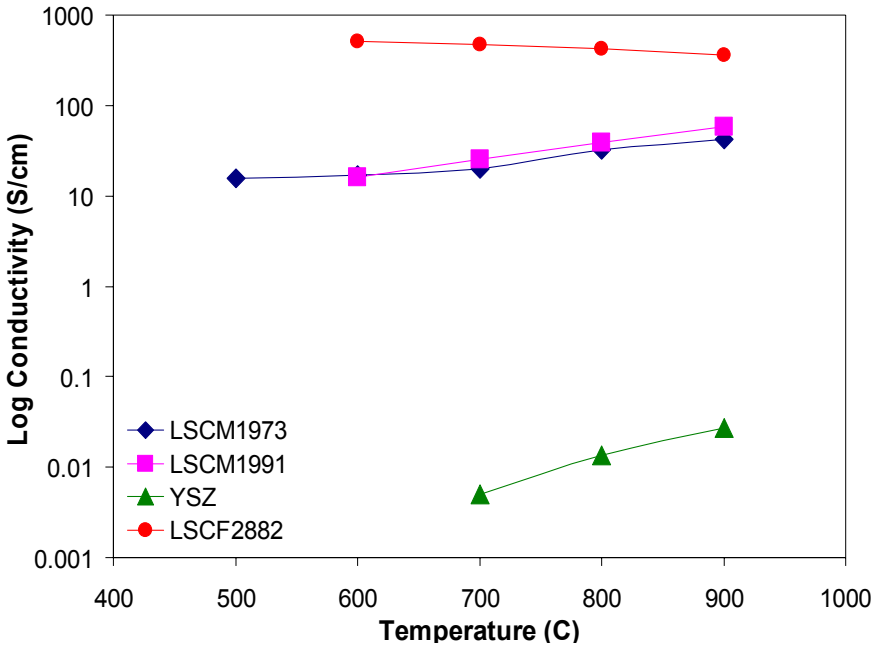
TGA Cycle of $La_{0.1}Sr_{0.9}Co_{0.7}Mn_{0.3}O_{3-\delta}$



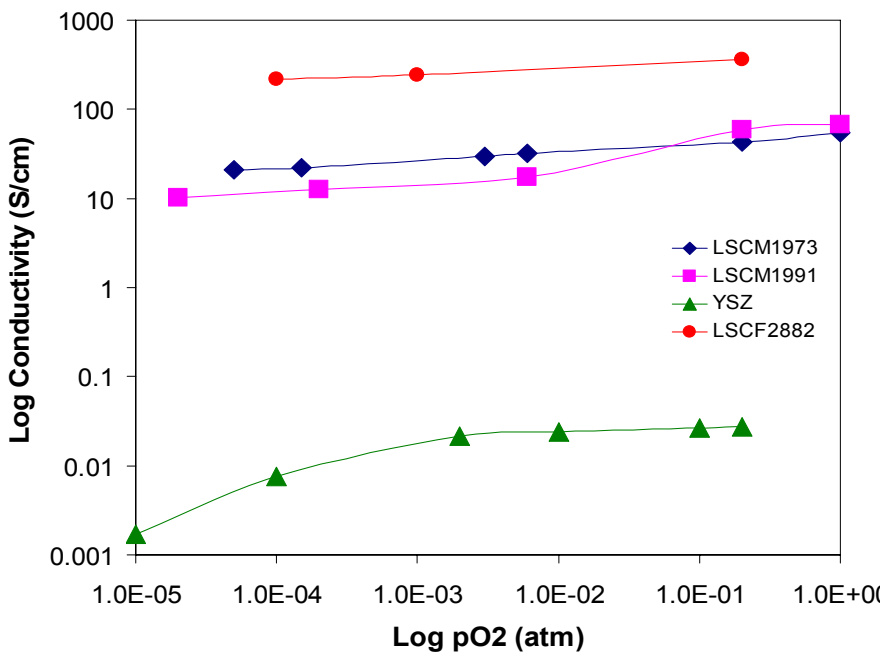
- The first part of the graph shows the weight change as the temperature is cycled between 50-850 °C, under a constant flow of O_2 gas. This describes an easily reversible temperature-swing adsorption/desorption of oxygen.
- The second part of the graph illustrates the reversible weight change as a function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



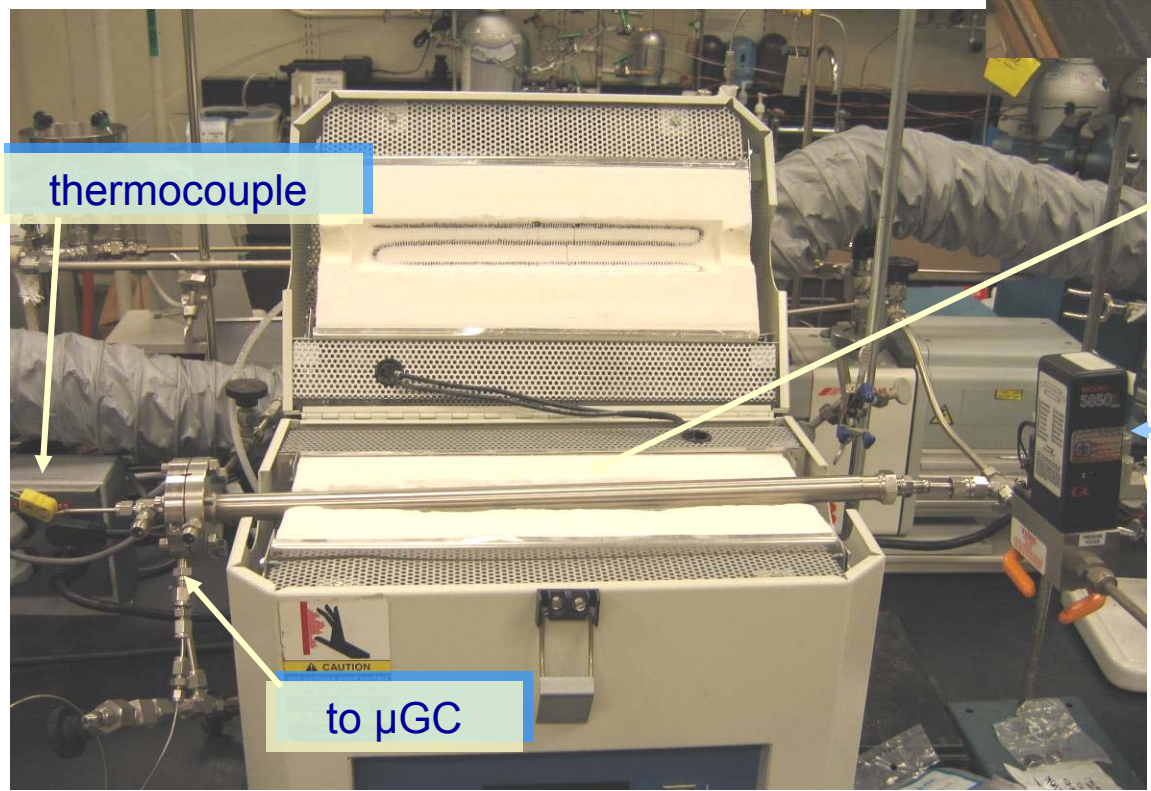
- Conductivity is several orders of magnitude better than YSZ
- Conductivity ↑ as temperature ↑ and pO_2 ↑
- Large magnitude implies electronic conductivity contribution
- Ionic contribution between 0.2 – 0.4 S/cm at 850 °C

Garino, SNL

Oxygen Permeation Unit

Constructed of Inconel 600 Ni alloy

membrane

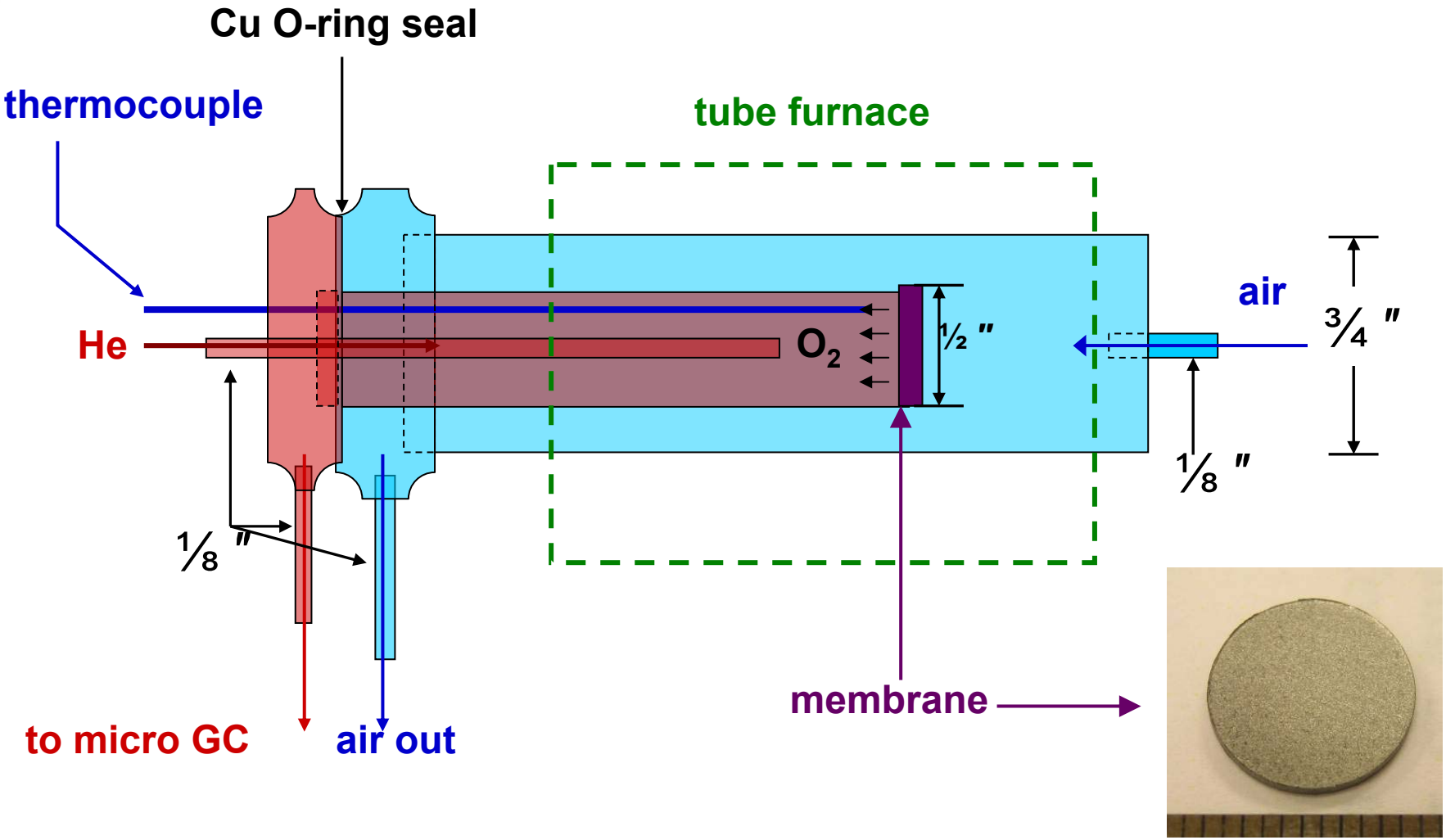


thermocouple

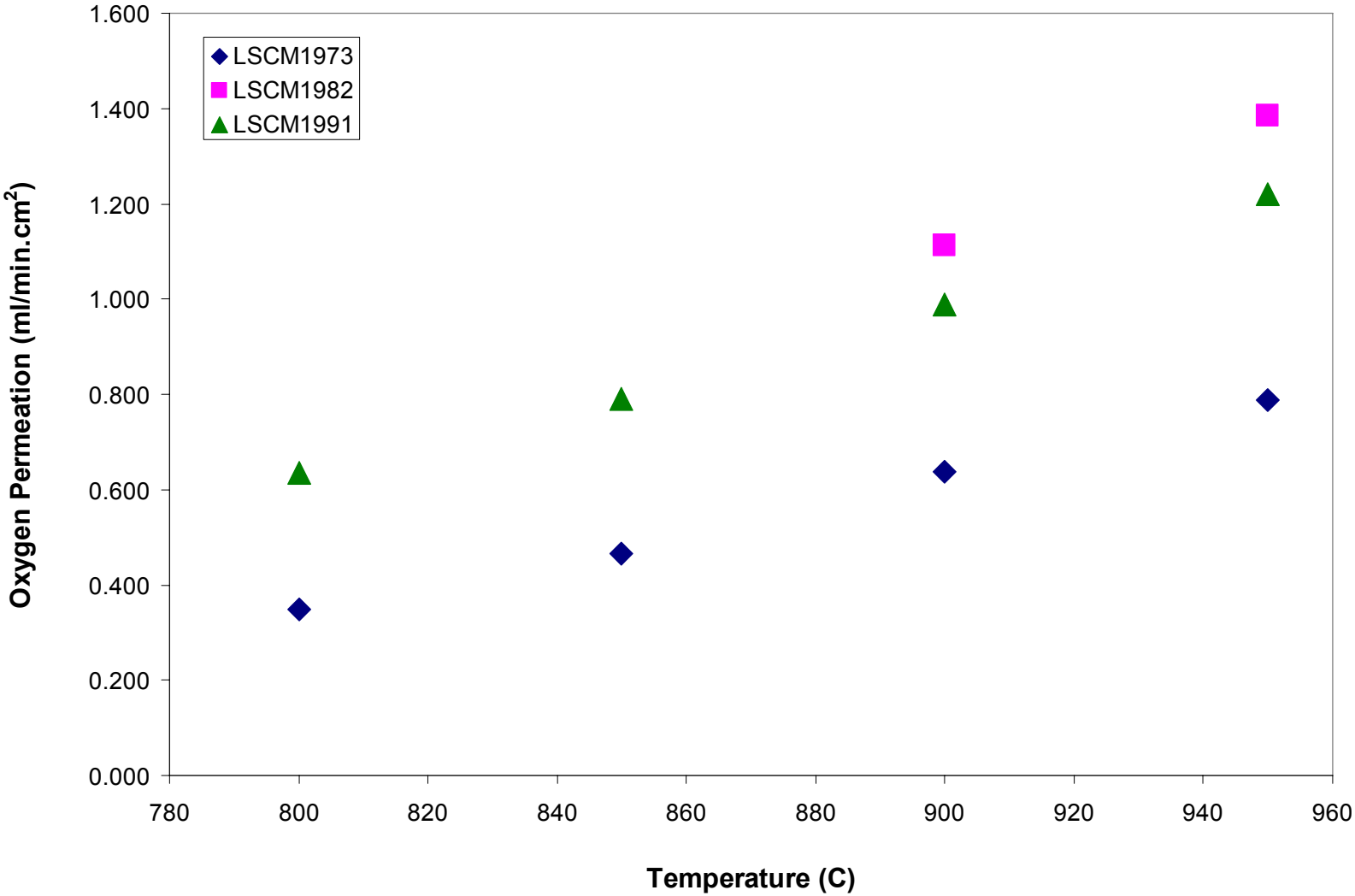
Mass flow controller (air)

to μGC

Permeation Unit - Design

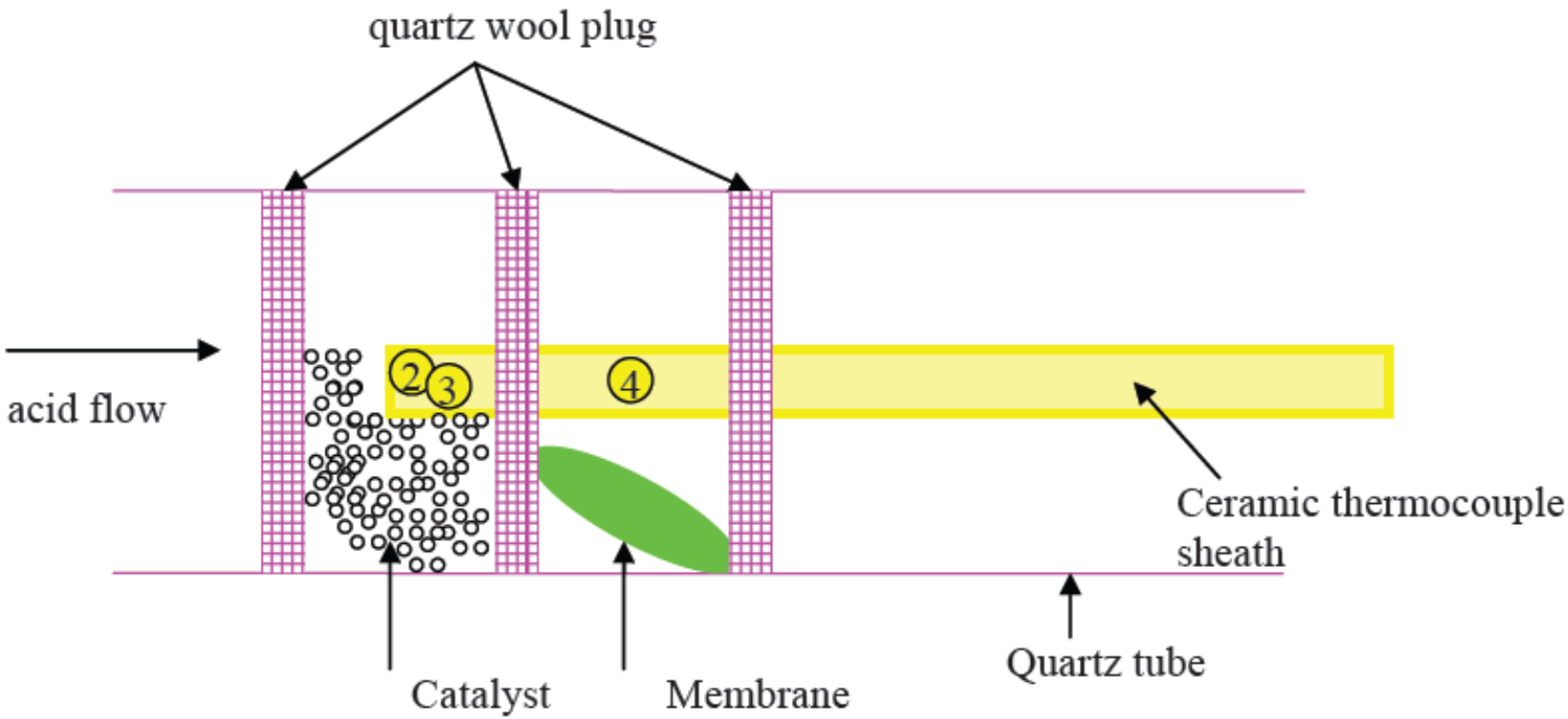


Permeation of LSCM Membranes



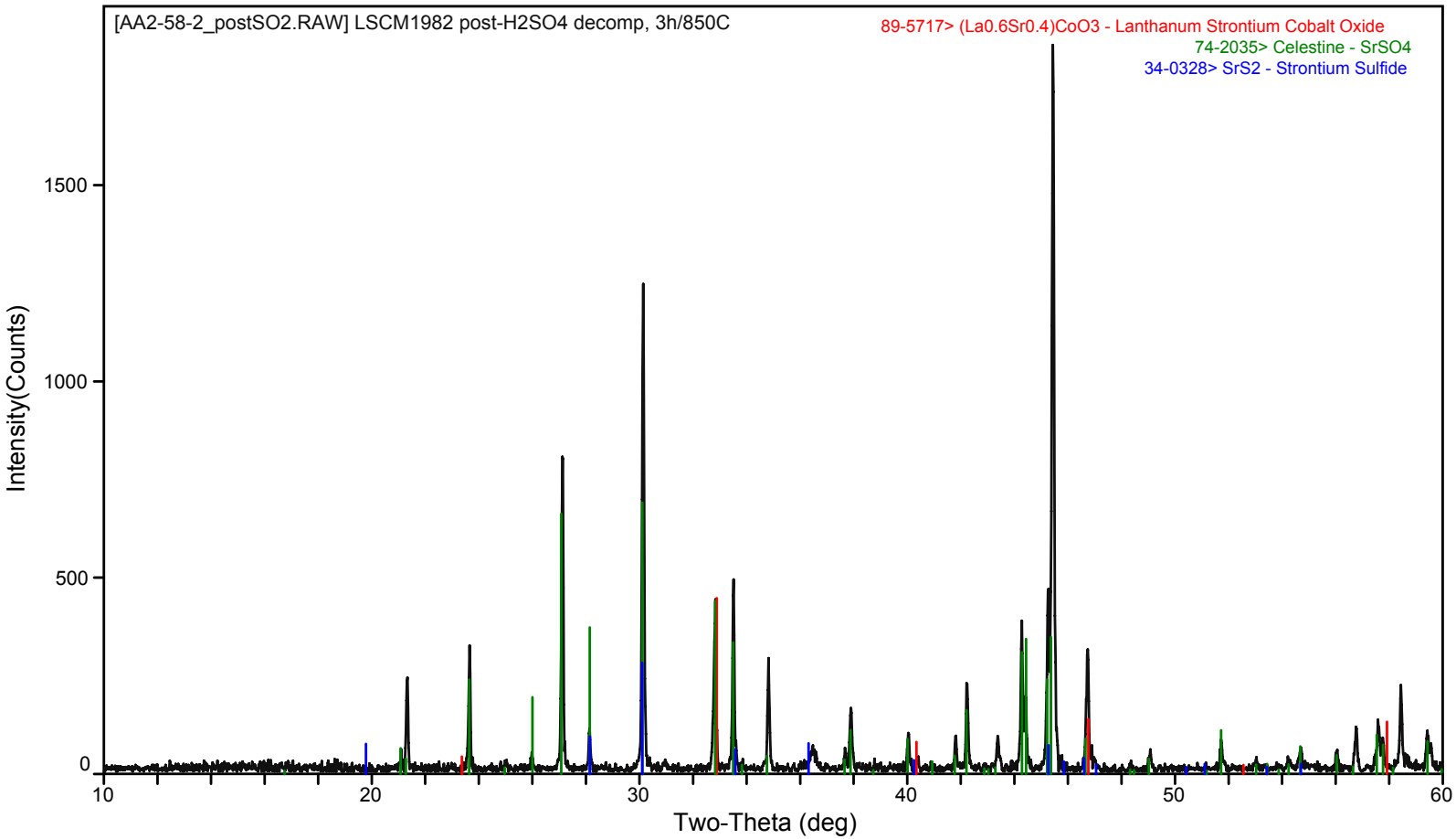
Mini H_2SO_4 Decomposition Reactor

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

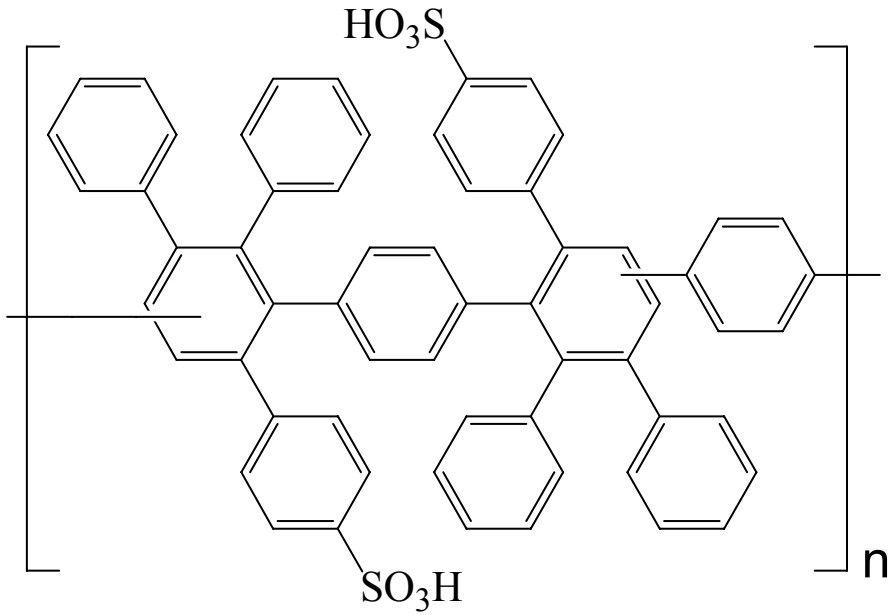
Ongoing Work

- 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.

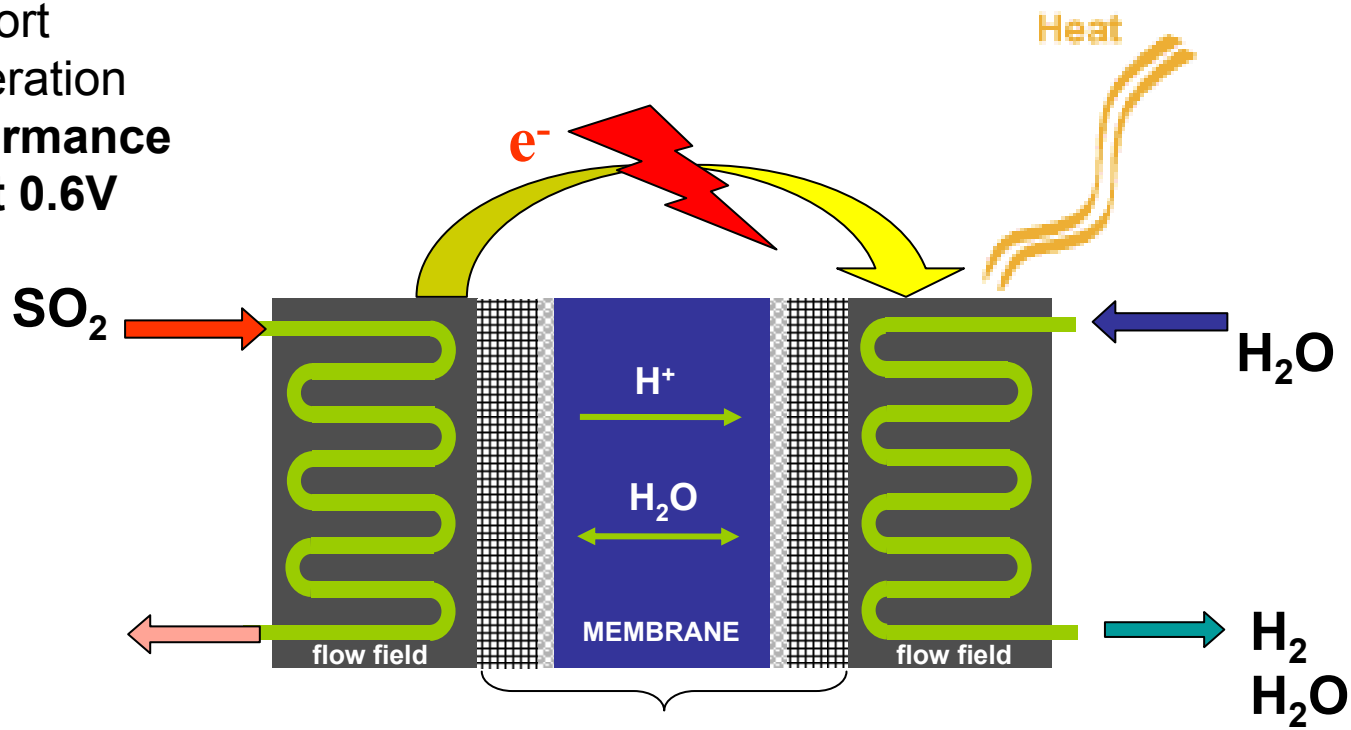
Fujimoto, C.H, Hickner, M.A., Cornelius, C.J., Loy, D.A.
Macromolecules **2005**, 38(12), 5010-5016.

Electrolyzer Schematic

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

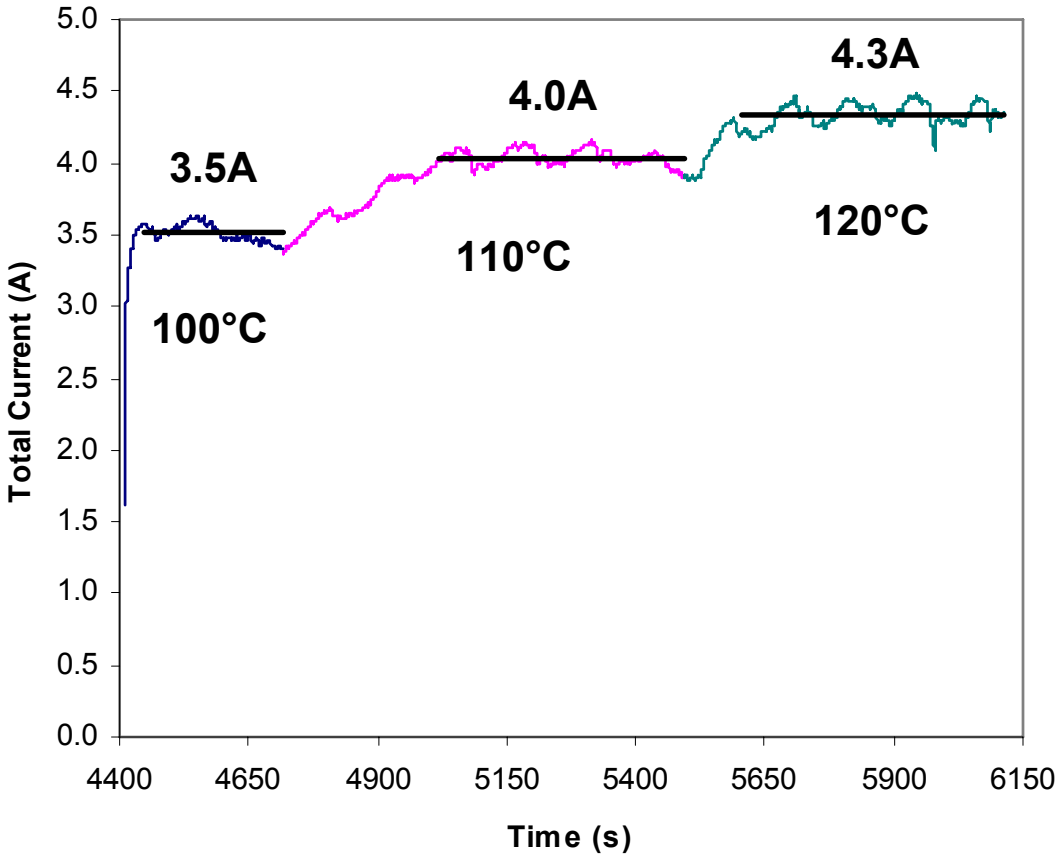
Membrane is critical for:
- low SO_2 crossover
- efficient water transport
- high temperature operation

SNL Membrane Performance Target: 0.5 mA/cm² at 0.6V



Membrane Electrode Assembly – MEA
Membrane
Catalyst layers
Gas diffusion layers

Increased Temperature Promotes Better Performance
High Temperature Enabled by SNL membranes

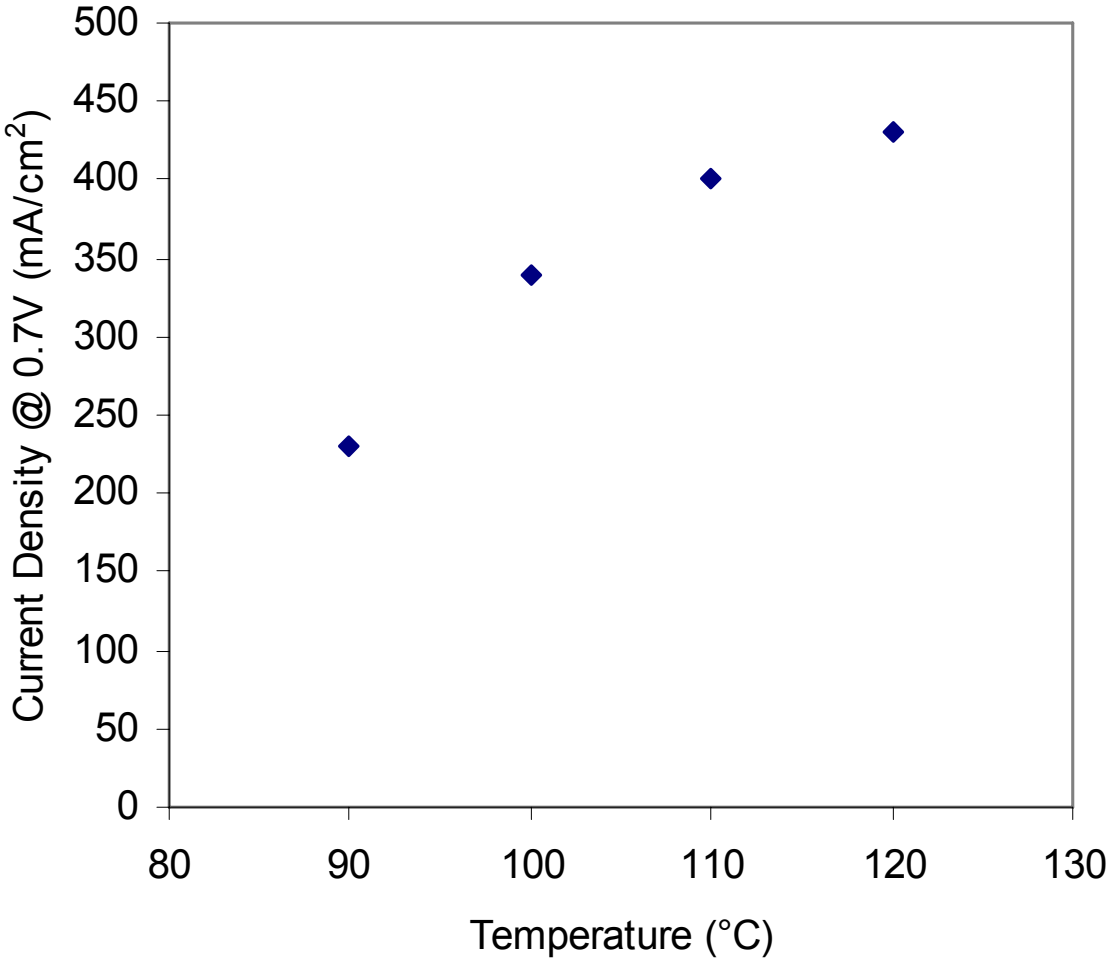


Total cell current at 0.7 V cell potential of SDAPP 2.2 meq/g electrolysis cell with time at 100°C, 110°C, and 120°C cell temperature.

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

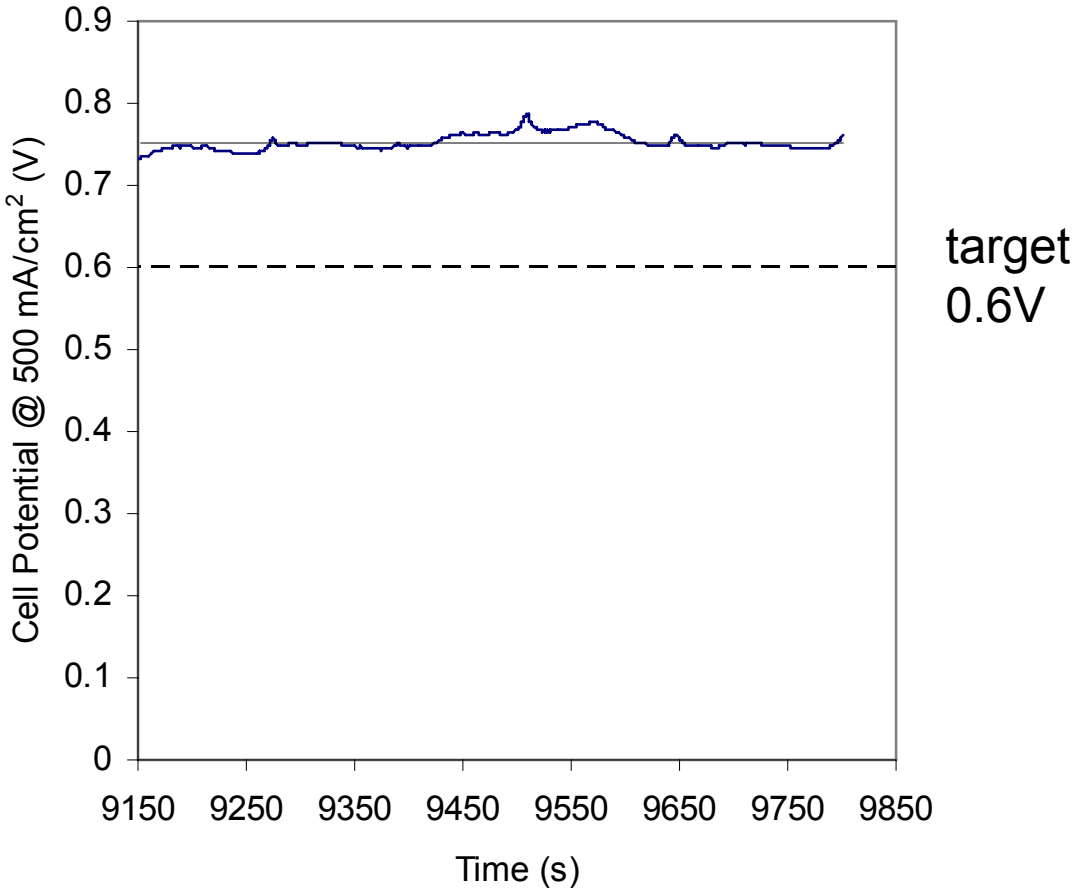
Performance increase of SNL Membrane Electrolysis Cell at 0.7 V



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

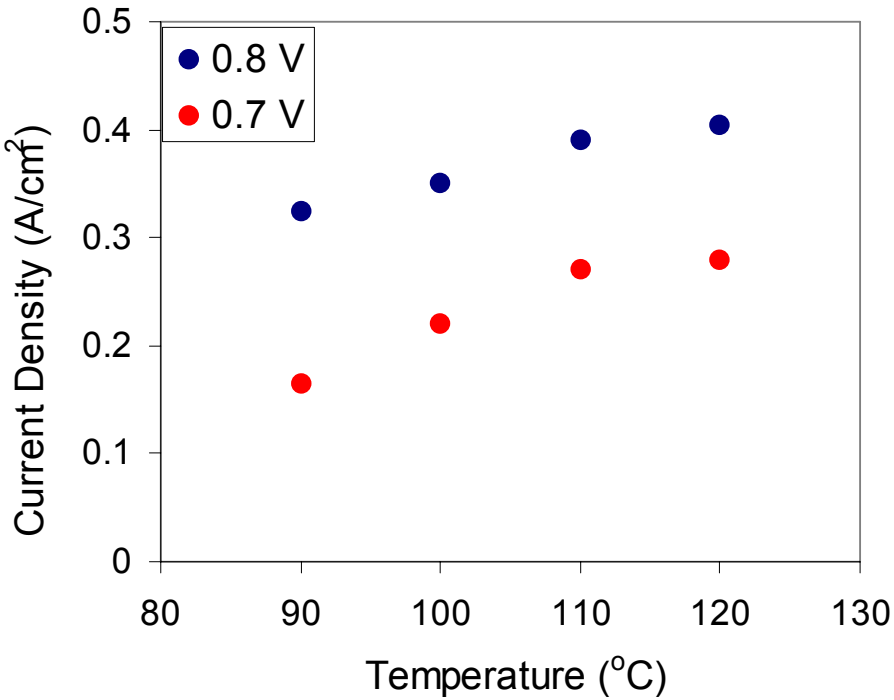
Galvanostatic Performance of SNL Membrane at 120°C

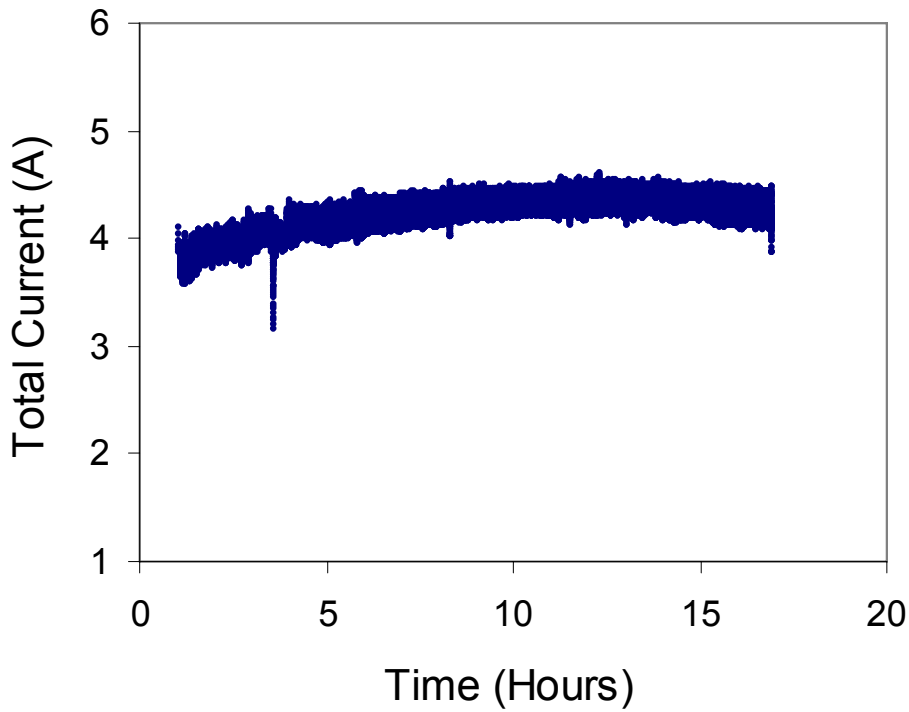
The average potential of the electrolysis cell for 10 minutes is 0.75 V. The previous best performance of this membrane was 0.83 V at 500 mA/cm^2 and 80°C as measured by University of South Carolina.



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

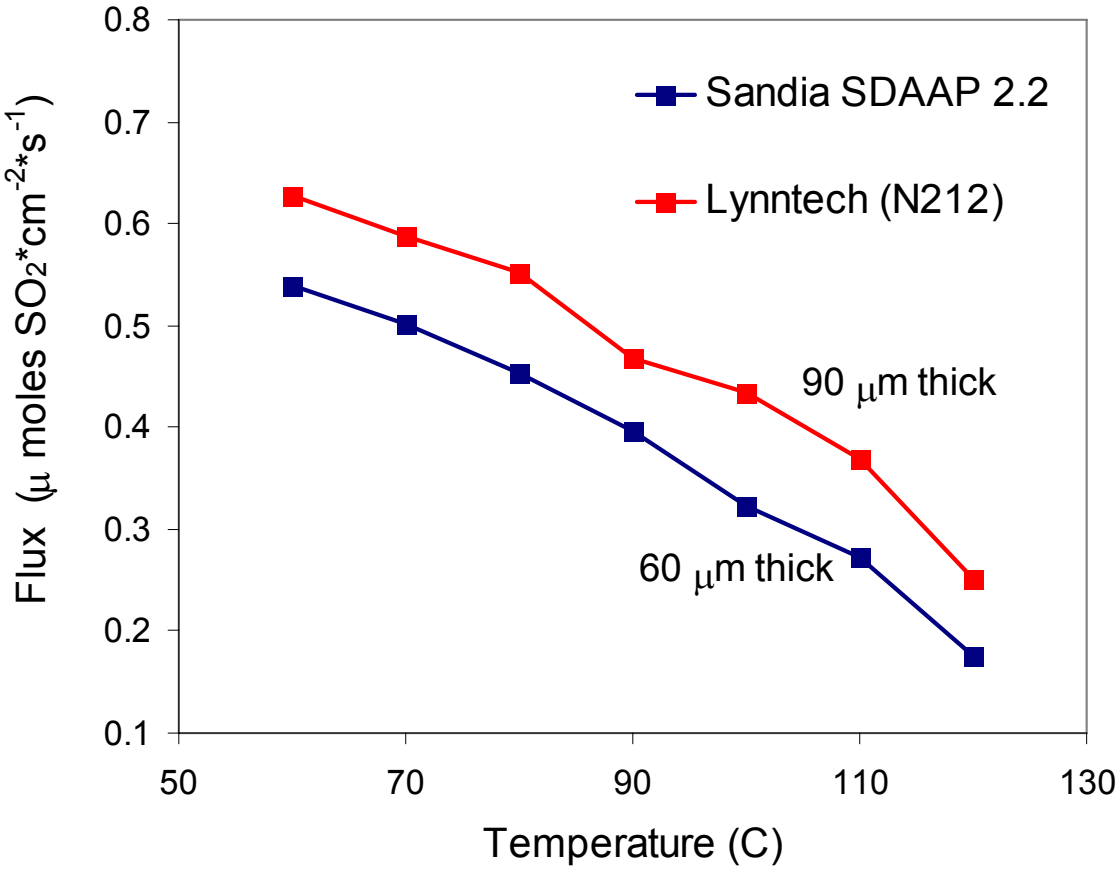
Performance and Lifetime of SNL (4-141-D) Membranes





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



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.

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

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	μmol SO_2/cm^2*s	μmol H_2/cm^2*s	μmol 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

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(UC Davis, Calorimetry)
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