



Porous Alumina Tubular Supported Ultra-thin Pd Membrane

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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

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 $1 \times 10^{-6} \text{ mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ [$6 \times 10^{-4} \text{ mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa}^{1/2})$] at 320°C.

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.

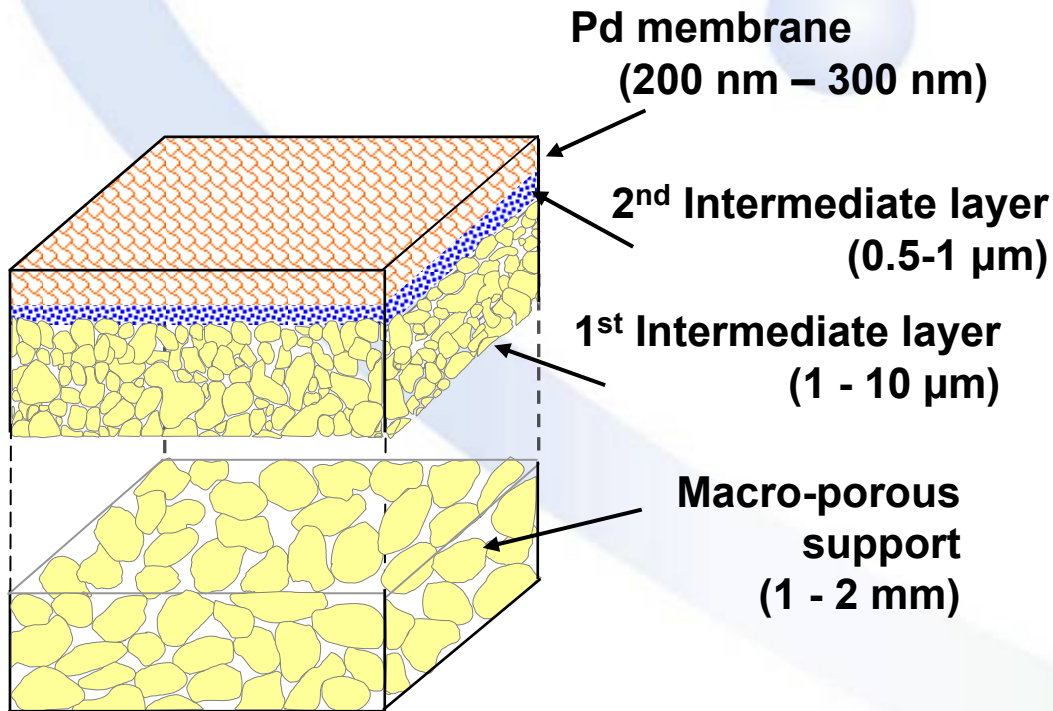
Benefits of MMCP Forming Method

- 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 H₂ permeability

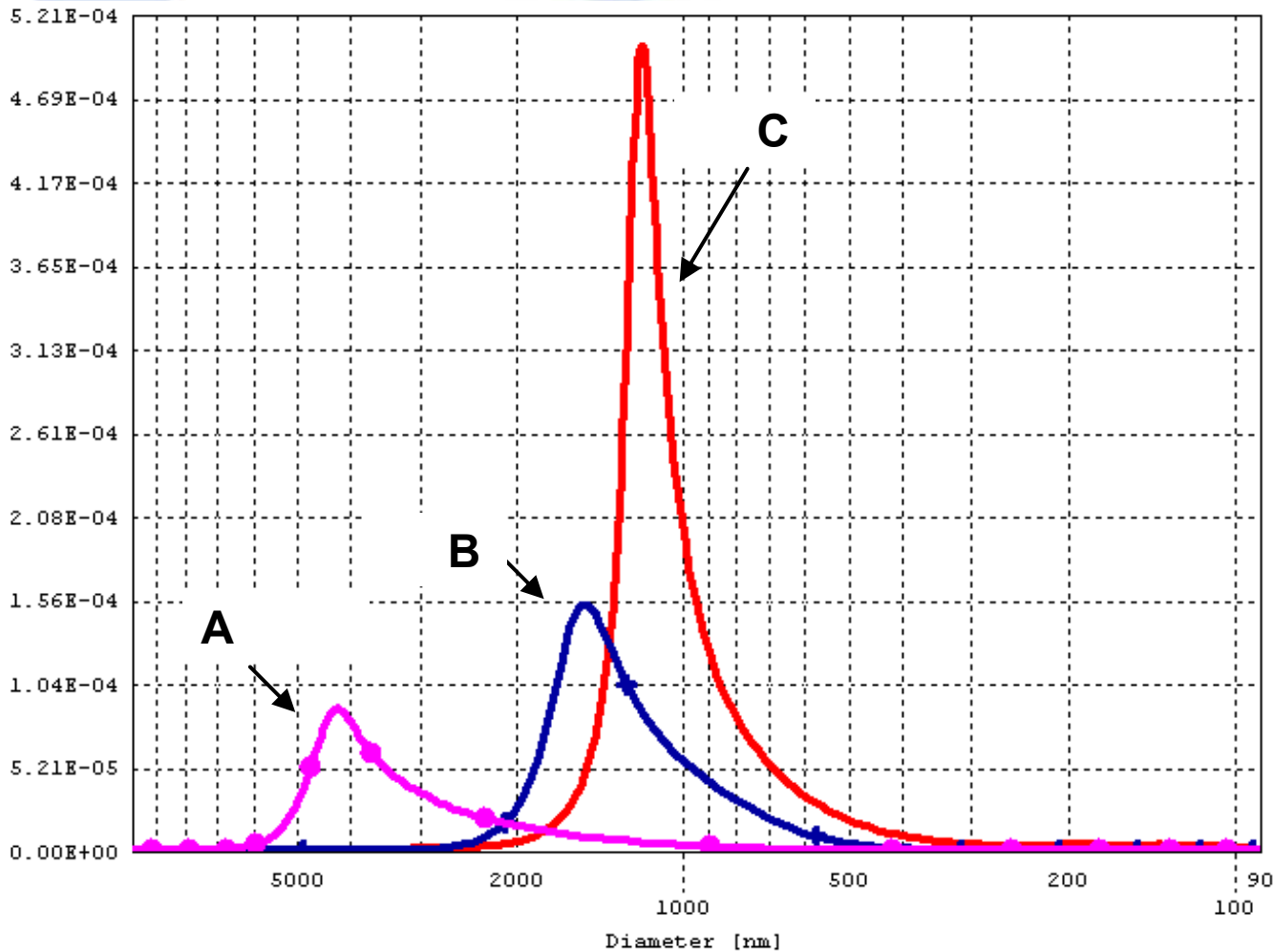
Approach - continued

- 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

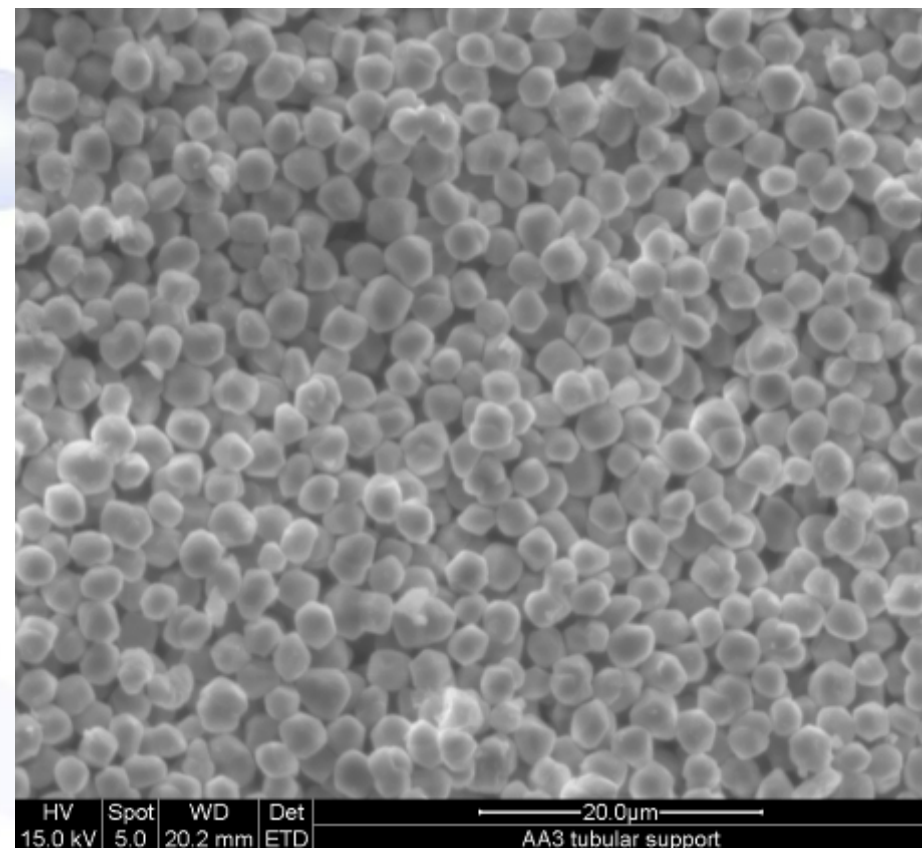
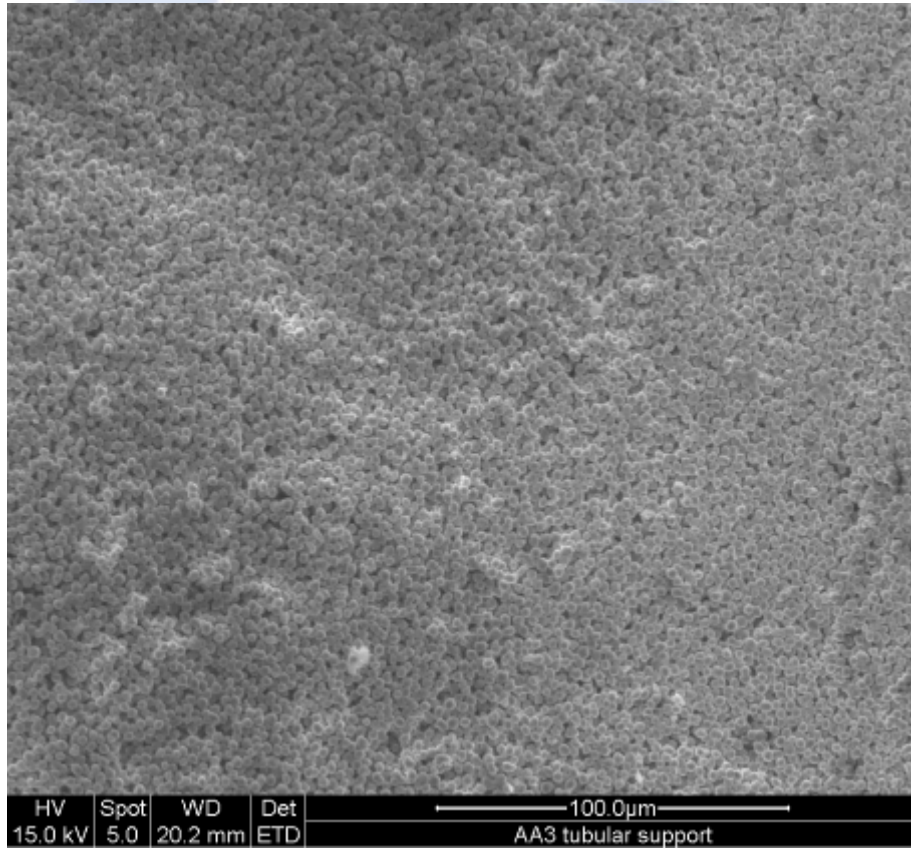
Properties of Supports - Hg porosimetry



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

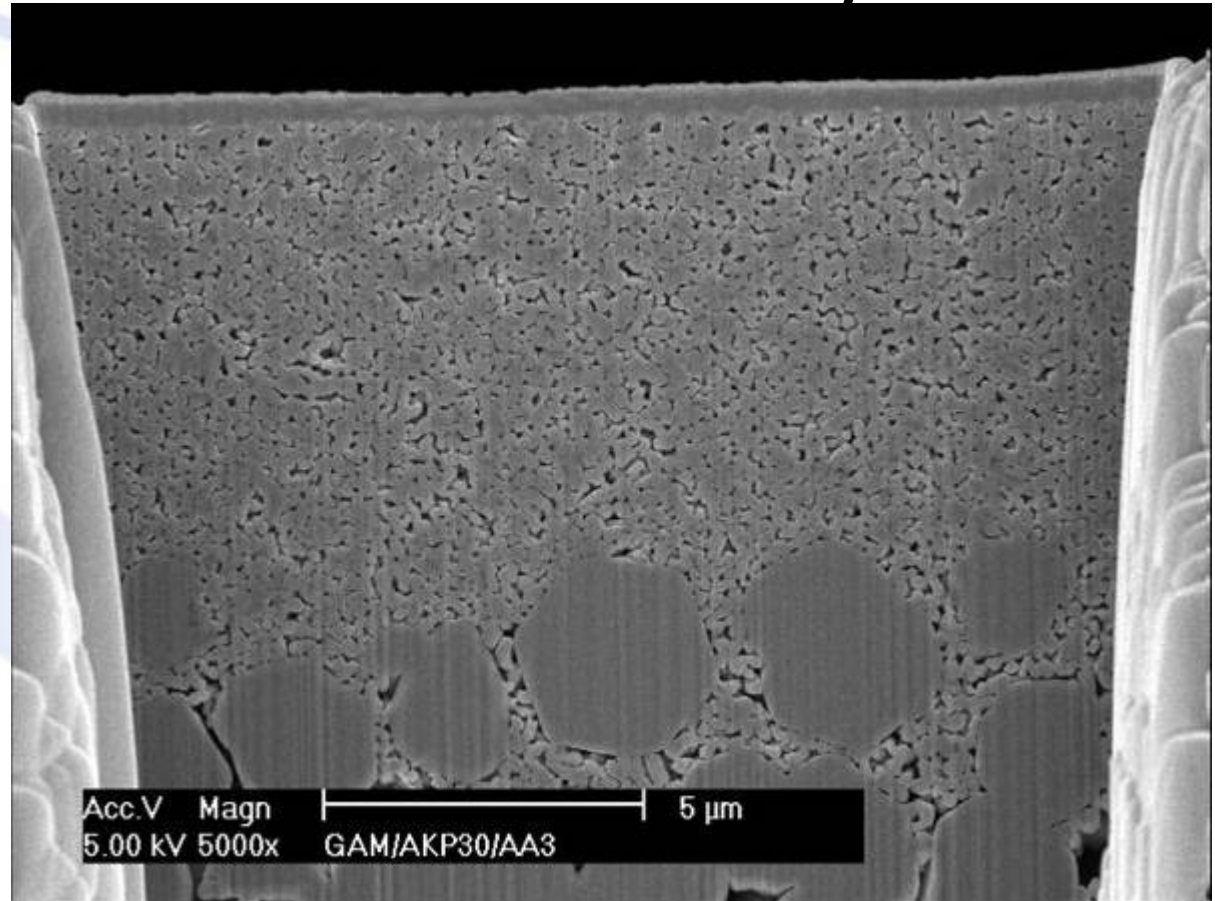
Microstructure of Supports - Fracture



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

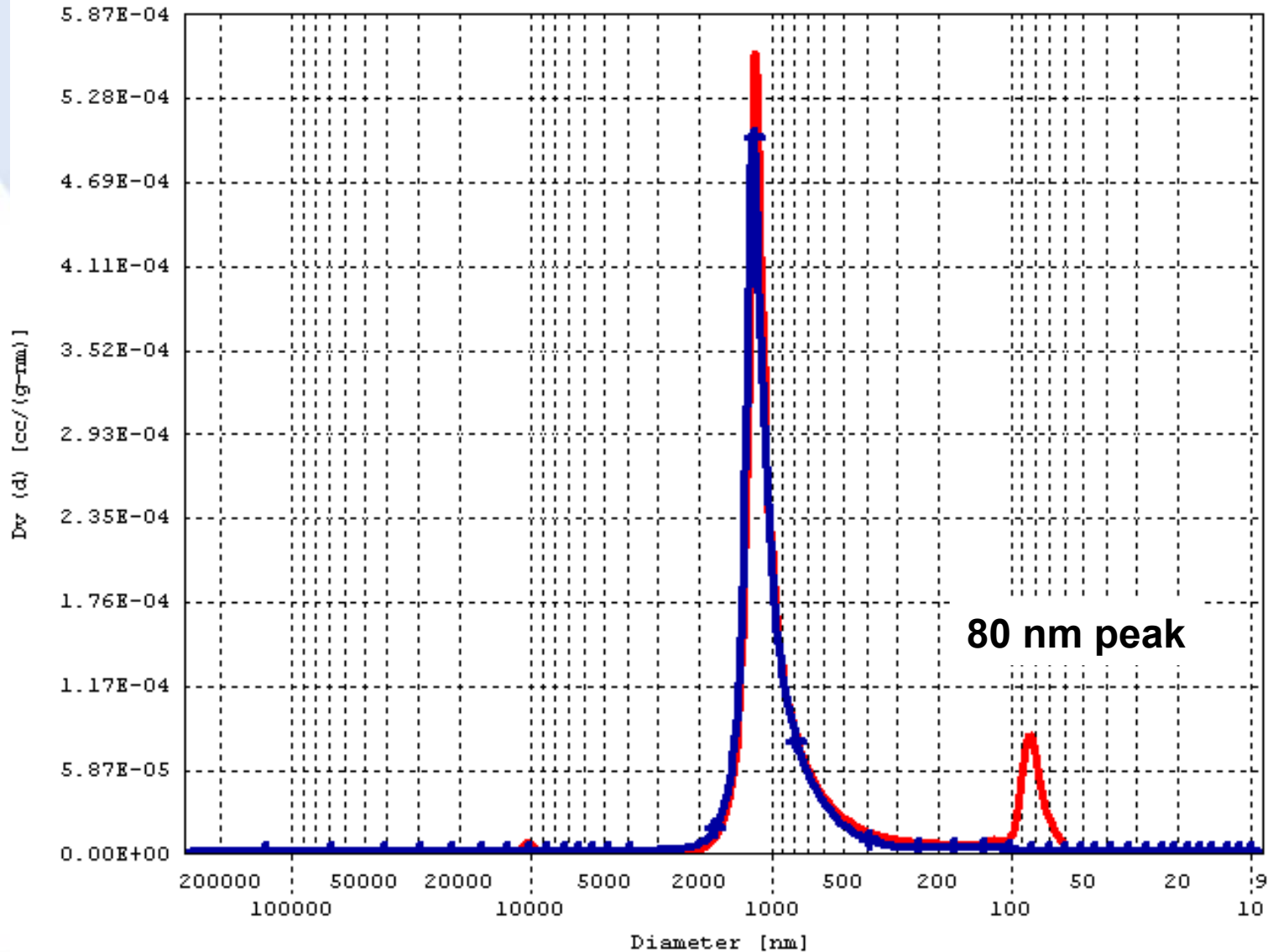
Dip-Coated Intermediate Layers

- 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

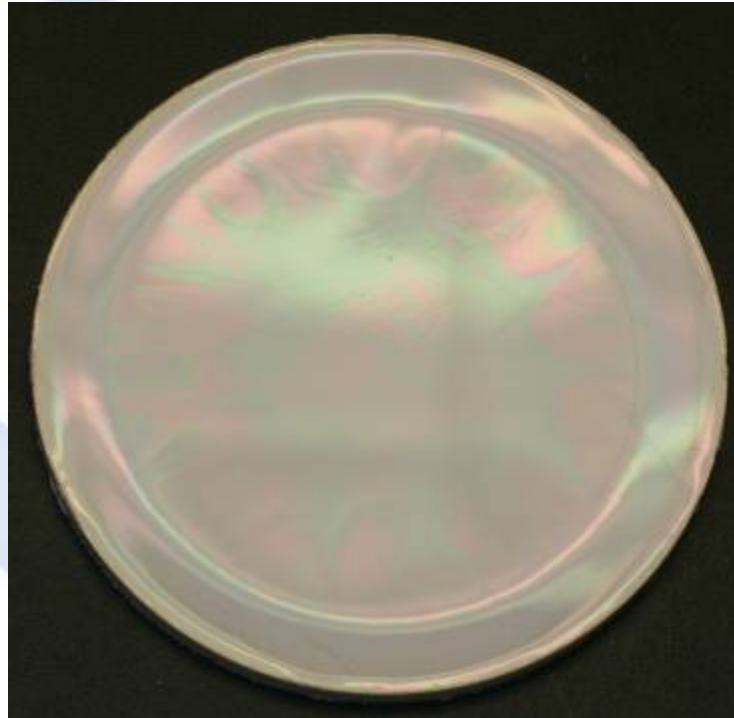


FIB cross-section

80 nm Pore Size in Intermediate Layer



Intermediate Layers on Supports

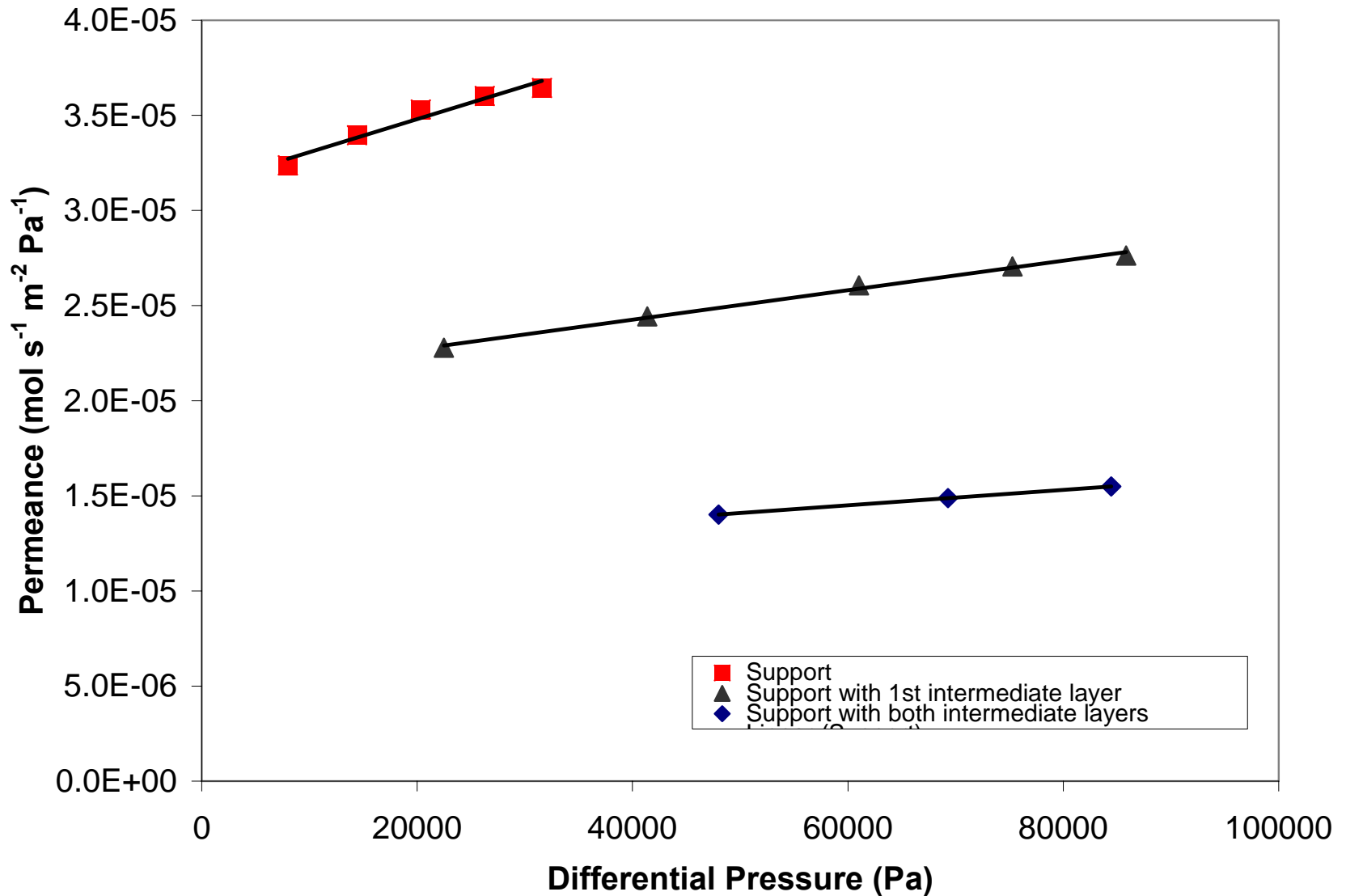


Planar



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)




Acc.V Spot Magn Det WD | 5 μ m
5.00 KV 3.0 4000x SE 8.7 AKP30-gamma-Pd comp_5 min

(5 micron bar)



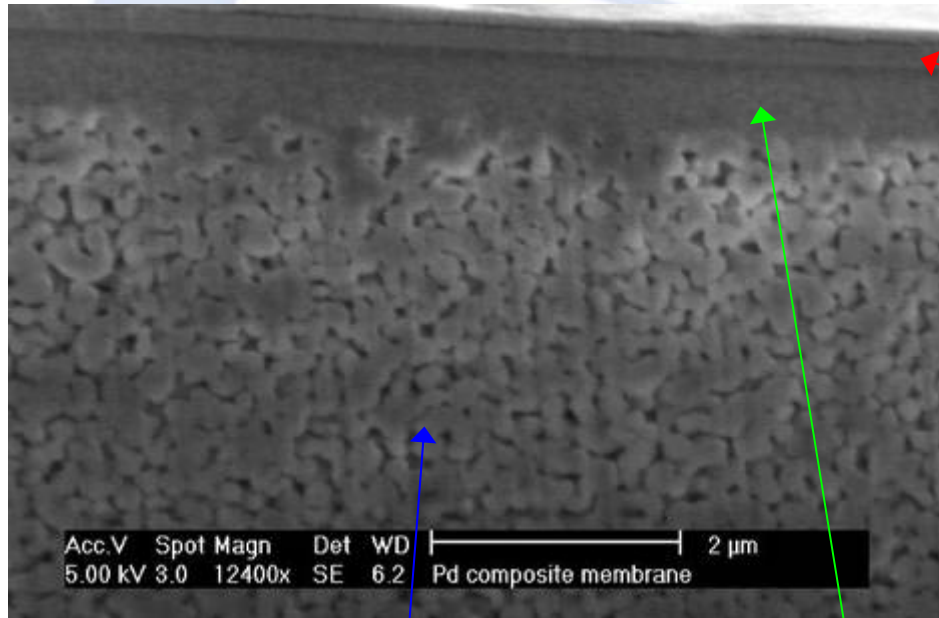
Acc.V Spot Magn Det WD | 500 nm
5.00 KV 3.0 32000x SE 8.7 AKP30-gamma-Pd comp_5 min

5 minutes for deposition



MATAMATERIA
(500 nm bar)

Pd Membrane Cross-Section (~285 nm thick)

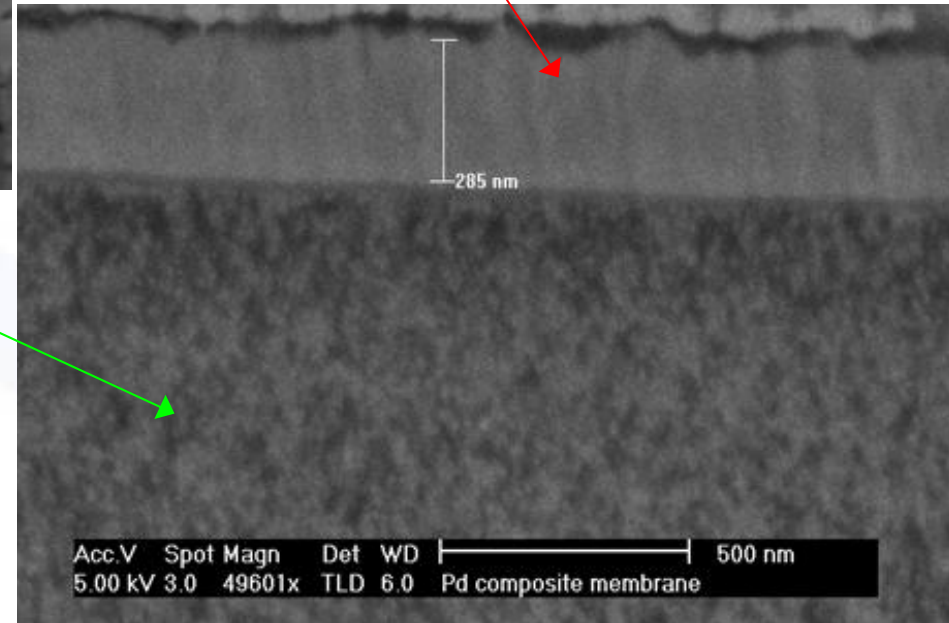


(2 micron bar)

2nd intermediate layer

1st intermediate layer

Pd layer



Photograph of 10 cm Membrane



Glass coatings at ends to improve sealing during testing

Permeance/Selectivity Data

<u>Structure</u>	Permeance (mol/(m ² ·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/(m²·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/(m²·s·Pa^{1/2}).
- Permeance value of the MMP/OSU membrane at 320°C is 6x10⁻⁴ expressed in the same units [mol/(m²·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

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