UT-BATTELLE

Microporous Inorganic Membranes for Hydrogen Purification

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Hydrogen Separation Membranes

- **Non-Porous**
  - Palladium based films
  - Ion transport membranes

- **Porous**
  - Ordered microporous membranes (IUPAC Recommendations 2001), e.g. zeolite membranes
  - Microporous membranes

Microporous Membranes

- IUPAC defines micropores as pores smaller than 2nm in diameter
- Generally a microporous membrane is made by applying 1 to 3 thin layers to a porous support
- Porous support can be ceramic or metallic
- Supports can be flat sheets, disks, or tubes
- Microporous layers are generally metal oxides, and are often silica

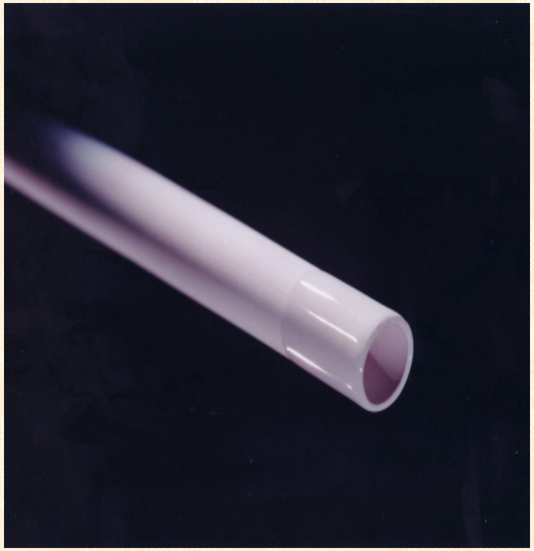
Supports

- Tubular supports allow scale-up using tube and shell configurations to make large multi-tube modules.
- Metal support tubes are easier to install into modules.
- Metal supports are more robust and are not prone to catastrophic failure like ceramic supports
- Metal supports have the potential for thermal expansion mismatch problems.

Photograph of an industrial system based on Pall's AccuSep™ inorganic membranes

Supports Can Be Made From Metals Or Ceramics

Photograph of an aluminum oxide tubular support showing ends sealed using glass glaze. Non-porous ends can be attached using metal to ceramic brazing technology.



Photograph of a stainless steel supported hydrogen membrane with non-porous ends to facilitate sealing into membrane module

Microporous Membranes

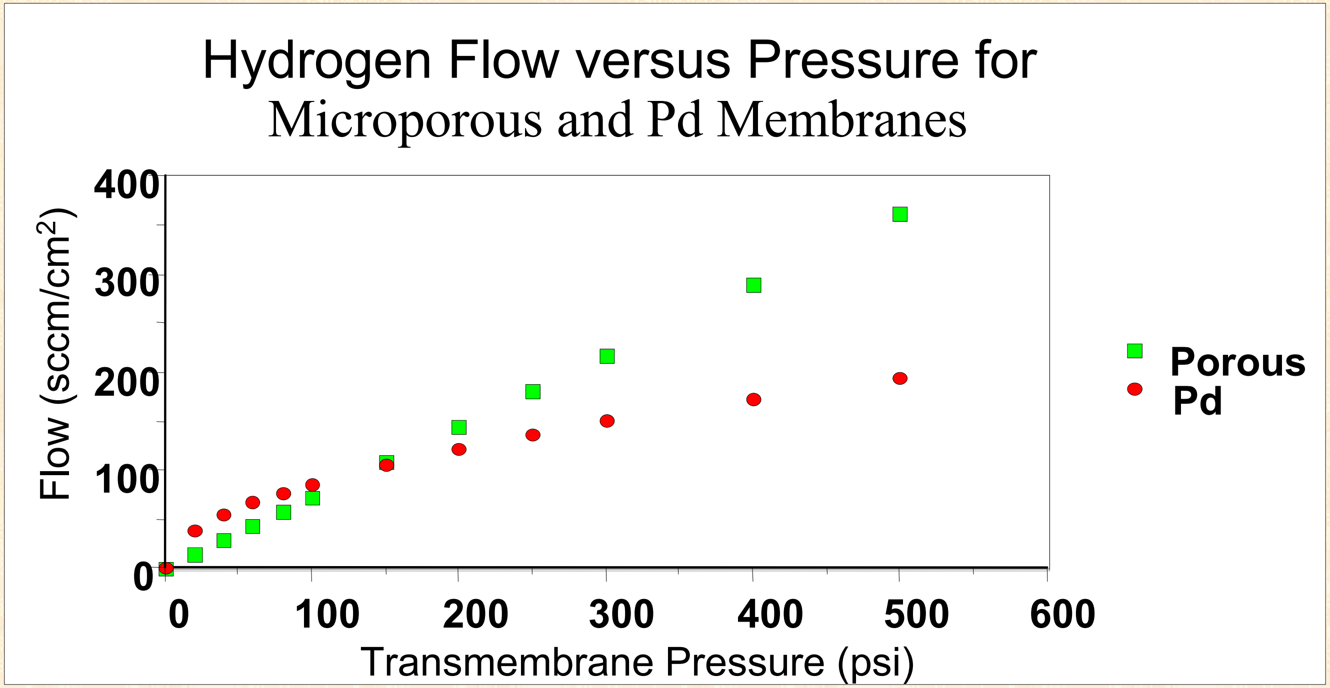
IUPAC defines micropores as pores smaller than 2nm in diameter. However, in order to efficiently separate hydrogen, pores must be less than 1 nm.

Gas	Molecular Diameters (nm)*
Hydrogen	0.283
Nitrogen	0.380
CO_2	0.399
Carbon Monoxide	0.394
Propane	0.512

*From Lennard-Jones force constants as determined from viscosity data

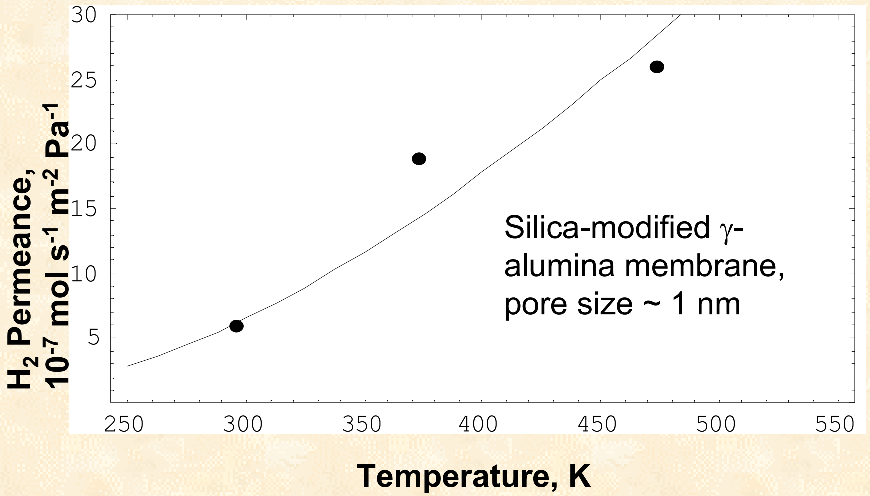
Performance Advantages

- Transport is by molecular gas diffusion which is not limited by solution diffusion and ionization kinetics
- Flux is proportional to transmembrane pressure ΔP. In Pd membranes, flux is proportional to square root of ΔP.

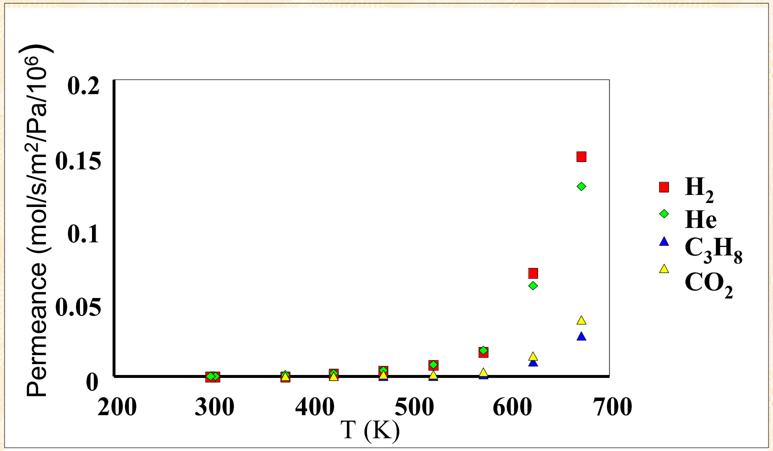


High Temperature Advantage

Permeance of hydrogen has been shown to increase rapidly as the temperature is increased.



R. J. R. Uhlhorn, K. Keizer, A. J. Burggraaf, J. Membrane Sci. 66 (1992) 259-287.



B.L. Bischoff, et. al, from Proceedings of 8th International Conference on Inorganic Membranes, (2004), 167-170.

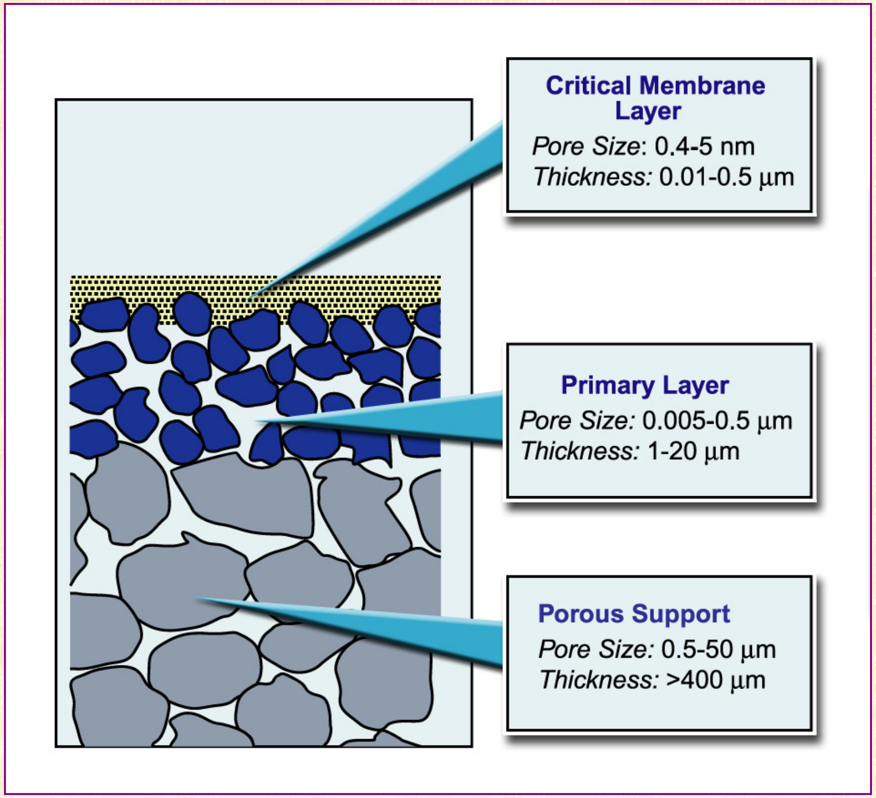
Materials Advantages

- Materials choice is not limited
  - Non-porous membranes require materials permeable to hydrogen but impermeable to other gases.
  - Zeolite membranes have limited materials selection to form ordered pore structure.
  - Materials can be chosen to be compatible with operational environment.
- Materials are not limited to exotic materials and thus manufacturing costs are much less.
- Membranes can operate at potentially much higher temperatures approaching 800 °C.
- Because virtually any metal, alloy, or ceramic may be used, materials compatibility with feedstocks/operating conditions/contaminants is not a major issue. Tars and oils could be problematic as a result of plugging.

Disadvantages

- Because a perfect membrane having discrete pore size is impossible to fabricate, infinite separation factor is unachievable. Separation factors of 100 have been achieved.
  – Single stage purity would be 99% with a separation factor of 100.
  – May require several stages to achieve desired purity. Two stages would result in 99.99% purity.
  – Hybrid systems (membranes + PSA) may be needed to achieve higher purity required for PEM fuel cells.
- Over-sized pores are a common defect and require additional R & D to eliminate.

Typical Properties of Microporous Membranes



Critical Membrane Layer

Separative layer, typically metal oxide including silica, alumina, etc.

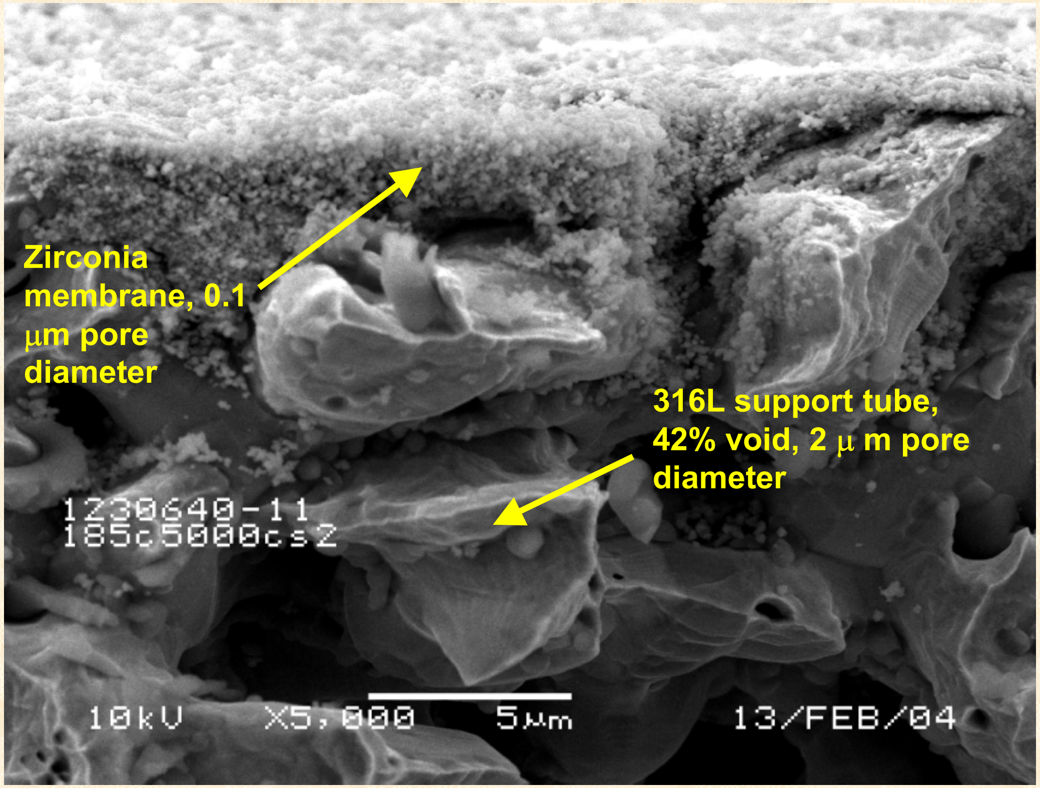
Primary Layer

Needed to bridge between support and separative layer.

Porous Support

Metal or Ceramic with pore size from 1-20 µ

Thin Separation Layer Allows High Permeance of Fluids Through Small Pore Membranes

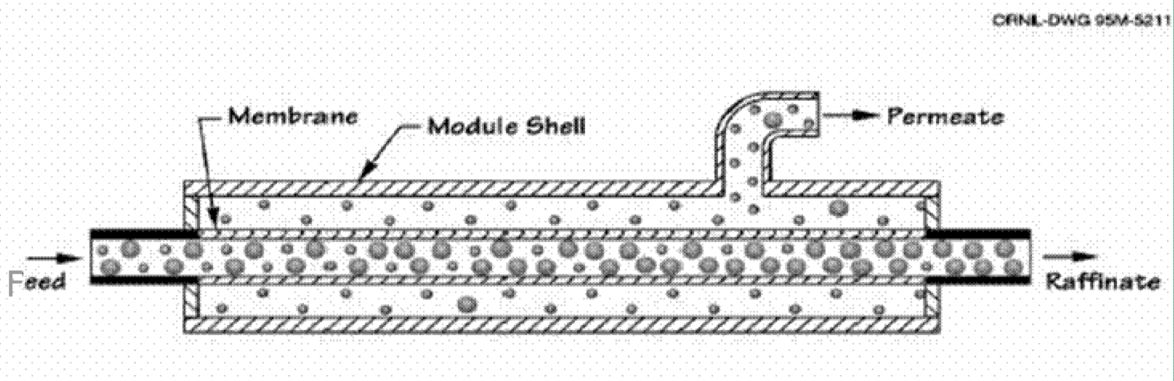


Performance of Microporous Membranes

Permeance Range: 1×10^{-8} to 1×10^{-6} mol/m^2/sec/Pa

Typical Separation Factors: 5 to over 1000 for H_2/CO_2

Most of the R & D in microporous membranes utilizes a separative layer made of silica. Silica membranes are stable in the presence of steam up to 500 °C.

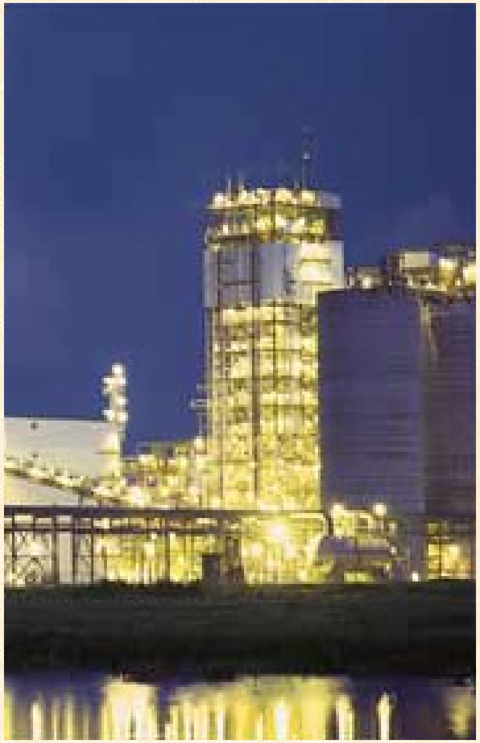


Separation Module Using Molecular Sieve Membrane to Separate Gases

Applications for Microporous Membranes

Reformed natural gas
Coal gasification
Refinery purge gases
Hydrogen separation in biomass derived H_2
Thermochemical cycles
High-temperature electrolysis

Conventional Hydrogen Production Plant



Coal Gasification Plant

Current State of Technology

•Inorganic membranes and filters are currently being commercialized by several companies including Ceramem and Pall Corporation. However, microporous hydrogen membranes have not yet been commercialized for large industrial use.

•Research on microporous membranes is being conducted at Air Liquide and Toto (Japan) and several government labs and universities, including Sandia National Laboratory, Virginia Tech, University of Wisconsin, and University of Twente (Netherlands).

•Current development is directed to production of hydrogen via coal gasification, but tests have only been performed on laboratory mixtures.

Current Status vs. DOE Targets

DOE Fossil Energy (Hydrogen from Coal) Hydrogen Separation Technical Targets

	Microporous	Membrane 2015 DOE Targets
Cost	<$100/ft^2	<$100/ft^2
Flux	> 150 scfh/ft^2 at 300 °C and 100 PSI ΔP.*	300 scfh/ft^2
Operating Temperature	Tested in lab up to 700 °C with pure gases	250-500 °C
Purity	99%	99.99%
Durability	Tested in lab for less than 1000 hours**	> 10 years

Also, must be resistant to S and CO able to operate at up to 1000 PSI

*Separation factor is generally inversely proportional to flux.

**Other inorganic membranes have been in use for over 40 years (350K hours).

Commercial Potential and Hurdles

•Microporous membranes may be used to separate hydrogen from the hydrogen reforming product stream or a membrane reactor that incorporates the membranes and shift catalysts in a single unit may be used to effect the production and separation/purification in a single concerted mechanism.

•A report by Parsons Infrastructure & Technology Group determined that there is a great potential to achieve a single-unit process by incorporating the shift catalyst into the membrane unit.

•The combined low-cost fabrication of the microporous membranes with the high flux and high separation factors make the microporous membranes very favorable economically.

•Microporous membranes have yet to be tested under industrial conditions for extended periods of time.

Key Hurdles to Overcome

- Over-sized pores are a common defect and require additional R&D to eliminate.
  - Higher quality support materials with a more uniform pore size and less surface roughness should improve the quality of the intermediate layer.
  - Improvements to membrane fabrication are key in controlling pore-size and pore-size distribution
- Improvements in fabrication process to optimize flux and selectivity are needed.
  - Need to fully understand thermally activated diffusion through extensive physical characterization of the membrane and flow properties of different gases under ranges of temperatures. A better understanding will allow a tailoring of the pore size to get both maximum flux and selectivity.
- Thermal stability
  - Long-term testing under industrial conditions are needed to guide membrane fabrication and materials selection

Acknowledgments

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