Ultra-thin supported inorganic membranes

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Structure of this talk

Description/definitions inorganic membranes

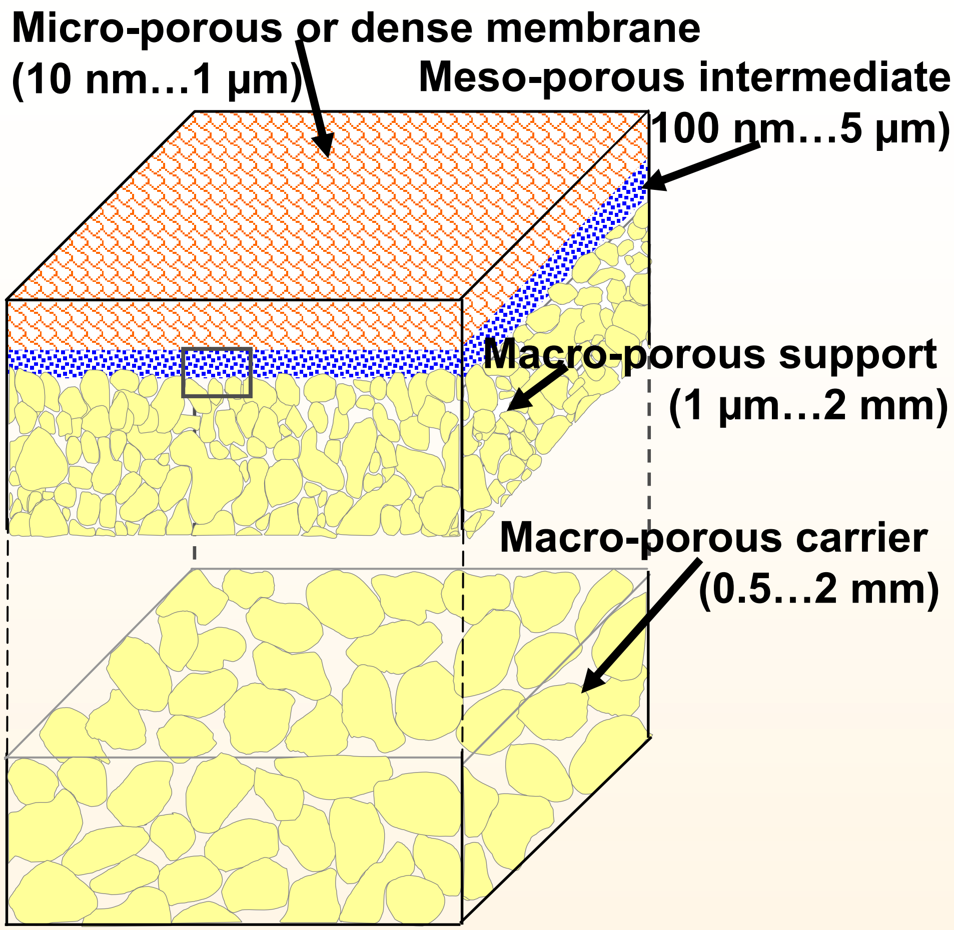
Long-term performance goals

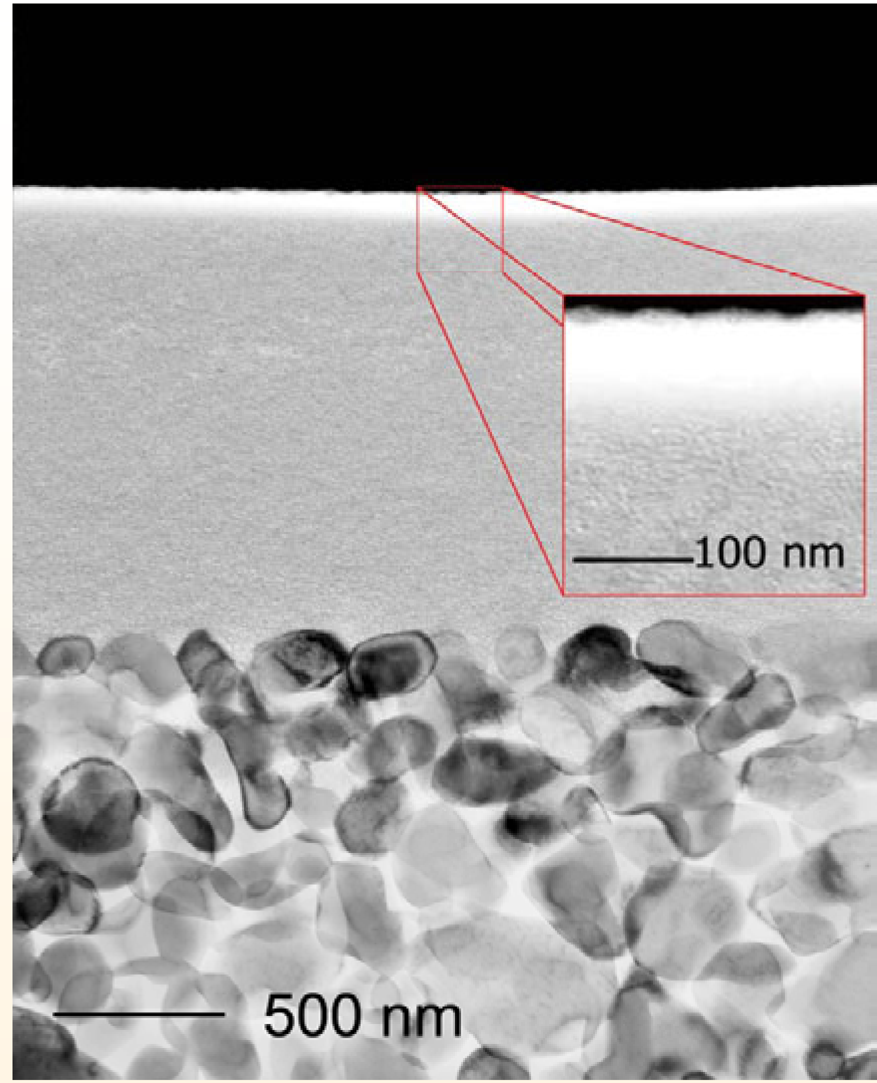
Micro-structural optimization <500 nm thickness

Examples

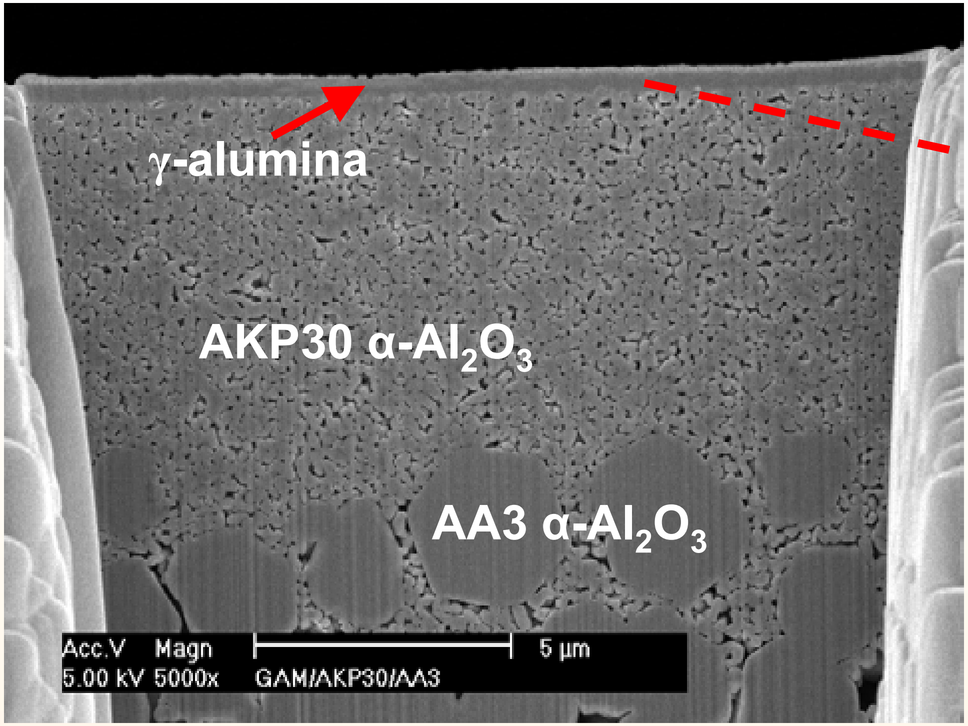
Conclusions and perspectives

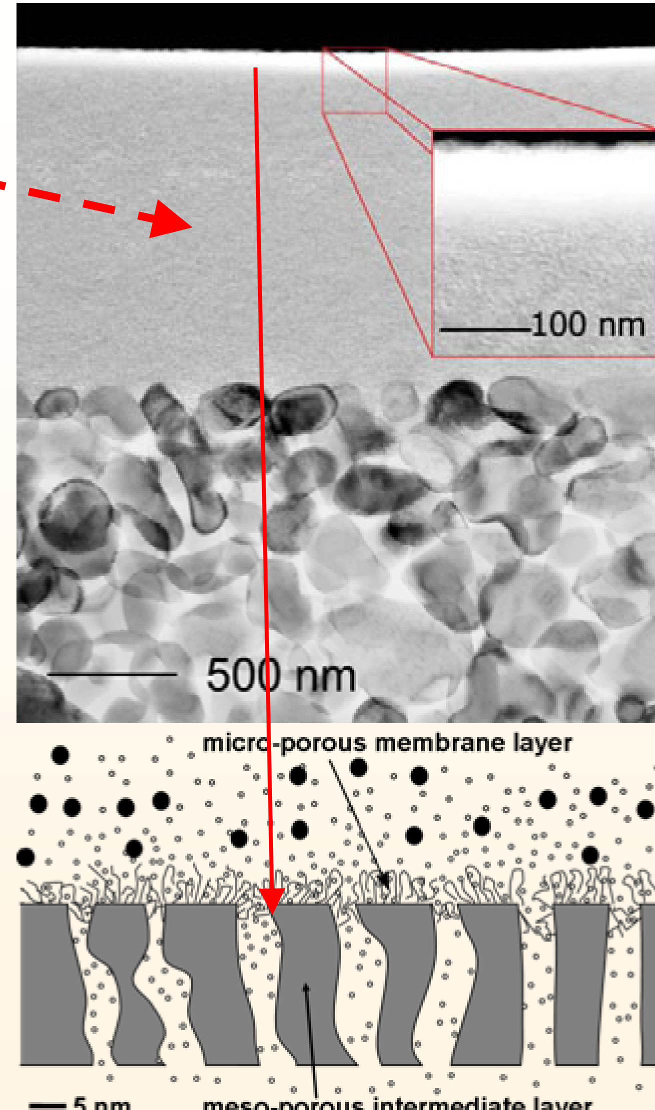
Example of designed and real structures





Four different length scales





2 mm thick multilayer structure for H_2, CO_2, air, water separation

Stretch goals

1. ***g-Permeance*** $k/\Delta p > 10^{-5}$ mol/(m^2·s·Pa); $\alpha > 100$
2. **Degradation** <50% **over** >10.000 **hrs**
3. **Production yield** >90%; **reproducibility** <10%
4. **Membrane surface density** >100 m^2/m^3
5. **Cost price** <\$500/m^2.
    - **Structural components: earth-abundant elements**
    - **Thin layer manufacturing time/step to <1'**

Options for H_2-permeable membranes

Material:	Sol-gel SiO_2	Pd-alloy	MIE (H^+,e^-)	Zeolite
Permeability	High	High	Low	High
Selectivity	Medium	High	High	Medium
Stability	Poor?	Poor?	Good	Excellent

General approach

Find very thin *selective* (1 nm…1 μm) film

- Identify *mechanism* for selective transport

Find very strong, smooth, permeable multi-layer

- No surface defects, (<1 nm…<1 μm) roughness
- *Design*: analysis/measurement transport
- Intermediate layers as thin as possible
- Carrier as thick/strong as possible

Deposit film defect-free on multi-layer

Make sure it can be **dirt-cheap**

- But do no work with dirt!

Why multi-layer defect control

Deviation from *quasi-homogeneous* structure

Connected pore defects:

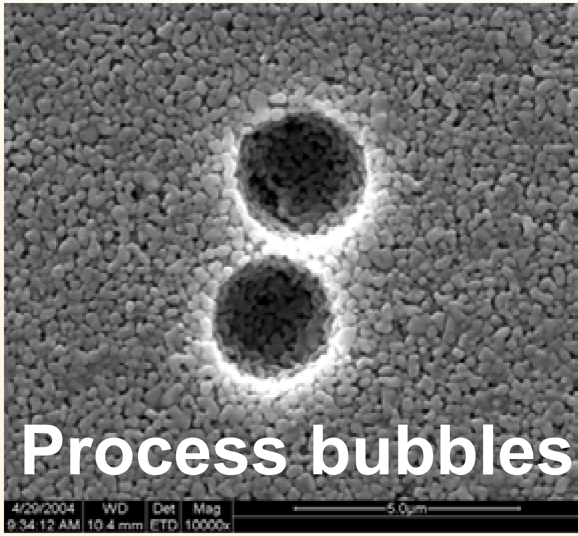
- ↓ selectivity

Surface defects:

- ~ in the next layer

All defects:

- ↓ life time
- ↓ reproducibility
- Hinder *basic research*



Approach to defect control

All layers: high ρ packing particles similar $\varnothing_s$

***Dispersion*, *colloidal* stabilization:**

- **$\varnothing_s$-selective purification**
- **US removal micro-bubbles**

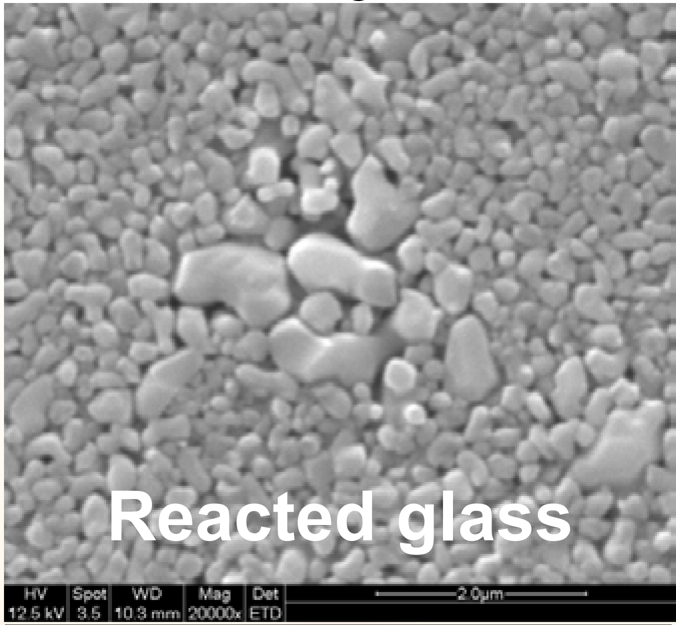
***Deposition*:**

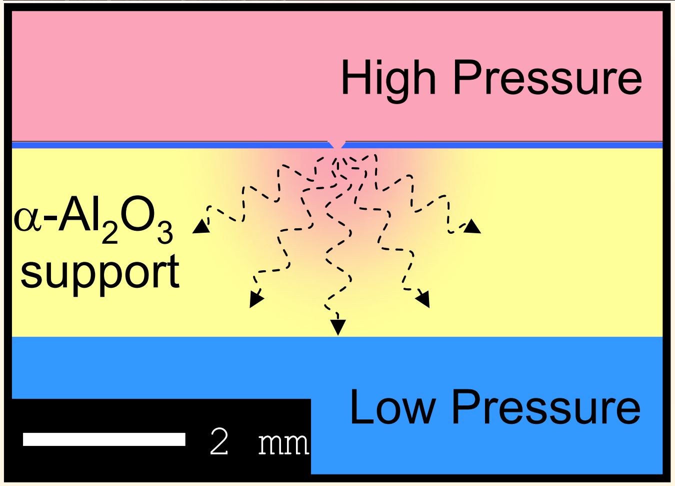
- **Colloidal filtration, casting**
- **Film, dip, spin deposition**

Dense in-situ/secundary growth

- **Template-free/epitaxial**

***Support* permeance ≫ membrane**





Colloidal fitration/casting

Dispersion of:

- ***homogenous* particles**

Stabilization by:

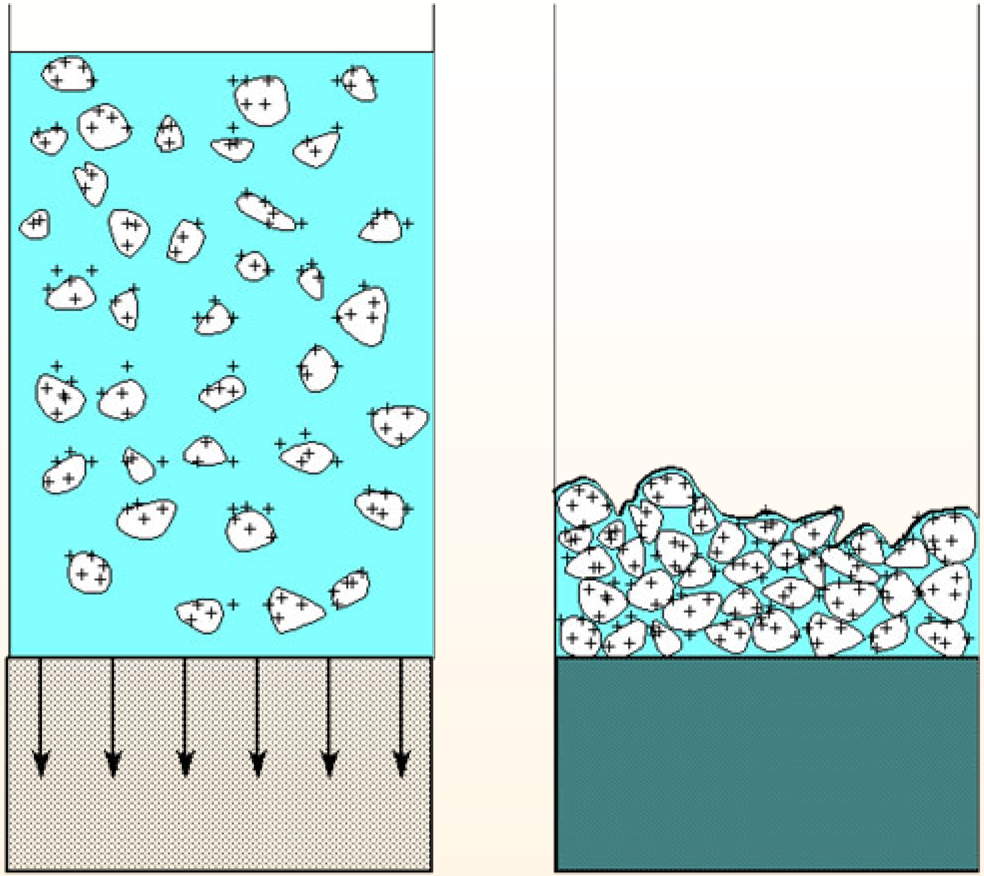
- ***Charge, steric***

Rheology by:

- ***Hydro polymers***

Deposition by:

- **Support *modification***



At 1 nm…10 μm length scale

AA3 α-Al_2O_3 carriers ($\varnothing_s$ = 3 μm)

Aqueous HNO_3; p_H = 2.0

33 wt% **AAA3**

Chilled **US 60 W for 10 min**

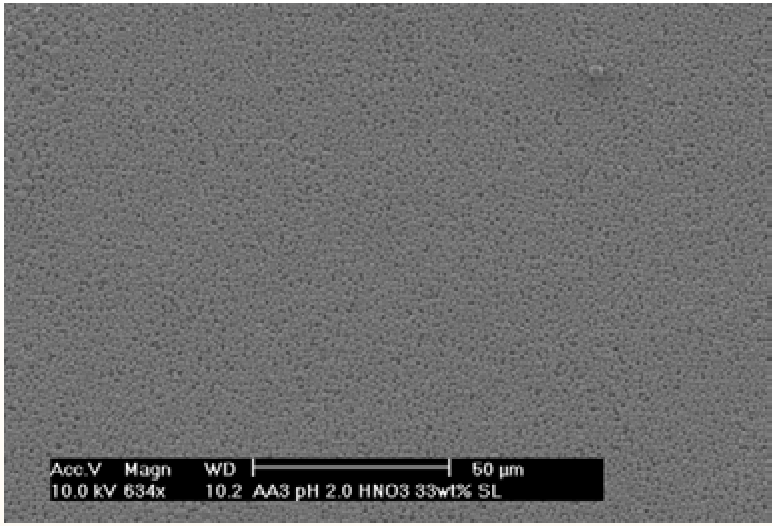
20 μm **# nylon screen**

Colloidal casting 43 mm Ø

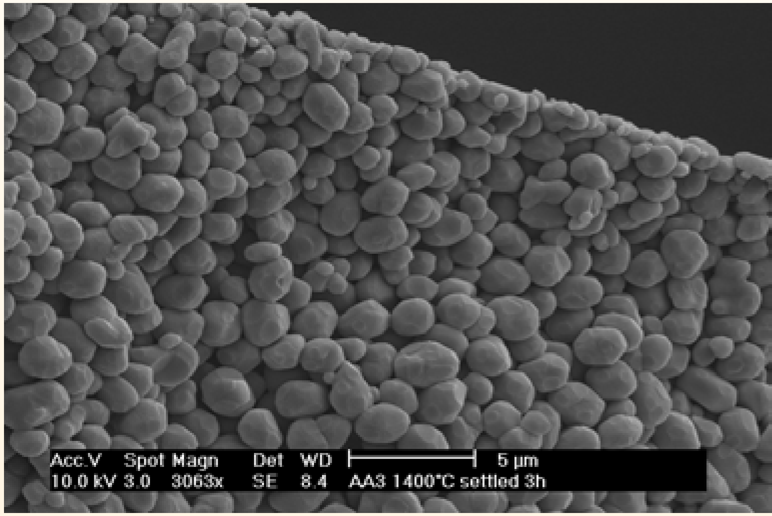
1300°C **for** 10 hrs

"Floaters" require:

- **Polyacrylate wetting agent**

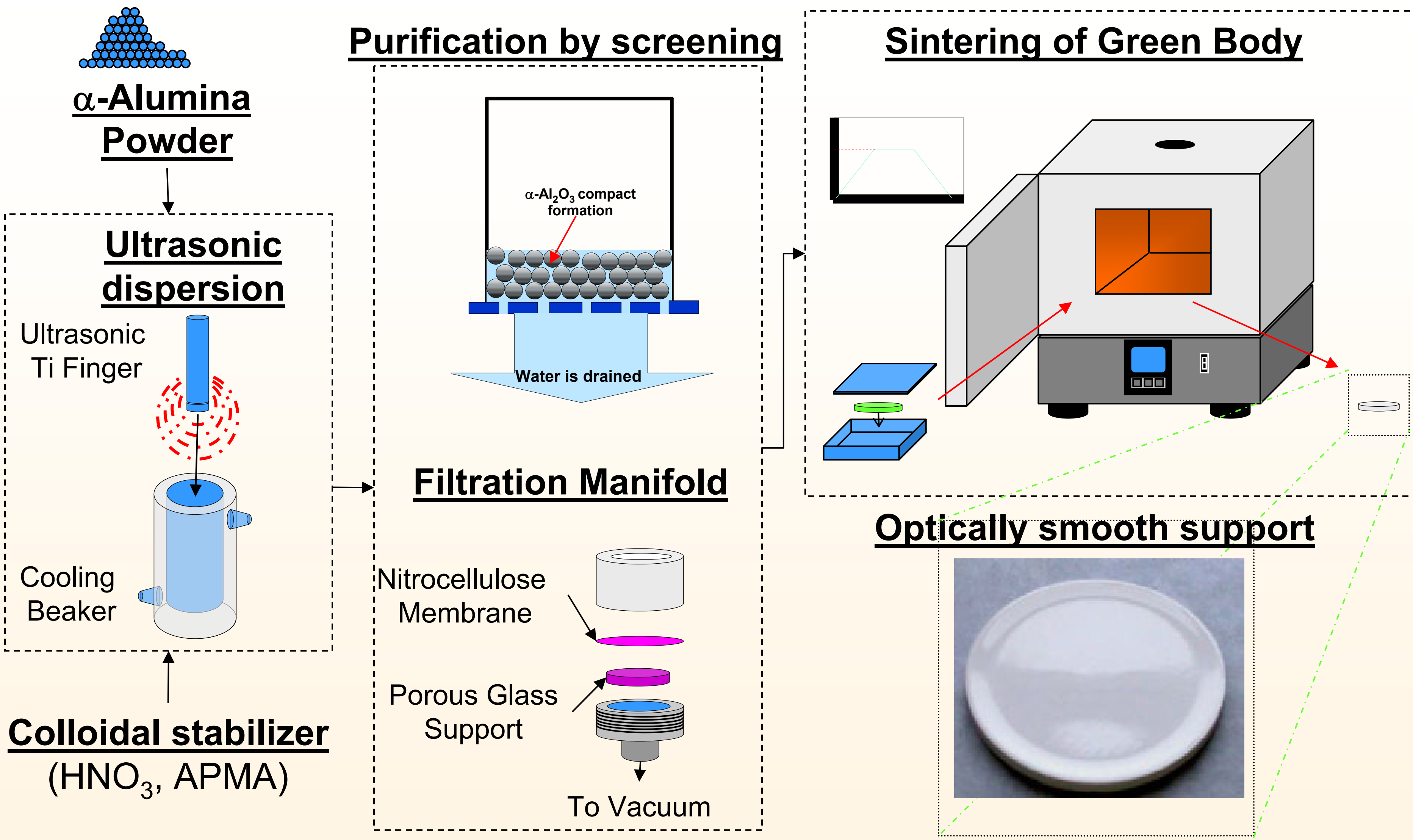


Surface morphology



Fracture morphology

Improving support layers ($\varnothing_p$ = 80 nm)

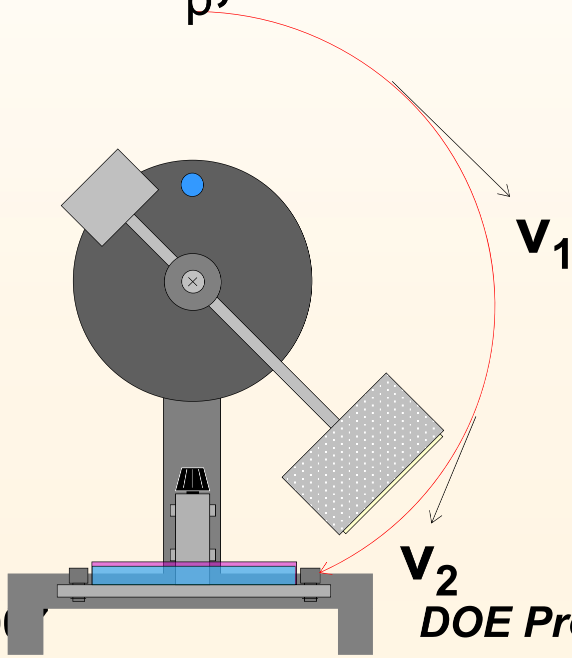


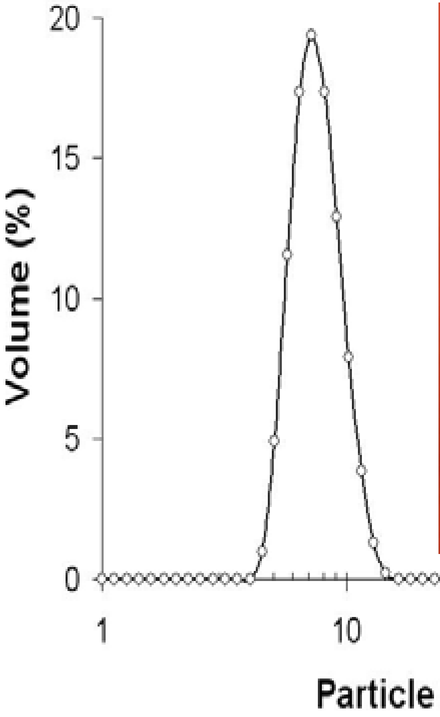
Homogeneous meso-porous intermediate

Water-clear dispersions (narrow PSD; Ø < 20 nm)

Modification with hydro-phyllic polymer chains:

- **Dip-coating rheology**
- **Drying lubrication**
- **Support $Ø_p$, and affinity**

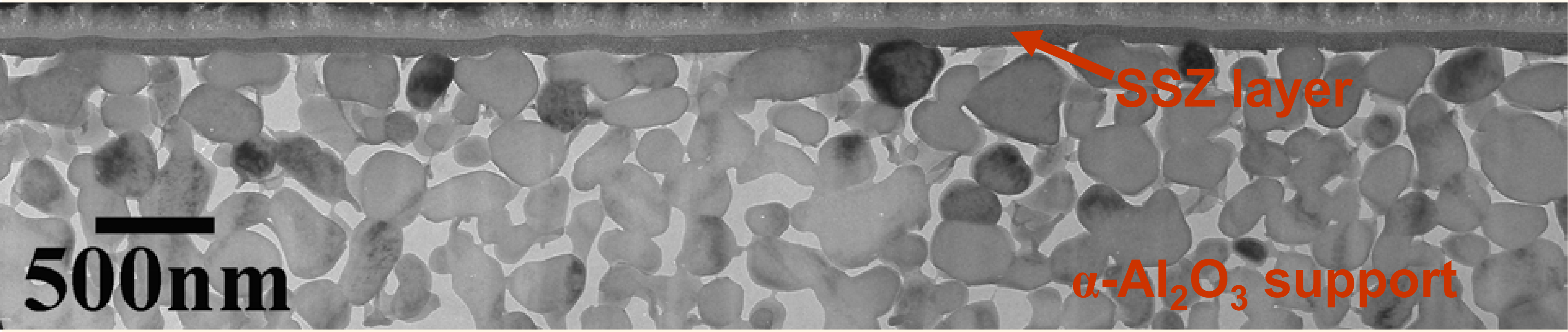




Homogeneous 50 nm thick SSZ zirconia

SSZ $\O_p$ = ~2 nm, X = 50 nm **on porous α-Al_2O_3**

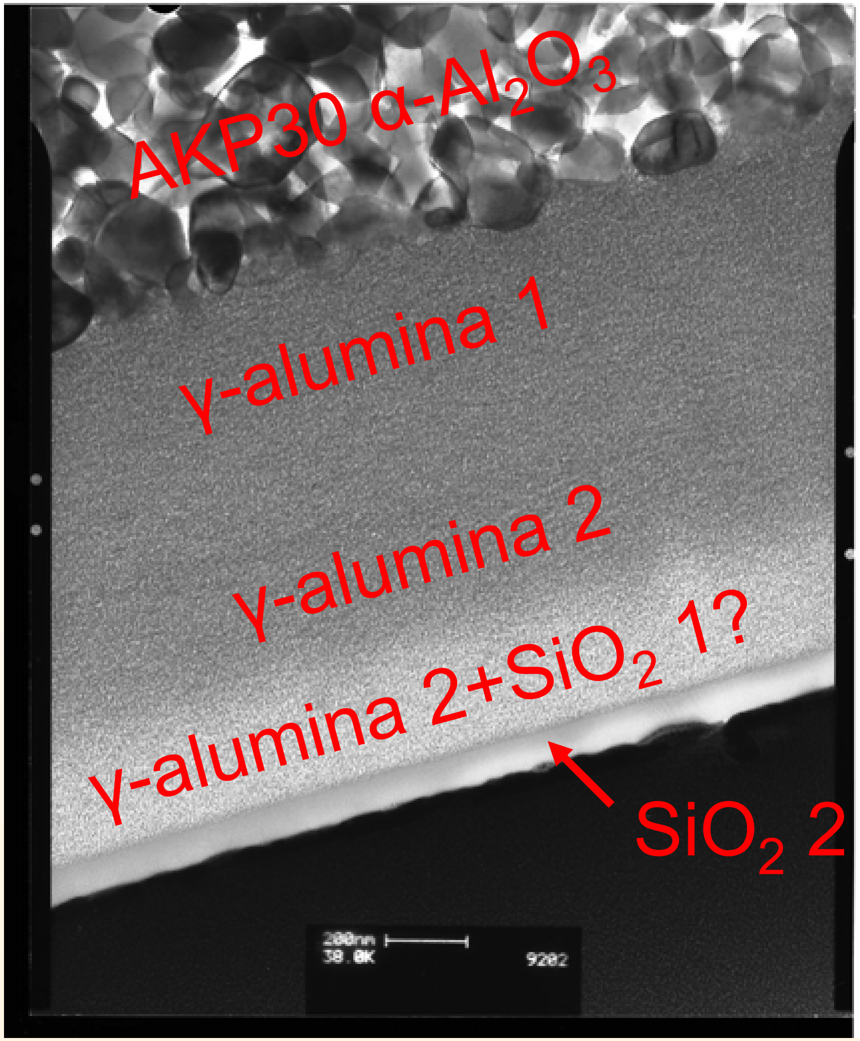
- **With industrial partner:**
  - ◊ **sono-chemical synthesis 3 nm SSZ particles**
- **Polymer-assisted film coating**



Recent example amorphous silica

Standard sol-gel SiO_2

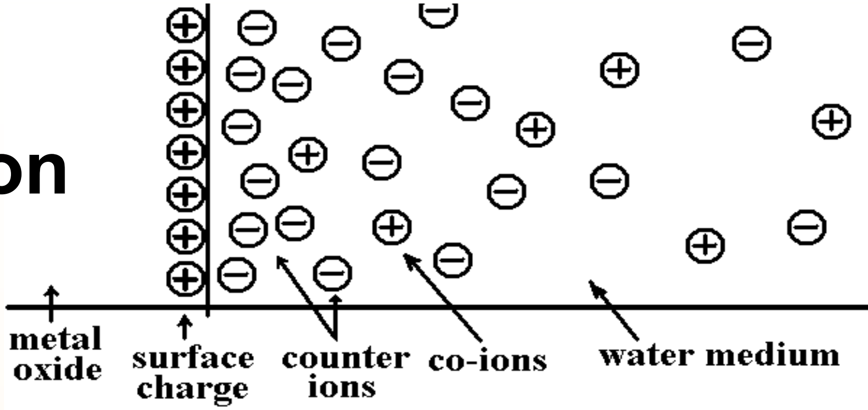
- $f_{H_2} = 3 \times 10^{-8}$ [SI], α>100
- *f* **lowered by** ***infusion*** **first layer?**
  - ◊ **Enhanced suction**
- **Good for stability**
- **Wil be explored with 50 nm thick** ZrO_2



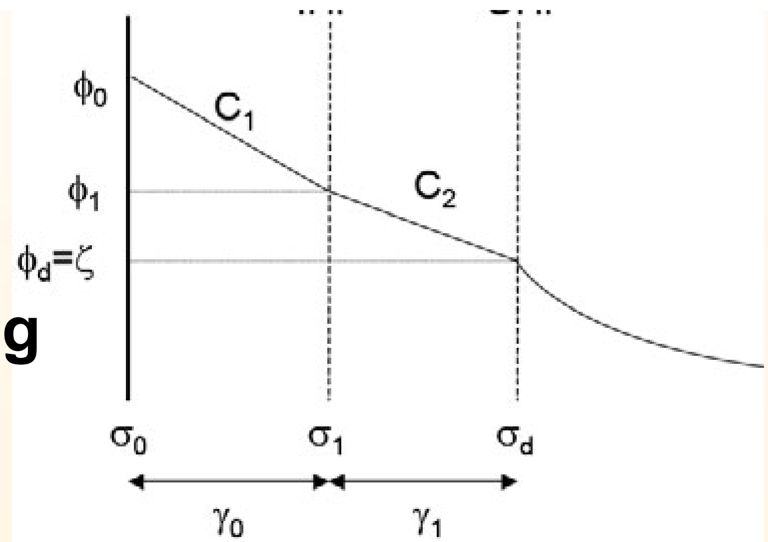
Deposition control: surface chemistry

Aqueous **medium:**

- **Spontaneous ion sorption**
- **Charges the surface**
- **Diffuse counter-charge**



Double layer model



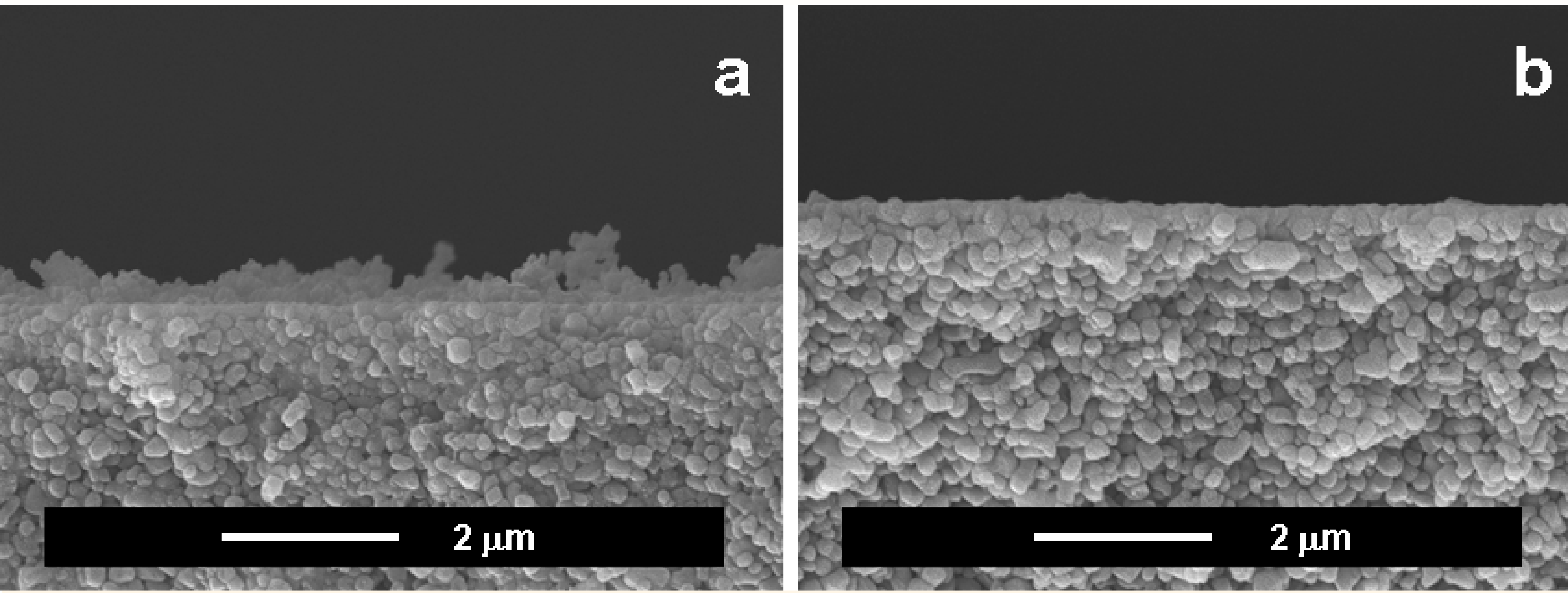
Control surface charge:

- **By specific ions, p_H**
- **Colloidal stability:**
  - ◊ **Homogeneous dense packing**
- ***Affinity*: orientation**

Characterization: ζ-*potential*

Zeolite Y deposition

Effect p_H = 8.5 (left) vs p_H = 11.5 (right)



And finally: one very new result

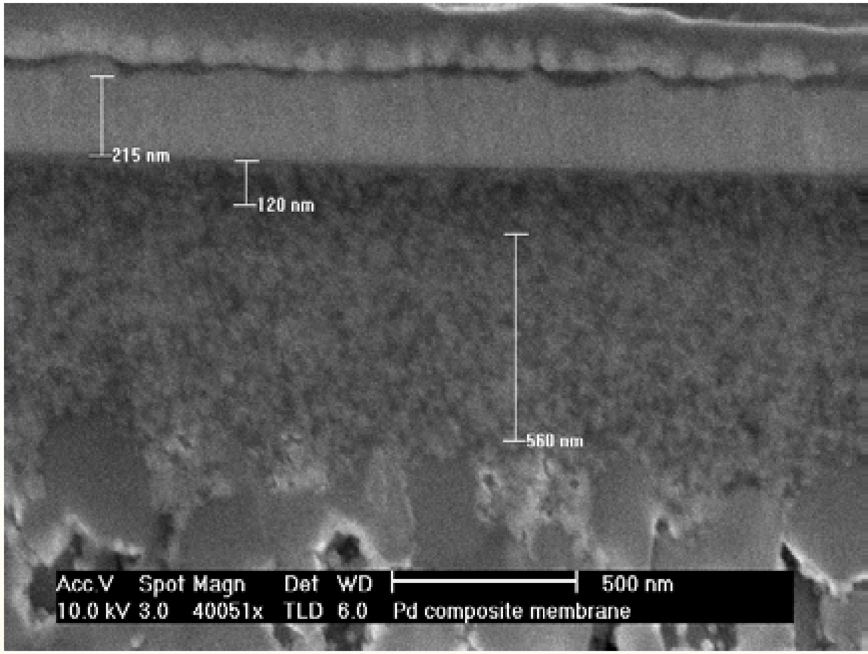
200 nm electroless Pd **on:**

120 nm layer

560 nm γ-alumina ($Ø_p$=4 nm)

5 µm α-Al_2O_3 ($Ø_p$=80 nm)

2 mm α-Al_2O_3 ($Ø_p$=700 nm)



Stable $j_{H_2} = 0.1...1\,(\mathrm{mol/m^2s})$: 260…320°C; 2→0 Bar.

- **Appears surface controlled**

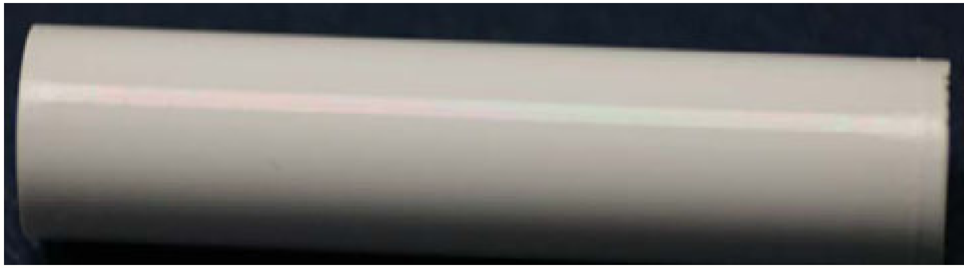
Selectivity >100

Further stabilization: alloys, meso-porous top layer

And the first tubes

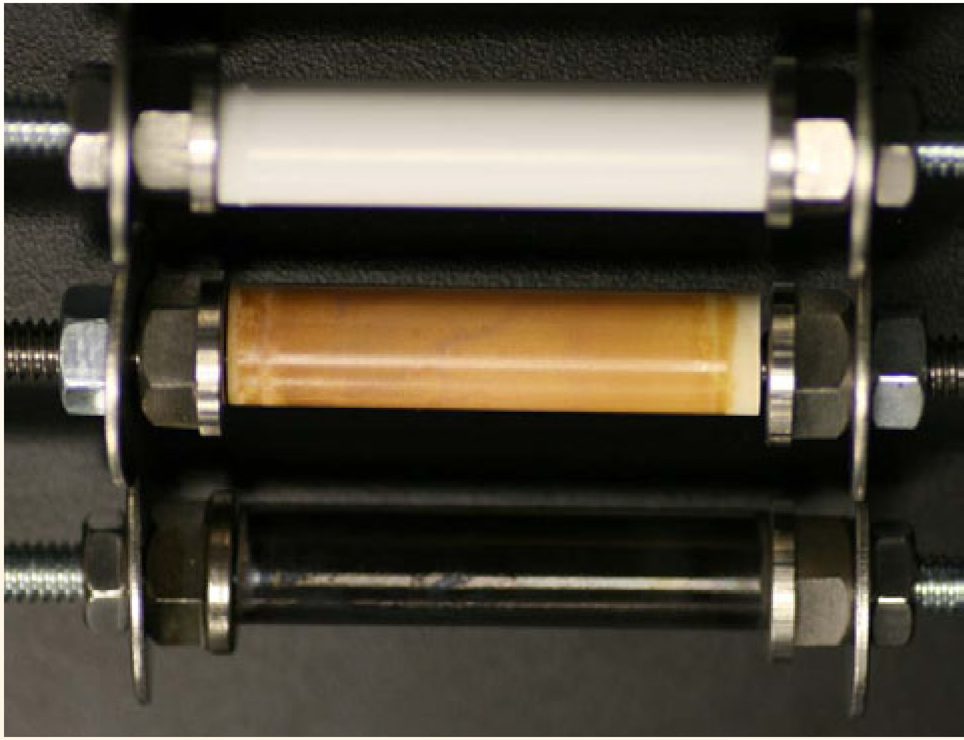
γ-alumina on AKP30 on coarse α-Al_2O_3

- **Green/magenta:** ***homogeneity***



Pd on γ-alumina

- **Brown *intermediate*:**
- **Gray <500 nm Pd:**
- **N_2-dense at RT**



Conclusions; status

Viable multi-layer syntheses become available:

- Several membrane separation concepts
- Surface pore Ø <1 μm
- Defects are becoming under control

Abundant use of *colloidal*, US-based methods

Further development defect detection needed

Further development of rapid methods needed

Now trying several membrane/fuel cell concepts

INORGANIC Materials Science

Acknowledgement

DOE

- **Hydrogen Production and Storage program**
- **BES Hydrogen Fuel Initiative**
- **EMTEC hydrogen program**

NSF

- **IGERT MEMD**

State of Ohio/OSU

- **Third Frontier program**
- **Hayes Investment program**

Questions?