UT-BATTELLE

Membrane Applications for Nuclear Hydrogen Production Processes

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OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

Project Overview

Budget ($K)

	Sulfur Cycles	High Temperature Electrolysis
FY2004	50	50
FY2005	170	60

Partners and Collaborators

- General Atomics
- Idaho Falls National Laboratory

Objectives

Sulfur Cycles

To assess the potential for high temperature inorganic membranes for use in the decomposition of sulfuric acid.

- **Evaluate stability of membrane materials in the corrosive SO_2/SO_3 environment.**
- **Fabricate membranes from compatible materials and initiate testing of membrane separation efficiency.**

HTE

To analyze the applicability of high temperature inorganic membranes, developed at ORNL, for the separation of hydrogen from steam at the outlet conditions of the solid oxide electrolyzer cells.

(See Notes page for further information)

Approach

Sulfur Cycles

The primary tasks are:

1) - Identification of candidate high temperature membrane materials

2) - Candidate membrane and support tube fabrication studies

3) - Membrane and support tube materials compatibility testing

4) - Conduct membrane separations tests

These initial studies will provide basis and initial separations for prioritizing further investigations on membrane materials for the high temperature step in the Sulfur cycles.

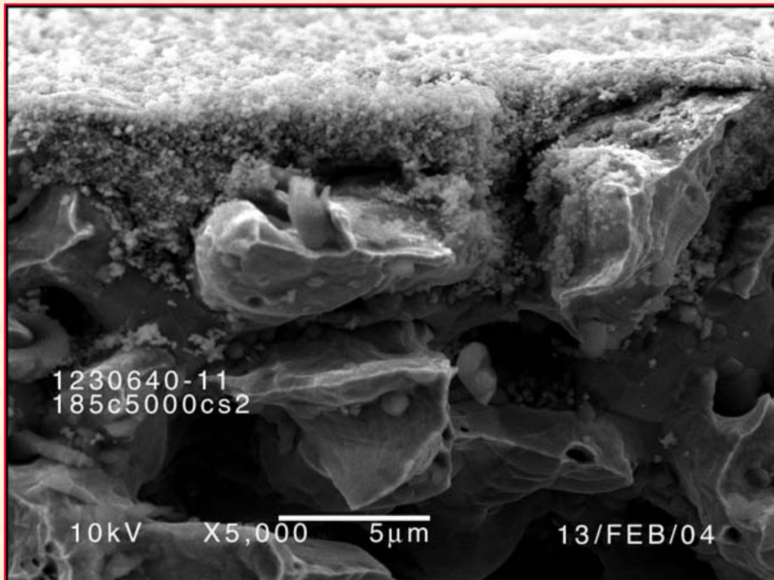
High Temperature Electrolysis

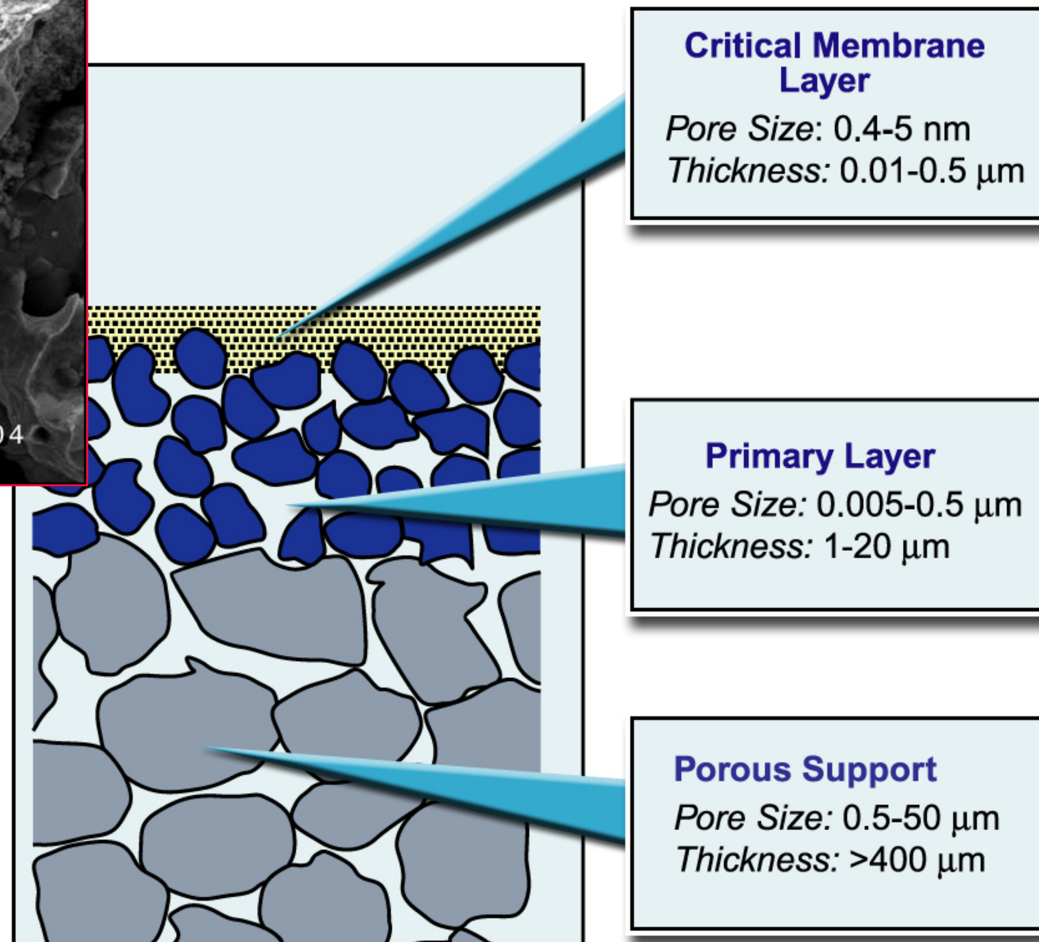
1) Analyze existing data or collect additional data to determine efficacy of inorganic membranes to separate hydrogen from steam at electrolyzer conditions.

ORNL's Inorganic Membrane Fabrication Process is Quite Versatile

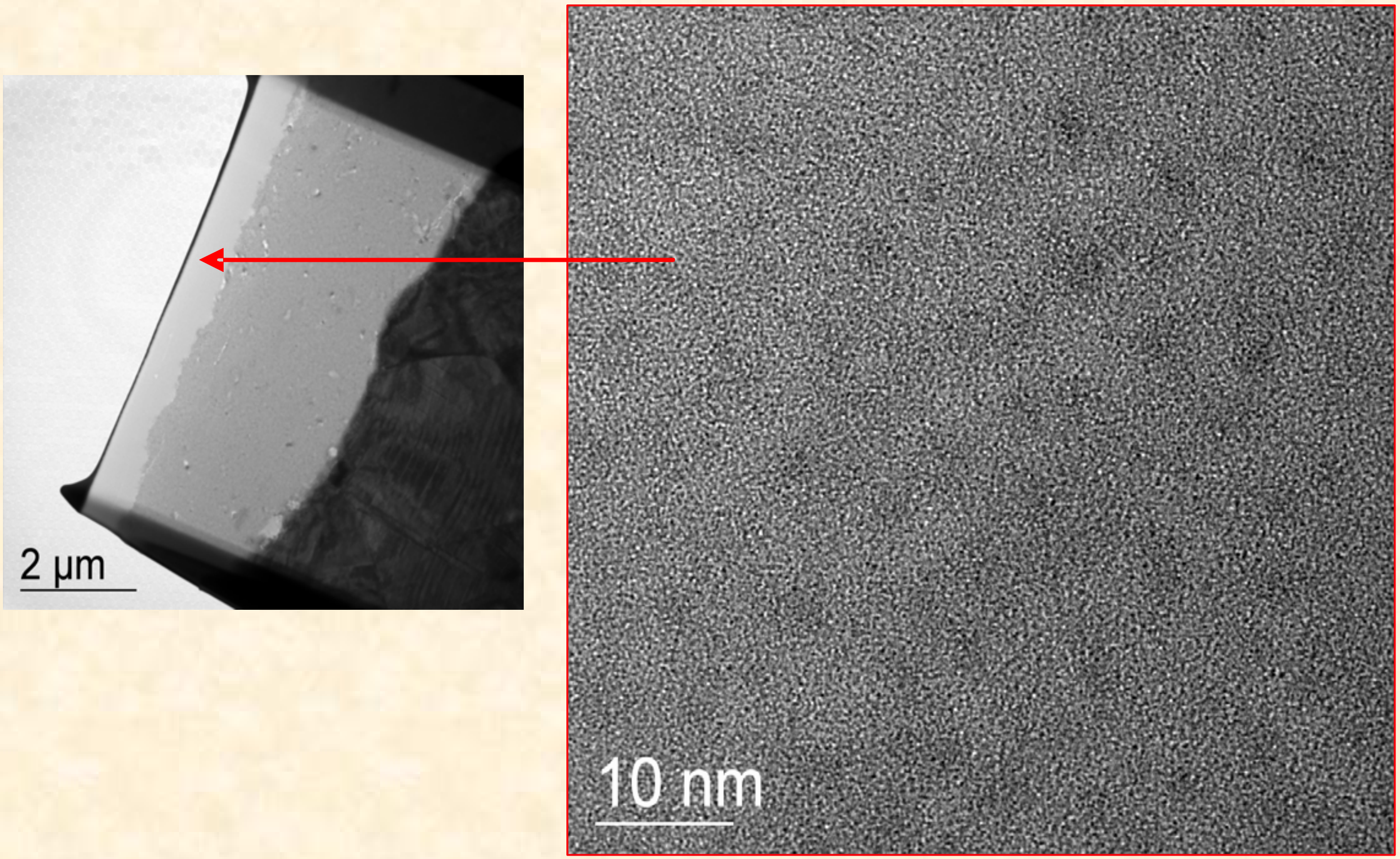
- Pore diameters of 0.5 nm – 20,000 nm; for H_2, pore diameters of <1 nm are preferred
- Tubular support structure and layer made of variety of metals and ceramics
- Excellent mechanical, thermal, and chemical stability
- Membrane layer(s) applied to inside of support tube
- Membrane layer thickness of 2 μm or less yields high gas flows at low pressure drop; small pores result in high selectivity
- Proven scalability

A Thin Separation Layer Allows High Flow of Gases Through Small Pore Membranes





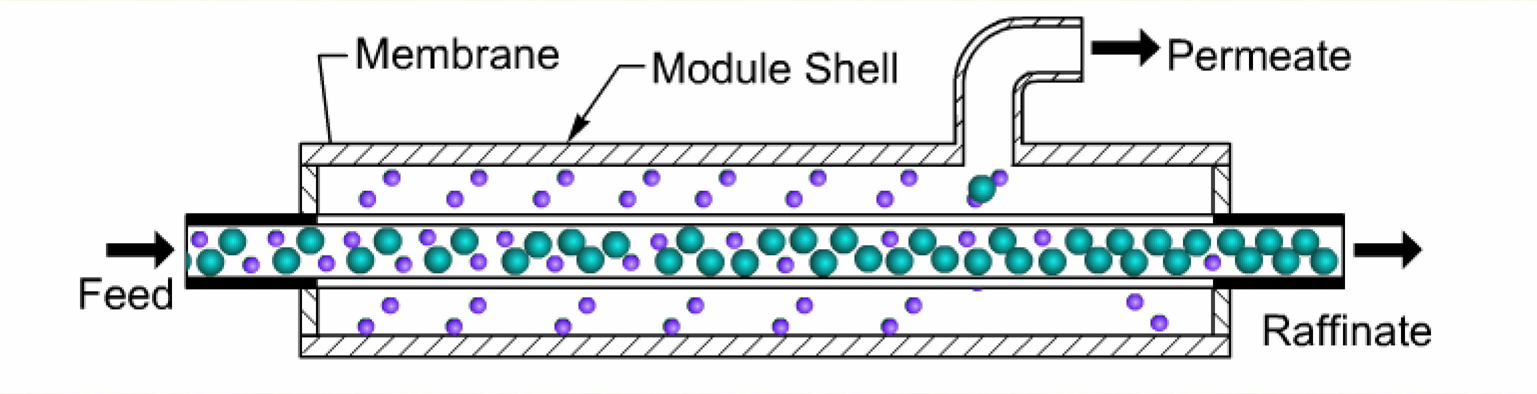
In Distinct Contrast To Palladium Or Ion Transport Membranes, These Are Porous



Membranes are descriptively nanoporous with pore sizes <2 nm, but IUPAC nomenclature is "microporous' (I didn't make the rules)

Permeance and Separation Factor are the Two Most Critical Attributes of Microporous Membranes

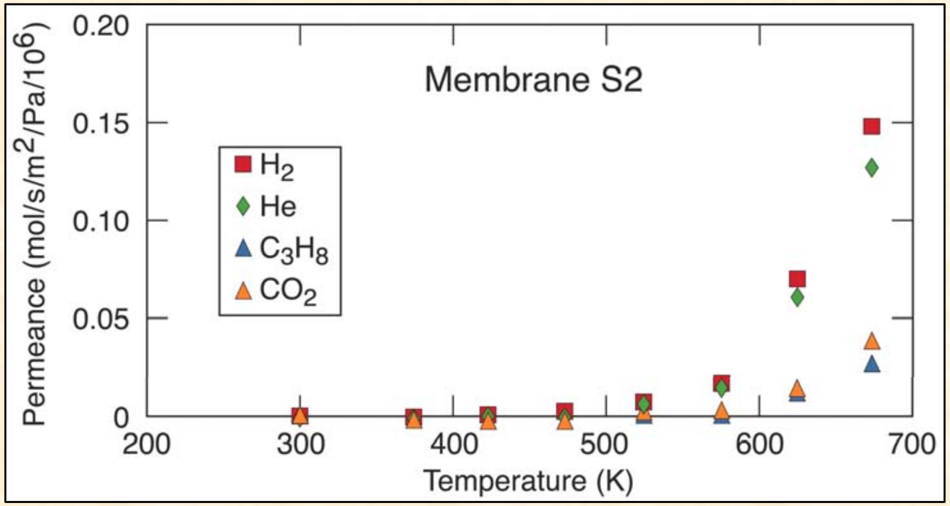
95%

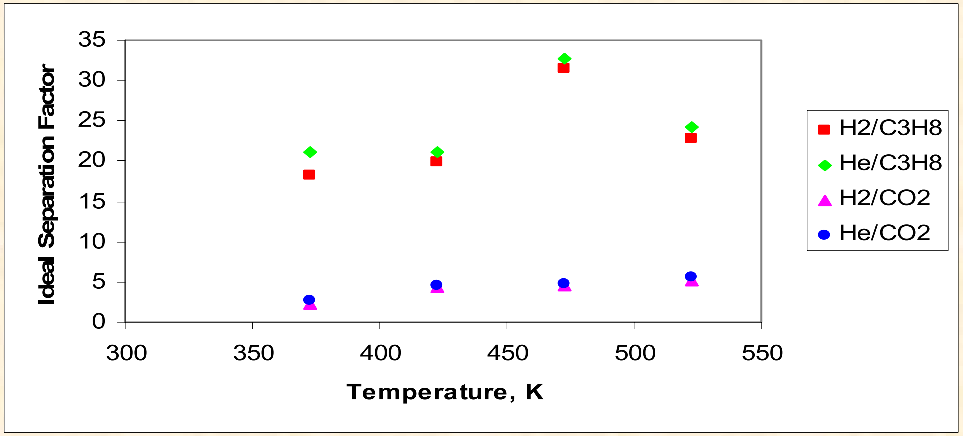


- *Permeance*: volumetric flow rate per unit of surface area per unit of transmembrane pressure (ΔP) at a particular temperature
- *Separation factor*: ratio of the flow of two gases in a binary gas mixture; indicator of selectivity of the membrane *(Separation factor depicted in figure is 19 and yields 95% hydrogen purity)*
- Design that achieves an appropriate balance of permeance and separation factor is <u>key</u>
- Both permeate gas flow and purity are affected by the "cut" (fraction of total gas flow that goes through the membrane)

High Operating Temperatures Result in Both Higher Permeances and Higher Separation Factors

As the temperature is increased, the permeance of hydrogen and helium increase faster than CO_2 and propane. This phenomenon results in larger separation factors as temperatures are increased.

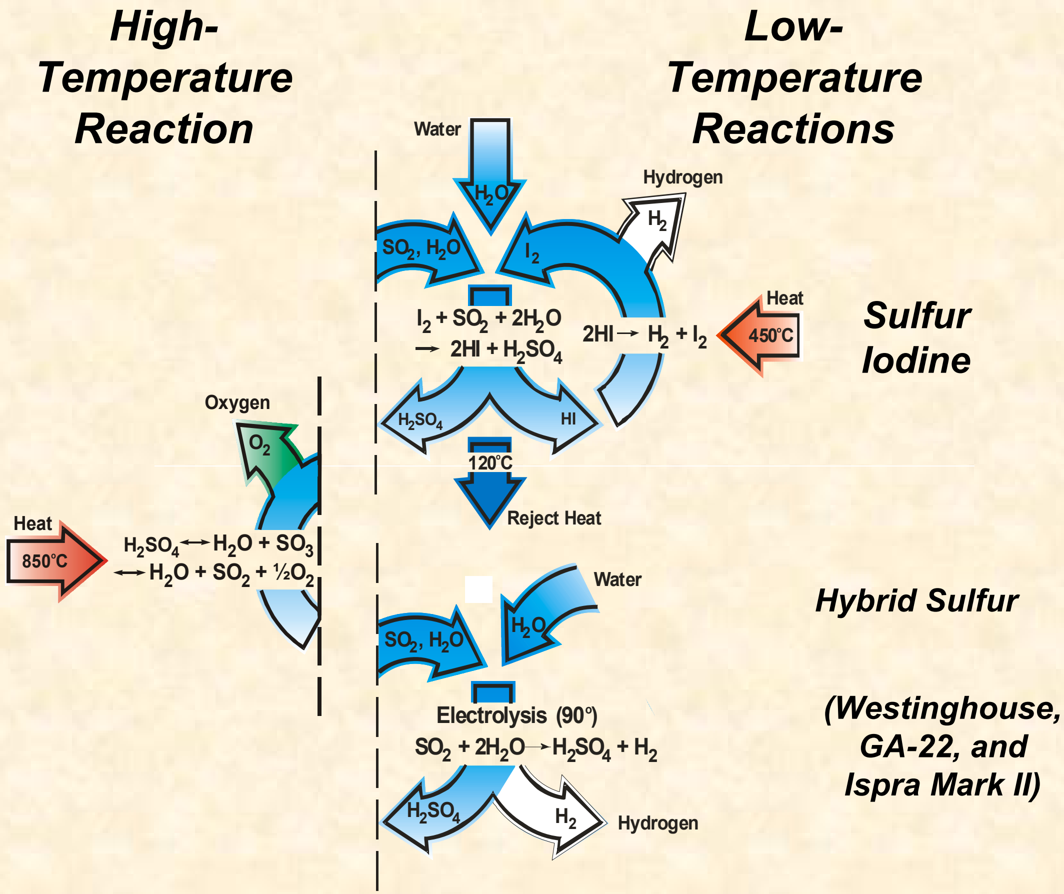




Thermochemical Cycles can be Used to Produce Hydrogen from Water

- Water + Heat $\Rightarrow$ Hydrogen + Oxygen
- Sulfur-based thermochemical cycles are the leading options
- Sulfur cycles require very high temperatures (850ºC)
  - At the limits of reactor technology
  - At the limits of practical materials
  - Large incentives exist to reduce temperatures
- A method to lower peak temperatures by 100 to 200ºC is being developed using inorganic membranes

Sulfur Family of Thermochemical Cycles



- **Shift the equilibrium of the high-temperature reaction to completion by removing the reaction products using inorganic membrane:**
- **Membrane separation of O_2, H_2O, and SO_2 from SO_3 drives reaction to the right, thus allowing high conversion at lower reaction temperatures**
- **Potential exists to reduce peak temperature to between 650 and 750°C**

Membrane Design and Fabrication

Molecular Diameters:

water: 0.2641 nm

oxygen: 0.3467 nm

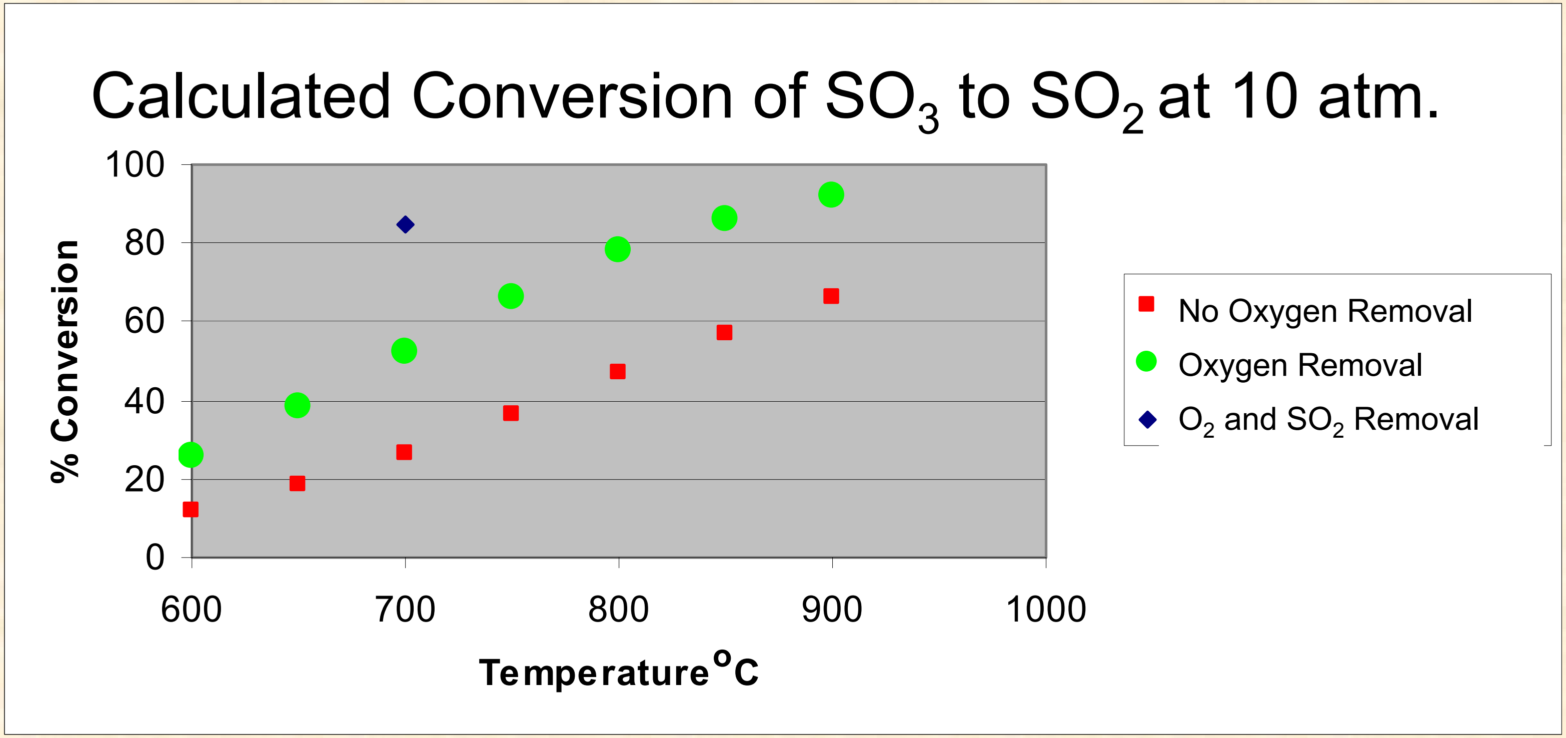
SO_2 : 0.4112 nm

SO_3 (a larger planar molecule)

First Generation Membrane – Experimental Characterizations

Tube	He Perm 250°C	SF6 Perm 250°C	Ideal Separation Factor	Hard Sphere Model Diameter nm
HT5021b	3.22E-03	2.39E-05	134.9	0.624
HT5022a	5.71E-03	1.32E-04	43.4	0.682
HT25210a	4.62E-03	1.17E-04	39.4	0.736
HT108b	6.51E-04	5.01E-05	13.0	0.895
HT54220a	2.88E-03	3.80E-04	7.6	0.895

Calculated Conversion of SO_3 to SO_2 using FactSage* Computer Program



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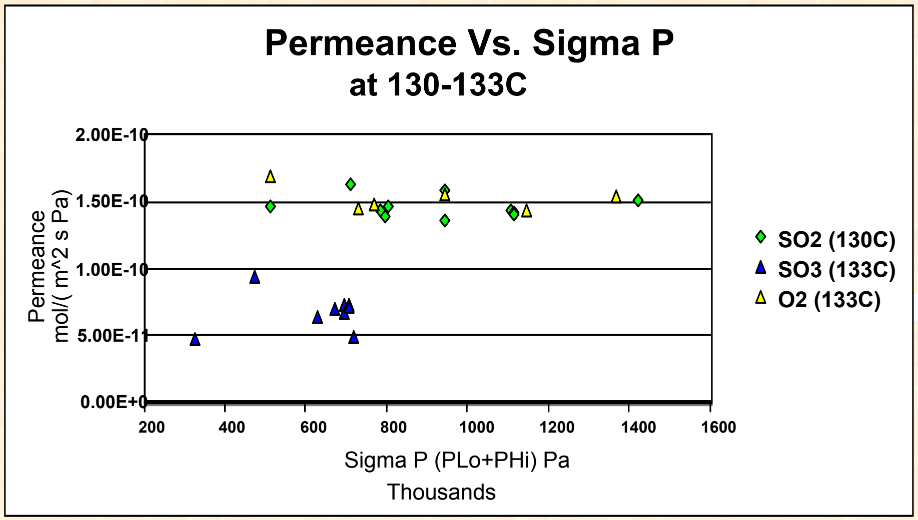
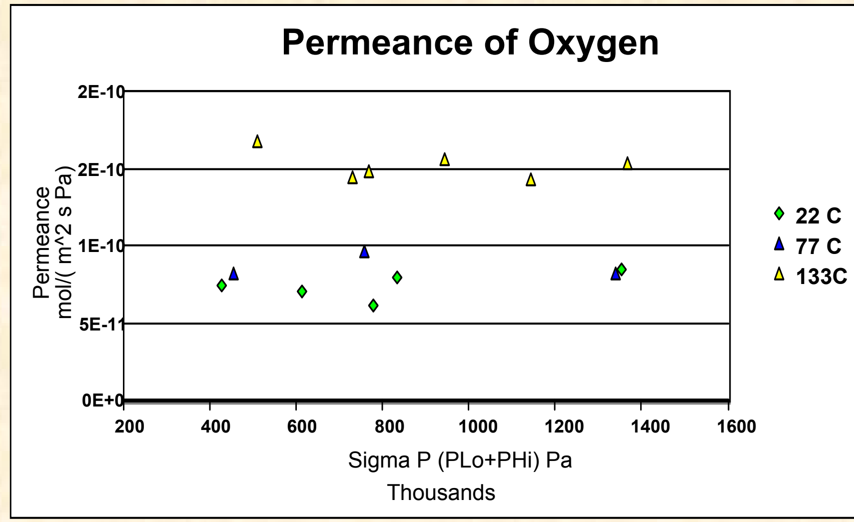
1st Generation Membrane Tests: SO_2 /SO_3 and O_2/SO_3 Separation Factors Exceed 2 in Low-Temperature Tests





SI Conclusions to Date

- The stainless steel 316L supported ceramic membranes are compatible with process chemicals up to 130 °C
- Initial experiments show nanopore diffusion with permeance increasing with temperature—the desired behavior for a sulfur thermochemical membrane
- Initial experiments with first-generation membranes show low-temperature separation of O_2 and SO_2 from SO_3
  - Separation factor for O_2/SO_3: 2.3
  - Separation factor for SO_2/SO_3: 2.2
- Preliminary work is highly encouraging and suggests that a practical separations membrane can be developed

Plan for FY 2005

- Conduct membrane fabrication studies for candidate high temperature membrane materials
- Fabricate exposure test system and conduct membrane compatibility studies to determine applicability for H_2SO_4 environment
- Conduct initial phase of candidate membrane separations tests

Status

The following materials have been identified as potential candidates for support tube fabrication

1) Hastelloy B2 or B3

2) Hastelloy C22

3) Hastelloy G

4) Monel

5) MA20Nb-3

6) MA825

7) Nickel-Copper alloy

Powders in the desired size and morphology of the following have been located and procured.

1) Hastelloy C22

2) Monel

Porous coupon-sized samples have been fabricated and sintered.

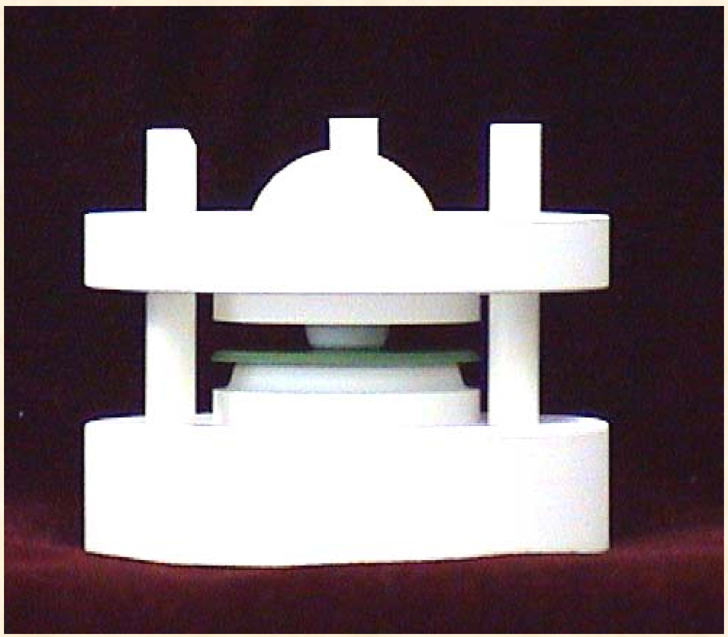
Plan for the Remaining FY

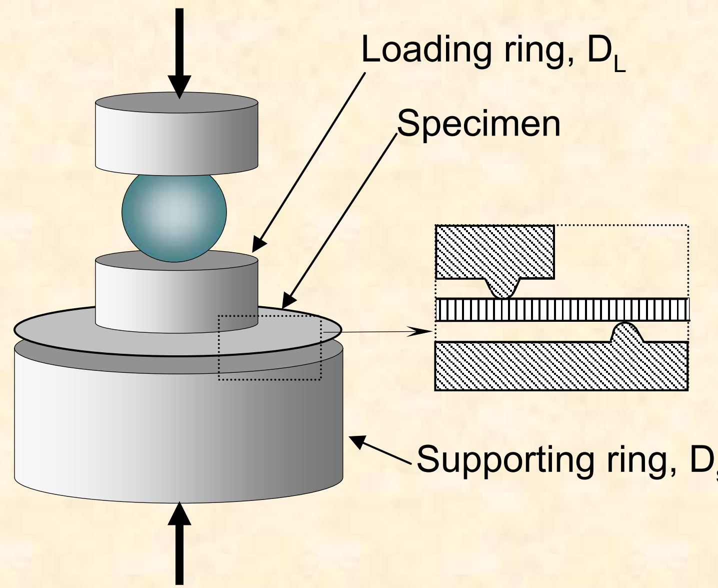
- Characterize coupon samples for flow properties and mechanical properties (elastic modulus and in-plane biaxial strength). Edgar Lara-Curzio (Metals and Ceramics) has developed these techniques which can be applied to our coupon samples.
- Expose samples to SO_3 and SO_2 at high temperatures of 500-900 °C.
- Characterize exposed samples to determine effect on support materials

Strength of Samples will be Tested Before and After Exposure

Biaxial Strength

Ring-on-ring Testing (ASTM C1499-01)





High Temperature Electrolysis

<u>Outlet of electrolyzer</u>

H_2 - 75-85 % with the balance steam at 600-900 °C and 1-5 MPa

Target is for membrane to produce hydrogen at 90-95% purity

Reject stream will be fed back into electrolyzer

Hydrogen is larger than Water molecule so separation cannot be accomplished by molecular sieving. Separation by Knudsen diffusion is

$$SF = \left(\frac{M_{Water}}{M_{Hydrogen}} \right)^{1/2} = 3$$

High Temperature Electrolysis

Measured Separation Factor (SF)

SF = (Conc. H_2 out/Conc. H_2 in)/(Conc. H_20 out/Conc. H_20 in)

For 75% H_2 One Stage Conc. H_2 = 90%

Two Stages Conc. H_2 = 96.4%

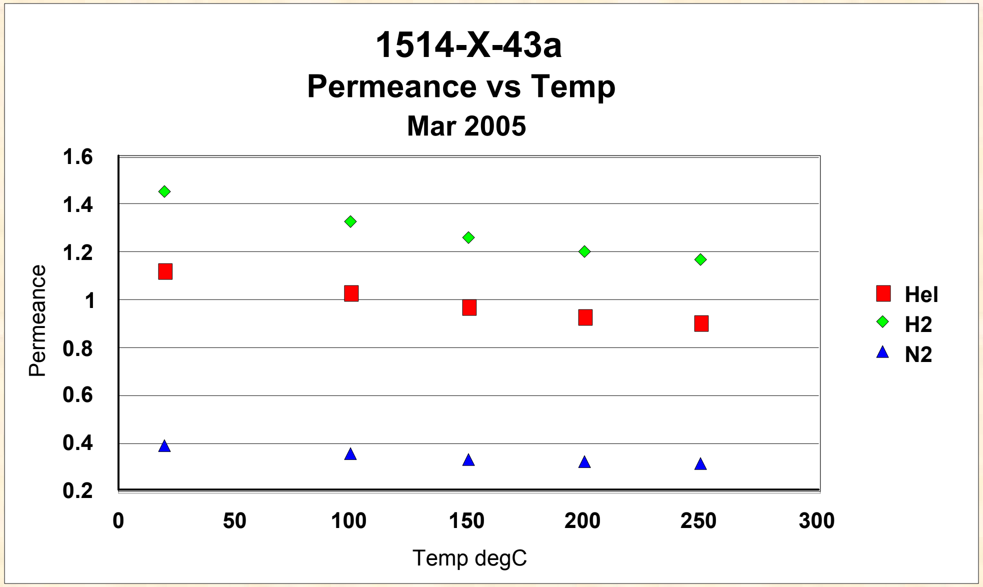
Three Stages Conc. H_2 = 98.8%

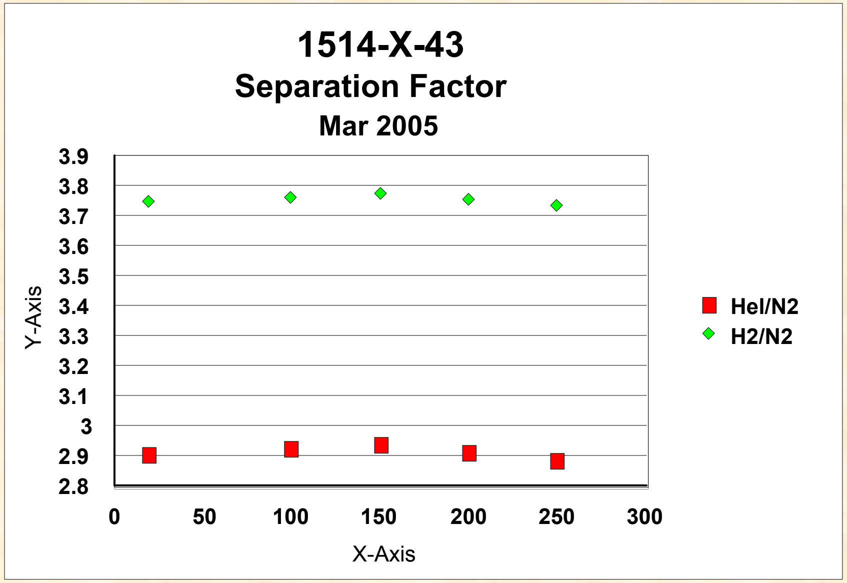
For 85% H_2 One Stage Conc. H_2 = 94.4%

Two Stages Conc. H_2 = 98.1%

Three Stages Conc. H_2 = 99.4%

Metal Supported 70 Å Alumina Membrane Achieves Knudsen Separation





<u>Theoretical Separation Factors</u>

H_2/N_2	3.74
He/N_2	2.65

HTE Status

- Knudsen diffusion will yield a separation factor for hydrogen from steam of 3 with very high permeances
- Required purity can be achieved in 2 stages.
- A metal supported alumina membrane was evaluated for the separation of hydrogen from nitrogen and was found to achieve Knudsen separations.
- Membranes should be less expensive to manufacture and more stable than microporous membranes used for SI process.

Project Safety

The most significant hazards are the use of sulfur dioxide and sulfur trioxide in our SI membrane test systems and hydrogen in the HTE project

Our approach to ensuring safe operation includes:

- Project has undergone "Integrated Safety Management Pre-Planning and Work Control" (Research Hazard Analysis and Control)
- Each work process is authorized on the basis of a Research Safety Summary (RSS) reviewed by ESH subject matter experts and approved by PI's and cognizant managers
- The RSS is reviewed/revised yearly, or sooner if a change in the work results in a need for modification.
- Experienced Subject Matter Experts are required for all Work Control for Hydrogen R&D including periodic safety reviews of installed systems
- Results of Work Control Process requires:
  - Complete SI system including gas bottles will reside in laboratory fume
  - Gas lines will be purged with inert gases upon completion of test
  - Monitoring hydrogen concentration at ceiling above test system. Alarm sounds at 50% LEL.
  - Personnel be present at all times when using hydrogen.
  - Evacuation of gas lines of air or purging with inert gas prior to introduction of hydrogen
  - Exhaust of gas lines containing hydrogen using eductors instead of electrically driven vacuum pumps.

Completed Membrane Test System for SO_2/SO_3 Separation in Hood