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Development of Dense Ceramic Membranes for Hydrogen Separation*

***U. (Balu) Balachandran*, T. H. Lee, C. Y. Park, J. J. Picciolo, J. E. Emerson, and S. E. Dorris**

DOE/NETL Project Manager: Richard Dunst
DOE/NETL Technology Manager: Dan Cicero

Project Start Date: FY 98
Project End Date: Project duration and direction determined annually by DOE-FE/NETL

Total project costs:
-DOE share 100%
Funding for FY 07: $750K
Funding for FY 08: $400K
FWP 49601

***Work supported by DOE, FE-NETL, Hydrogen & Syngas Program.**

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Project Objectives

Develop dense ceramic & cermet membranes for separating hydrogen from product streams generated during coal gasification (coal-to-hydrogen production process) conditions. 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, NH_3, Hg, halides, etc.

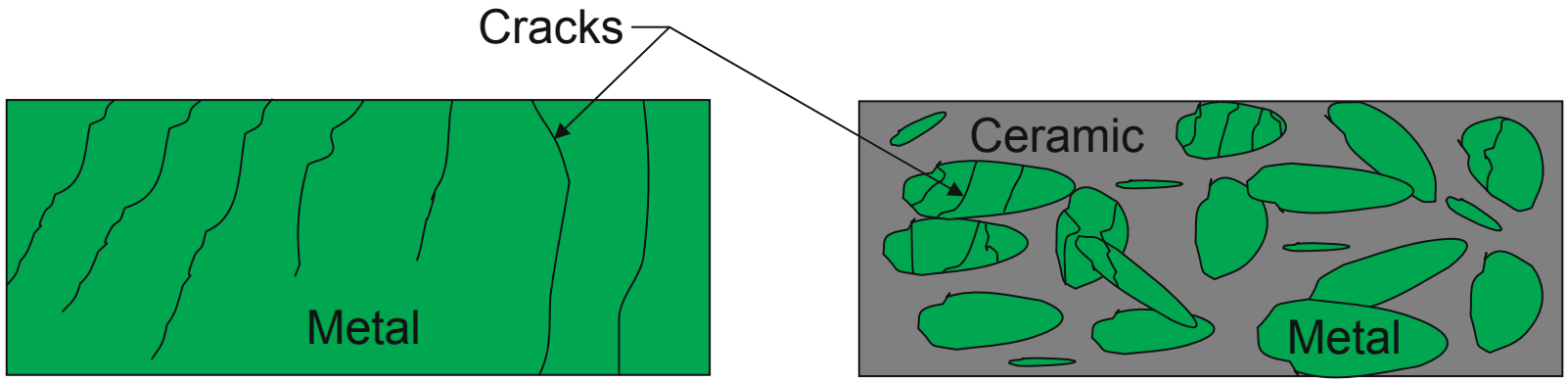
Types of Membranes:

- *Metallic membranes (Pd, Pd alloys, Group IV – V elements, etc.)*
- *Porous membranes (micro-, nano-porous materials)*
- *Polymeric membranes (low-temperature organic materials)*
- *Dense ceramic membranes (mixed-conductors)*
- *Dense ceramic/metal composite (cermet) membranes*

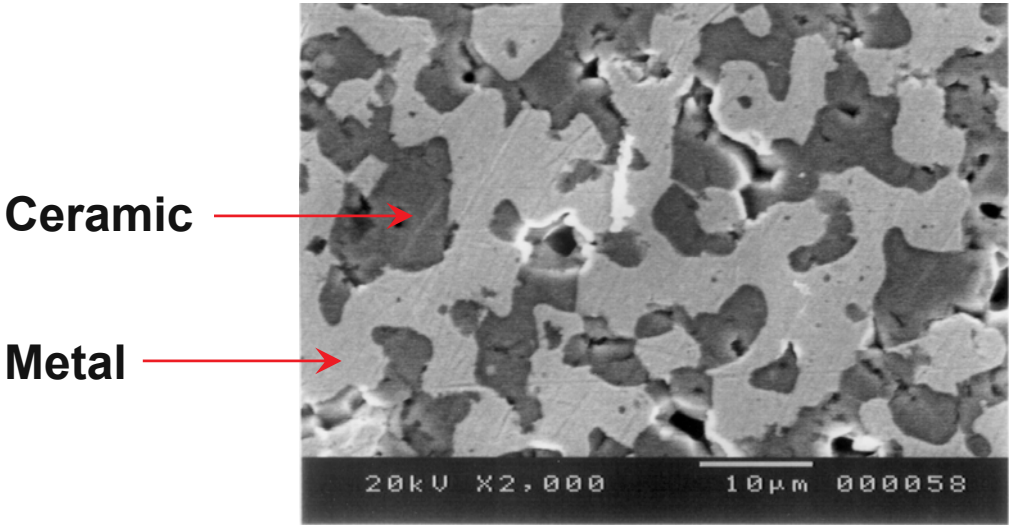
Advantages of Argonne's Cermet Membrane

- Major concern for metallic membrane (free standing or supported)
  - Dissolved hydrogen tends to cause lattice expansion in metals leading to rupture
  - Cracking will cause total failure/loss of mechanical integrity of metallic membrane
- Argonne's membrane is a ceramic/metal homogeneously mixed composite (cermet)
  - Ceramic phase provides three-dimensional mechanical support that can blunt/deflect crack propagation
  - Argonne membranes have been tested at high pressures & temperature conditions

Cermet vs. Metallic Membranes

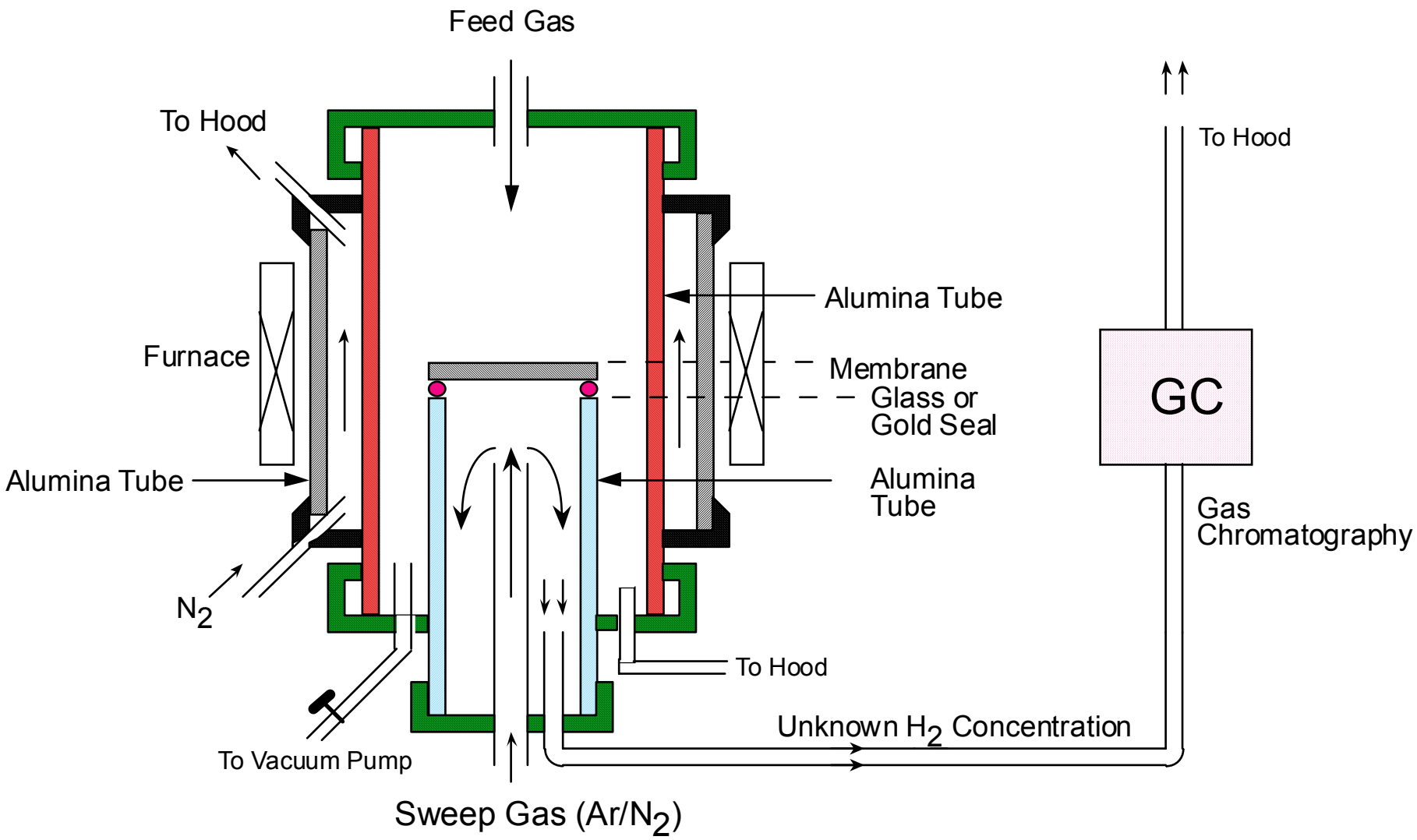


Metallic Membrane **Cermet Membrane**



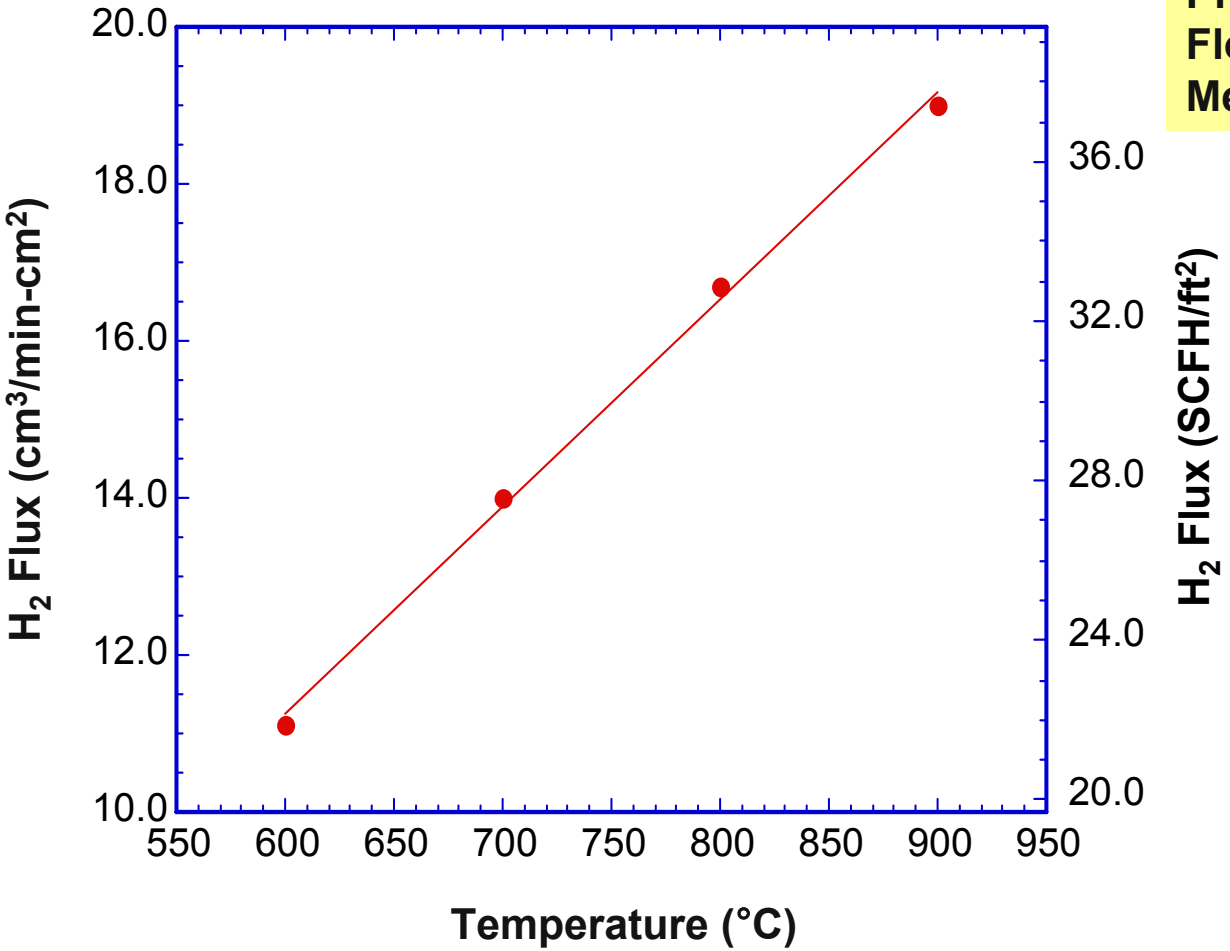
Cermet Microstructure

Schematic of Experimental Setup



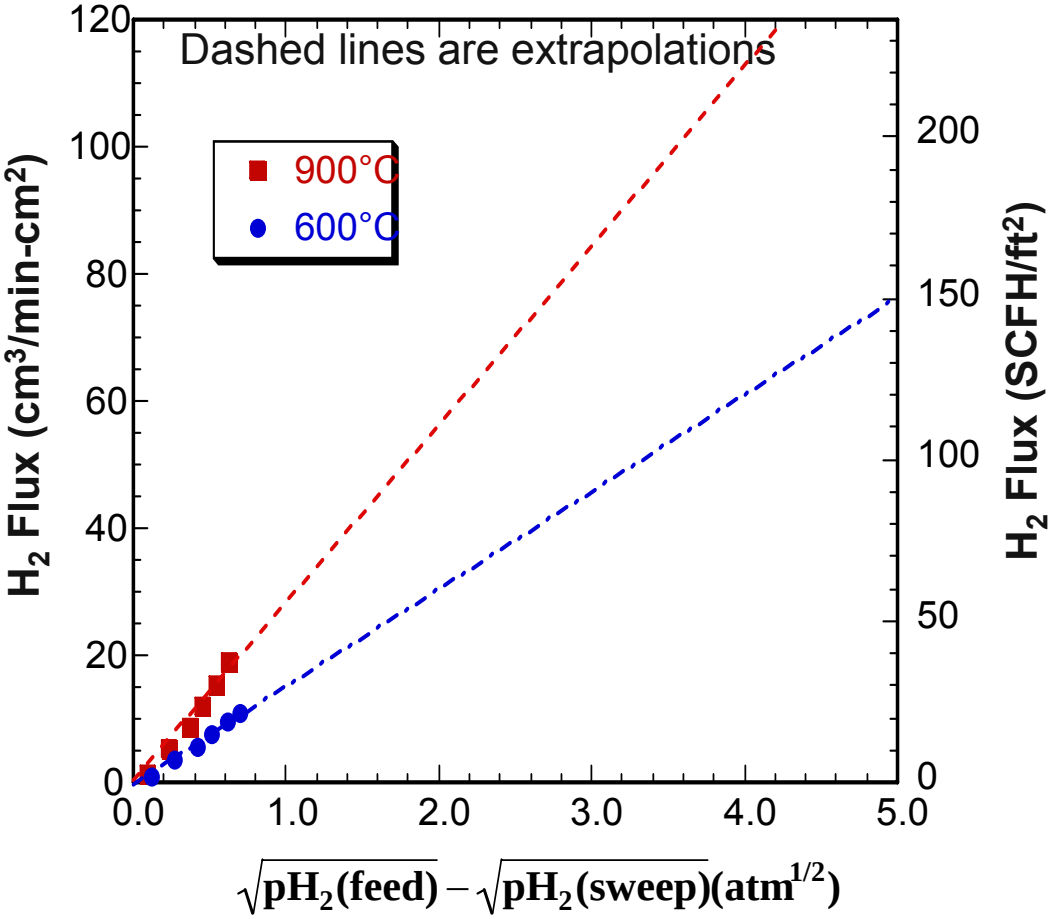
H_2 Permeation Rate vs. Temperature YSZ/Pd Cermet Membrane

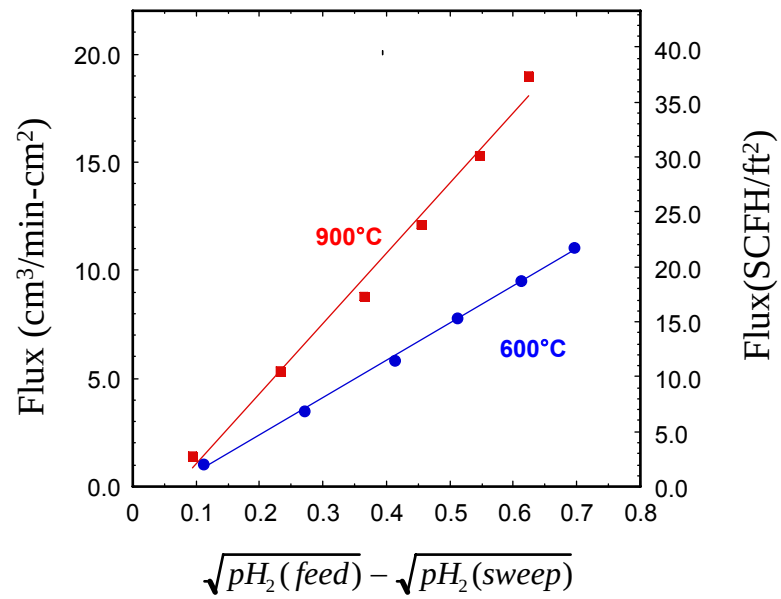
Feed: 90% H_2/Bal. He, **Sweep:** N_2
Pressure: Ambient, $\Delta P \approx 0$ psi
Flow rates: 150-200 cc/min
Membrane Thickness ≈ 22 μm



Dependence of H_2 Flux on pH_2(feed) and pH_2(sweep) for Self-Supported Cermet Membrane

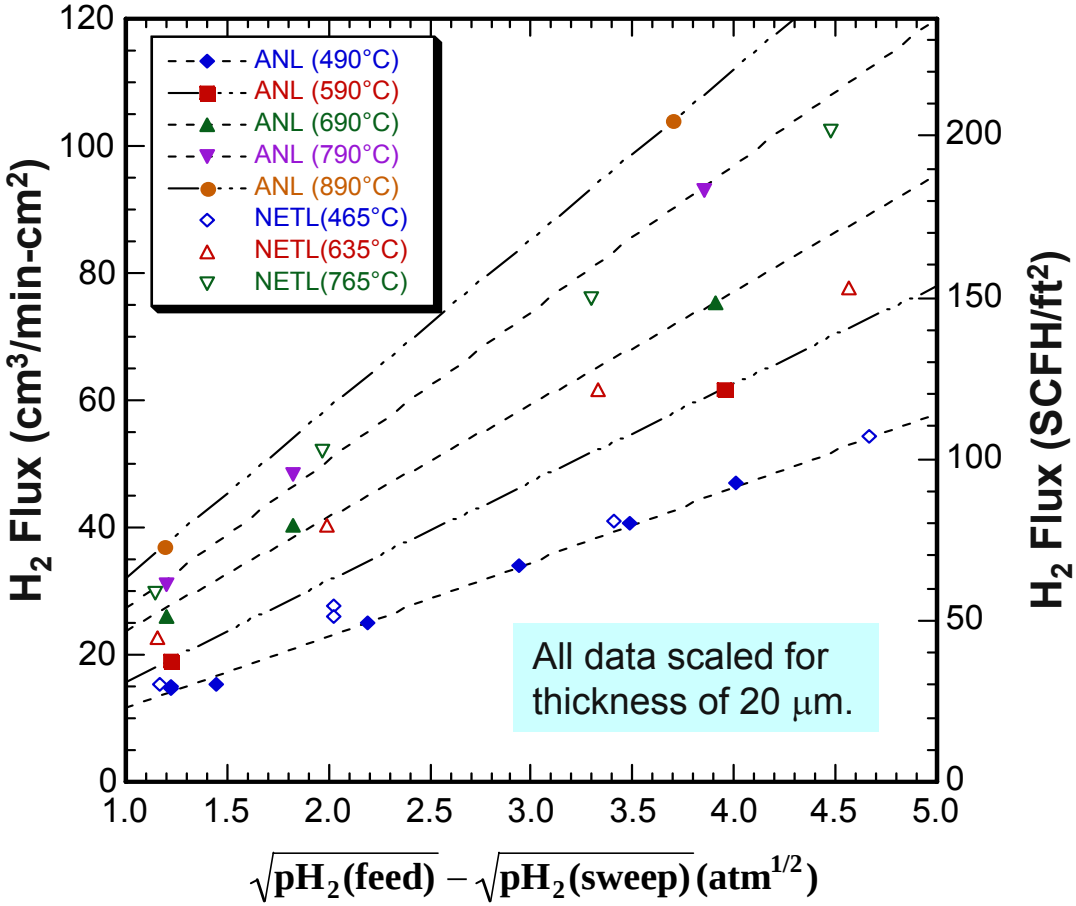
Feed: 4-90% H_2/Bal. He, **Sweep:** N_2
Pressure: Ambient, $\Delta P \approx 0$ psi
Flow rates: ≈200 cc/min
Membrane: YSZ-Pd Cermet
Thickness: ≈ 20 μm





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

H_2 Flux of Cermet Membranes at High Feed Gas Pressures (Measured at Argonne and NETL)



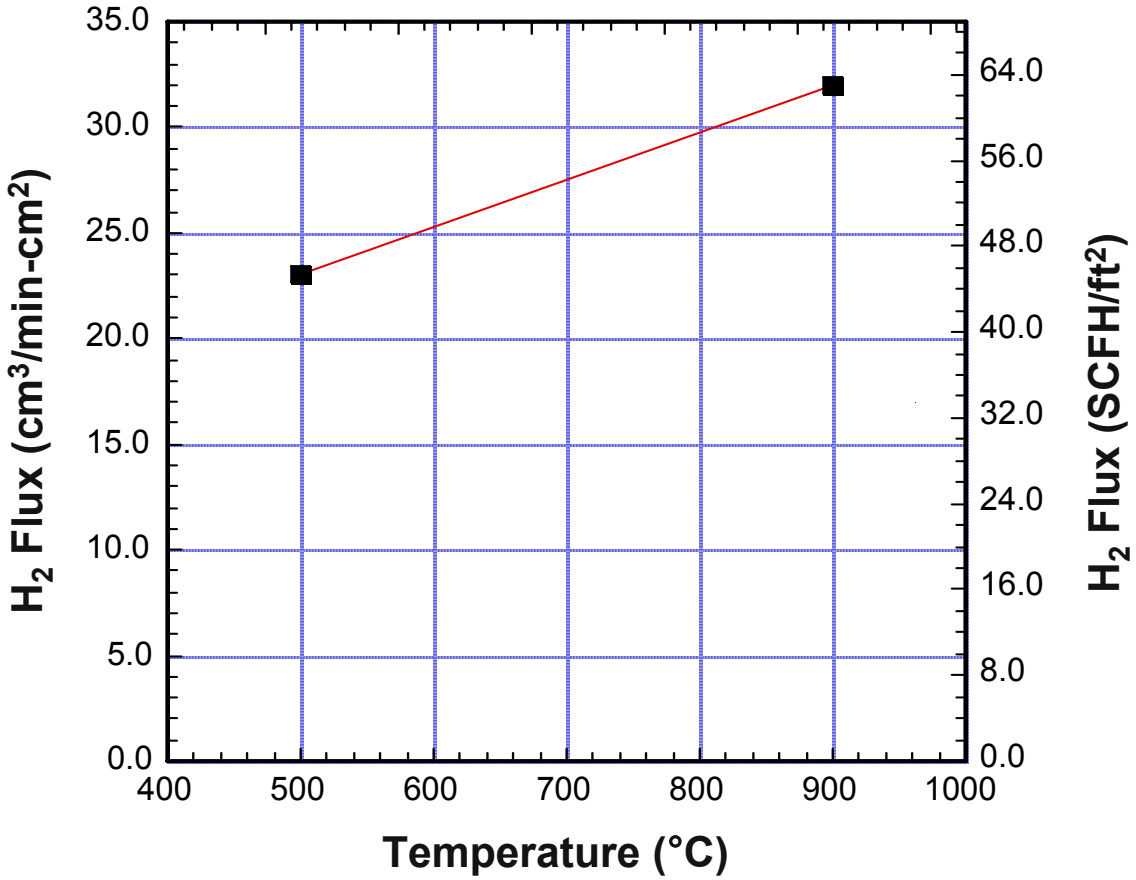
Argonne:
Feed: 90% H_2/Bal. He, **Sweep:** N_2
Pressure: 20-300 psig, $\Delta P<5$ psi
Flow rates: 200 cc/min
Membrane Thickness: ≈0.8 mm

NETL:
Feed: 90% H_2/Bal. He, **Sweep:** Ar
Pressure: 20-400 psig, $\Delta P<20$ psi
Flow rates: ≈100 cc/min
Membrane Thickness: ≈0.8 mm

- **Extrapolated values fall in line with values measured at high pressures at both Argonne and NETL.**

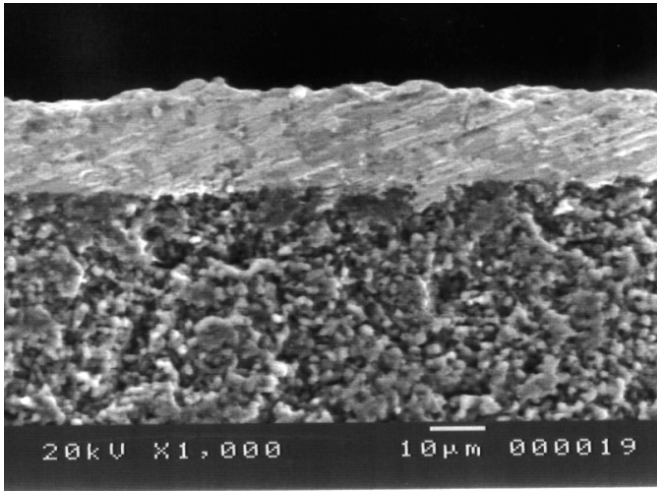
Measurements at NETL were made by M. Ciocco and R. Killmeyer

H_2 Flux through Thin Film Cermet Membrane on Porous Al_2O_3 Substrate

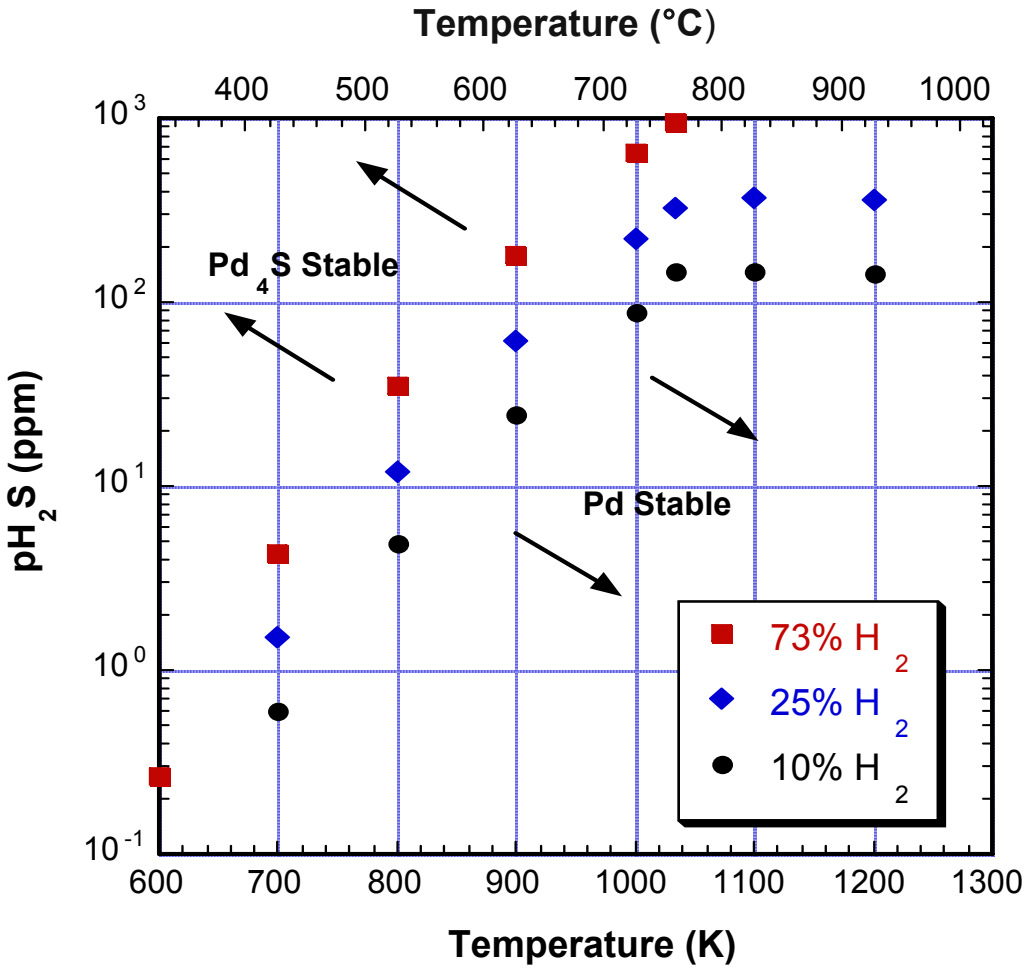


Feed: 100% H_2, **Sweep:** N_2
Pressure: Ambient
Flow rates: 150 cc/min
Membrane: YSZ-Pd Cermet
Thickness: ≈15 μm

SEM of dense cermet on porous support

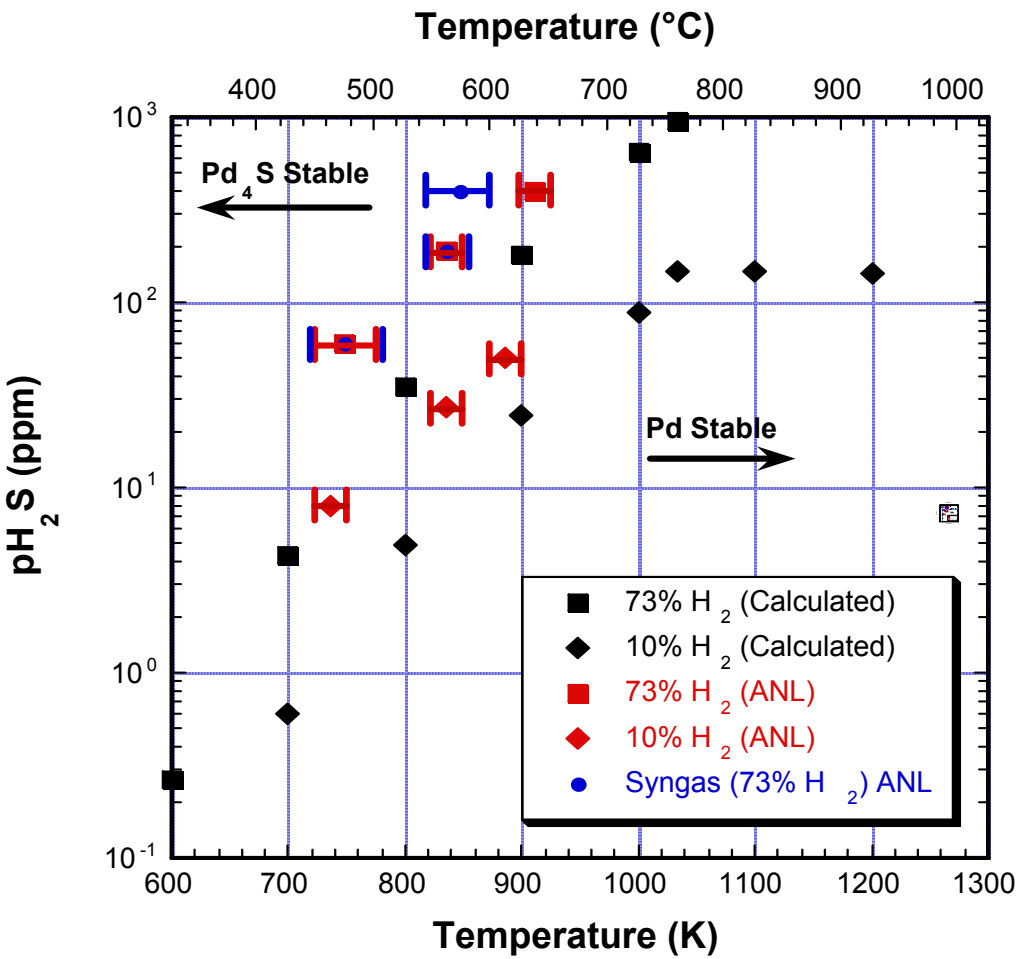


Pd/Pd_4S phase boundary calculated for various H_2 concentrations using data from literature



J. R. Taylor, Met. Trans., 16B, 143, 1985; O. Knacke, et al., Thermochemical Properties of Inorganic Substances I, Springer-Verlag, Berlin, 1991.

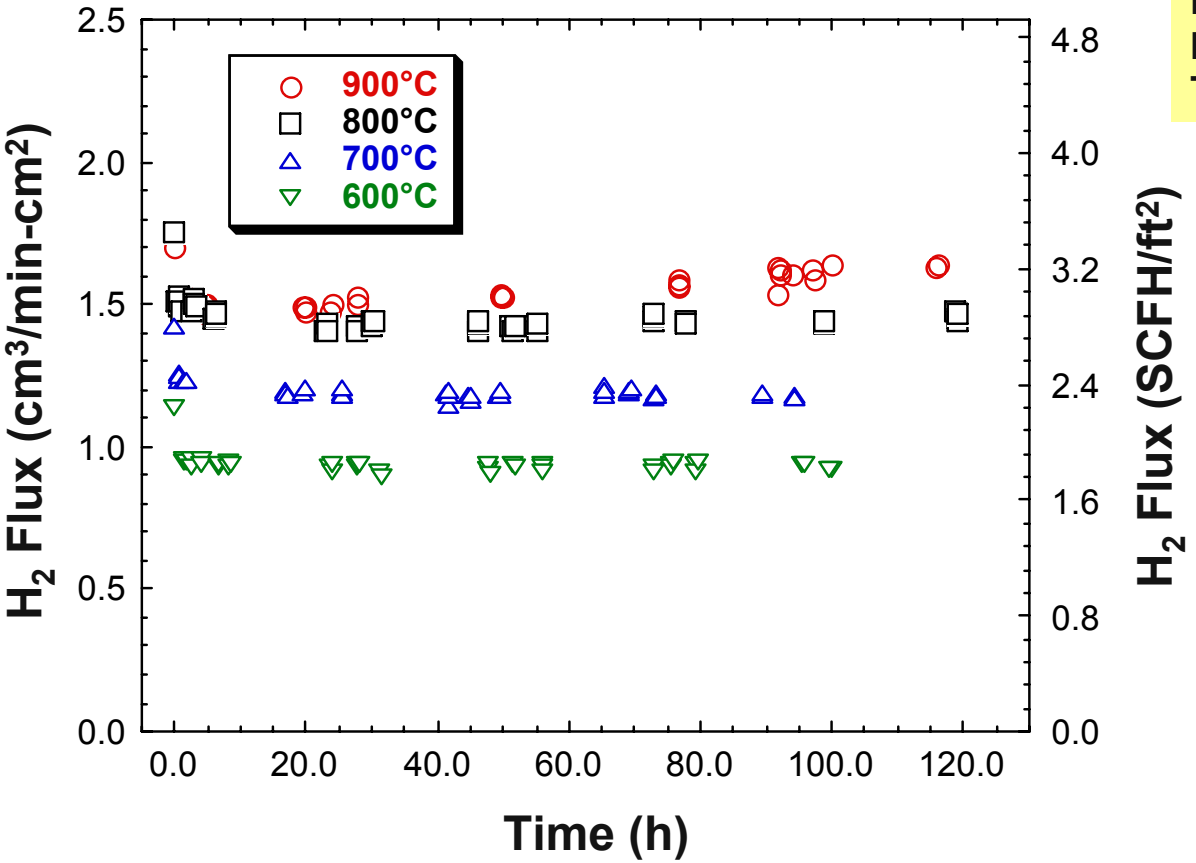
Pd/Pd_4S Phase Boundary for Cermet Membrane Determined at Argonne



Colored bars show results obtained at Argonne by equilibrating samples at various temperatures with feed gas of: (Red) 73% H_2 with 400, 190, or 60 ppm H_2S or 10% H_2 with 50, 27, or 8 ppm H_2S; (Blue) 73% H_2, 0.5% CH_4, 6.2% CO_2, 7.8% CO, with 400, 190, or 60 ppm H_2S. All gases at ambient pressure.

Chemical Stability of Argonne's Cermet Membrane

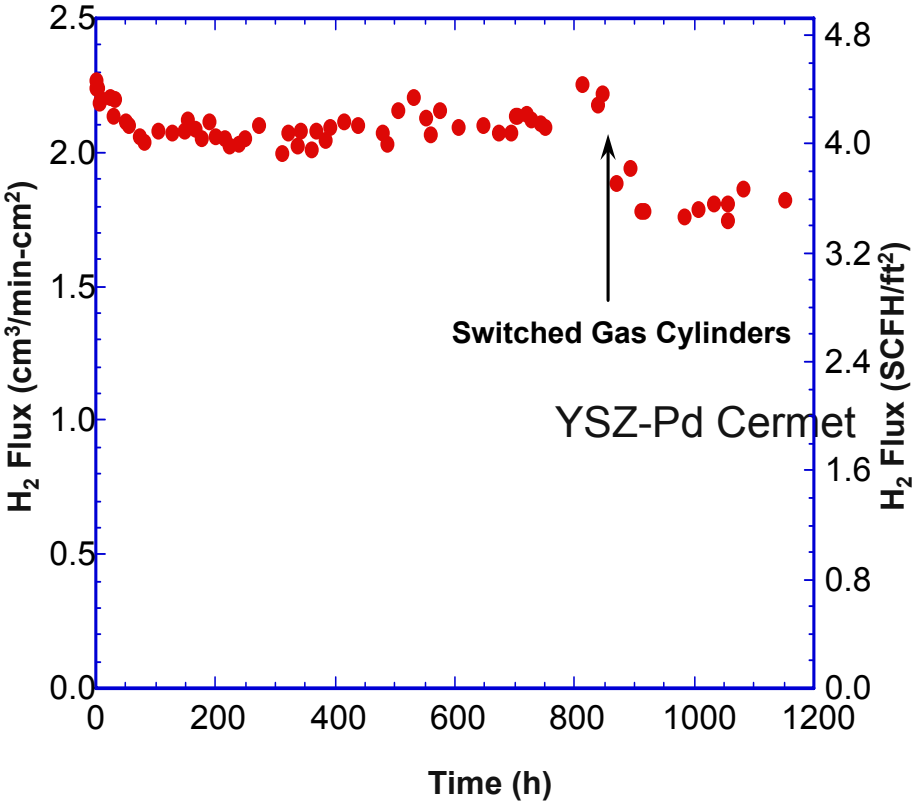
Feed: 20% H_2, 51 ppm H_2S, Bal. He
Sweep: N_2
Pressure: Ambient
Flow rates: 150 cc/min
Membrane: YSZ-Pd Cermet
Thickness: ≈0.10 mm



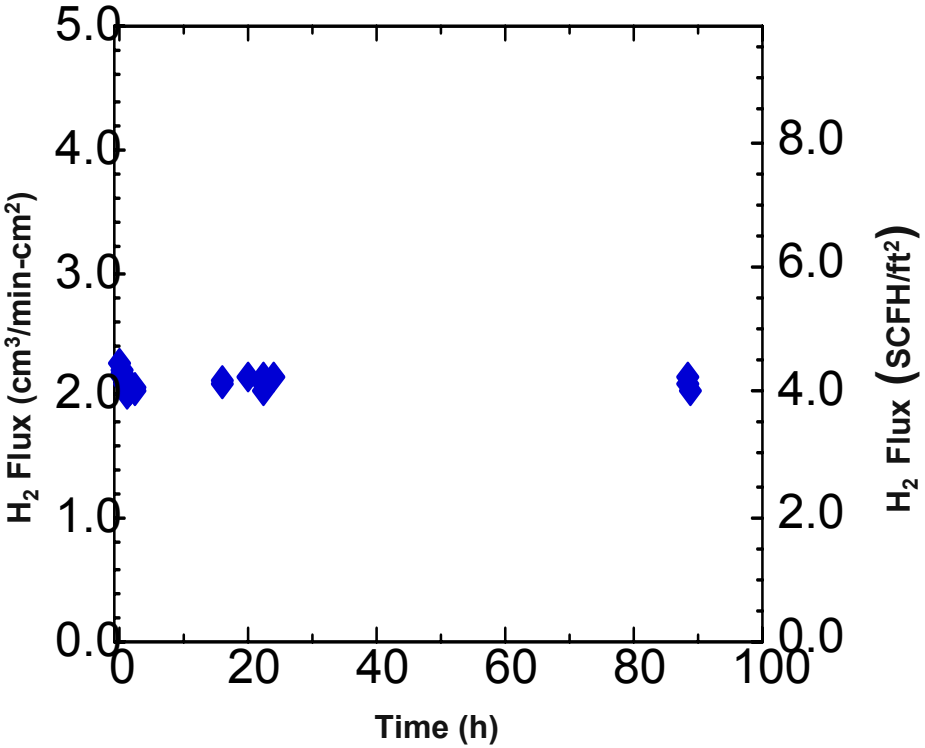
- **HTM appears stable at low temperatures in ≈50 ppm H_2S (20% H_2).**

Chemical Stability of Argonne's Cermet Membrane

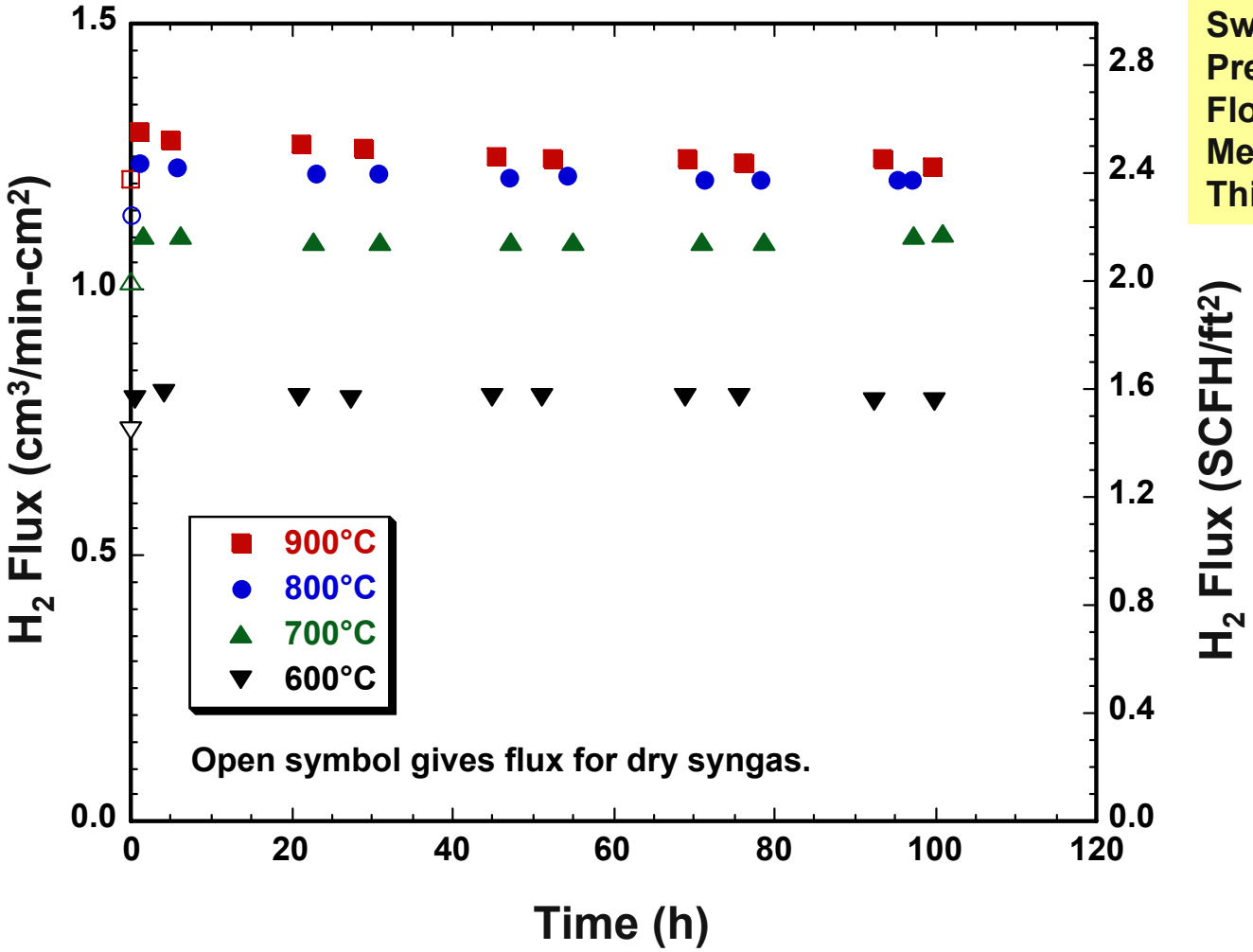
Feed: 73% H_2, 400 ppm H_2S, Bal. He
Sweep: N_2
Pressure: Ambient
Flow rates: 150 cc/min
Temperature: 900°C
Thickness: ≈0.20 mm
Membrane: YSZ-Pd Cermet



Feed: 61.3% H_2, 8.2% CH_4, 11.5% CO, 9.0% CO_2, 10% He, 100 ppm H_2S
Sweep: N_2
Pressure: Ambient
Flow rates: 150 cc/min
Temperature: 900°C
Thickness: ≈0.20 mm
Membrane: YSZ-Pd Cermet

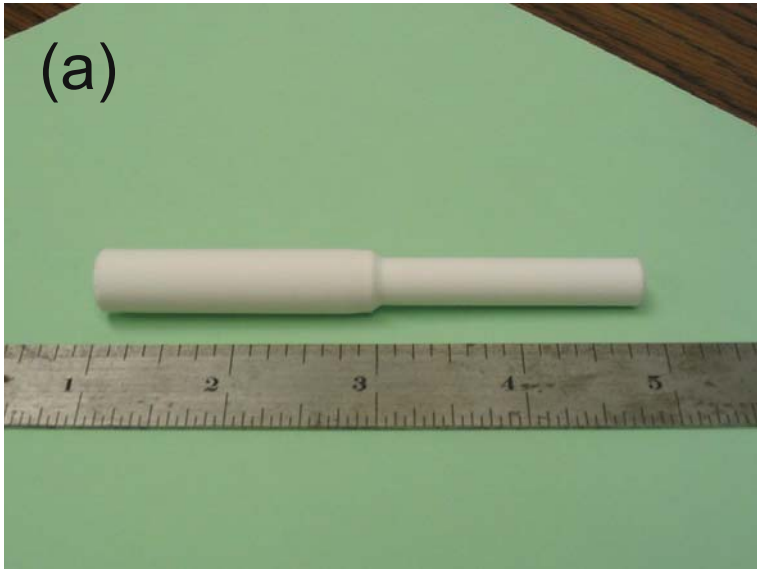


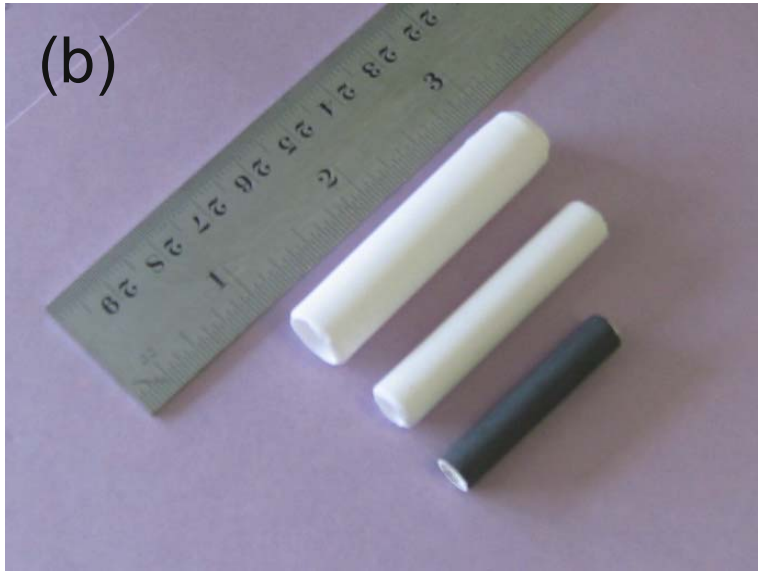
Stability of Cermet Membrane in Steam-Containing Mixed Gas Stream



Feed: 53% H_2, 1% CH_4, 10% CO, 8% CO_2, 21% H_2O, Bal. He
Sweep: N_2
Pressure: Ambient
Flow rates: 150 cc/min
Membrane: YSZ-Pd Cermet
Thickness: ≈0.27 mm

Tubular HTM Membranes





a) Porous alumina support tube pre-sintered for 5 h at 700°C in air.
b) Pre-sintered porous alumina support tubes coated with cermet HTM and then sintered for 5 h at 1400°C in air.

H_2 permeation of small tubes (Length ≈8 cm; Diameter ≈0.9 cm OD; Surface Area ≈24 cm^2) exceeded 150 cc/min (0.32 SCFH) in the temperature range 600-900°C at ambient pressure.

Fracture Toughness of HTM Membrane (YSZ/Pd Cermet)

Temperature [°C]	K^*_{IC} [MPa(m)$^{-1/2}$]
20	7.79
25	7.98
600	6.58
900	5.22
1000	5.24
1100	4.64
1200	4.72
Al_2O_3 tubes	2.50

Measured by K. Salama & G. Majkic at University of Houston

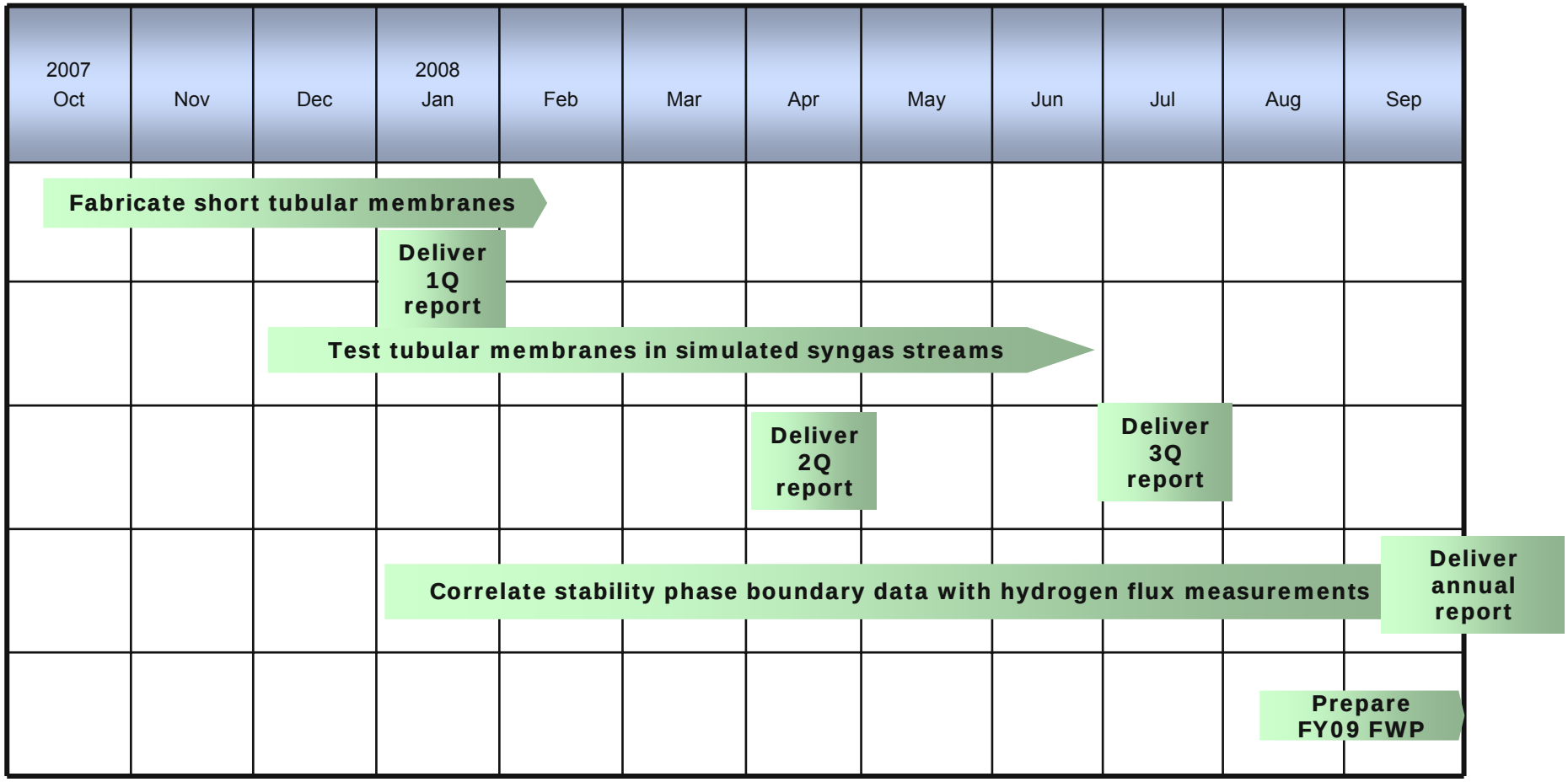
Issues/Technical Challenges

- Effect of particulates impacting the membrane surface
- Effect of trace contaminants such as NH_3, Hg, halides, etc. in coal-gas streams
- Steam corrosion
- Compatibility of membranes with shift catalyst at reaction temperatures
- Leak-proof metal/ceramic seals to withstand high-pressures and thermal cycling
- Long-term stability and failure limits of materials under “real-world” operating conditions.

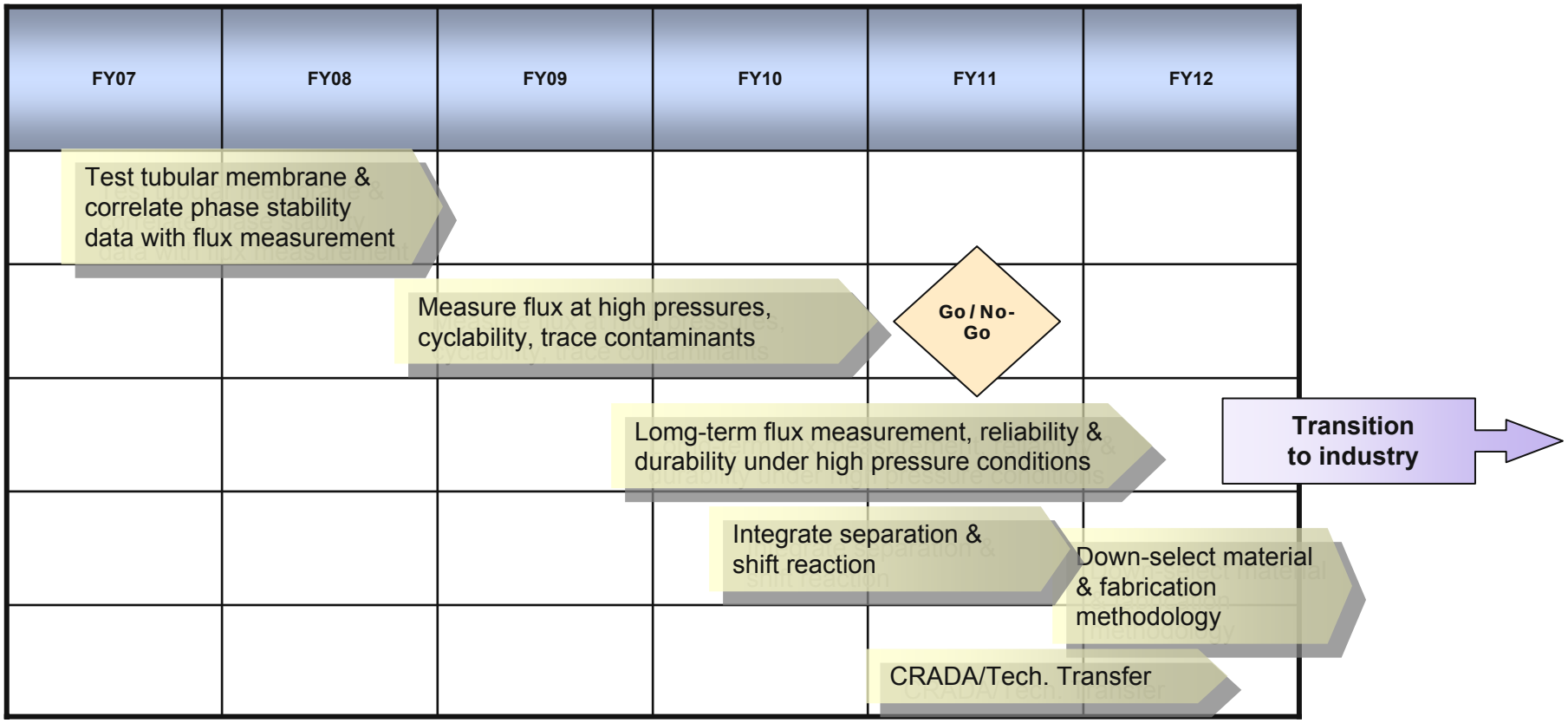
Future Work

- Boundary layer transport appears to be limiting the hydrogen flux, at least under conditions where hydrogen concentration in the feed gas is low. Fabricate & test tubular membranes at high flow rates and changing flow directions to overcome the external transport phenomena that is rate-limiting.
- Test thermal & feed gas concentration cyclability of membranes.
- Study the effects of trace contaminants such as NH_3, Hg, halides, etc.
- Measure flux at high pressures using simulated syngas streams.
- Perform experiments integrating H_2 separation & shift reaction.
- Make long-term flux measurements & demonstrate reliability and durability of membranes under high pressure conditions.
- Down-select material and fabrication methodology for practical applications.

Project Schedule: Timeline for FY 08



Project Schedule



Summary of Technical Accomplishments

- Developed dense cermet membranes that nongalvanically separate hydrogen from mixed-gas streams (gasification/reforming).
- Highest H_2 flux (≈64 scfh/ft^2 at 900°C and ≈46 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 (>200 cc/min/cm^2) can be achieved with hydrogen pressure at ≈350 psi in feed gas. Measurements made at high pressures both at Argonne & NETL support this conclusion.
- Hydrogen permeation exceeding 150 cc/min (0.32 scfh) were measured in short (≈8 cm long) tubular membranes at 600°C (at ambient pressure feed).
- Cermet membranes were stable in the range 600-900°C in simulated syngas mixtures containing ≈20% steam.
- Flux was stable for ≈1200 h in feed stream with 400 ppm H_2S at 900°C.
- Regeneration of sulfur-poisoned cermet membrane was observed.
- High temperature mechanical properties were measured.

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Coal-Assisted H_2 Production via Water Dissociation using Ceramic Membranes*

***U. (Balu) Balachandran*, T. H. Lee, C. Y. Park, J. J. Picciolo, J. E. Emerson, and S. E. Dorris**

DOE/NETL Project Manager: Richard Dunst
DOE/NETL Technology Manager: Dan Cicero

Project Start Date: FY 03
Project End Date: Project duration and direction determined annually by DOE-FE/NETL

Total project costs:
-DOE share 100%
Funding for FY 07: $400K
Funding for FY 08: $400K
FWP# 49347

***Work supported by DOE, FE-NETL, Hydrogen & Syngas Program.**

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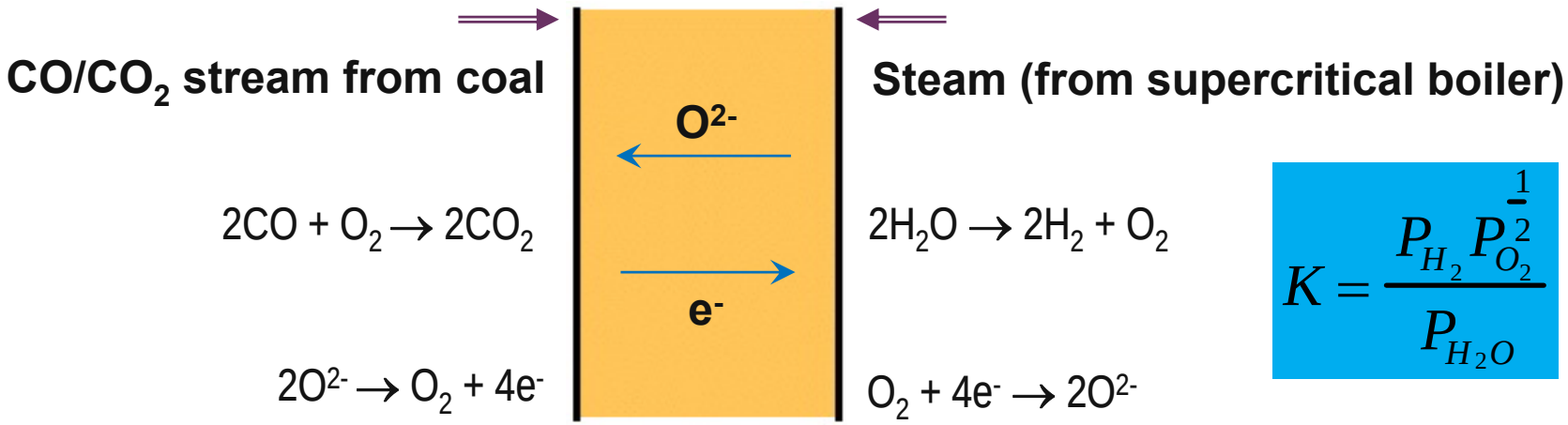
Project Objectives

Develop oxygen transport membrane that will utilize off-gases from coal plants to generate hydrogen by water (steam) splitting. This approach would increase the efficiency of coal plants, simplify the capture of greenhouse gases, and provide versatility to co-produce hydrogen and electricity. Membranes must combine several structural and functional properties:

- high permeability and species selectivity
- sufficient mechanical, chemical, and thermal stability under applied operating conditions
- low foul rate
- long & reliable operation
- cost effective production

Schematic of Coal-Assisted H_2 Production via Steam Splitting using Dense Oxygen Transport Membranes



$$K = \frac{P_{H_2} P_{O_2}^{\frac{1}{2}}}{P_{H_2O}}$$

- No electrical circuitry or power supply
- Non-galvanic

$C + CO_2 + \text{heat} \rightarrow 2CO$ (reverse Boudouard)

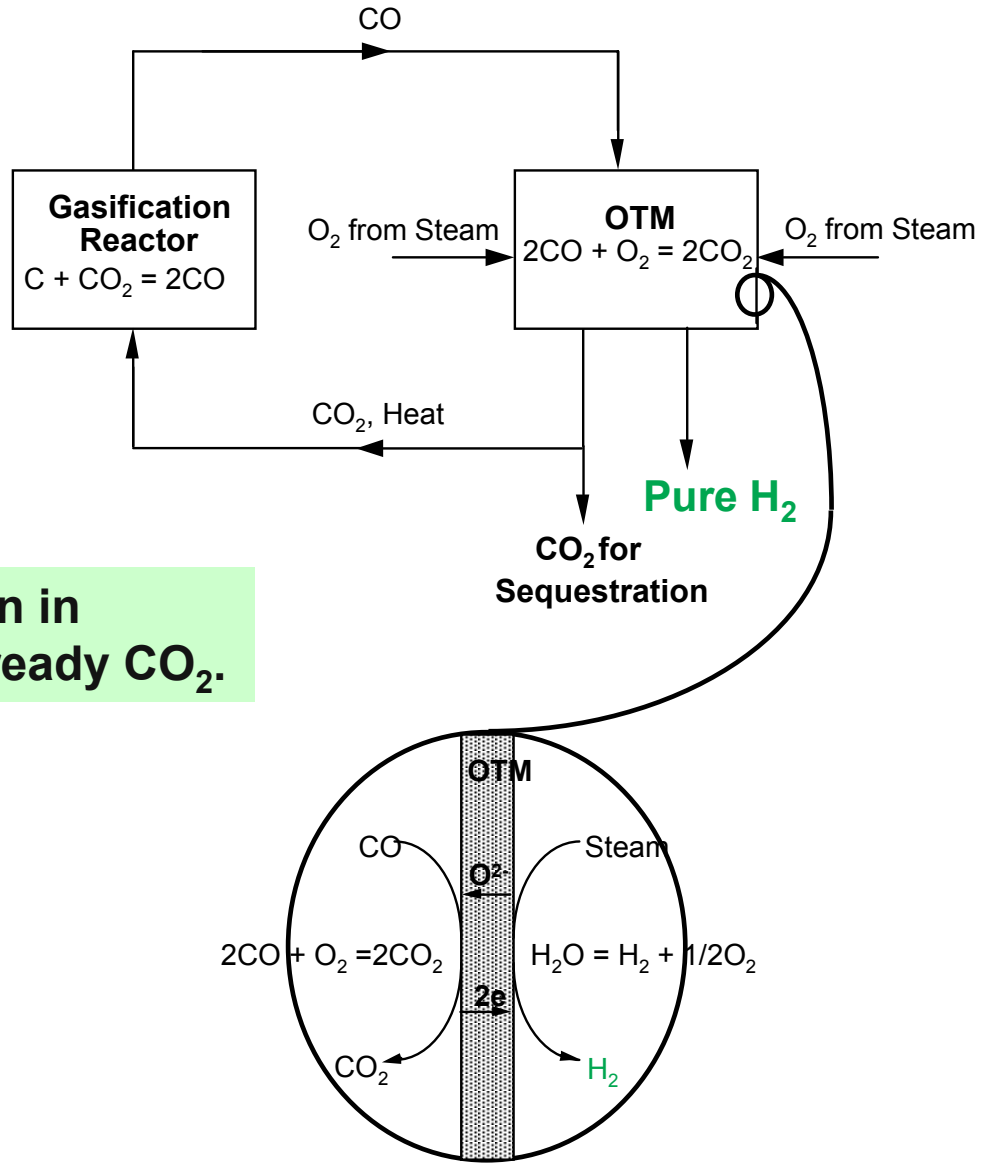
$2CO + O_2 \rightarrow 2CO_2 + \text{heat}$ (in OTM reactor)

$C + O_2 \rightarrow CO_2 + \text{heat}$ (overall reaction)

$2H_2O \rightarrow 2H_2 + O_2$ (in OTM reactor)

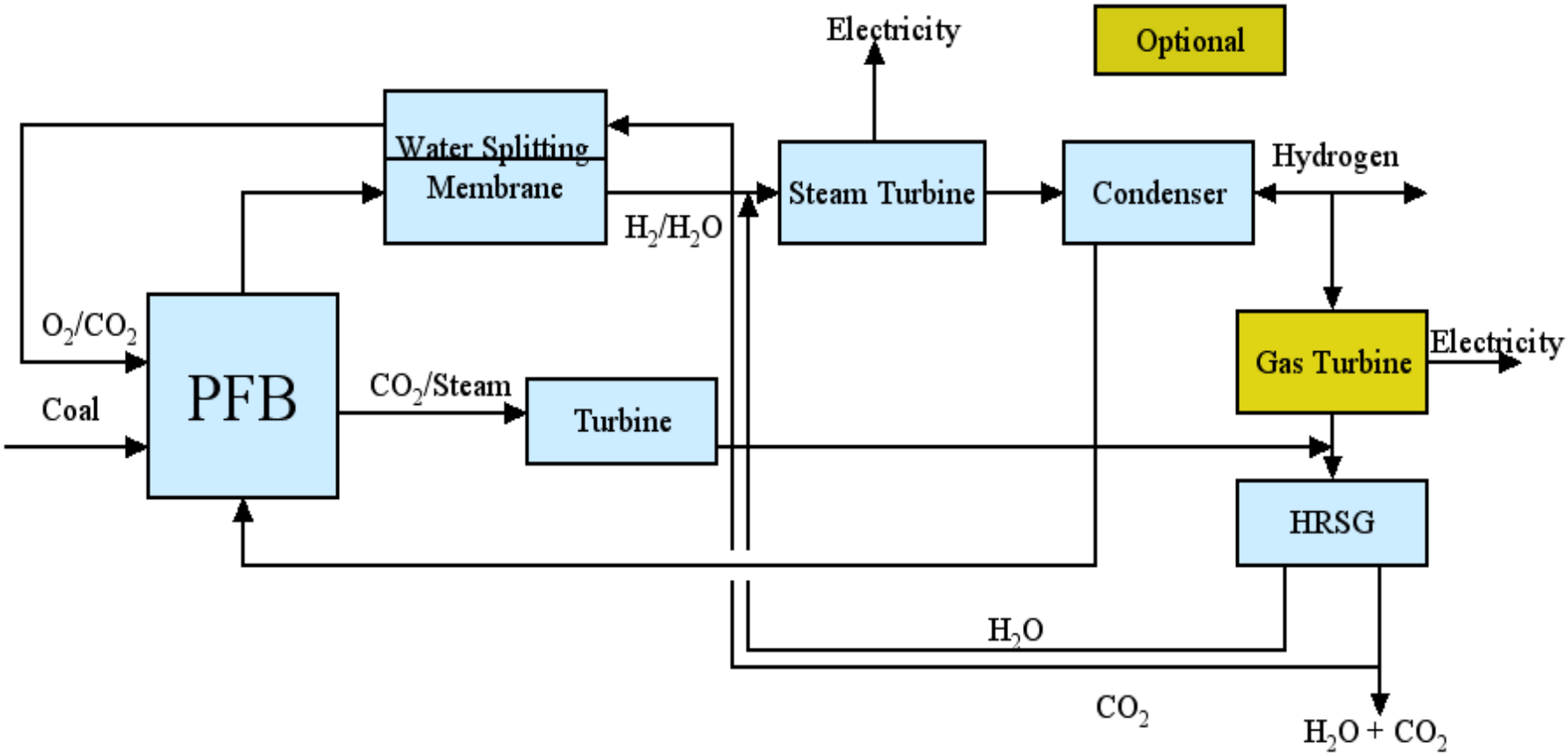
U. Balachandran et al., Int. J. Hydrogen Energy, 29, 291, 2004; U.S. Patent 7,087,211, Aug. 8, 2006.

Schematics for generating H_2 & CO_2-rich stream ready for sequestration



Process will yield hydrogen in addition to sequestration-ready CO_2.

PFB for H_2/Power Using Steam-Splitting Membrane



Ref: Gary Stiegel, NETL,

Schematic of Experimental Setup – Disk-Type Membrane

OTM Compositions

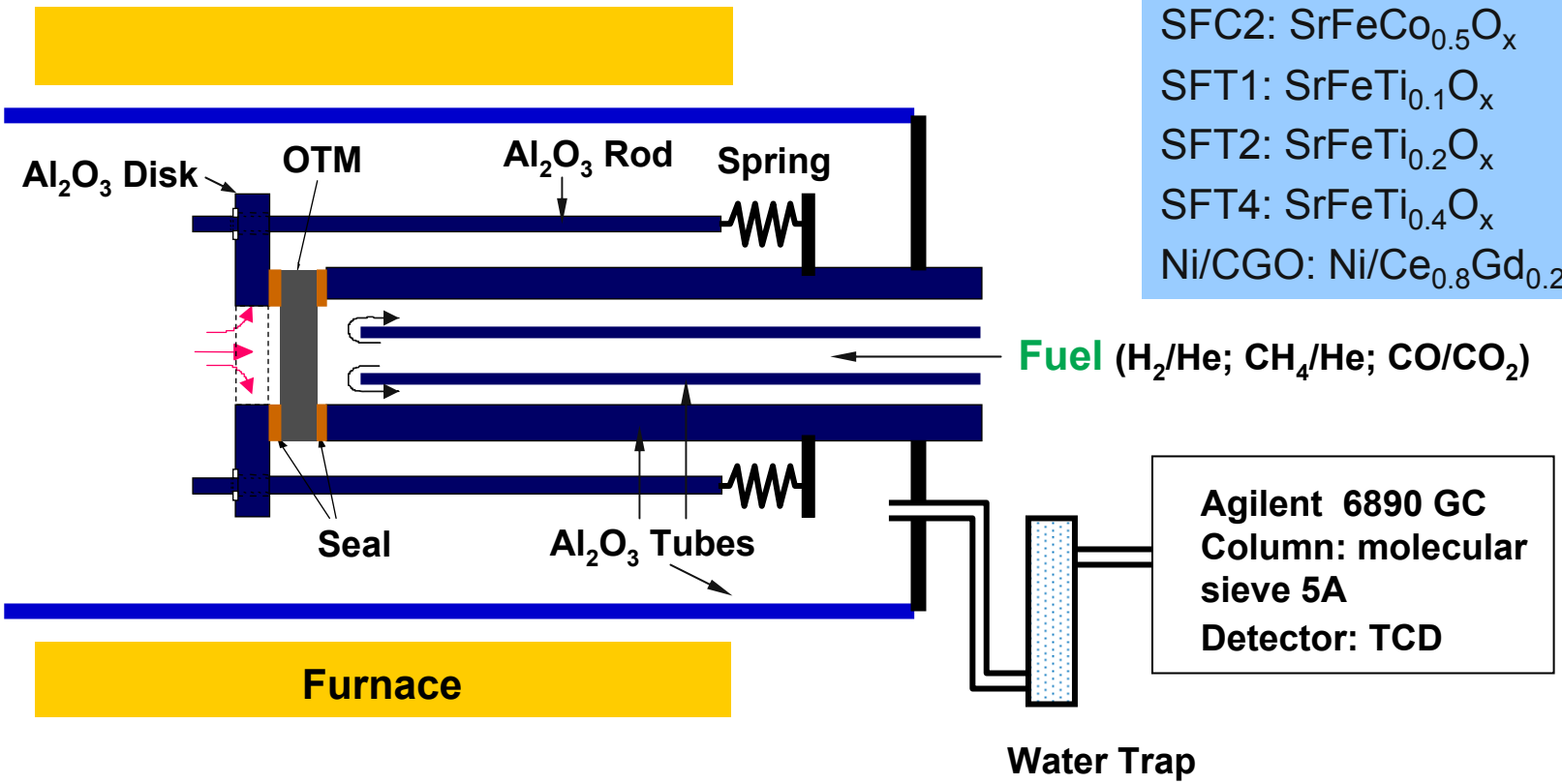
SFC2: $SrFeCo_{0.5}O_x$

SFT1: $SrFeTi_{0.1}O_x$

SFT2: $SrFeTi_{0.2}O_x$

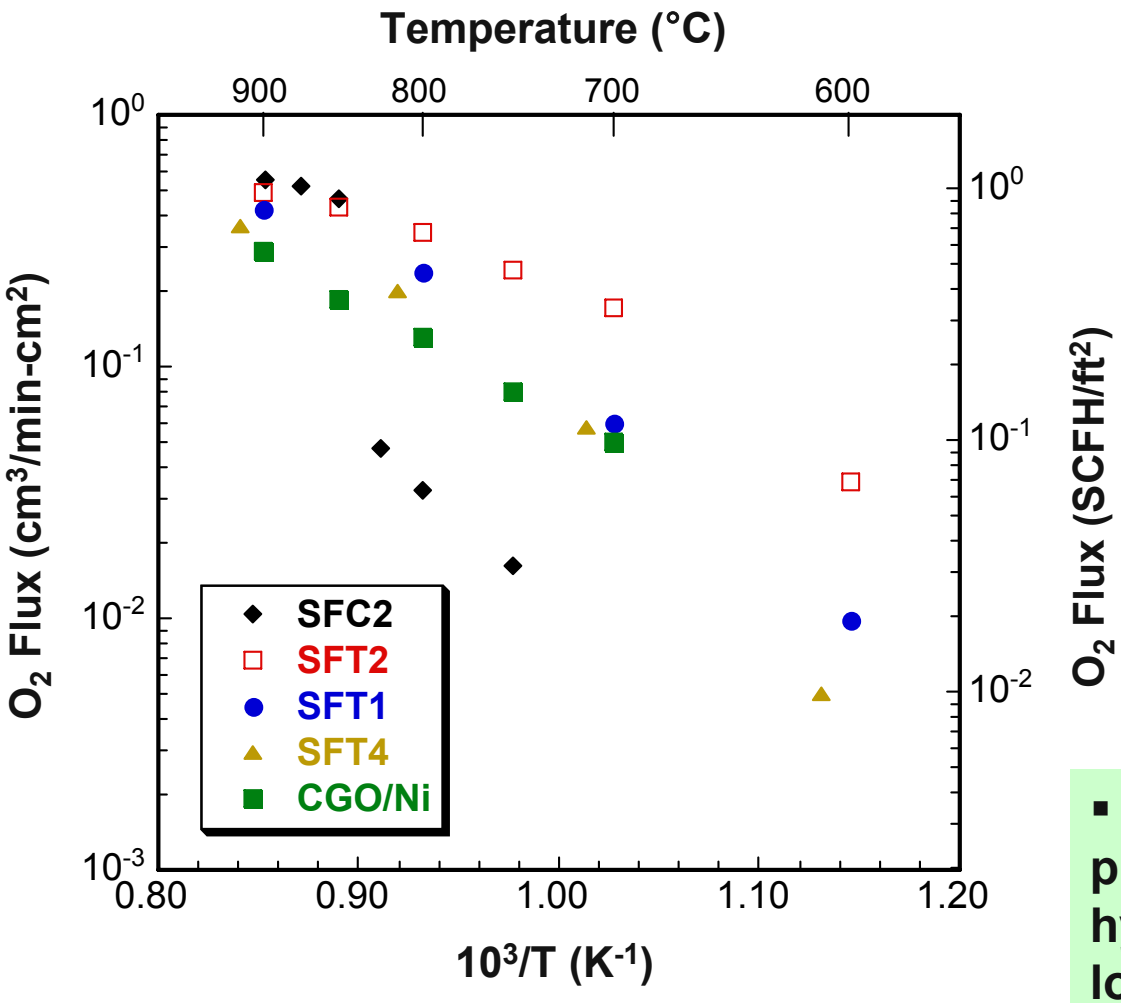
SFT4: $SrFeTi_{0.4}O_x$

Ni/CGO: $Ni/Ce_{0.8}Gd_{0.2}O_x$



- Flow rates: ≈200 cc/min
- OTM sample size: ≈20 mm dia.
- Feed concentration: H_2/He; CH_4/He; CO/CO_2)
- Temperature: 500-900°C

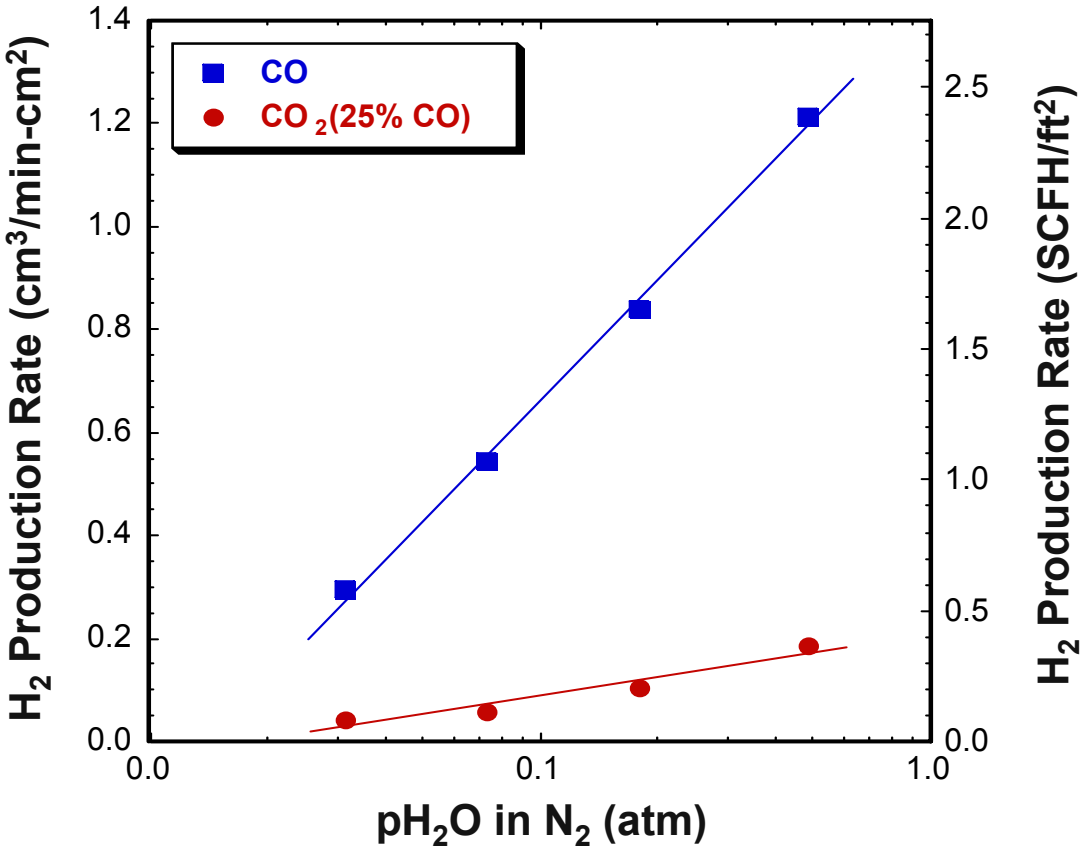
Optimizing OTM Performance by Doping



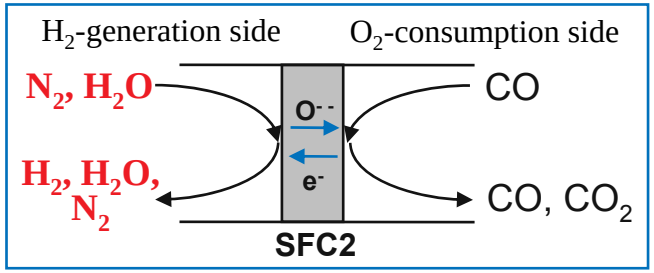
Membrane: Various Compositions
Thickness: ≈1 mm(all membranes)
Gas 1: 4% H_2/Balance He
Gas 2: N_2/3% H_2O
Flow Rates: 150 cc/min
Gas Pressures: Ambient

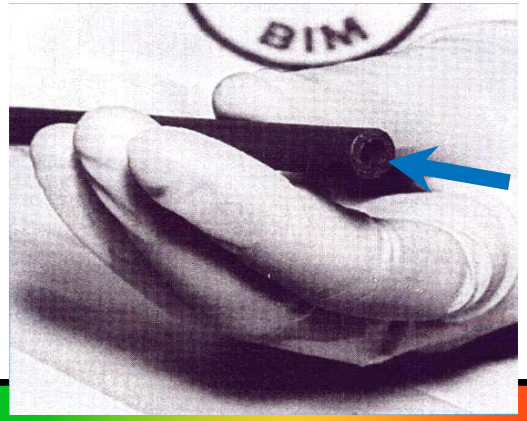
- **Proper doping eliminates phase transition and gives high hydrogen production rate at low temperatures (<825°C).**

Coal-gas (CO_2, CO) assisted H_2 Production using OTM via Steam Splitting: H_2 Production rate of tubular membrane

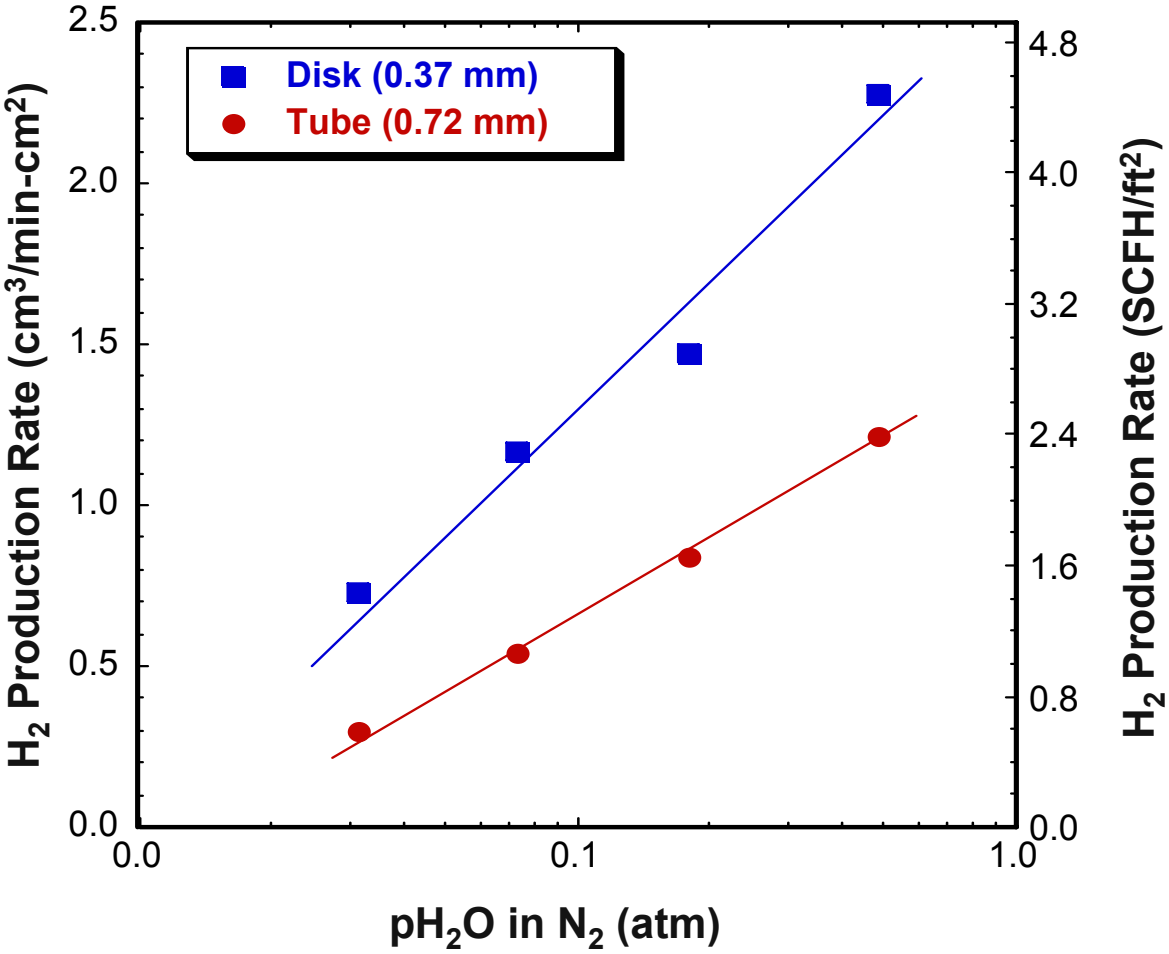


Membrane: SFC2 Tube
Thickness: 0.72 mm
Temperature: 900°C
Gas 1: CO or CO_2(25% CO)
Flow Rate: 200 cc/min
Gas 2: N_2 (3-49% H_2O)
Flow Rate: 400 cc/min
Gas Pressures: Ambient





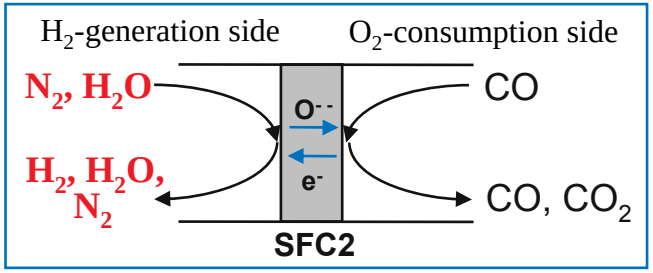
Hydrogen Production Rate of OTM Tube and Disk Effect of Thickness



Membrane: SFC2 Tube or Disk
Thickness: Given in Legend
Temperature: 900°C
Gas 1: CO
- **Flow Rate:** 200 cc/min (Tube)
- **Flow Rate:** 150 cc/min (Disk)

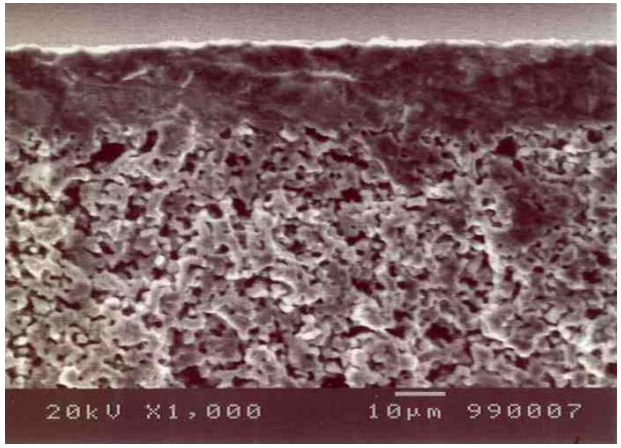
Gas 2: N_2 (3-49% H_2O)
- **Flow Rate:** 400 cc/min (Tube)
- **Flow Rate:** 150 cc/min (Disk)

Gas Pressures: Ambient

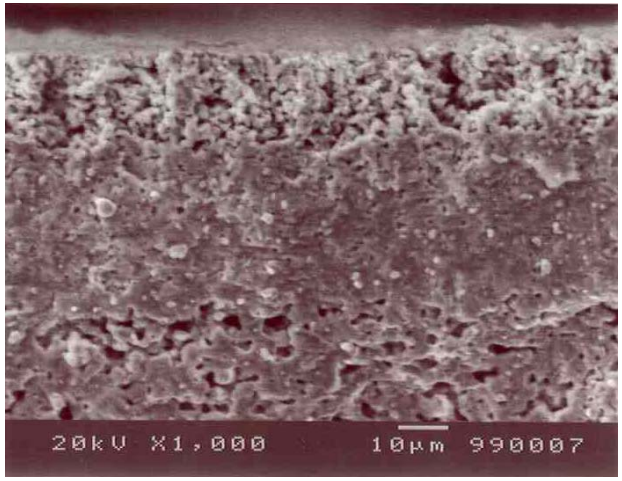


Fabricating Thinner OTMs to Enhance Hydrogen Production Rate

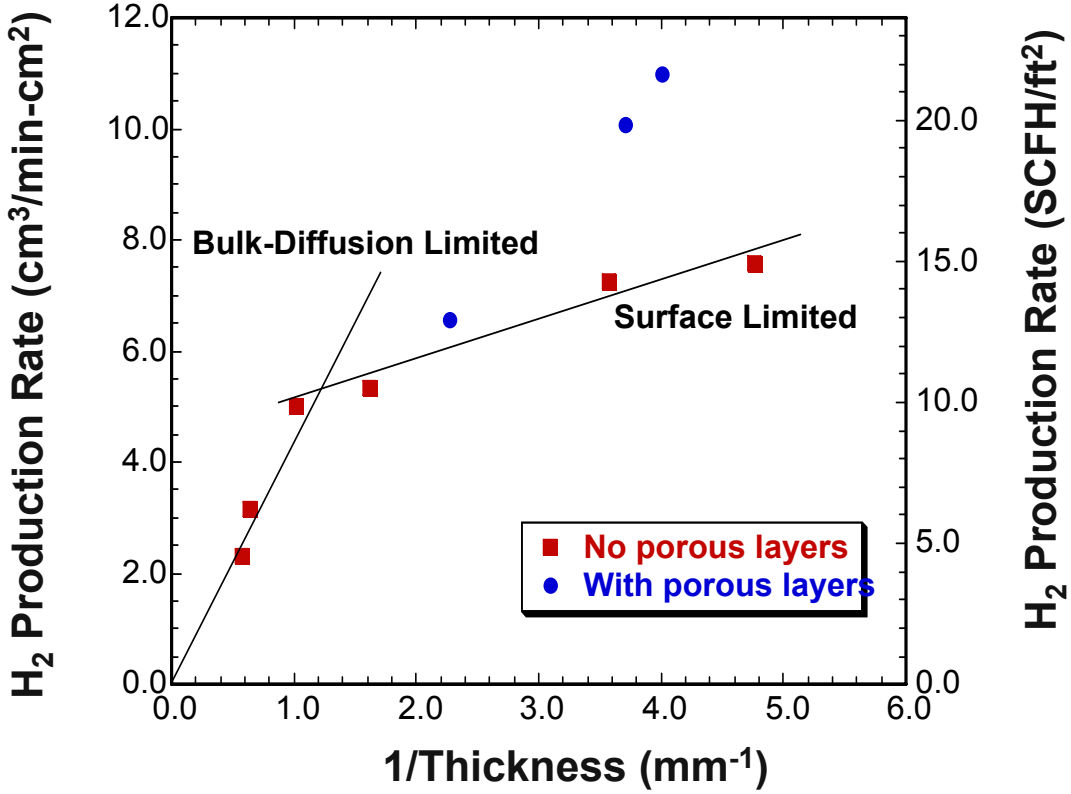
Membranes: SFC2
Gases: 80% H_2/Balance He // N_2(49% H_2O)
Flow Rates: 150 cc/min, **Gas Pressures:** Ambient
Temperature: 900°C



Porous layer on one surface

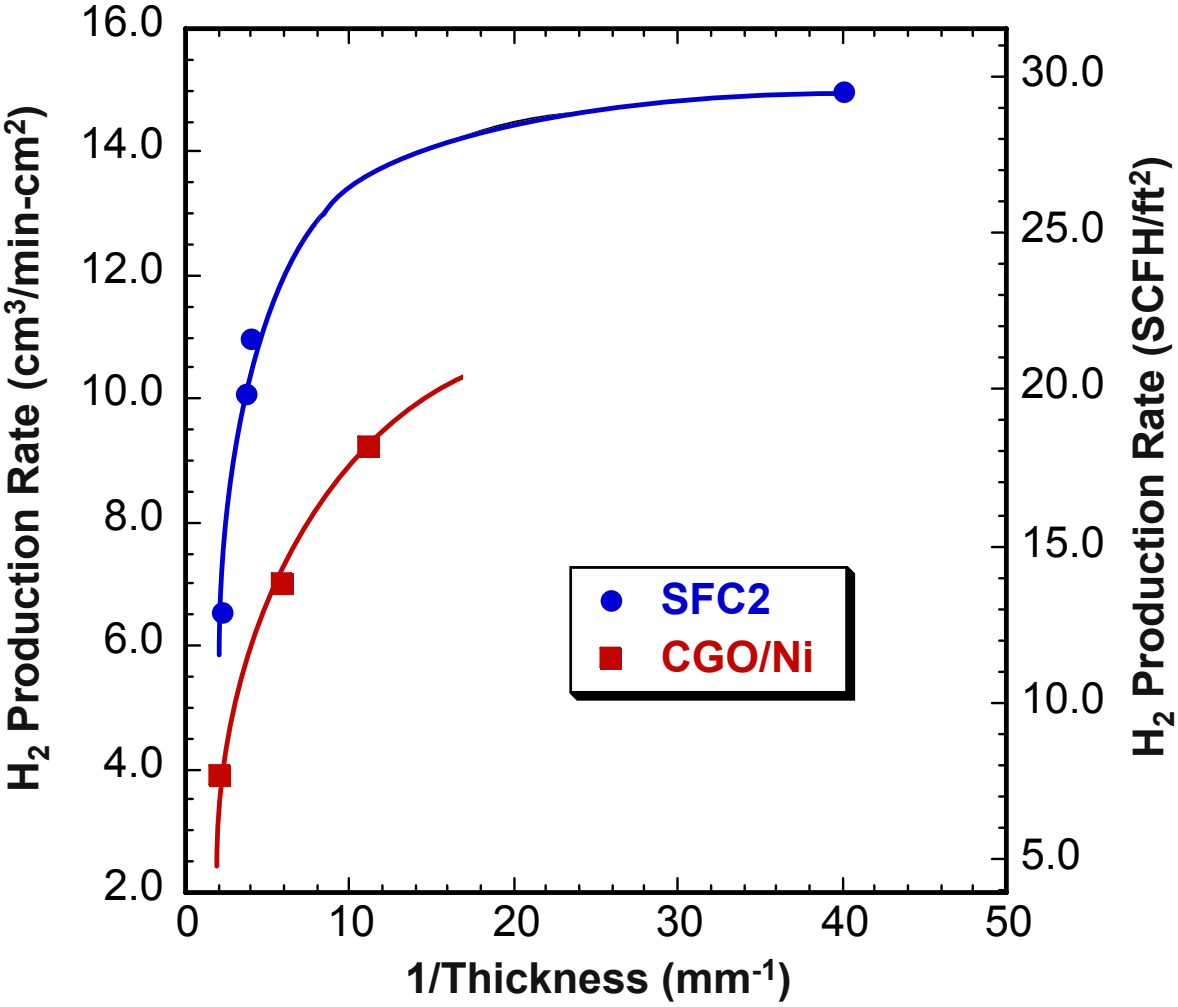


Porous layer on both surfaces



- Reducing OTM thickness increases hydrogen production rate, but porous layers are needed to overcome limitations from surface reaction kinetics.

Hydrogen Production Rate vs. Inverse of Membrane Thickness



Membrane: SFC2 or CGO/Ni
Temperature: 900°C
Gas 1: 80% H_2/Balance He
Gas 2: N_2/49% H_2O
Flow Rates: 150 cc/min
Gas Pressures: Ambient

- 25 μm-thick SFC2 film (1/Thickness = 40 mm^{-1}) gave H_2 production rate of ≈36 SCFH/ft^2 using N_2/69% H_2O.

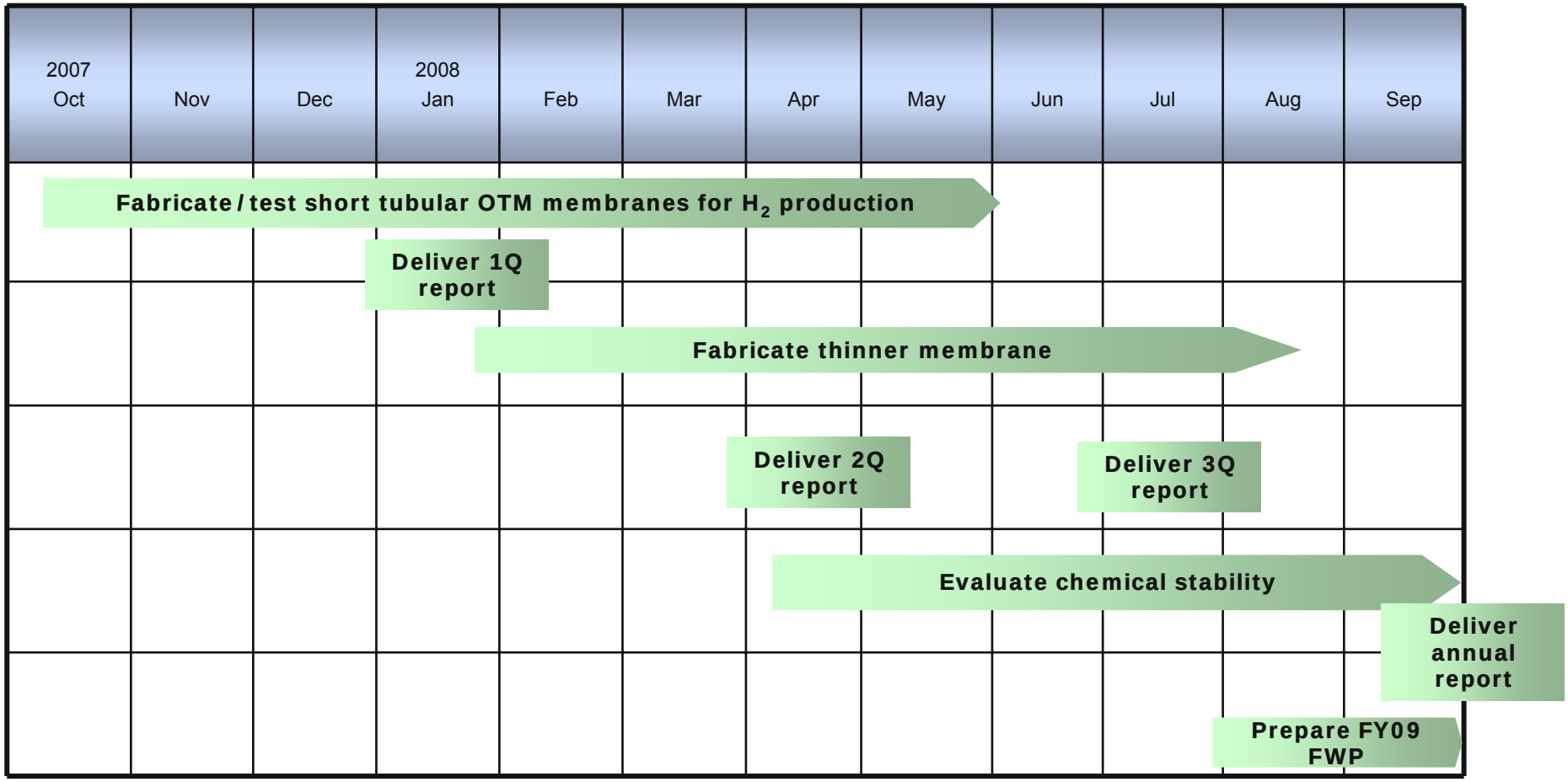
Issues/Technical Challenges

- Stability of membrane in presence of trace contaminants (H_2S, NH_3, Hg, halides, etc.) and at high pressures of steam (steam corrosion)
- Enhancement of oxygen flux under practical application conditions (i.e., high pressure steam on one side & CO_2/CO mixture on the other side)
- Leak-proof metal/ceramic seal to withstand high pressure steam & coal gas streams and thermal cyclability
- System analysis to determine the advantages of this new approach for coal-assisted hydrogen production

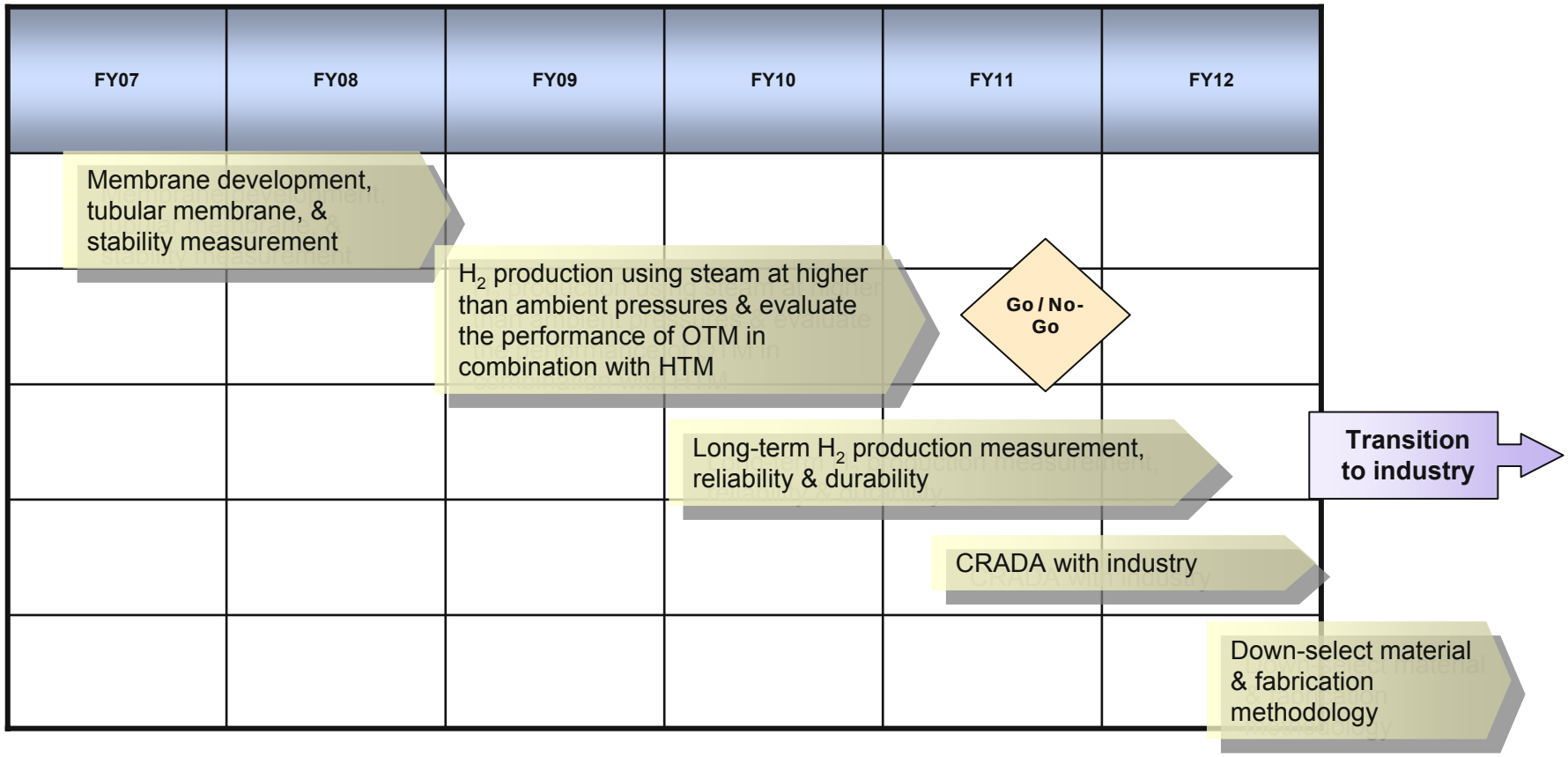
Future Work

- Continue to develop new membrane with enhanced flux under practical operating conditions
- Evaluate the stability of the membrane (steam corrosion, high pressure streams, trace impurities, etc.)
- Fabricate tubular membranes and address the boundary layer transport limited conditions
- Measure hydrogen production with steam at higher pressures
- Make long-term hydrogen production measurements & demonstrate reliability and durability of membranes
- Study scale-up issues

Project Schedule: *Timeline for FY 08*



Project Schedule



SUMMARY

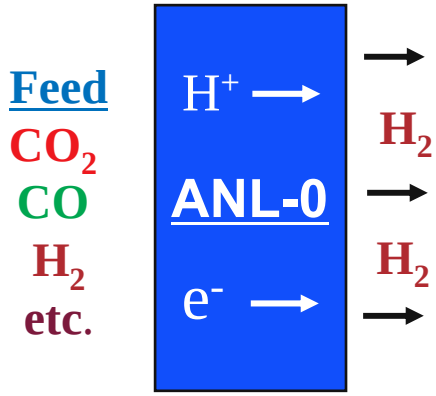
- Developing mixed-conducting dense oxygen transport membranes for coal-assisted hydrogen production via steam splitting.
- Preliminary concept of coal-gas assisted H_2 production using dense membranes via steam dissociation has been demonstrated.
- H_2 production rate as high as ≈36 SCFH/ft^2 was measured with 25-μm-thick OTM membrane.
- H_2 production rate increased with both increasing steam concentration and pO_2 gradient, and with decreasing membrane thickness.
- Production rate will be increased with high pressure steam (from supercritical boilers) and by enhancing the surface exchange kinetics.

Backup Slides

Argonne's Approach to H_2 Membrane Development

(Dorris, Lee, and Balachandran, U.S. Patent 6,569,266, May 27, 2003)

Single-Phase Mixed Conductor

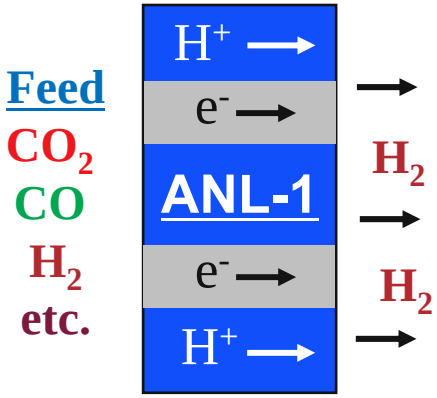


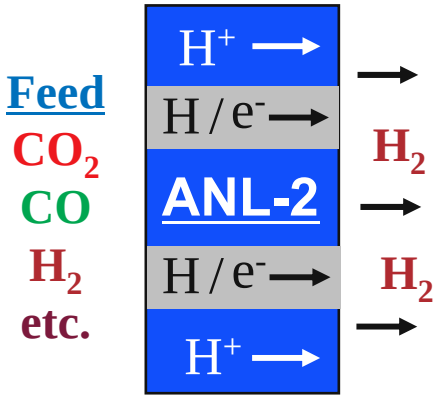
$$J_{H_2} = \frac{RT}{16F^2 l} \cdot \sigma_{amb} \cdot \ln \frac{p_{H_2}^{II}}{p_{H_2}^{I}}$$

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

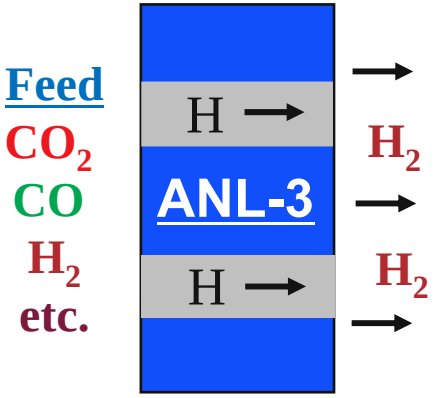
- Low σ_{e-}
- Low Flux
- Poor Mechanical Integrity

Mixed Conductor With Metal





Structural Ceramic With Hydrogen Transport Metal

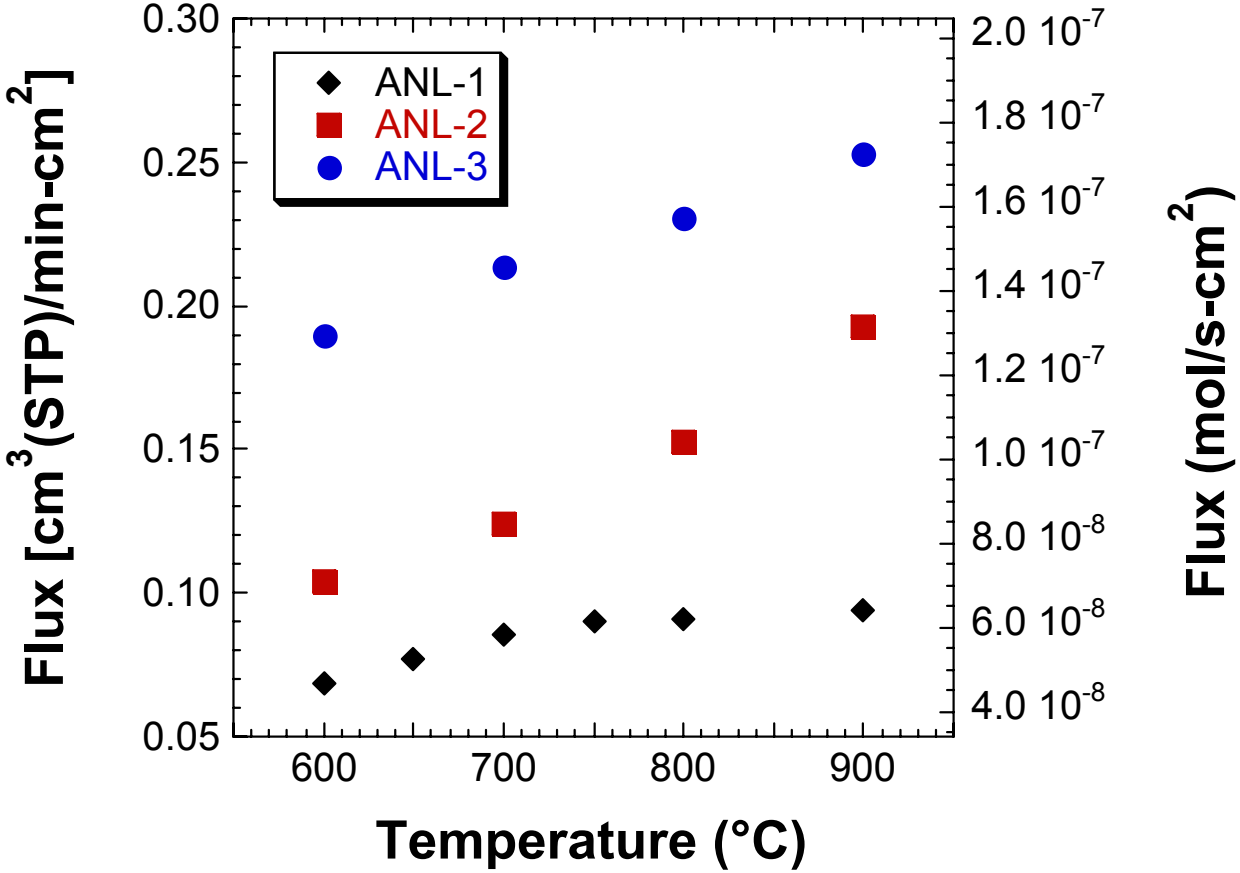


$$J_{H_2} = \frac{A\Phi}{l}\left(\sqrt{p_{H_2}^{feed}} - \sqrt{p_{H_2}^{sweep}}\right)$$

- High Flux
- High Selectivity
- Good Mechanical Integrity

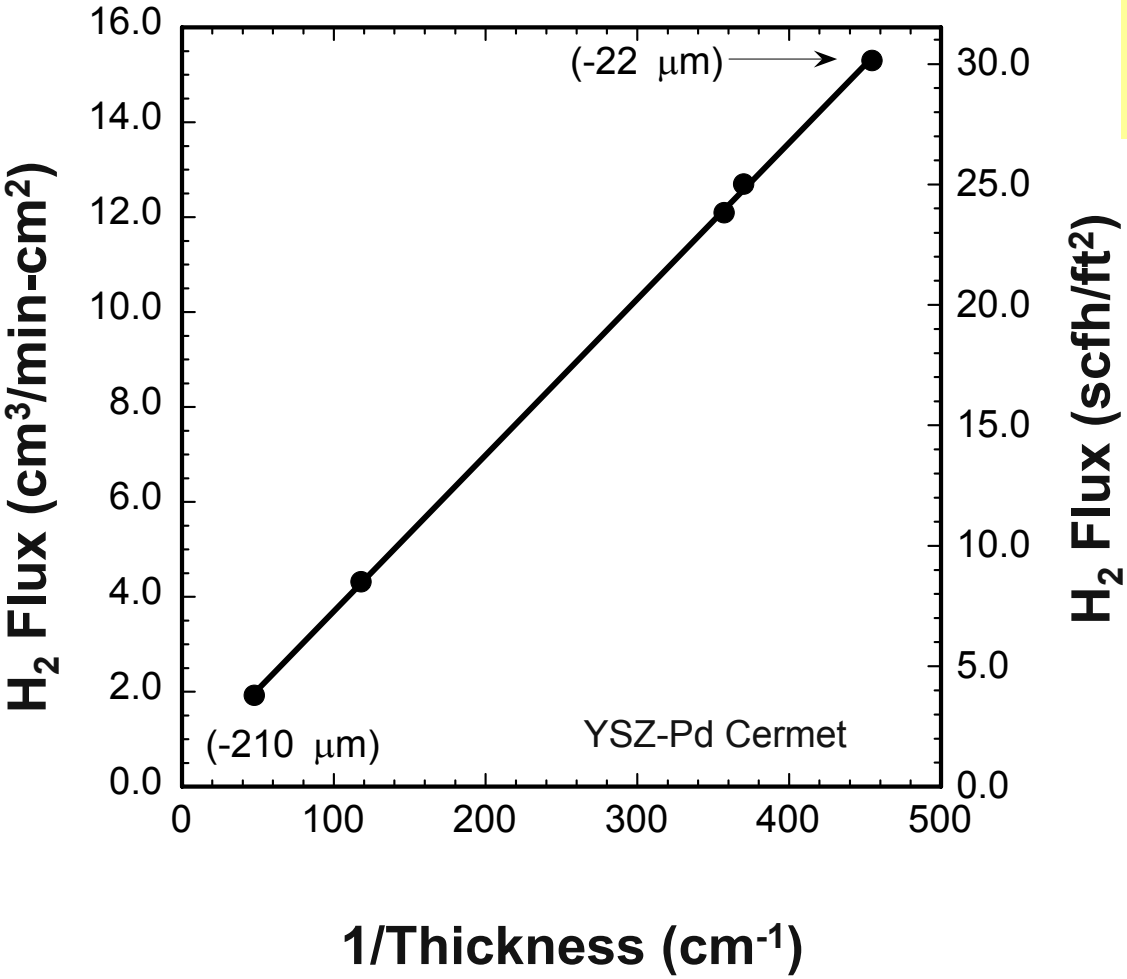
Comparison of Cermet Membranes

Feed Gas: 4% H_2/Ar, Sweep: N_2; Ambient Pressure; Mem. Thickness = 0.50 mm



ANL-3 is primary focus due to its significantly higher H_2 flux.

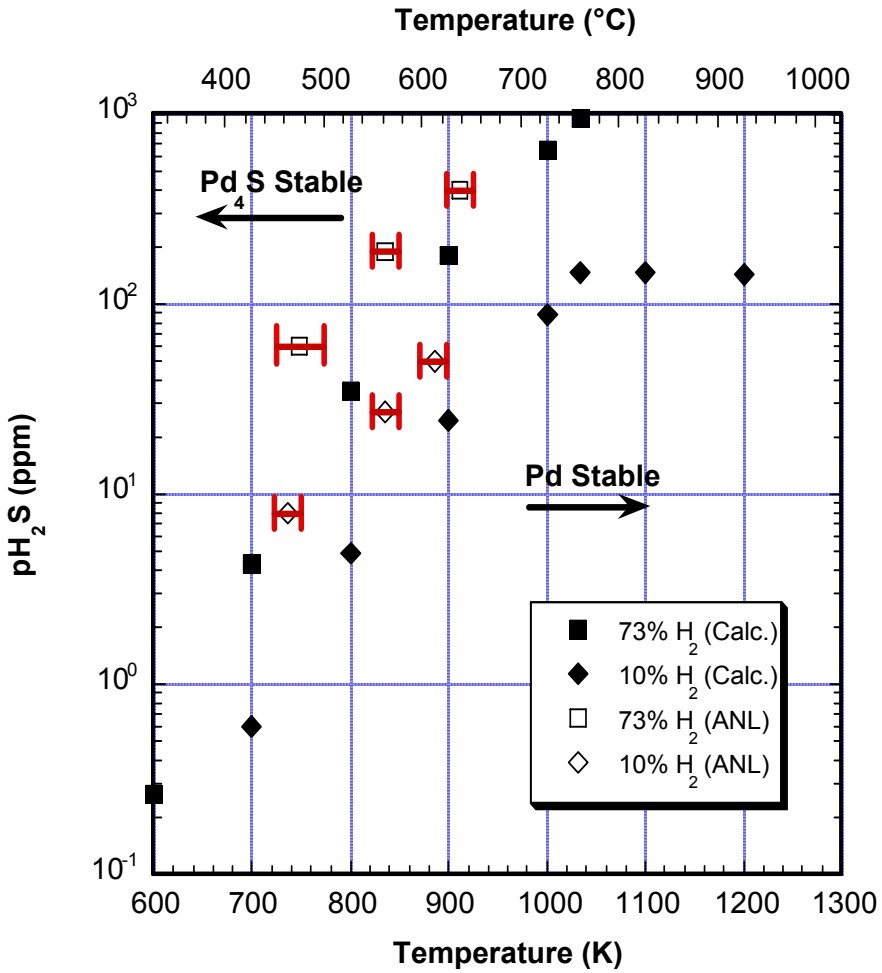
H_2 Flux vs. Inverse HTM Thickness



Feed: 80% H_2/He, **Sweep:** N_2
Pressure: Ambient, $\Delta P \approx 0$ psi
Flow rates: 150-200 cc/min
Temperature: 900°C

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

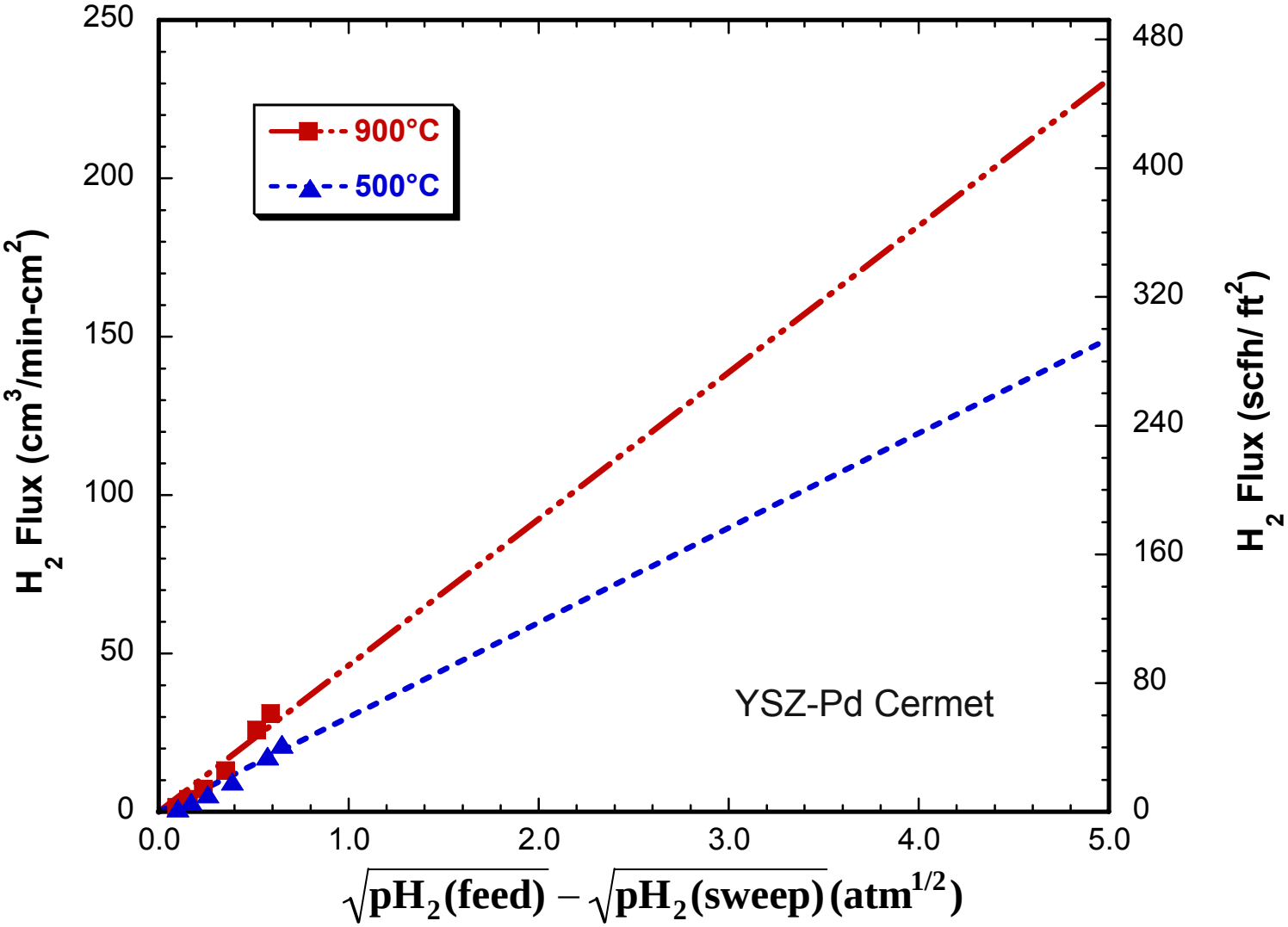
Pd/Pd_4S Phase Boundary for Cermet Membrane determined at Argonne



Red bars summarize results obtained at Argonne by equilibrating samples at various temperatures with feed gas of 73% H_2 with 400, 190, or 60 ppm of H_2S (□); 10% H_2 with 50, 27, or 8 ppm H_2S (◇). All gases at ambient pressure.

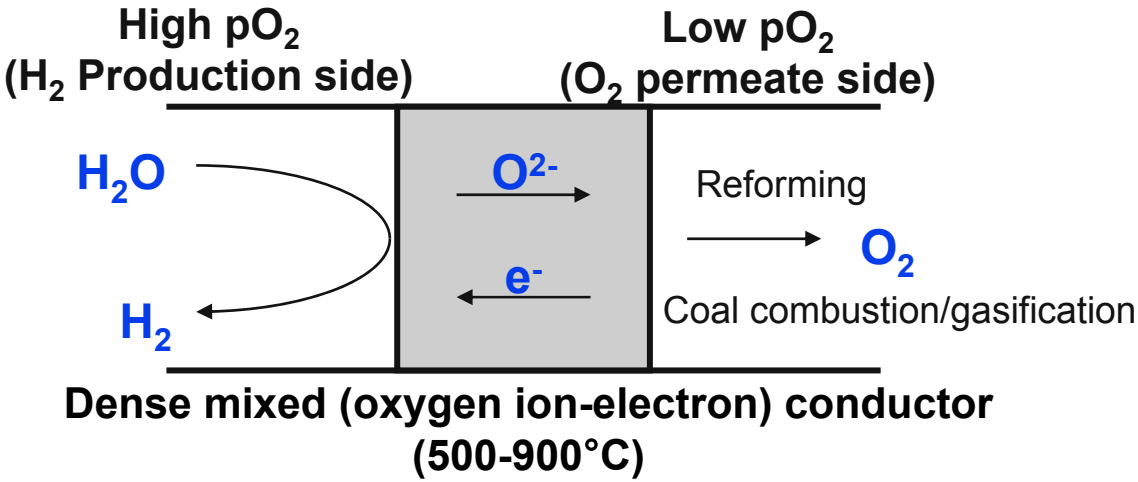
Calculated data from literature: J. R. Taylor, Met. Trans., 16B, 143, 1985; O. Knacke, et al., Thermochemical Properties of Inorganic Substances I, Springer-Verlag, Berlin, 1991

H_2 flux through 15–μm thick supported cermet membrane vs. difference in square root of p_{H2} for the feed & sweep gases



Hydrogen Production from Steam Using Mixed Conducting Ceramic Membranes

- Oxygen is removed by membrane.
- Non-galvanic (no electrodes/ electrical circuitry)



$$H_2O \Leftrightarrow H_2 + 1/2\ O_2$$

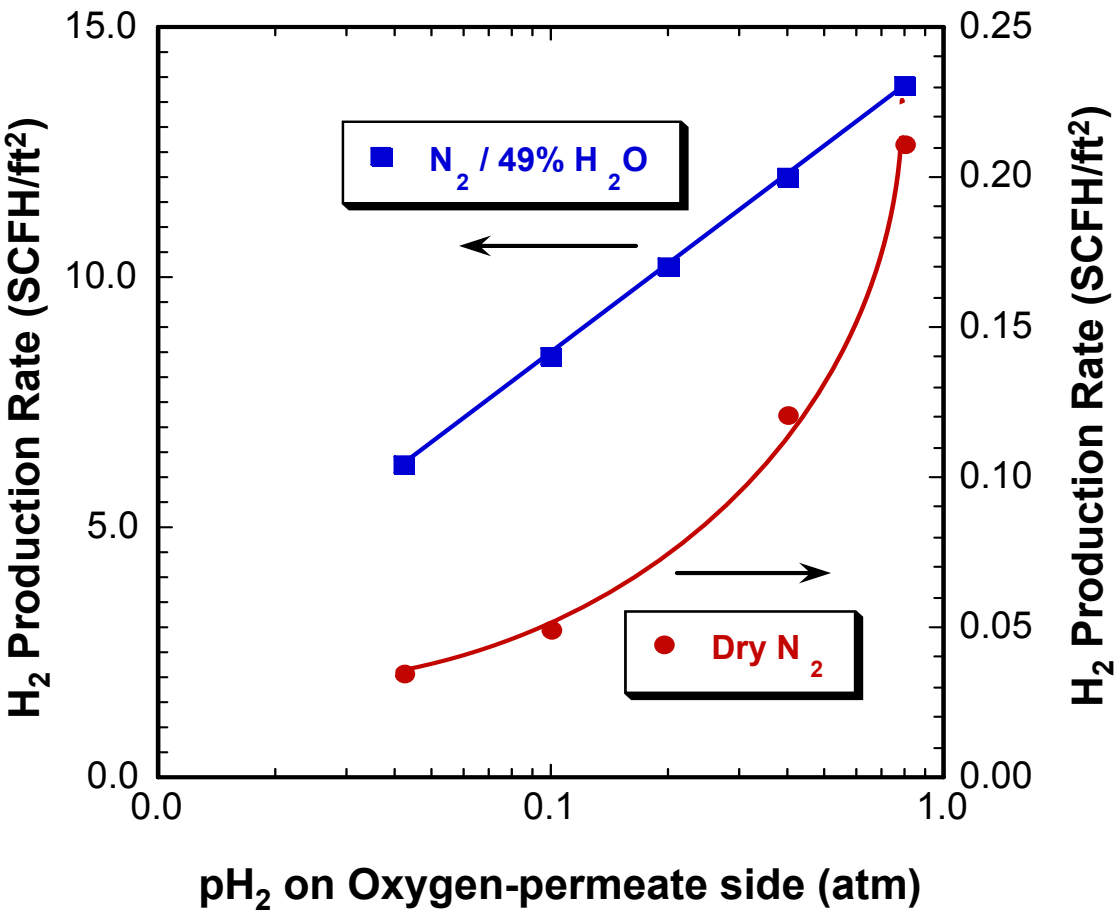
- Very low concentrations of H_2 and O_2 are generated even at relatively high temperatures (0.1 and 0.042% for H_2 and O_2, respectively, at 1600°C).
- Significant amounts of H_2 can be generated at moderate temperatures if the reaction is shifted toward dissociation by removing either O_2, H_2, or both.

$$K = \frac{P_{H_2} P_{O_2}^{\frac{1}{2}}}{P_{H_2O}}$$

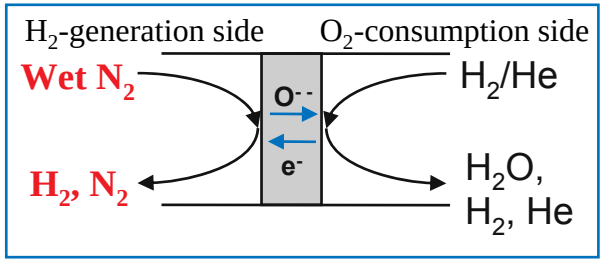
U. Balachandran et al., Int. J. Hydrogen Energy, 29, 291, 2004; U.S. Patent 7,087,211, Aug. 8, 2006.

Proof of Principle

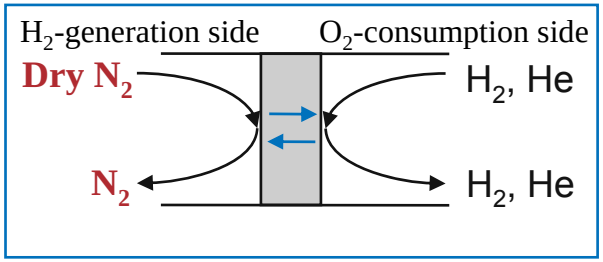
Hydrogen Production Rate with Dry and Wet N_2



Membrane: CGO/Ni
Thickness: 0.17 mm
Temperature: 900°C
Gases: H_2, He // N_2, H_2O
Flow Rates: 150 cc/min

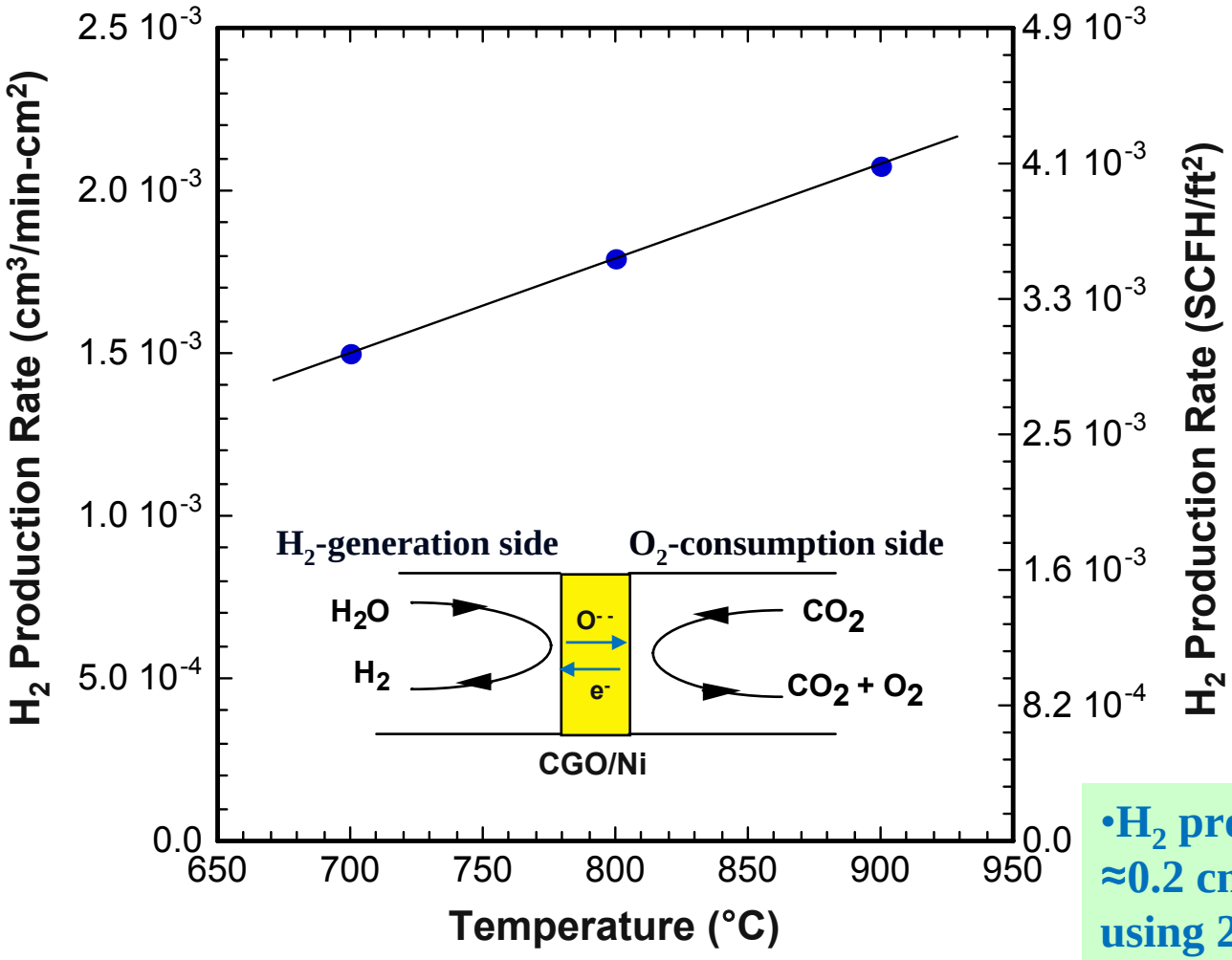


H_2 Production



No H_2 production

Coal-Gas (CO_2, CO) Assisted H_2 Production Using Ceramic Membrane via H_2O Splitting

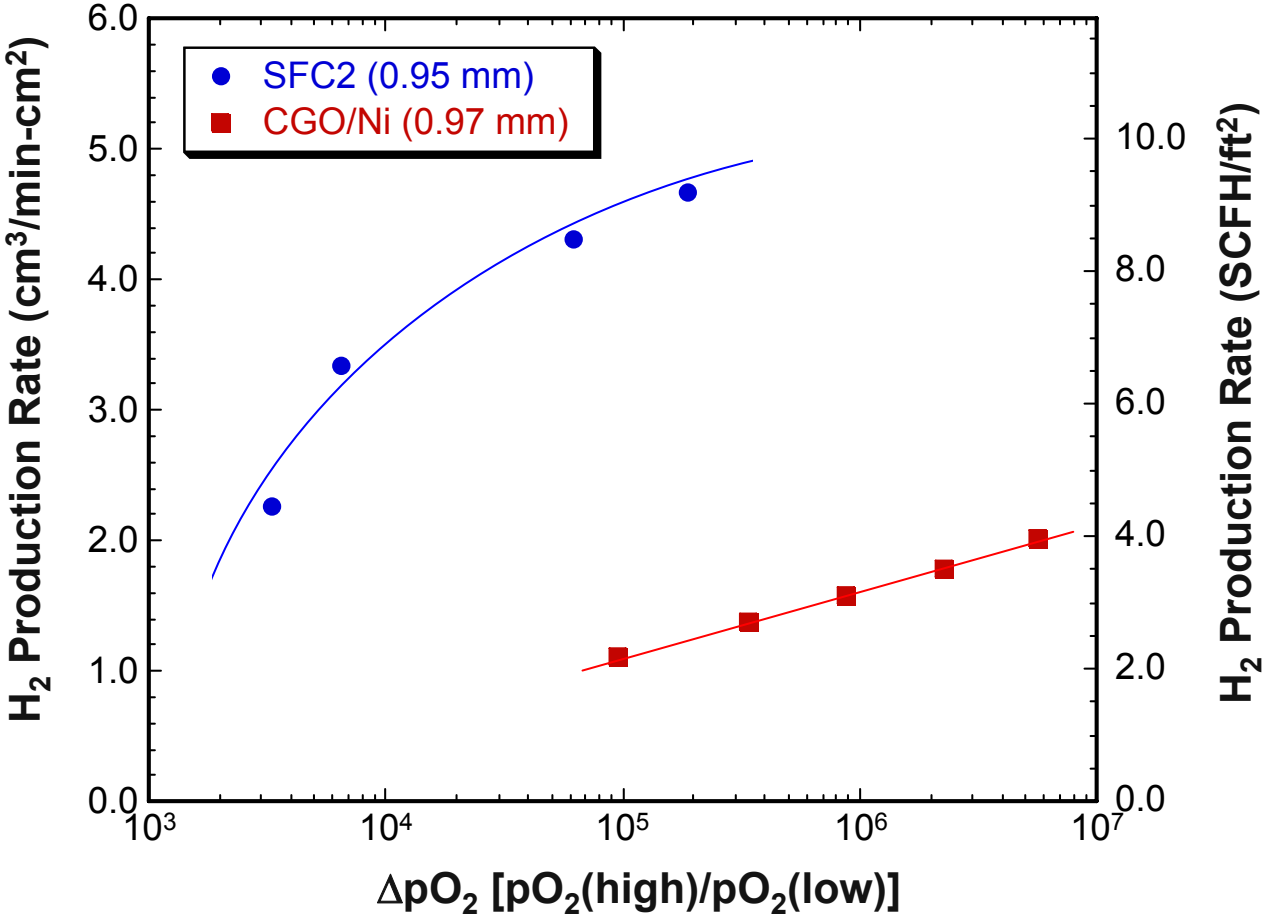


Membrane: CGO/Ni
Thickness: 0.3 mm
Gases: CO_2
N_2(0.3 atm H_2O)
Flow Rates: 150 cc/min

- **H_2 production rate increased to ≈0.2 cm^3/min-cm^2 (≈0.4 SCFH/ft^2) using 20% CO/balance CO_2.**

H_2 production rate vs. pO_2 differential across the membrane

Membranes: Compositions in Legend
Gases: 4-80% H_2/Balance He // N_2(49% H_2O), **Flow Rates:** 150 cc/min, **Gas Pressures:** Ambient
Temperature: 900°C



- Decreasing membrane thickness should enhance H_2 production rate.