Porous Alumina Tubular Supported Ultra-thin Pd Membrane

Dan Edson, PhD
MetaMateria Partners
Columbus, OH

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Outline

- Overview
- Background of hydrogen program
- Description of forming method
- Approach for multilayer membrane
- Properties of supports
- Properties of intermediate layers
- Properties of electroless Pd membrane layer
- Future Work
- Conclusions

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Overview

- This project used capabilities at **MetaMateria Partners** and **Ohio State University** to prepare hydrogen membrane
- **MetaMateria Capabilities**
  - Novel method for preparing porous ceramic support tubes
  - Colloids for preparation of thin film membranes
- **Ohio State Capabilities**
  - Experience with preparation & characterization of thin membranes
- Membrane Developed
  - Uses two thin intermediate layers, a dense, gas-tight palladium membrane layer deposited onto alumina supports via electroless deposition with a thickness of ~250 nm.
  - Measured hydrogen permeability of the composite membrane is $1x10^{-6}$ mol/(m^2•s•Pa) [$6x10^{-4}$ mol/(m^2•s•$Pa^{1/2}$)] at 320°C.

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Background on Work

- Development funded through DOE for commercialization of a high-flux, highly selective hydrogen separation membrane

- Approach combined supported inorganic membrane technology developed by Prof. Henk Verweij and team at The Ohio State University using a planar geometry with a high-quality porous ceramic cathode tubular support and colloids developed by MetaMateria that uses a novel colloidal method (MMCP)
  - Development also uses core technologies at MetaMateria for producing clear nanoparticle dispersions and nanostructured thin films from these dispersions.

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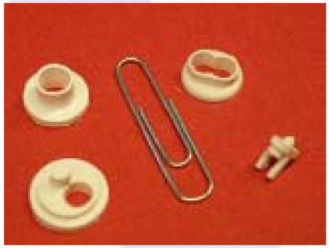
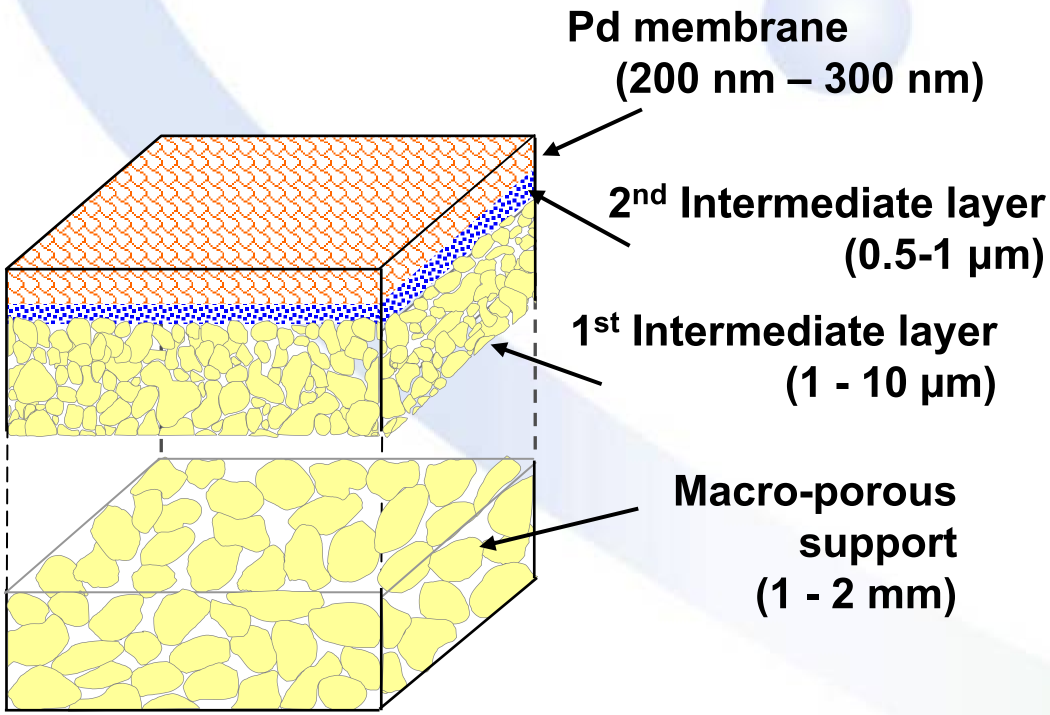
Benefits of MMCP Forming Method

- **Low-cost, low-organic, water-based ceramic forming method (MMCP) used with low-pressure injection molding**
  - Thermo-reversible binder system
    - enables demolding 2-5 minutes following injection
  - 2-3 weight percent total organic content
    - Short debind cycle time
  - Colloidal processing methods improve part uniformity
  - Highly interconnected porosity following drying
  - Binder system is used for several ceramic materials
    - Al_2O_3, ZrO_2, YSZ, LSM, SiC, B_4C, SiO_2
    - Traditional processing parameters
      - pH, surfactants, particle size distributions, sintering aids, etc.
  - Dense or porous ceramic parts can be produced

Examples of MMCP Parts



Multi-layer Membrane Approach



- **Standard architecture** maximizes flux by minimizing thickness of lower-permeability layers
- Subsequent layers must be thicker than largest defect in previous layer
  - Processing control determines attainable performance
- Benefits:
  - Strong carrier
  - Reduced Pd costs
  - Limited metallic inter-diffusion/poisoning
  - High H_2 permeability

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Approach - continued

- Developed a sintered macro-porous (>1 micron; >30% porous) alumina support tube 10 cm in length using MMCP and low-pressure injection molding
- Transfer technology from OSU on using aqueous ceramic suspensions for the intermediate layers
- Use OSU-developed method for deposition of dense, ultra-thin (200-300 nm) Pd membrane layer
- OSU conducted performance testing, which was limited due to time/budget constraints

MMP porous alumina supports

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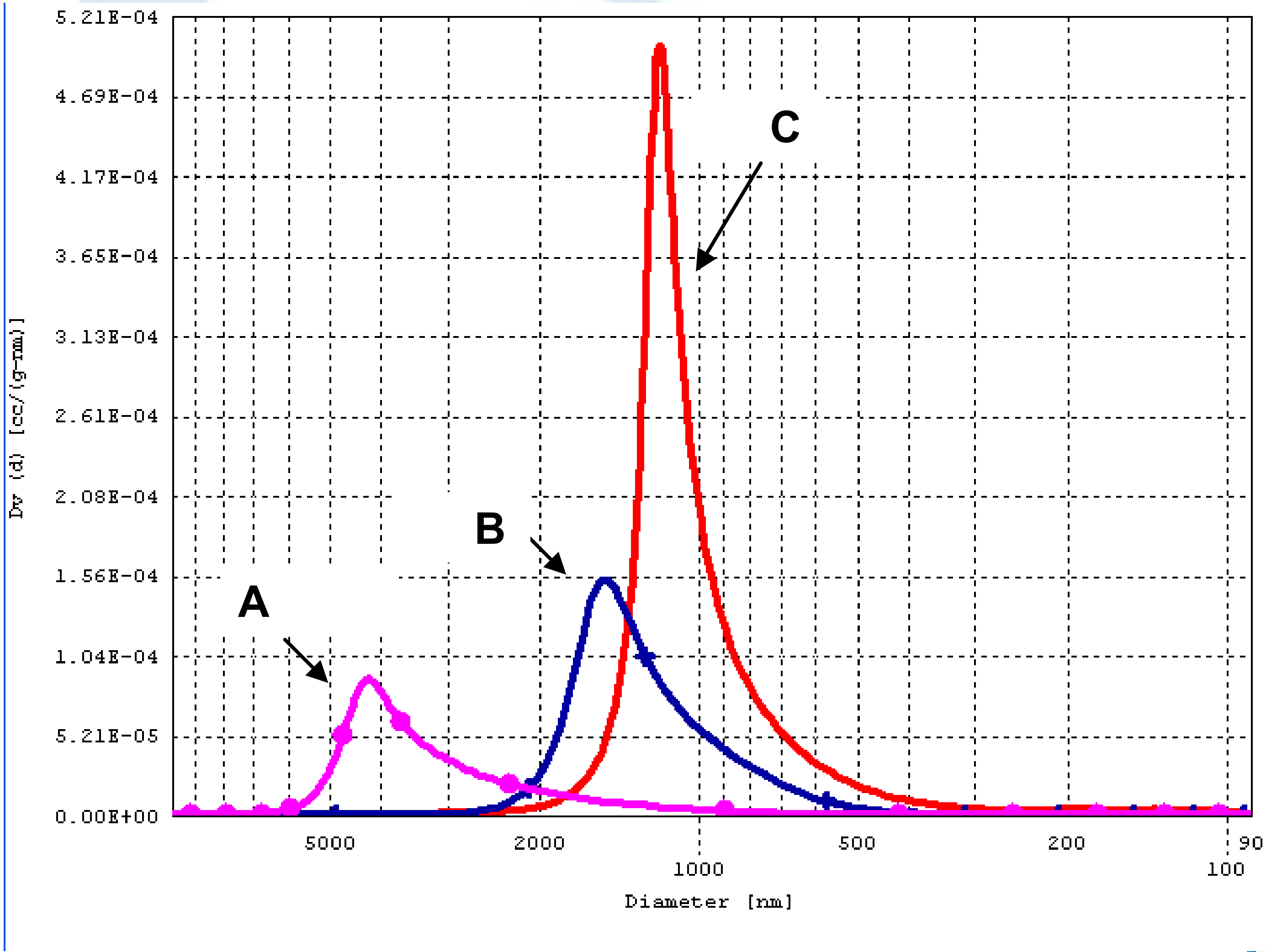
Properties of Supports – Hg porosimetry



Volume of porosity is about 36% in final supports

Pore size can be controlled by MMCP method and exhibits a sharp mono-modal size distribution

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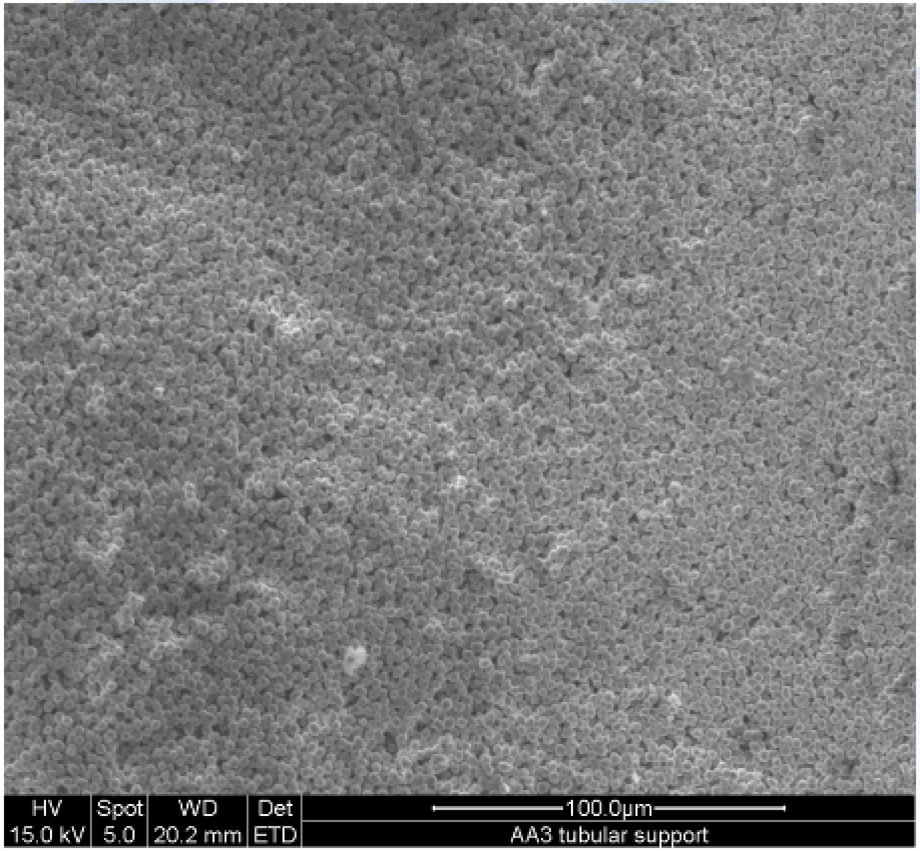
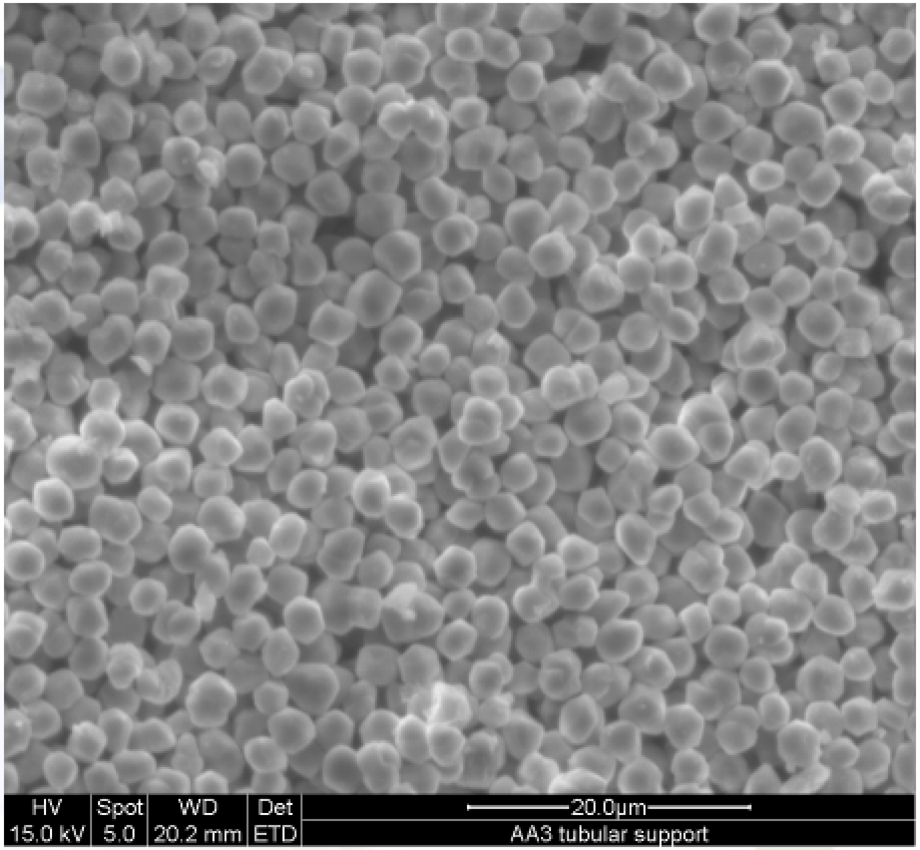
Microstructure of Supports - Fracture





Porosity controlled by particle interstices rather than more exotic pore forming methods to minimize defects which would need to be repaired

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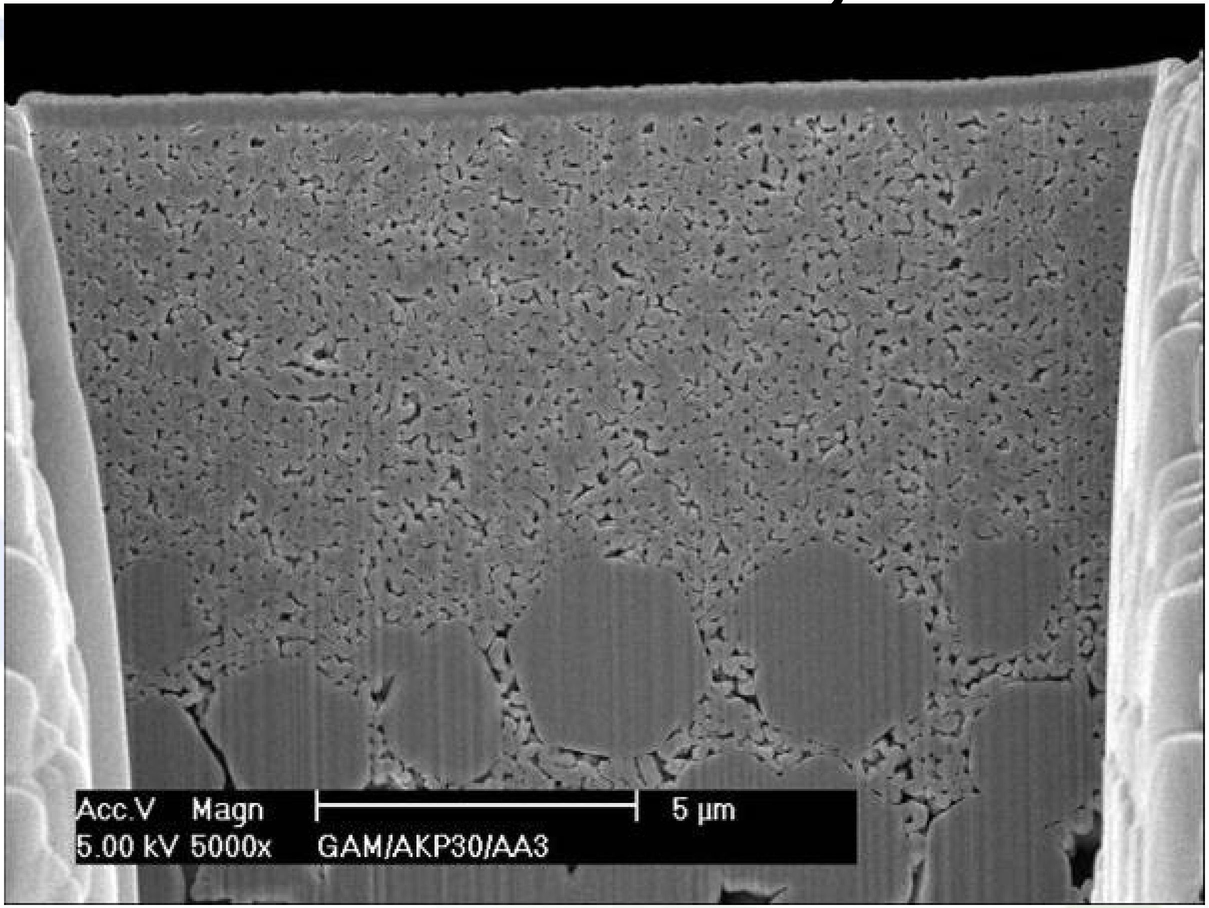
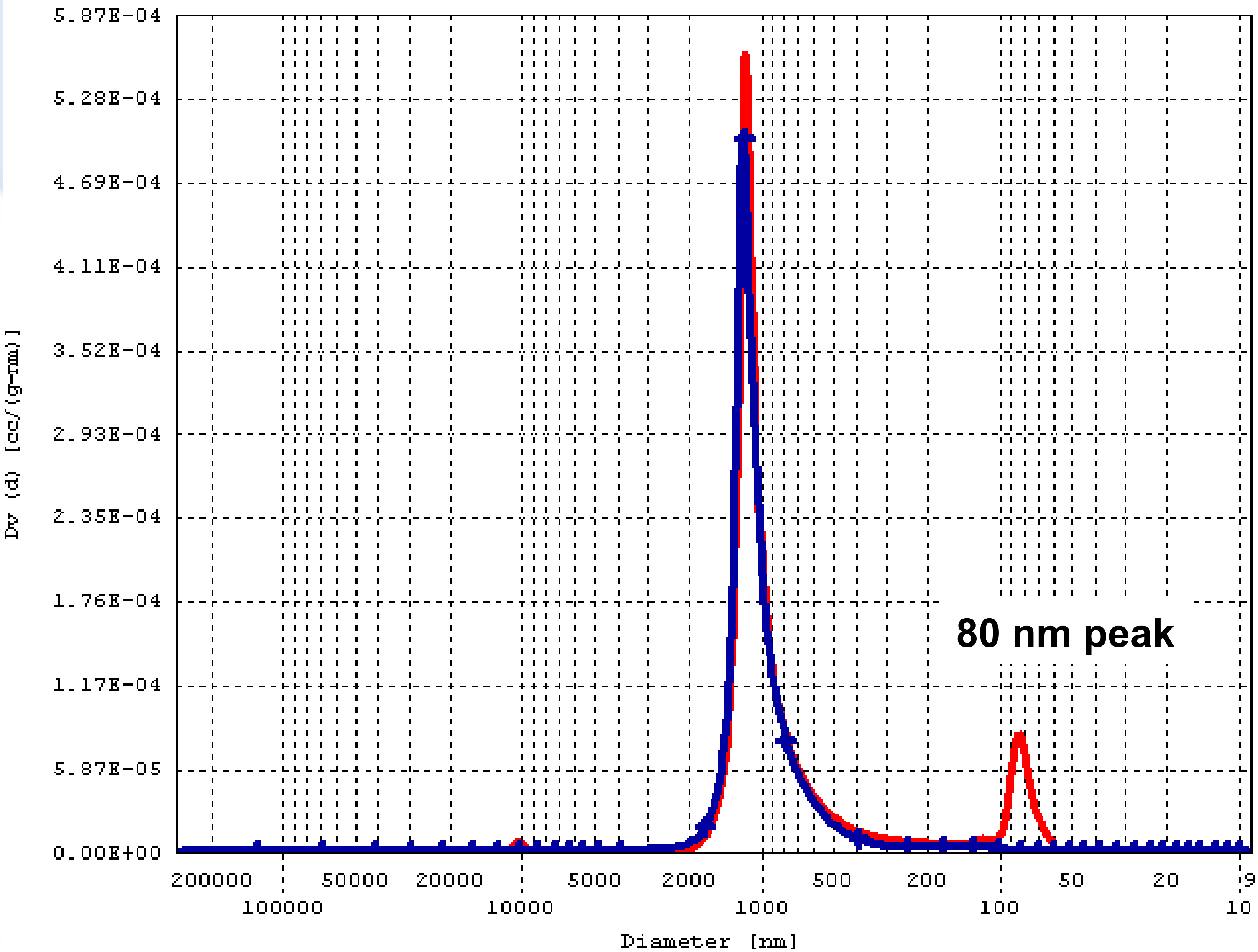
Dip-Coated Intermediate Layers

- Two alumina intermediate layers designed to reduce pore size to 80 nm then 4 nm.
- Thickness of 1st layer about 8 microns
- Thickness of second layer <1 micron

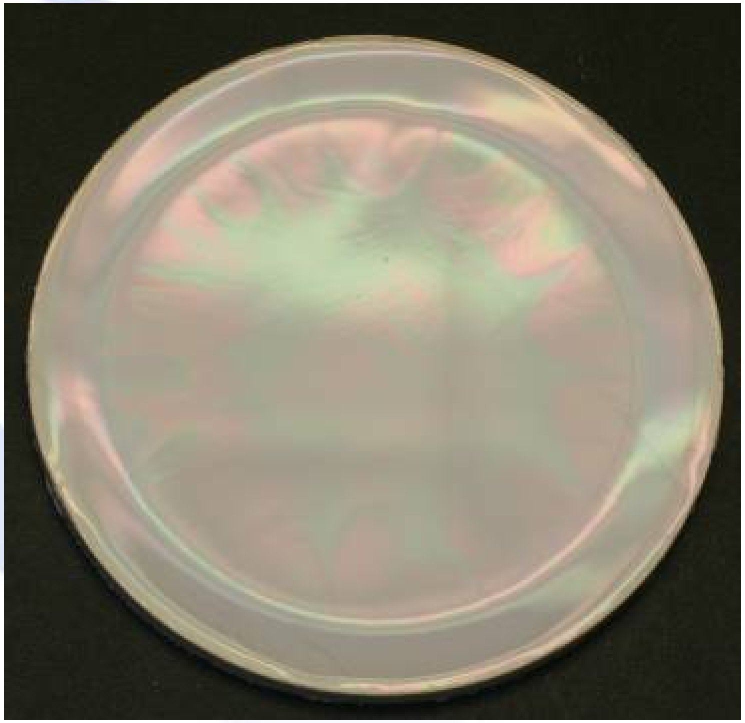


FIB cross-section

80 nm Pore Size in Intermediate Layer

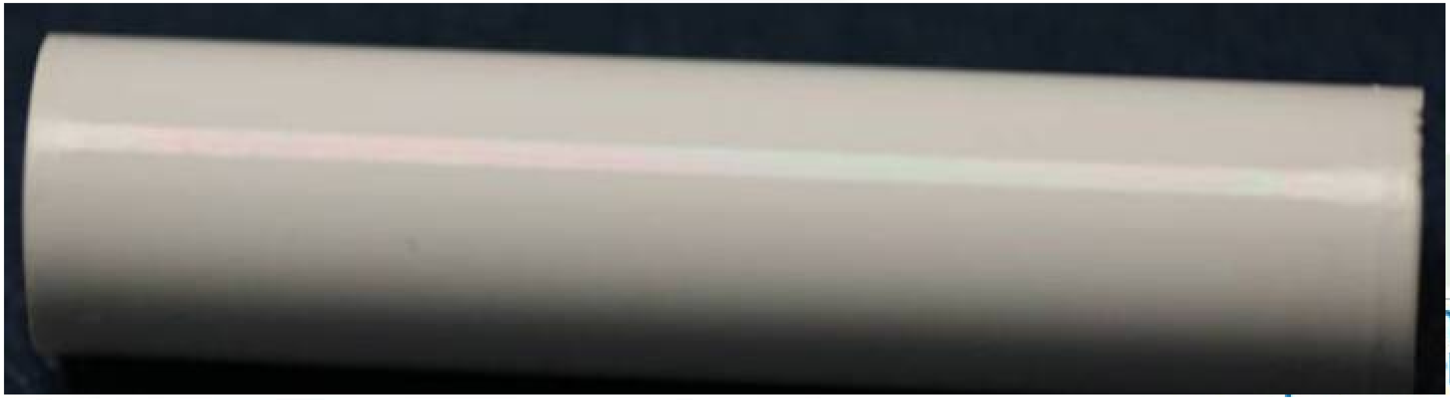


Intermediate Layers on Supports

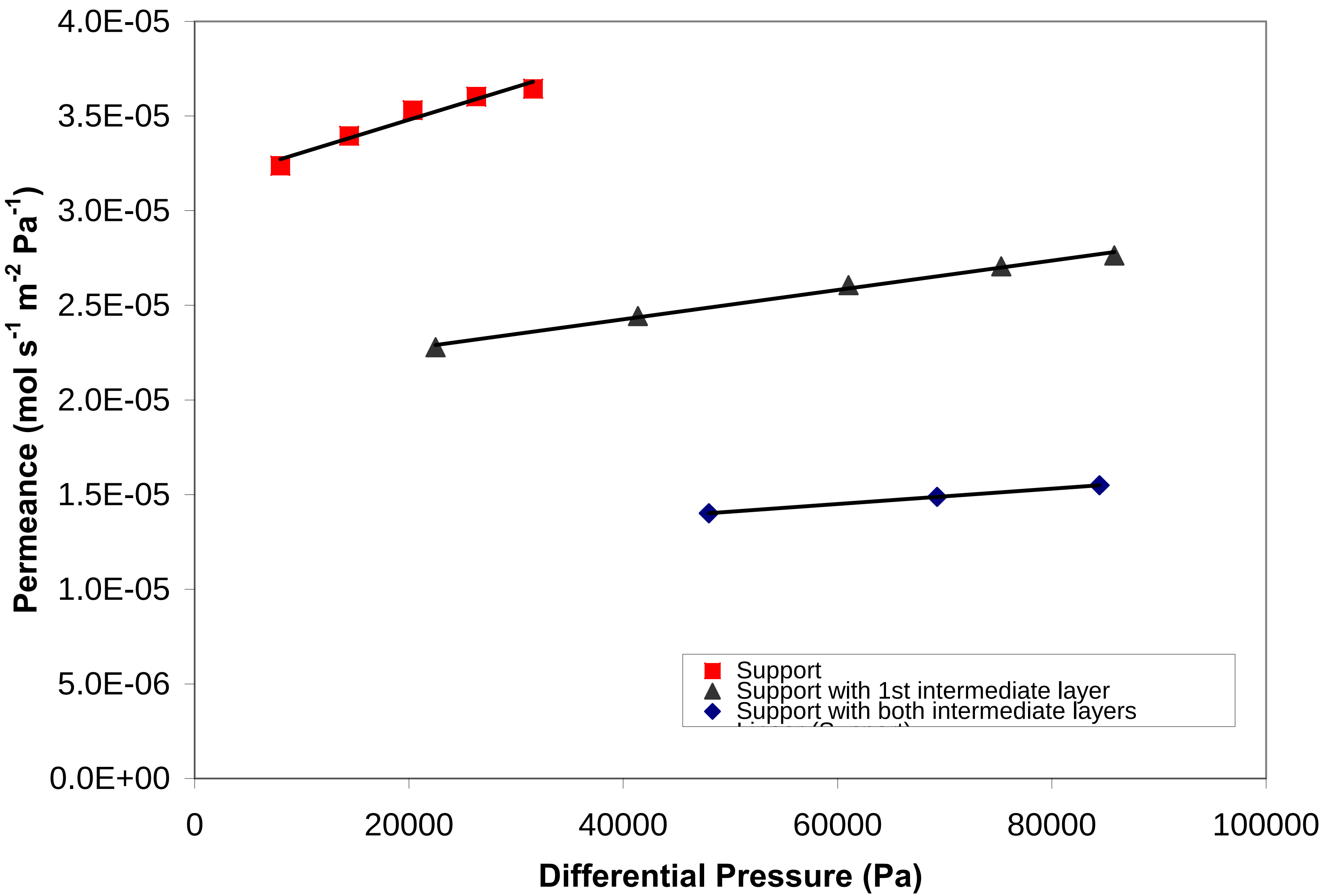


Planar

Tubular

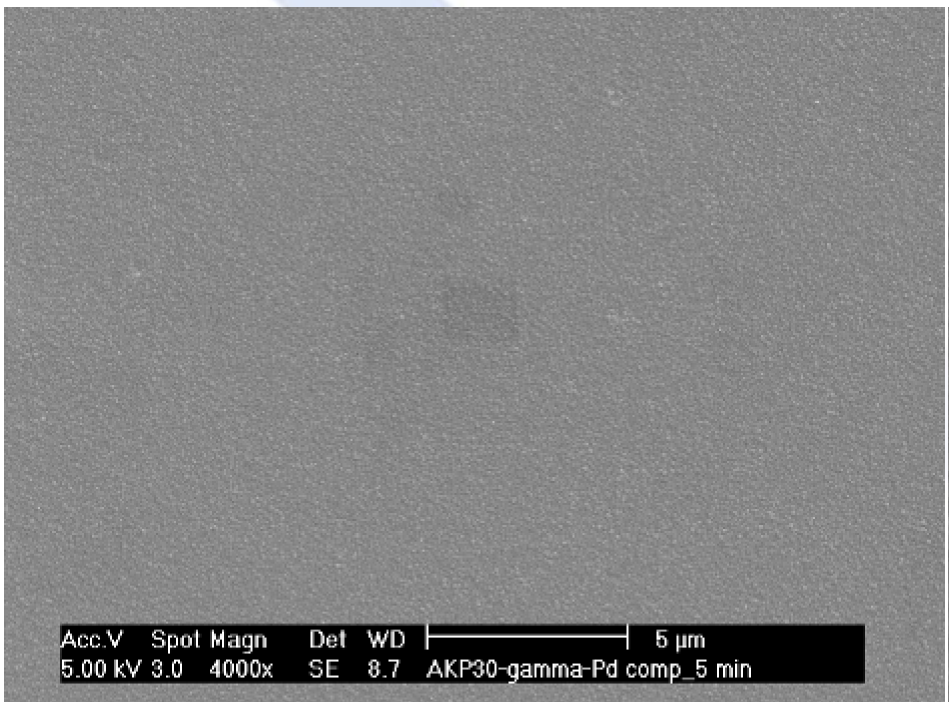


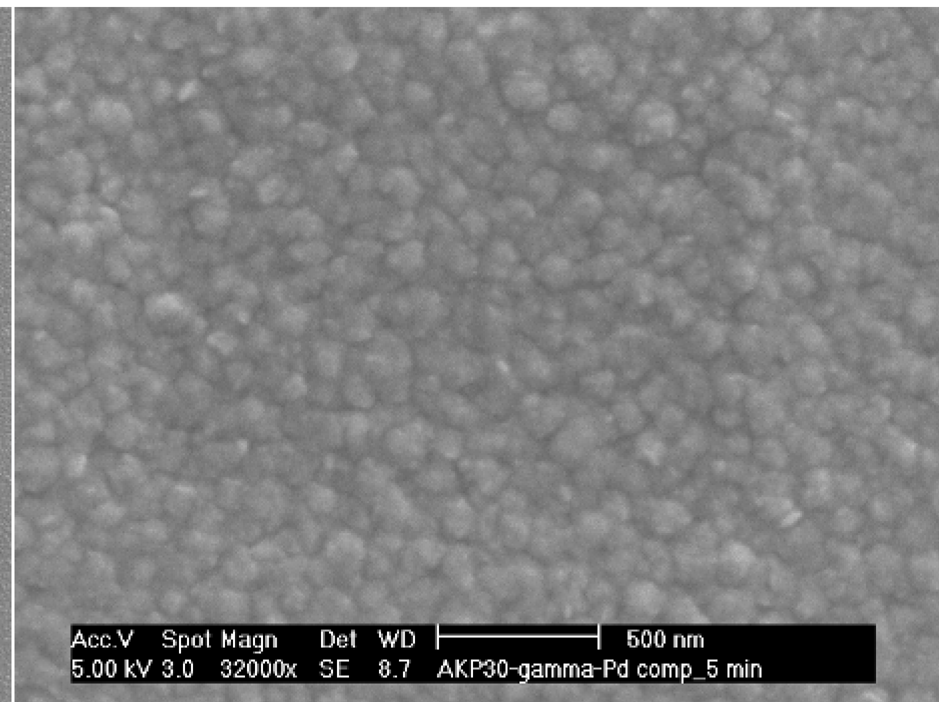
Minimal Impact on Permeability



Patent-Pending Electroless Deposition

- Electroless deposition is a standard method to create a dense palladium membrane layer.
  - OSU developed electroless deposition method for making a continuous, gas-tight palladium layer that develops in 5 to 10 minutes (thickness of 200 to 300 nm)



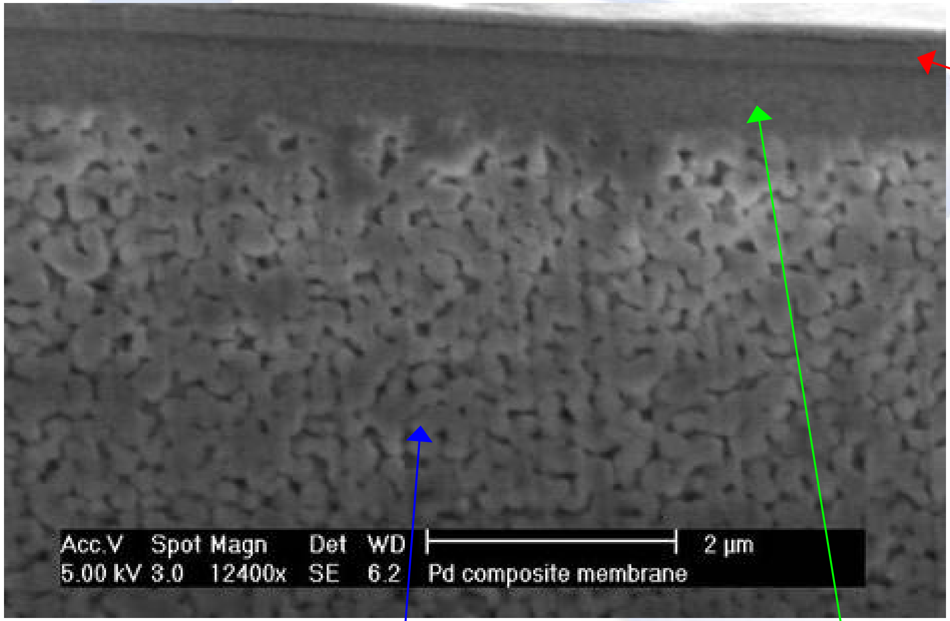


(5 micron bar)

5 minutes for deposition

(500 nm bar)

Pd Membrane Cross-Section (~285 nm thick)

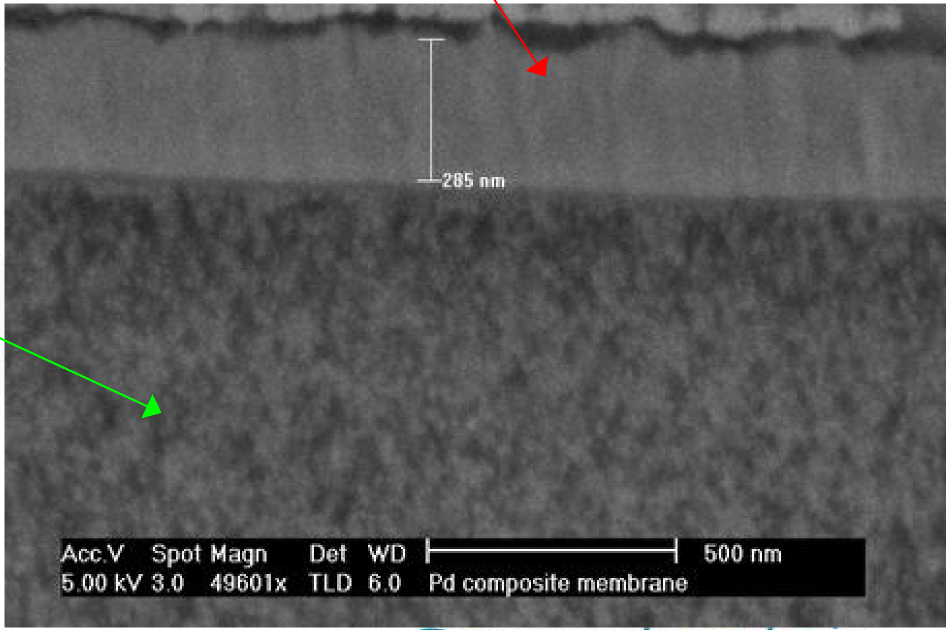


(2 micron bar)

Pd layer

2nd intermediate layer

1st intermediate layer



(500 nm bar)

Photograph of 10 cm Membrane

Glass coatings at ends to improve sealing during testing

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Permeance/Selectivity Data

Structure	Permeance (mol/(m²·s·Pa))			
	H_2	He	Ar	N_2
Support (Room temp)	na	1 x10^{-5}	na	4 x10^{-6}
Support with intermediate layers (room temp)	na	1 x10^{-5}	na	4 x10^{-6}
Complete membrane (200°C)	2 x10^{-8}	1 x10^{-8}	2 x10^{-9}	5 x10^{-9}
Complete Membrane (260°C)	1 x10^{-8}	na	na	na
Complete Membrane (320°C)	1 x10^{-6}	na	na	na

- Best literature value is 9.6x10^{-4} mol/(m^2·s·$Pa^{1/2}$) at 500°C for a membrane on a macroporous stainless steel tube. (Tong *et al*, *J. Mem. Sci.* **260** (2005))
- At 320°C same membrane had permeance of about 3.7x10^{-4} mol/(m^2·s·$Pa^{1/2}$).
- Permeance value of the MMP/OSU membrane at 320°C is 6x10^{-4} expressed in the same units [mol/(m^2·s·$Pa^{1/2}$)].

Looking to the Future

- Hydrogen work on hold while looking for funding partners for this promising approach
- Proposal pending for additional STTR DOE funding
- Investigating alternate industrial funding to further develop porous ceramics and membranes for other water, fluid and/or gas separation applications
- Anticipate that use of Pd-alloys will improve transport values and overcome lifetime issues as reported by others
- Much further testing and development needed

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Conclusions

- Capability to prepare high-quality, porous ceramic tubular supports using low-organic, aqueous-based ceramic processing demonstrated

- Addition of intermediate layers via dip-coating demonstrated to produce graded pore structure which exhibited minimal impact on gas transport properties

- Development and deposition of high-selectivity, ultra-thin Pd membrane
  - Higher performance observed than any other Pd membrane found in literature
  - Gas-tight at RT for nitrogen suggests quality of Pd layer and underlying support layers

- Porous supports useful for wide range of separation applications

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