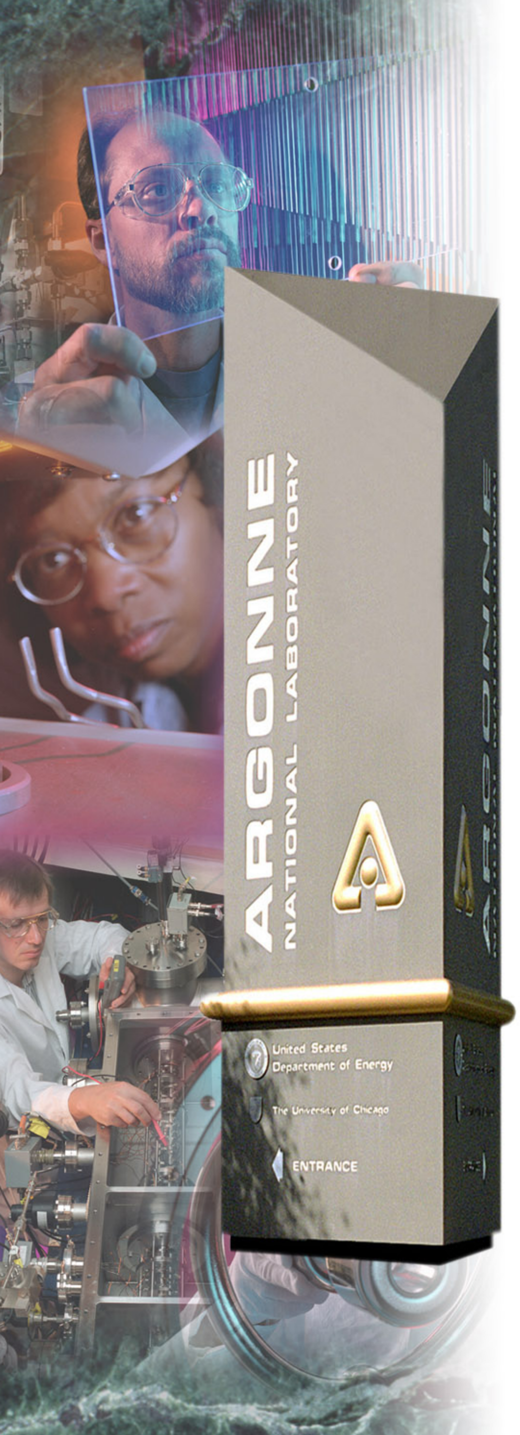


Development of Dense Ceramic Membranes for Hydrogen Separation*

U. (Balu) Balachandran

May 25, 2005

*Work supported by U.S. DOE, Office of Fossil Energy,
National Energy Technology Laboratory.

Overview

Timeline

- This is ongoing DOE Lab work funded by Fossil Energy on an annual basis.
- Started FY 1998.

Barriers to “Separations and Other Cross-Cutting H_2 Production”

(L) Hydrogen Transport Membrane (HTM) will be durable at high temp./pressure.

(M) HTM is stable in steam, CO, CO_2, CH_4, and H_2S.

(O) Selectivity is infinite.

(Q) HTMs give industrially significant flux.

(S) Cermet HTM reduces membrane cost.

Budget

- Total Funding: $3350K (DOE)
- FY 2004 Funding: $400K
- FY2005 Funding: $550K

Partner

NETL - National Energy Technology Laboratory

Objectives

Develop dense ceramic membranes for separating hydrogen from mixed gases at commercially significant fluxes under industrially relevant operating conditions. Product streams from coal gasification and methane reforming are of particular interest. Membrane must:

- have low cost
- have high selectivity for H_2
- give industrially significant flux
- withstand high pressure and temperature
- be chemically stable in presence of steam, CO, CO_2, CH_4, H_2S, etc.

Approach

Our three-pronged approach aims to develop:

- Pure mixed proton-electron conductors e.g., acceptor-doped cerates and zirconates
- Cermets (i.e., ceramic-metal composites) that contain mixed conductors and a metal that enhances the membrane's ambipolar conductivity and flux
- Cermets composed of mechanically durable ceramic and a metal/alloy with high hydrogen permeability

Approach - Continued

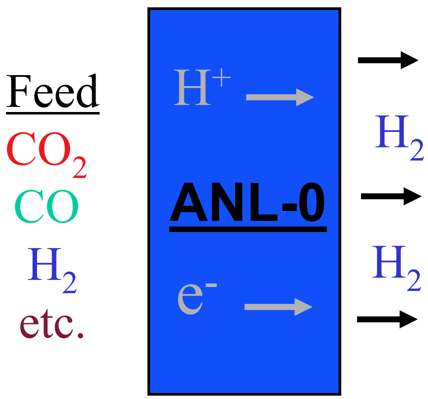
- Select/fabricate candidate materials based on fundamental principles of defect chemistry and mass transport.
- Measure hydrogen flux of candidate material versus temperature.
- If flux is high, test short-term (≈100 h) chemical stability in gases containing H_2S, CO, CO_2, H_2O, etc.
- If membrane seems chemically stable, measure mechanical properties (fracture strength, creep).
- Measure hydrogen flux at high pressures (NETL).
- Optimize fabrication methods to reduce membrane thickness and maximize flux.
- Test long-term (≈1000 h) chemical stability in simulated coal gasification atmospheres.
- Under guidance from NETL program managers, transfer membrane technology through industrial collaborations.

Advantages of Dense Cermet Membranes for Hydrogen Separation

- Selectivity is theoretically infinite.
- Flux rates >200 $cm^3/min\text{-}cm^2$ (400 $scfh/ft^2$) are attainable under "real-world" pressure conditions.
  - flux >30 $cm^3/min\text{-}cm^2$ (60 $scfh/ft^2$) already shown at ambient P
- Commercial, well-proven ceramic processing is used.
  - device will be economical
- Will accept high-temperature and high-pressure gas streams
  - suitable for FutureGen plants
- No pore plugging/closure
- Tolerates steam, CO, CO_2, CH_4, and H_2S
- Supplies CO_2 stream at high temperatures and pressures
  - important for carbon sequestration
- Can enhance equilibrium product conversion

ANL's Approach to HTM Development
(U.S. Patent 6,569,226, May 27, 2003)

Single-Phase Mixed Conductor

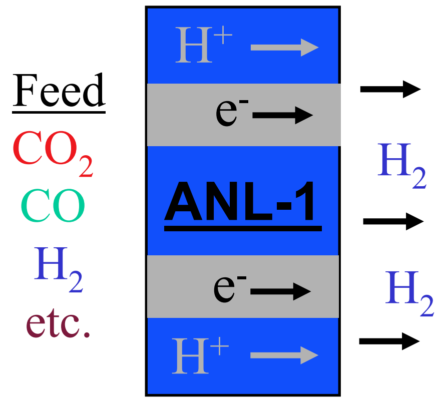


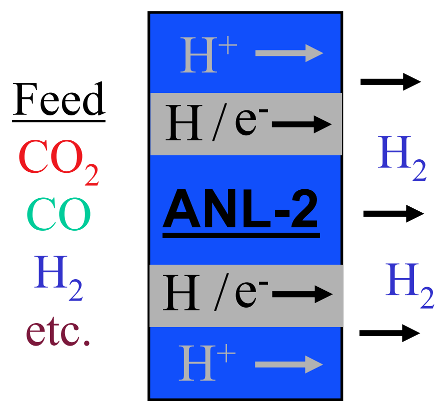
$$J_{H_2} = \frac{RT}{4F^2 l} \cdot \sigma_{amb} \cdot \ln \frac{p_{H_2}^{II}}{p_{H_2}^{I}}$$

$$\sigma_{amb} = \frac{\sigma_{H^+} \bullet \sigma_{e^-}}{\sigma_{H^+} + \sigma_{e^-}}$$

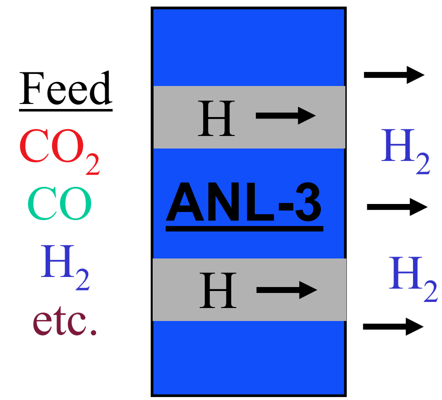
- Low σ_{e-}
- Low Flux
- Poor Mechanical Integrity

Mixed Conductor With Metal





Structural Ceramic With Hydrogen Transport Metal



$$J_{H_2} = \frac{A\Phi}{l}\left(\sqrt{p_{H_2}^{feed}} - \sqrt{p_{H_2}^{sweep}}\right)$$

- High Flux
- High Selectivity
- Good Mechanical Integrity

ANL Membrane Compositions

Membrane	Matrix	Metal
ANL-0	BCY	----
ANL-1a	BCY	Ni
ANL-1c	TZ-8Y	Ni
ANL-2a	BCY	Pd
ANL-2b	CMO	Pd/Ag(23 wt.%)
ANL-3a	Al_2O_3	Pd
ANL-3b	$BaTiO_3$	Pd/Ag(23 wt.%)
ANL-3c	Al_2O_3	Nb
ANL-3d	Al_2O_3	Pd/Ag(23 wt.%)
ANL-3e	TZ-3Y	Pd
ANL-3f	TZ-8Y	Pd
ANL-3g	$CaZrO_3$	Pd
ANL-4a	Cu	Nb

ANL Membranes (HTMs)

ANL-0: Mixed conductor (e.g., BCY)

ANL-1: Mixed conductor + metal with low H_2 permeability (e.g., Ni)

ANL-2: Mixed conductor + metal with high H_2 permeability (e.g., Pd, alloys, etc.)

ANL-3: Structural ceramic (e.g., Al_2O_3) + metal with high H_2 permeability (e.g., Pd, alloys, etc.)

ANL-4: Ductile metal + metal with high H_2 permeability (e.g., Pd, alloys, etc.)

Notes:

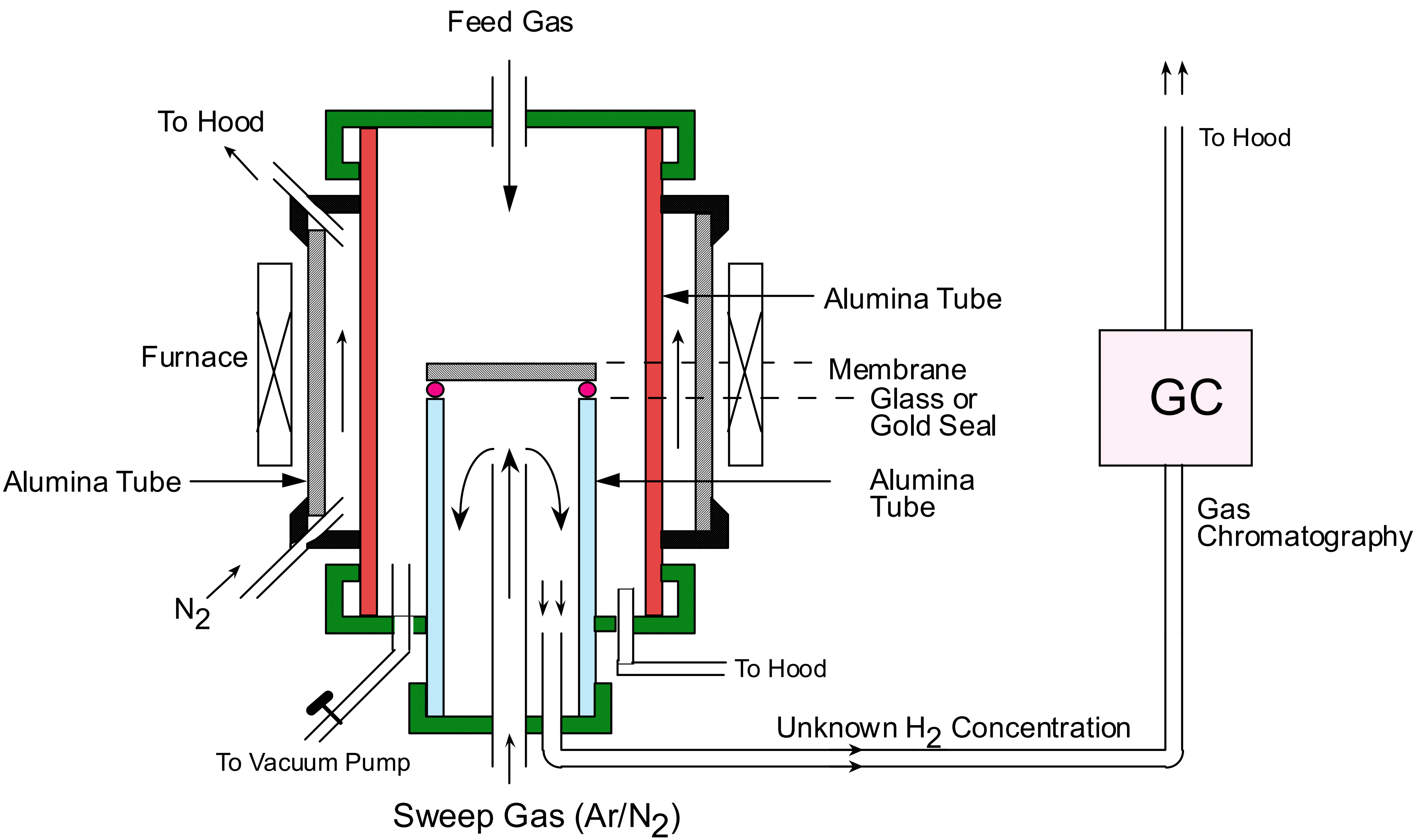
BCY = $BaCe_{0.8}Y_{0.2}O_{3-\partial}$

CMO = $Ce_{1-x}M_xO_{2-\partial}$ (M: Gd, Y)

TZ-3Y = ZrO_2 (3 mol.% Y_2O_3)

TZ-8Y = ZrO_2 (8 mol.% Y_2O_3)

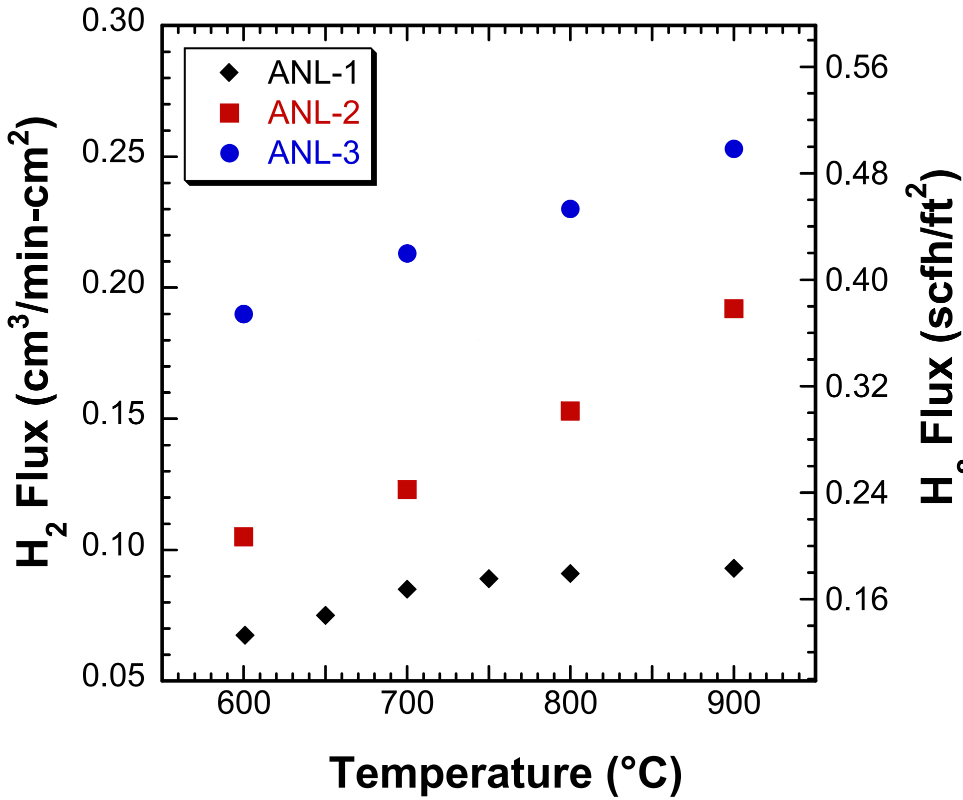
Schematic of Experimental Setup



Comparison of Cermet Membranes

Feed Gas: 4% H_2 in Ar @ Ambient Pressure

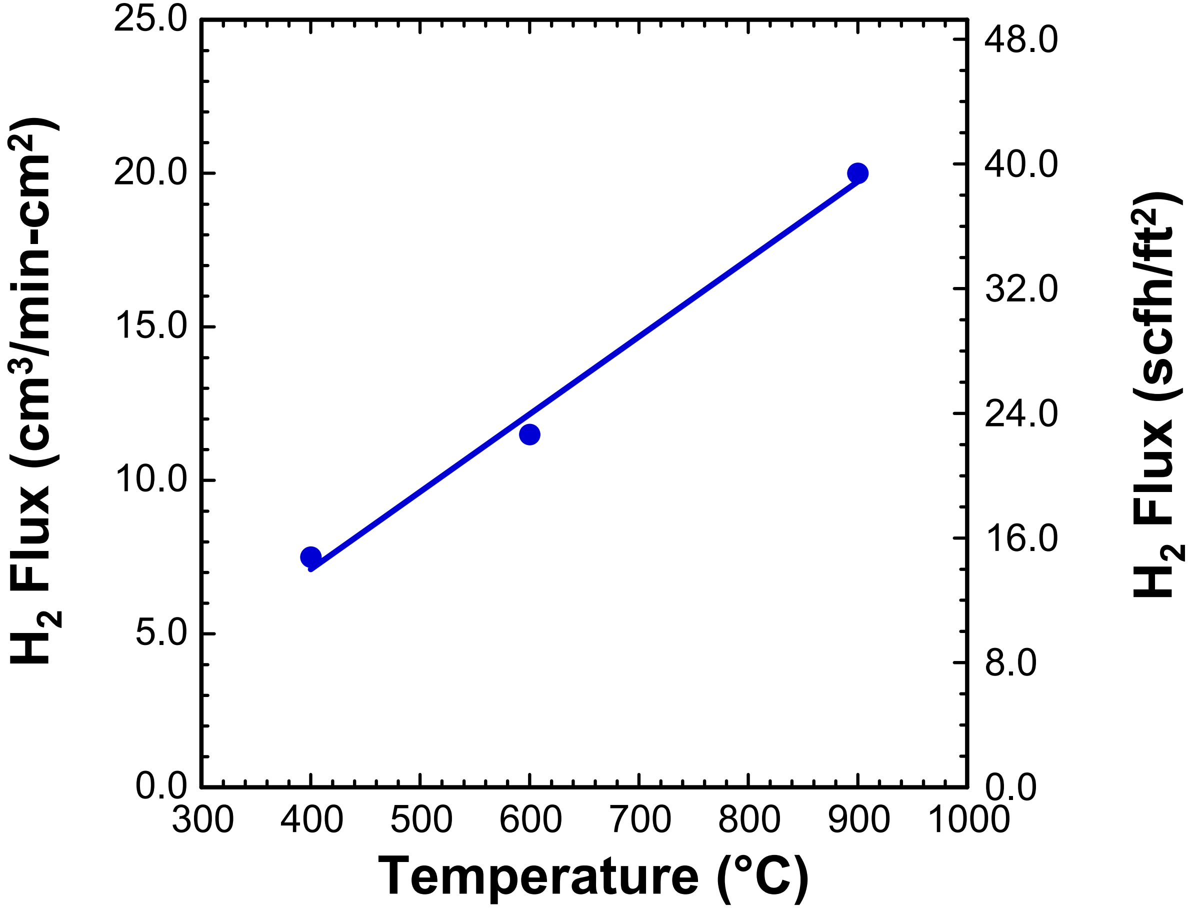
Membrane Thickness = 0.50 mm



- **ANL-3 HTMs give highest H_2 flux of ANL membranes.**

H_2 Flux (ANL-3a) vs. Temperature

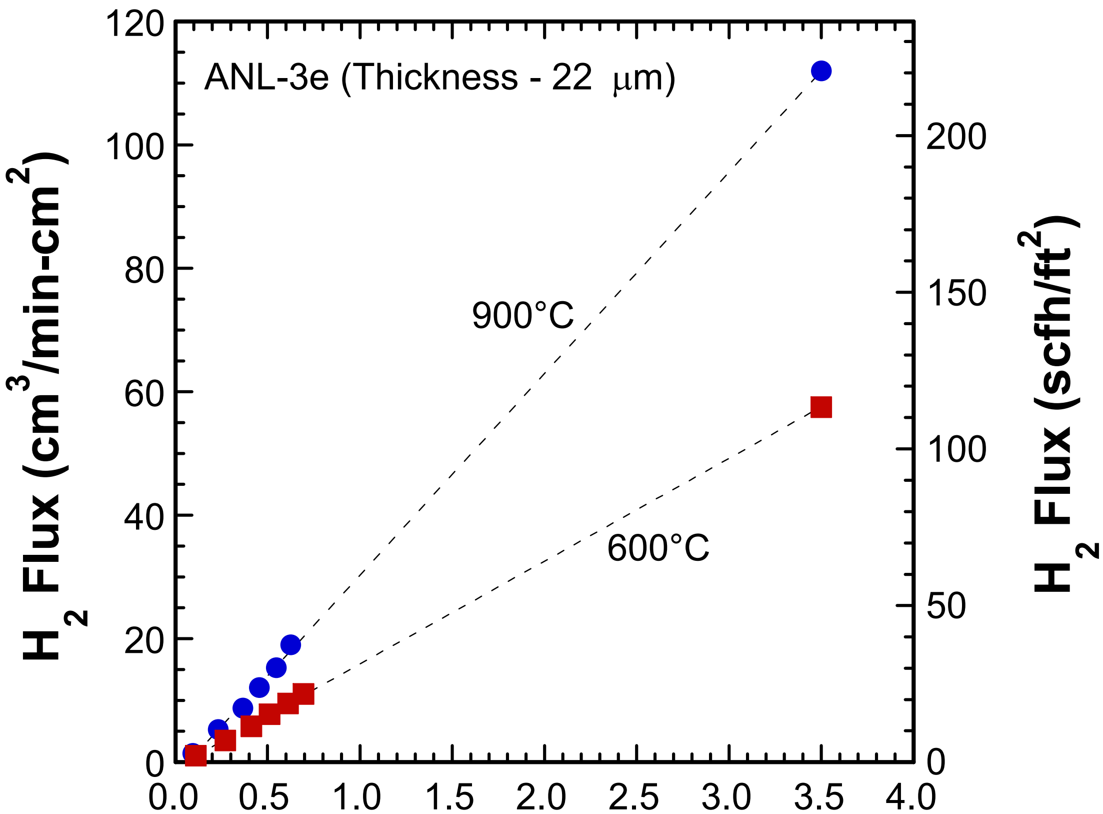
Thickness ≈ 40 μm, Feed Gas: 100% H_2 at ambient pressure



- **ANL-3a gives highest flux of self-supported HTMs.**

H_2 Flux vs. $\Delta pH_2^{1/2}$

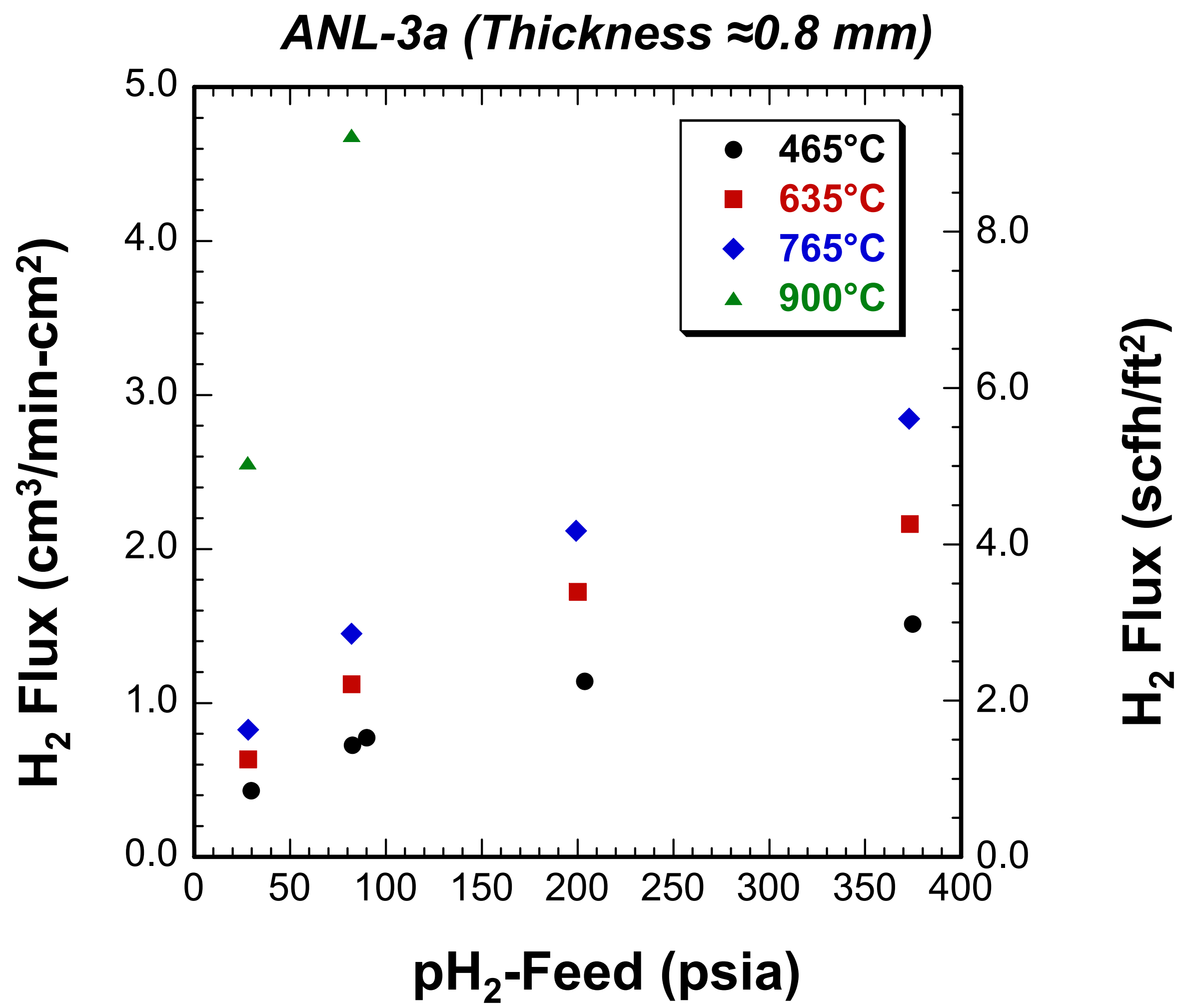
- **Linear dependence of H_2 flux on $\Delta pH_2^{1/2}$ shows flux is limited by bulk diffusion.**
- **Extrapolation shows stand-alone ANL-3e HTM should yield H_2 flux >200 scfh/ft² at 900°C with feed gas at ≈300 psi.**



$$\Delta pH_2^{1/2} \equiv \sqrt{pH_2(feed)} - \sqrt{pH_2(sweep)}\,(atm^{1/2})$$

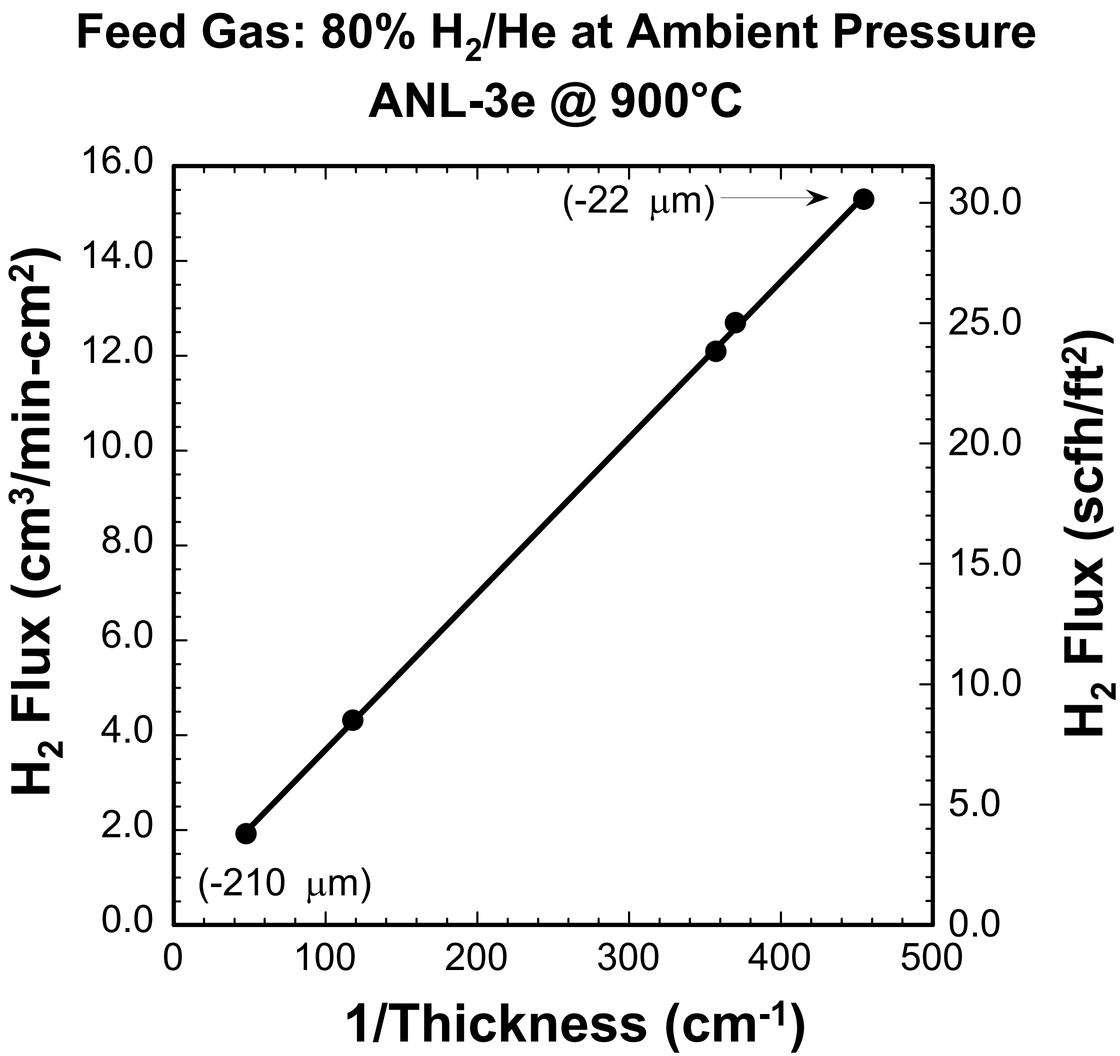
$$H_2\ Flow\ Rate = \frac{A\Phi}{l}\left(\sqrt{p_{H_2}^{feed}} - \sqrt{p_{H_2}^{sweep}}\right)$$

H_2 Flux at High Feed Gas Pressures



- **Measured flux values agree with extrapolated values.**

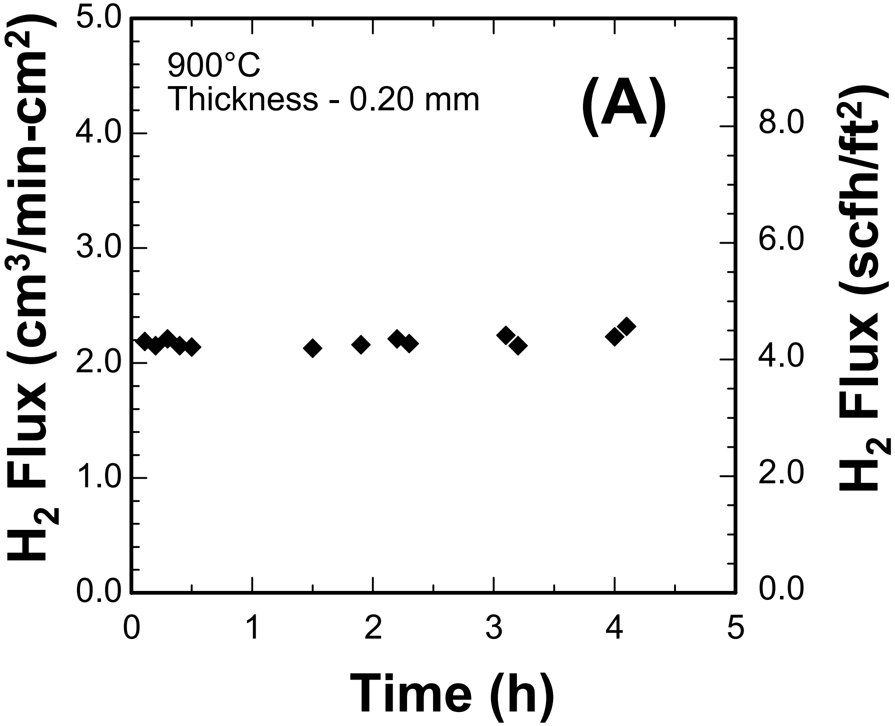
H_2 Flux vs. Inverse HTM Thickness



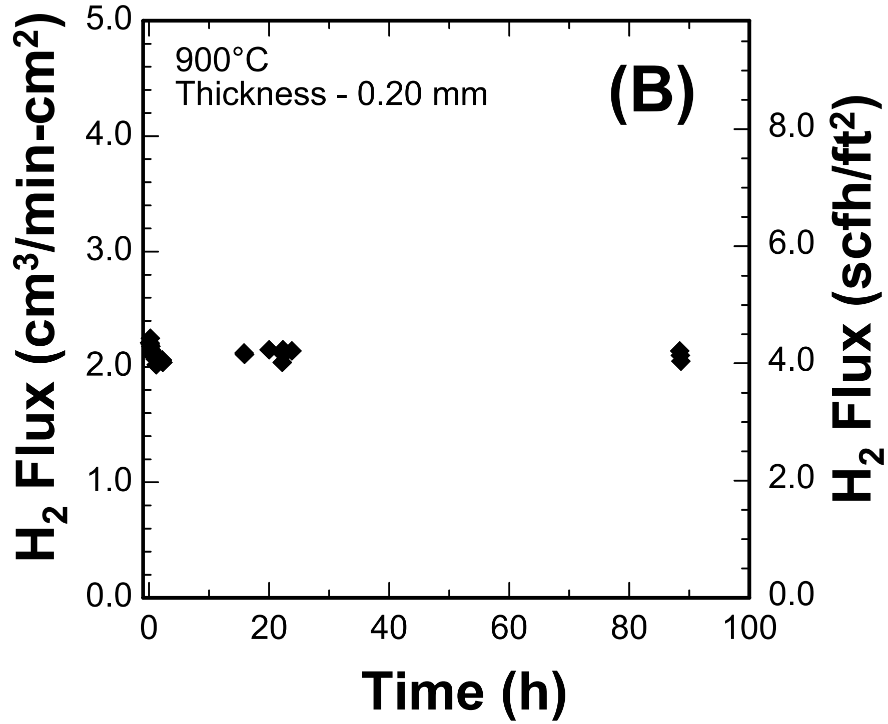
- **Flux data indicate that reducing HTM thickness should increase H_2 flux.**

Chemical Stability of ANL-3 Membranes

Feed Gas: 61.3% H_2, 8.2% CH_4, 11.5% CO, 9.0% CO_2, 10% He (Ambient Pressure)



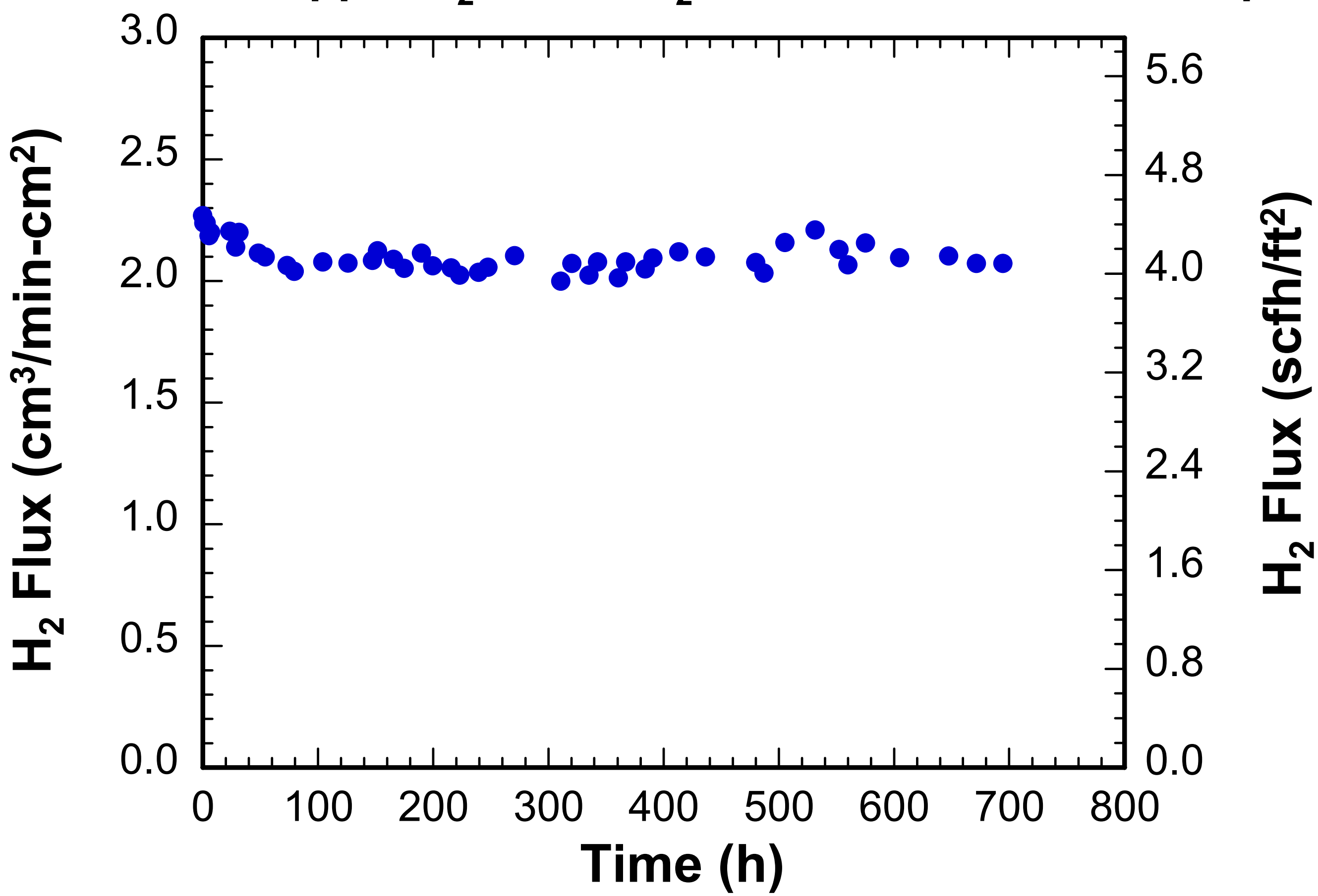
Feed Gas: Same as (A) + 100 ppm H_2S



- **ANL-3 membranes are chemically stable in CO, CO_2, CH_4 and H_2S.**

Chemical Stability of ANL-3 Membrane

ANL-3e (Thickness ≈ 0.20 mm)
Feed Gas: 400 ppm H_2S, 73% H_2, Balance He at ambient pressure

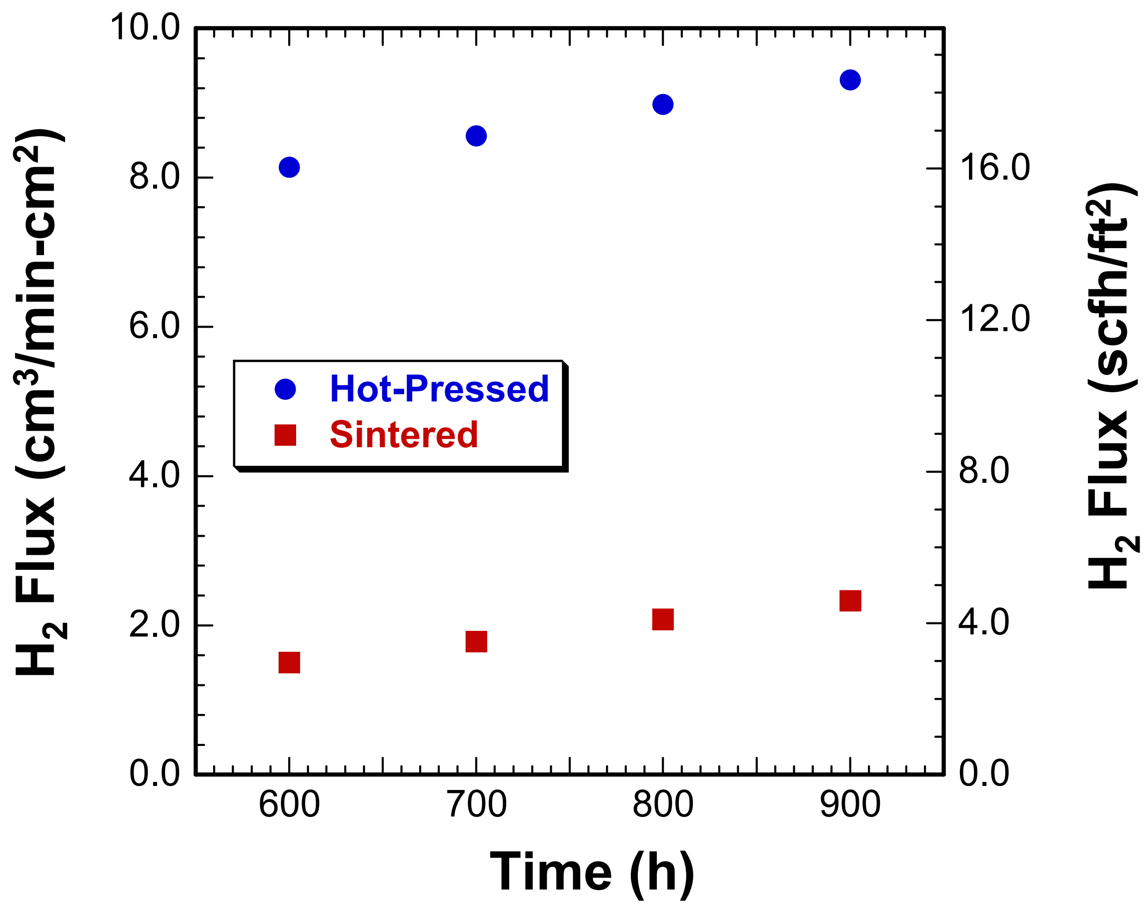


- **ANL-3 HTM appears to be stable in 400 ppm H_2S.**

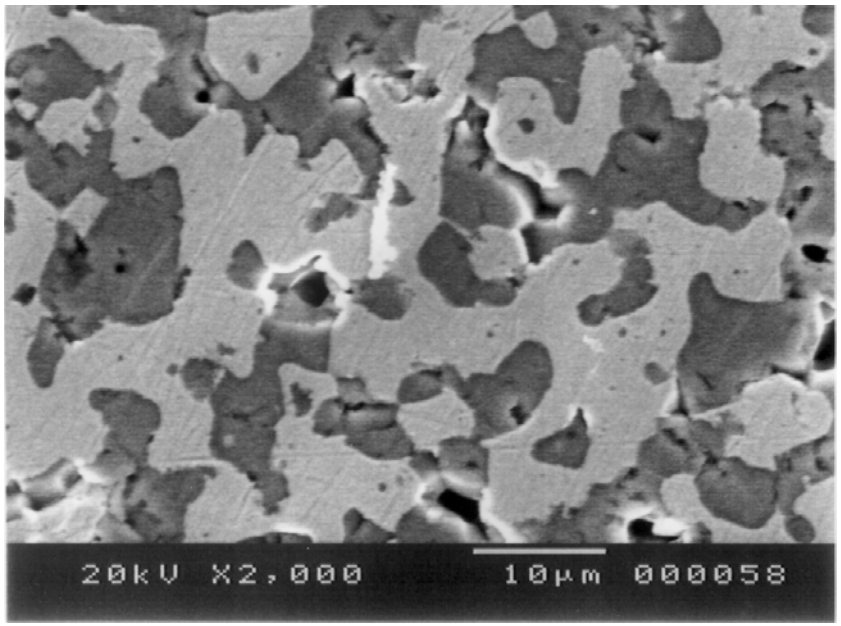
H_2 Flux Values of Conventionally Sintered and Hot-Pressed ANL-3a Membranes

- **Flux depends on microstructure.**
- **Hot-pressing gives higher flux.**

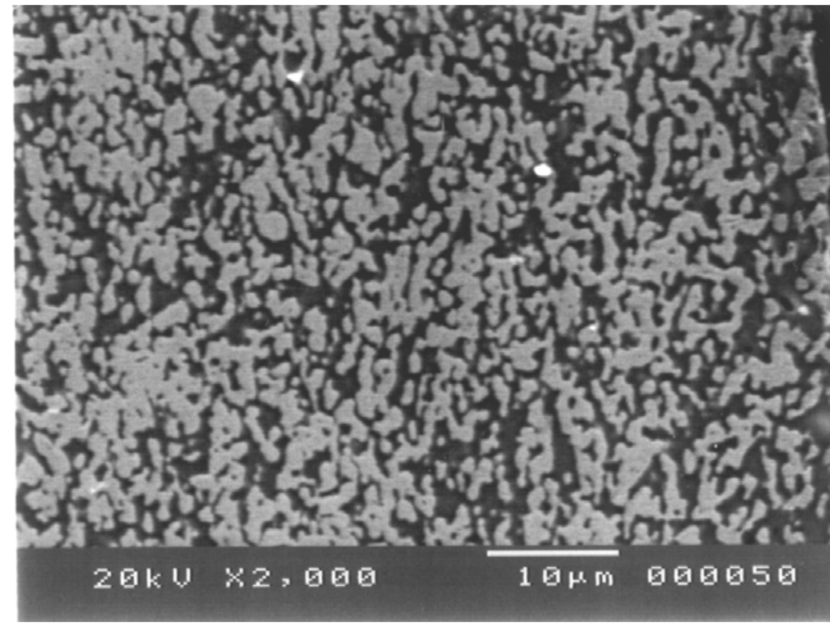
Feed Gas: 80% H_2/Balance N_2 at ambient pressure
Thickness ≈0.40 mm



Microstructures of Conventionally Sintered and Hot-Pressed ANL-3a Membranes



Conventionally Sintered
1500°C/10 h/air

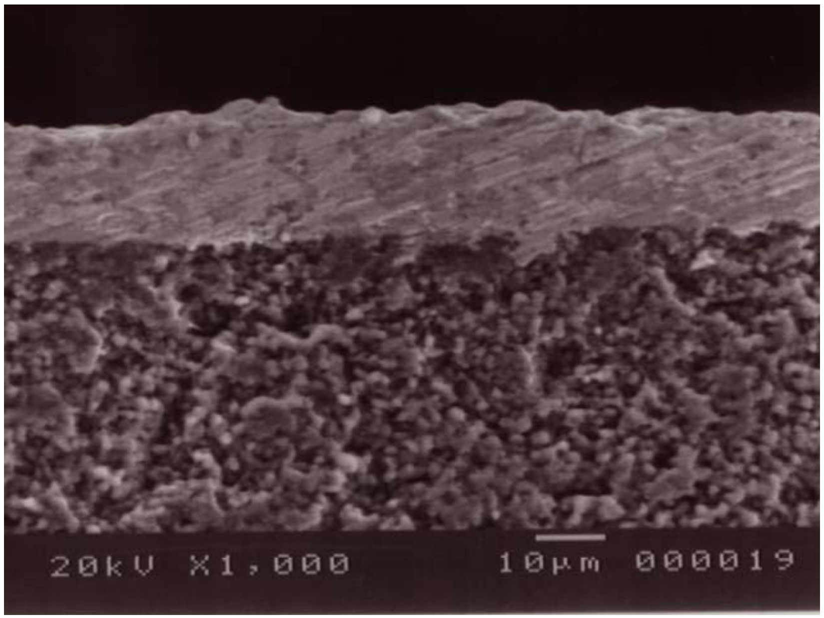


Hot-Pressed
1250°C/25 min/N_2

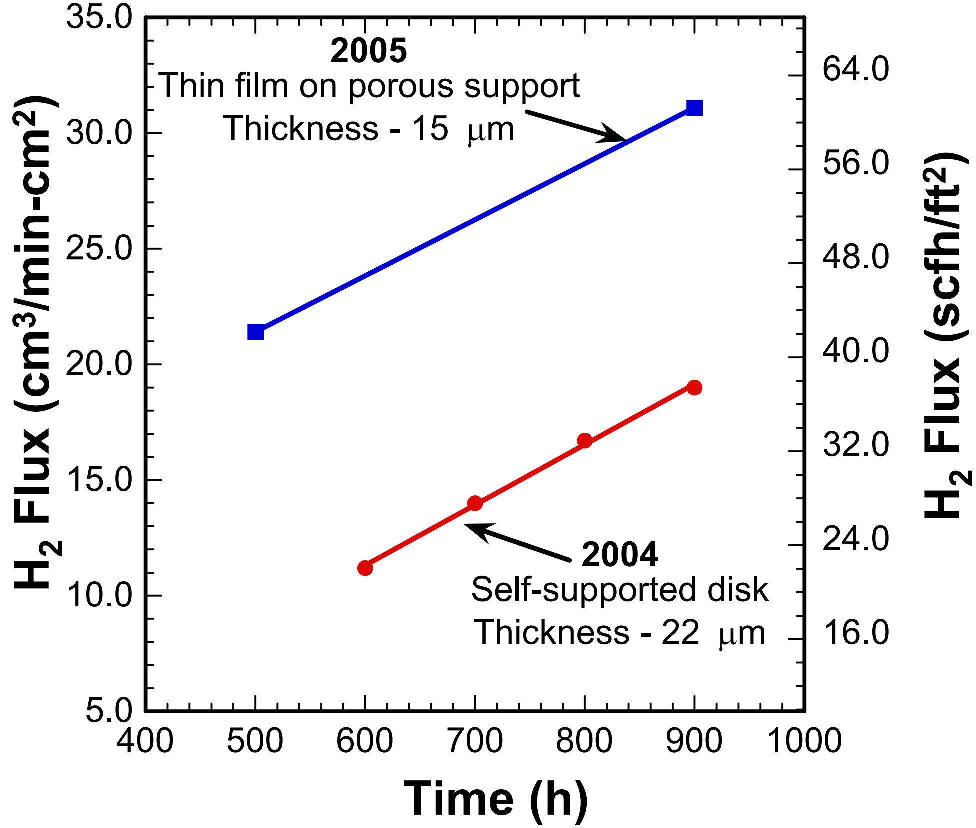
- **Hot-pressing gives much finer microstructure due to shorter processing time at lower temperature.**

Improvements in H_2 Flux (2004 vs. 2005)

ANL-3e Thin Film on Porous Support

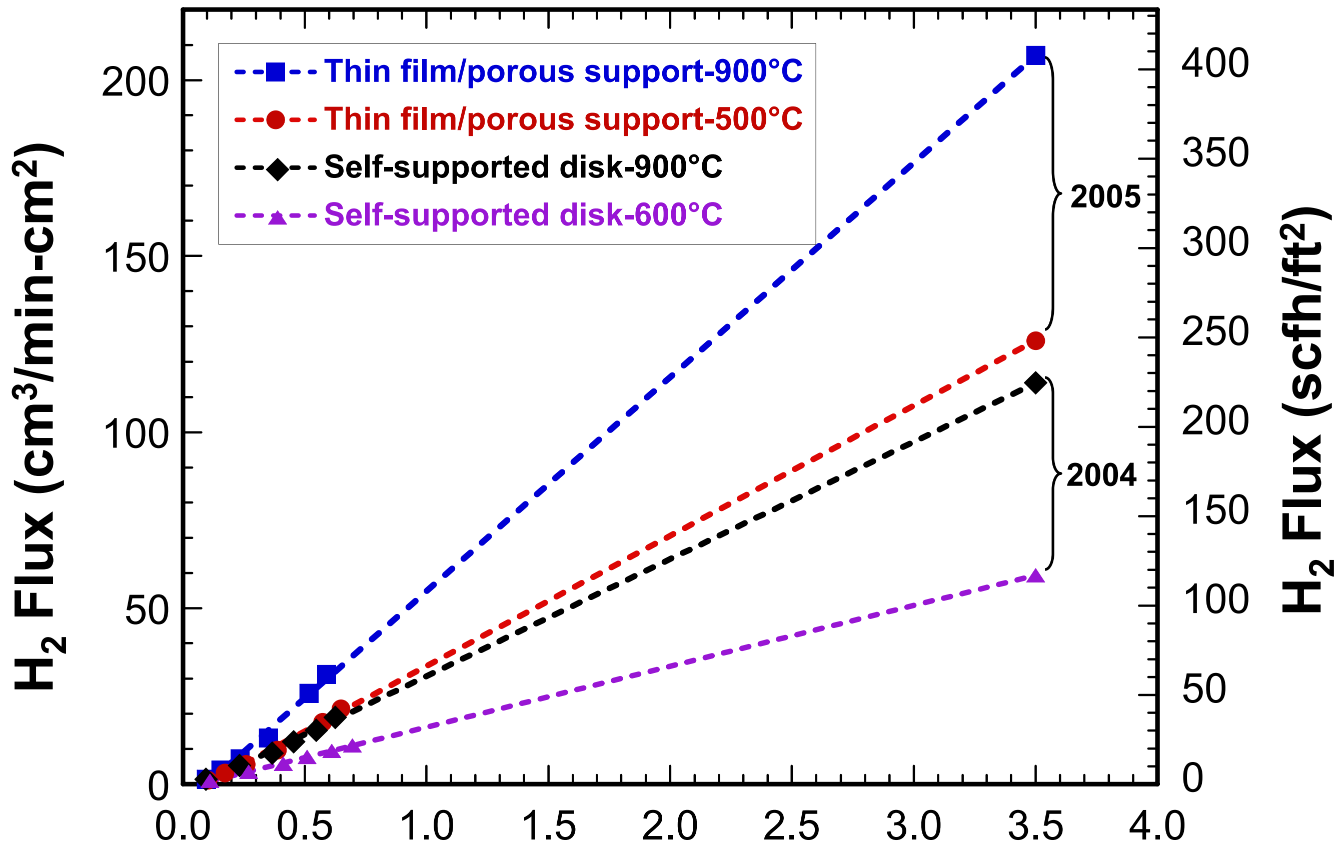


Feed: 100% H_2 at ambient pressure



- **Thin film HTM gives significantly higher flux.**

H_2 Flux (ANL-3e) vs. $\Delta pH_2^{1/2}$

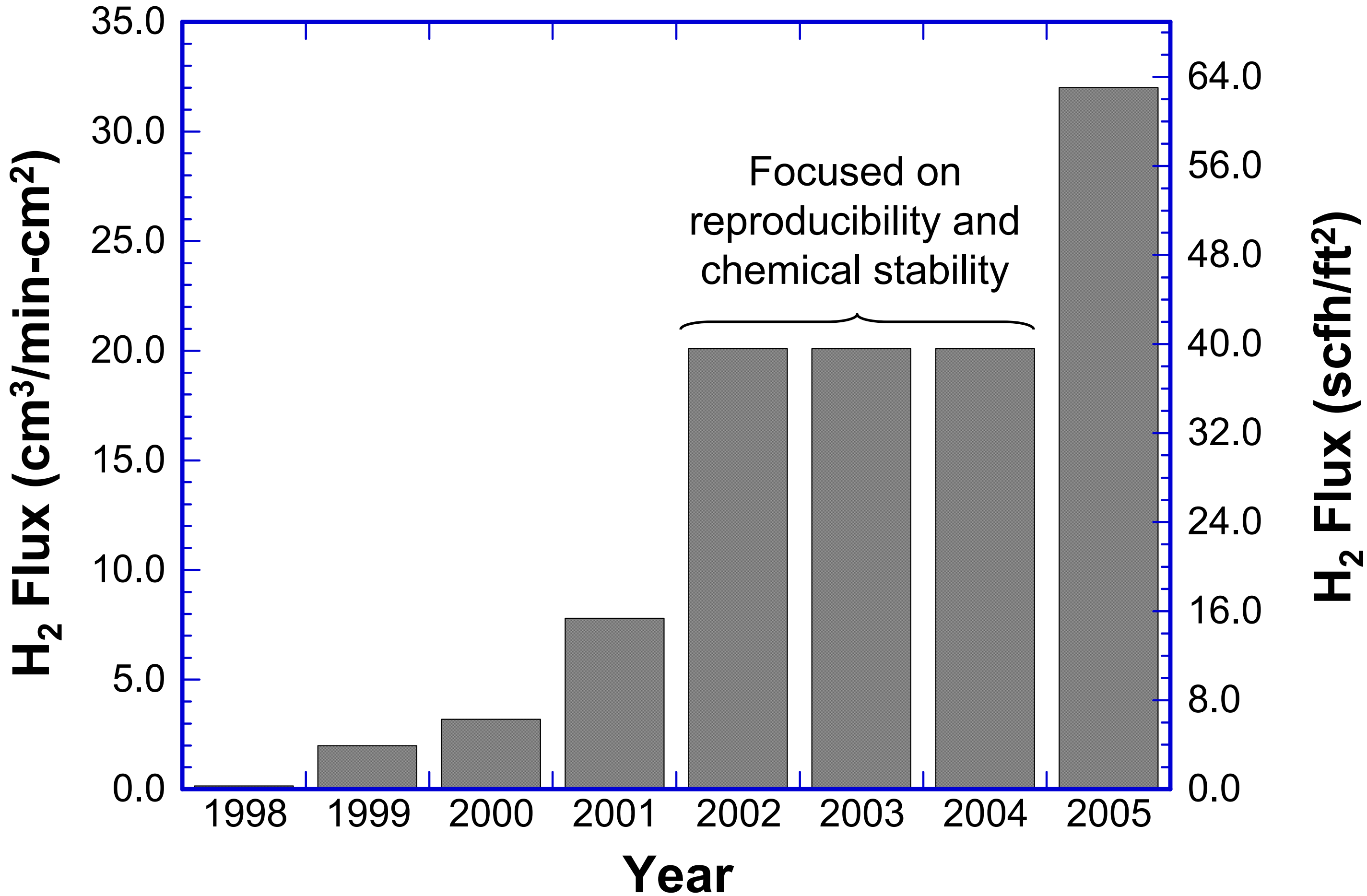


$$\Delta pH_2^{1/2} \equiv \sqrt{pH_2(\text{feed})} - \sqrt{pH_2(\text{sweep})}\ (\text{atm}^{1/2})$$

- **Flux >400 scfh/ft^2 can be achieved at feed pH_2 ≈300 psi.**

Progress in Membrane Development at ANL

Temperature: 900°C, Feed Gas: 100% H_2 at ambient pressure



- **HTM development has shown steady progress.**

FE Reviewers' Comments

- **FY 1999: Increase flux to >1 cm^3/min-cm^2 (2 scfh/ft^2).**
  - Increased flux of ANL-2a HTM to >2 cm^3/min-cm^2 (4 scfh/ft^2).
- **FY 2000-2001: Enhance performance of mixed conductors.**
  - Studied doping and surface modifications to increase flux.
  - Studied chemical stability in CO_2-containing atmospheres.
- **FY 2002: Increase flux to >10 cm^3/min-cm^2 (20 scfh/ft^2).**
  - Increased flux of ANL-3a HTM to ≈20 cm^3/min-cm^2 (40 scfh/ft^2) at 900°C.
- **FY 2003-2004: Study chemical stability of membrane.**
  - Studied effects of CO, CO_2, CH_4, and H_2S on HTM performance.
  - Showed ANL-3e is stable for >700 h in 400 ppm H_2S at 900°C.
- **FY 2005: Reduce operating temperature to 500°C.**
  - Increased flux of ANL-3e to ≈20 cm^3/min-cm^2 @ 500°C.

Future Work

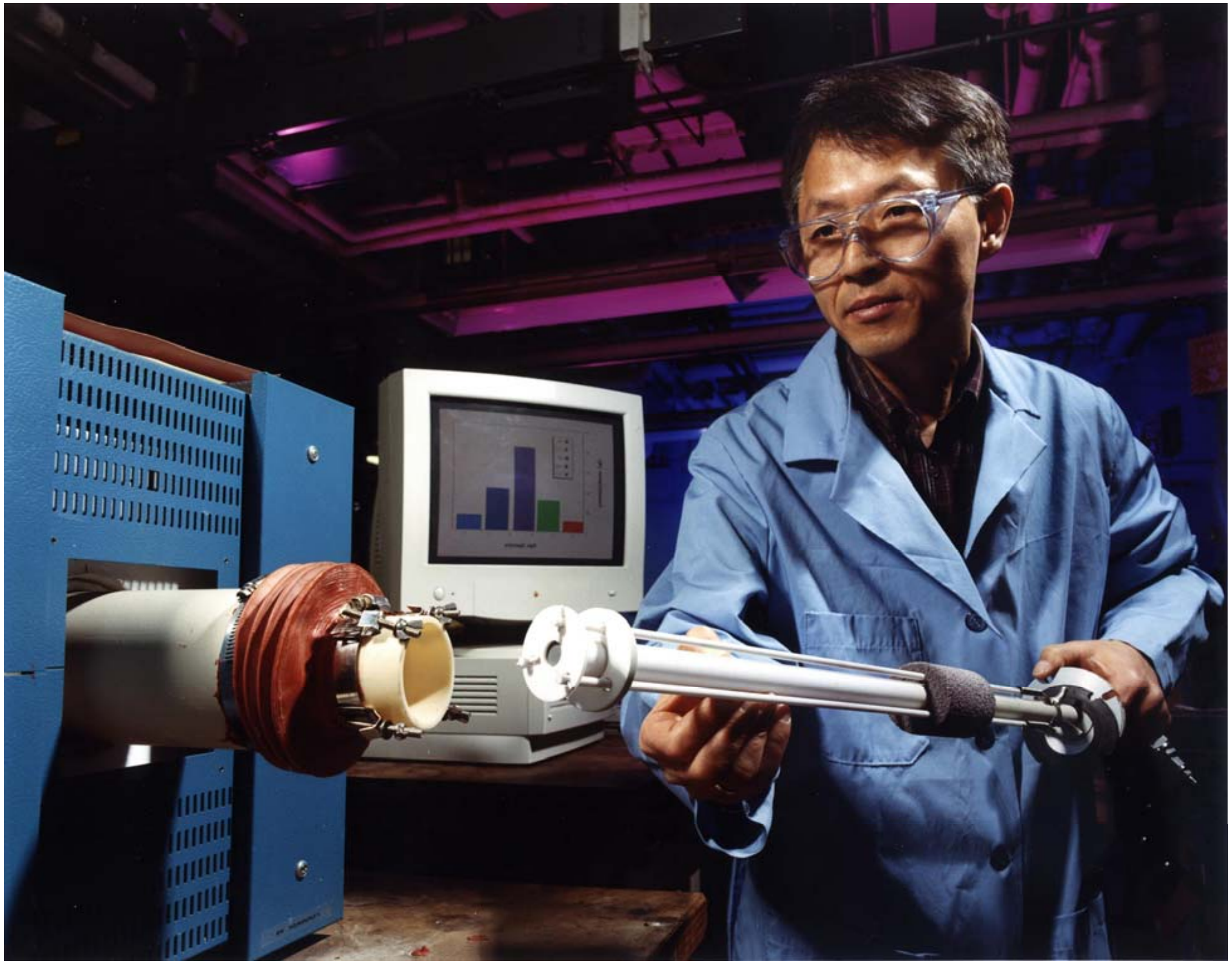
- Test long-term chemical stability of selected HTMs in atmospheres typical of coal gasifiers.
- Evaluate HTM microstucture before and after long-term tests in coal-gasifier-type atmospheres.
- Continue fabricating/testing thinner HTMs to maximize hydrogen flux.
- Evaluate HTM mechanical properties (fracture strength, creep) before and after exposure to hydrogen.
- Continue developing new HTMs to reduce cost, increase flux, and improve mechanical/chemical stability.
- Transfer membrane technology through industrial collaborations.

Summary

- Developed dual-phase dense membranes that nongalvanically separate hydrogen.
- Flux is proportional to the difference in the square-root of hydrogen partial pressure on two sides of membrane.
- Highest H_2 flux (≈66 scfh/ft^2 at 900°C and ≈42 scfh/ft^2 at 500°C) was measured on ≈15-μm-thick HTM using feed of 1 atm H_2.
- Flux >400 scfh/ft^2 can be achieved with hydrogen partial pressure ≈300 psi in feed gas.
- Short-term measurements showed stable flux in feed streams that contained CO, CO_2, CH_4, H_2O, and H_2S.
- Flux was stable for ≈700 h in feed stream with 400 ppm H_2S.

Supplemental Slides

R&D 100 Award in 2004



• Argonne's HTM was recognized as one of 2004's 100 "most significant technological developments."

Contributors

ANL

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NETL

Richard Killmeyer

Mike Ciocco

Hydrogen Safety - Hazards

- The most significant hydrogen hazard associated with this project is the potential for fire and/or explosion resulting from the release of hydrogen into the ambient atmosphere.
- Release of hydrogen from the reactor is the most serious hazard, because hydrogen in the reactor is at high temperature and/or pressure.
- Hydrogen flame can be especially hazardous to personnel in vicinity, because it is invisible.

Hydrogen Safety - Hazard Mitigation

- **The approach to deal with a potential release of hydrogen to the atmosphere is:**
  - Structural
    - *Sensors detect hazardous H_2 concentrations.*
    - *Vented gas cabinets shut down H_2 flow if H_2 concentration or H_2 flow exceeds safe levels.*
    - *Reactor has secondary containment purged by N_2.*
  - Procedural
    - *Establish standard operating procedures.*
    - *Perform safety review of equipment/procedures.*
    - *Permit work only by authorized personnel.*