Defect-free Thin Film Membranes for H_2 Separation and Isolation

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DOE / H_2, Fuel Cells & Infrastructure Technologies
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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94-AL85000

Sandia National Laboratories

Objectives

Goal: Synthesis of robust microporous zeolite membranes to improve on the H_2 separation technologies of polymers and precious metals

Relevance to Hydrogen:

Need to produce H_2 reliably, at low cost

Use of reforming to produce H_2

Steam Reforming: $CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$

Dry Reforming (MCFC): $CH_4 + CO_2 \rightarrow 2CO + 2H_2$

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Objectives

Synthesis

Defect-free Inorganic crystalline thin-film membranes:
Synthesis efforts with Al/Si & Si phases
Film growth on variety of supports (oxides, SS316, composite)
Testing on-line at various temperatures

Permeation

Testing new membranes, RT and elevated Temps:

pure: H_2, N_2, CO, CO_2, O_2, He, H_2O, CH_4, H_2S & SF_6;
mixed: 50/50 CH_4/H_2 , CO_2/H_2 ; simulated reformate stream

Modeling/Simulation

Light gases through 1D ZSM-22 and compare to ZSM-5

Validation through permeation testing

Business Partners/Collaborations

Basic research “directed” toward commercialization

Industry (manufacturers, end-users), University

Budget

Total FY04 funding: ≈ $211K*

DOE: $200K/year

$180K to Sandia

$20K subcontracted to NMSU (modeling)

In-kind funding (approximate: labor, samples, testing, travel):

$ 1K Mesofuels, Inc.

$ 5K Pall Corporation

$ 5K G.E. Dolbear & Associates, Inc

*(anticipated in-kind, awaiting NDA signing)

Total FY03:

DOE: $250K

In-kind: ≈ $6K (Mesofuels, Pall)

Technical Barriers and Targets

DOE Technical Barriers for Separation Membranes (for H_2 Production):

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance (O&M)
- C. Feedstock and Water Issues
- E. Control and Safety
- G. Efficiency of Gasification, Pyrolysis, & Reforming Technology
- AB. Hydrogen Separation and Purification

DOE Technical Targets for Separation Membranes for 2010 (Pd membranes):

- Flux Rate = 200 scfh/ft^2
- Cost = <$100/ft^2
- Durability = 100K hours
- Operating Temp = 300-600 °C
- Parasitic Power* = 2.8 kWh/1000 scfh

  * recompress H_2 gas to 200psi

Approach

Development of Defect-free thin film zeolite membranes for Hydrogen Production:

1) Synthesize membranes with Silicate-based frameworks
   use supports that are industrially relevant

2) Model/Simulate/Validate permeation of light gases through the frameworks

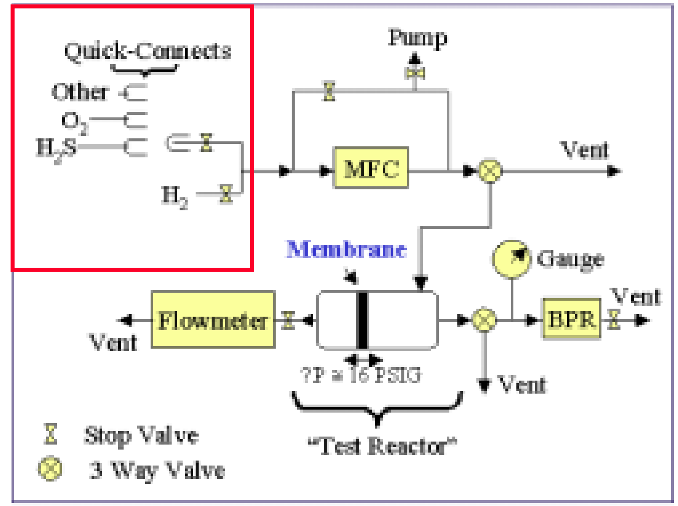
3) Analyze flux and permeation of gases (pure, binary, mixed gas streams)
   at ambient and varying temperatures/pressures

4) Optimize membranes' flux, permeation and durability

5) Foster industrial contacts for membrane stream and pilot-scale testing,
   and future commercialization partnerships

Project Safety

- H_2 separate from O_2 & other gases by plumbing
- Entire permeation unit is located inside a fume hood
- H_2S and CO sensors set according to OSHA limits (tested yearly)



- Thorough analysis of gas, equipment specs, process & pressure testing to ensure safety AND to pass Sandia's corporate ES&H regulations (SOPs, PHS, PSDP)

- All operators in compliance with required corporate training policies

Project Timeline

4/00-1/04	2/04-12/04	1/05-9/06
Phase I	✥Phase II	Phase III

1,2 3 4,5,6 7,8 9 10

- Phase I: Membrane synthesis and characterization
  1. Membrane composition
  2. Permeation unit construction
  3. Pure Gas testing
- Phase II: Membrane Optimization
  4. Various substrates for membranes
  5. Mixed gas testing
  6. Variable temperature testing
- Phase III: Applied to commercialization
  7. Optimize membrane support
  8. Industrial Gas Streams (Industry involvement; Lab & pilot-scale)
  9. Scale up
  10. Commercialization Processes

✥ current status

Technical Accomplishments/Progress

- Permeation Unit: testing **mixed gases (RT & higher)**, received H_2S testing approval

- Defect-free Silicalite and ZSM-5 (Al/Si) membranes synthesized & permeation tested
  50/50, mixed gases (initial: amended reforming stream)

- At various temperatures (RT, 90°C, 120°C), silicalite membranes maintain good
  selectivity for H_2 in both binary and mixed gas streams
  Selectivities between 10-100

- Comparison between **defect-free vs. defect "filled"** data indicates selective H_2
  separation for both, but improved results with >Knudsen diffusion (defect-free)

- Initial Studies on stream contaminants at RT: membranes are not selective for **H_2S**

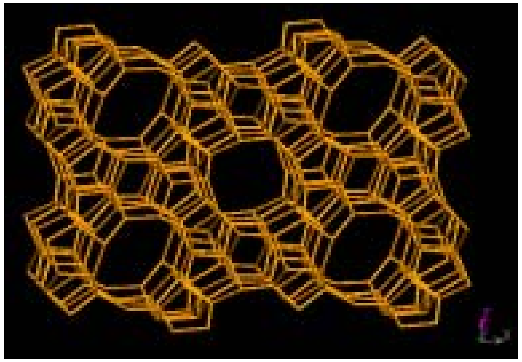
- Utilizing ceramic membrane supports: Inoceramic Alumina disks/tubes
  Oxide-coated SS316 (TiO_2; SiO_2/Al_2O_3; ZrO_2 coatings)
  Pall Corp. ZrO_2 coated SS316 tubes

Technical Accomplishments/Progress

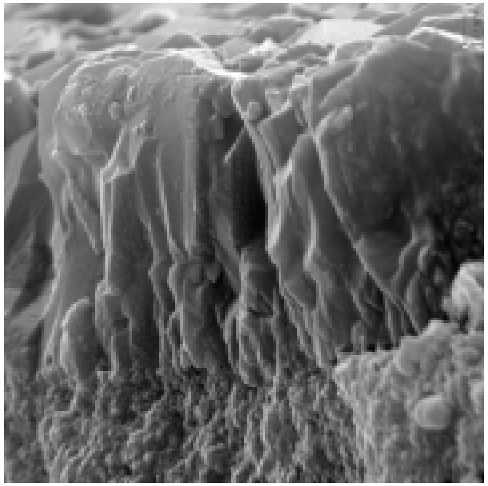
ZSM-5 ≈ 10^{-6} mole/(m^2 Pa sec)	Silicalite ≈ 10^{-6} - 10^{-7} mole/(m^2 Pa sec)
RT, Pure Gases	RT, Pure Gases
$H_2/N_2 \geq 61$	$H_2/N_2 = 1.4$
$H_2/CH_4 = 7$	$H_2/CH_4 = 0.625$
$He/N_2 \geq 7$	$He/N_2 = 1.1$
$CH_4/N_2 \geq 1.4$	$CH_4/N_2 = 2.28$
$H_2/CO_2 \geq 80$	$H_2/CO_2 \geq 0.34$
$H_2/O_2 \geq 11$	$H_2/O_2 = 1.7$
$CH_4/CO_2 \geq 11$	$CH_4/CO_2 = 0.54$
*$H_2/CO \approx 70$**	$H_2/CO = 1.43$

re-dehydrated membrane

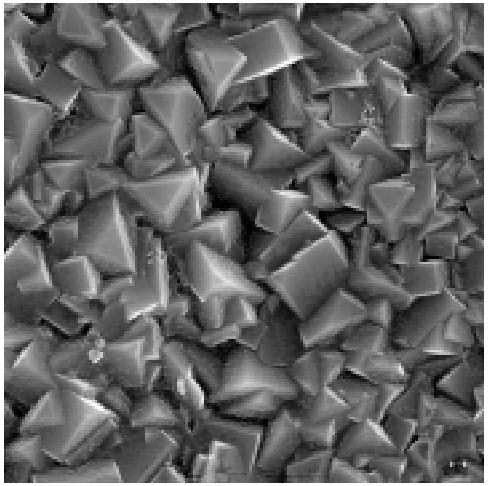
ZSM-5, Silicalite



ZSM-5 on Oxide Coated SS
Good intercrystalline growth
≈ 7microns thick



1.0 Micron



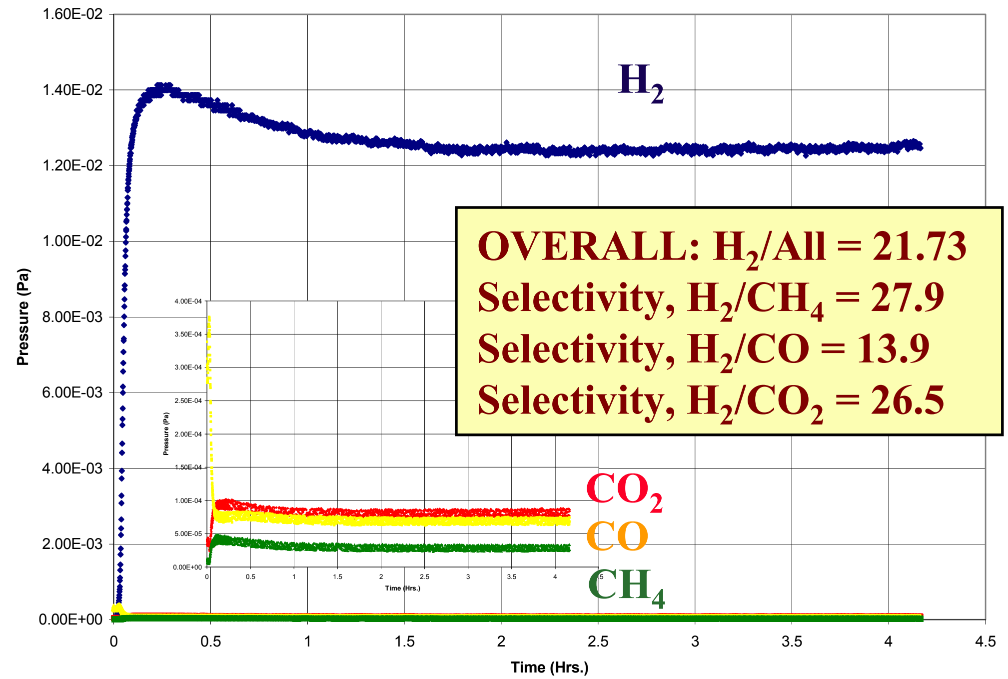
1.0 Micron

Technical Accomplishments/Progress (con't)

Silicalite Membrane, RT

Amended MesoFuel Inc.
reforming stream composition
(water removed for initial studies):

- 76% H_2
- 13.6% CO_2
- 6.8% CO
- 3.4 % CH_4



Silicalite, variable temperatures

	23°C	90°C	120°C
H_2/CO_2 (50/50)	21.51	29.29	19.57
H_2/CH_4 (50/50)	23.87	68.20	
Reformate, H/All	16.82	40.00	

ZSM-5, RT

	Defect Filled	Defect Free
H_2/CO_2 (50/50)	26.76	60.11
H_2/CH_4 (50/50)	16.67	39.43
Reformate, H/All	16.60	58.74*

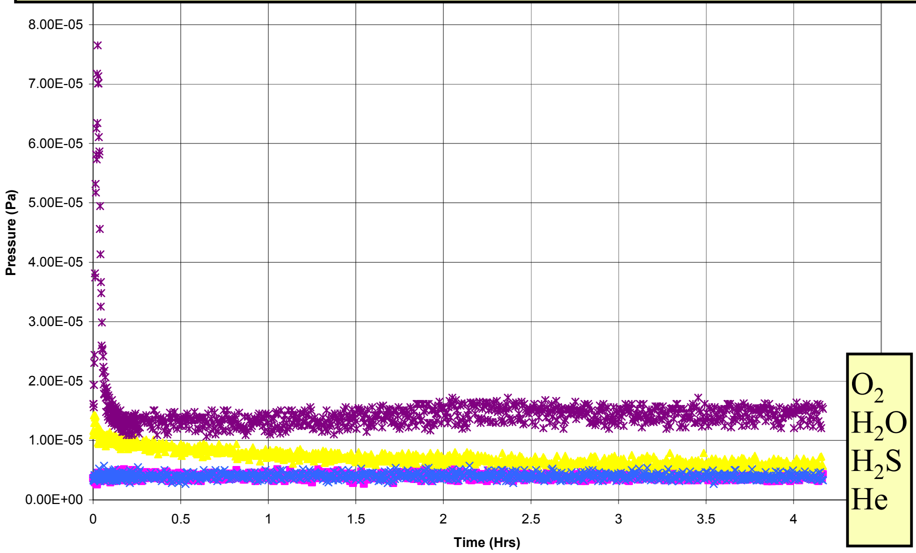
**need to replicate*

Technical Accomplishments/Progress (con't)

Initial Studies with caustic elements. Showed membrane survives (at room temp).
Further Study Required!

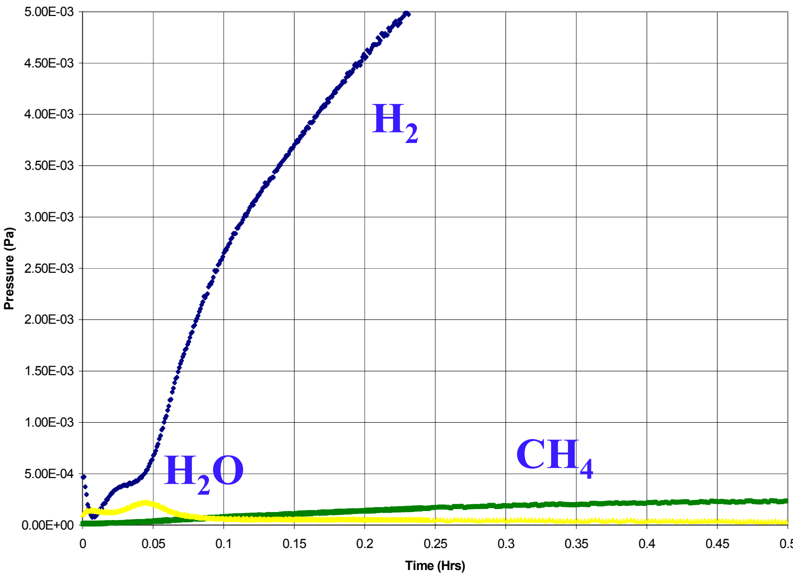
• H_2S (≈ 200ppm) in N_2 stream

N_2 equilibrium partial pressure (not shown) at 6 x 10^{-4}



H_2S does not permeate thru defect-free ZSM-5 membrane.
No short term damage

• Wet Stream



50/50 H_2/CH_4 flowing thru defect free Silicalite
"Zoom in" on H_2O partial pressure

Interactions & Collaborations

Presentations:

T. M. Nenoff, M. E. Welk, "Defect-Free Thin Film Membranes for H_2 Purification" Poster, Fuel Cell Symposium, Miami, FL, 11/6/03

T. M. Nenoff, M. E. Welk, "Defect-Free Thin Film Membranes for H_2 Separation and Isolation", 14th International Zeolite Conference, Cape Town, South Africa, 4/26/2004

2x M.E. Welk, Nenoff, T. M., "Zeolite Membranes for H_2 Purification"
8th International Inorganic Membrane Conference, Cincinnati, OH, 7/18/04
3rd International Zeolite Membrane Conference, Breckenridge, CO, 7/25/04

Publications:

Bonhomme, F.; Welk, M. E.; Nenoff, T. M. "CO_2 Selectivity and Lifetimes of Silicalite Membranes". *Micro. & Meso. Materials*, **2003,** *66*, 181.

Mitchell, M.; Gallo, M.; Nenoff, T. M. "Molecular dynamics simulations of binary mixtures of methane and hydrogen in titanosilicates", *J. Phys. Chem*., **2004**, in press.

Welk, M. E., Nenoff, T. M. "Mixed Gas Permeation Studies Through Defect Free ZSM-5 and Silicalite Zeolite Membranes.", *J. Membrane Science*, **2004**, in press.

Symposium:

"Modeling and Simulation in Surface and Colloid Science"; Tina M. Nenoff, Martha Mitchell, Marcus Martin, *Co-Organizers* ACS National Fall Meeting, NYC, NY Sept 7-13, 2003

Interactions & Collaborations (con't)

Industrial Partners:

- Mesofuels, Inc., Anand Chellappa: Reforming Gas Steam Composition
- Pall Corporation, Jim Acquaviva: Membrane Supports, Visits to both facilities
- G.E. Dolbear & Associates, Inc.: Non-disclosure Agreement in process, testing our membranes at elevated temps

Academic Partner:

- New Mexico State University, Martha Mitchell, Dept. of Chemical Engineering: modeling and simulation

DOE Workshops:

- Workshop Panel participant for H_2 Production:
  - US DOE/Italy Joint Workshop on H_2 Research, Sacramento, CA, 9/15/03
  - US DOE/UK Joint Workshop on H_2 Research, Albuquerque, NM, 10/8/03

Responses to Previous Year Reviewer's Comments

Reviewers Comments are all helpful in guiding our project!

1) Too many materials:

We have focused on MFI Al/Si and Si versions of membranes on various substrates. Using for mixed gas & variable temperature studies

Secondary research into Si/Ti membranes for comparison studies, on-going

2) Improved Permeation Rates to Match H_2 delivery Demands:

With improving membranes (synthesis techniques) we are improving our separations values

research direction: increased temperatures and pressures
compare mixed gas results to other supports
new reformate streams

Responses to Previous Year Reviewer's Comments (con't)

3) Membranes tested under realistic conditions:

We have concentrated on mixed gas studies including initial results on

- binary gases (50/50 H_2 with CO_2, CH_4)
- multicomponent mixed gas (76%H_2, 13.6%CO_2, 6.8%CO, 3.4 %CH_4)
- industrial streams; including H_2O, H_2S and N_2
  (we now have ES&H approval for H_2S in our system!)

We will focus on expanding this field

Future Work

- **Remainder of FY04:**

  Temperature: continue to increase on Mesofuel simulated stream
  H_2O: simulated reforming stream with H_2O and begin testing
  Begin mixed gas testing on MFIs w/various substrates

- **FY05:**

  Reconfigure permeation unit for high temperatures (>300°C)
  Testing on different reforming stream compositions
  Testing with industrial on-line hydrogen purification
  - G.E. Dolbear & Associates
  - Mesofuels Inc.

  Investigate H_2S scrubbing with membrane catalytic coatings*