Materials development for inorganic membrane layers at ECN

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ECN

Energy research Centre of the Netherlands

Materials Development for Inorganic Membrane Layers at ECN.

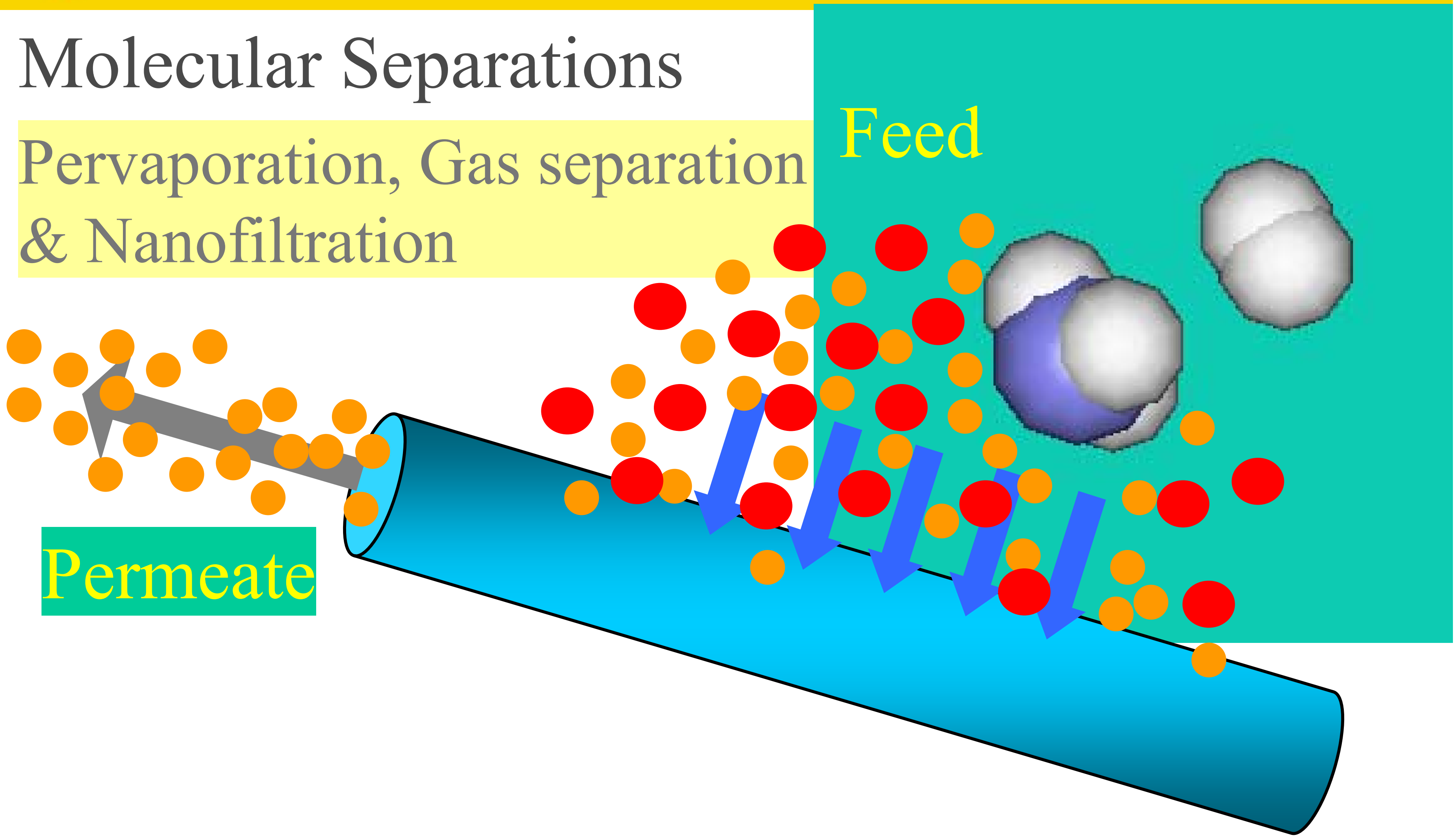
Ben C. Bonekamp

ECN

What about ?

Molecular Separations

Pervaporation, Gas separation & Nanofiltration

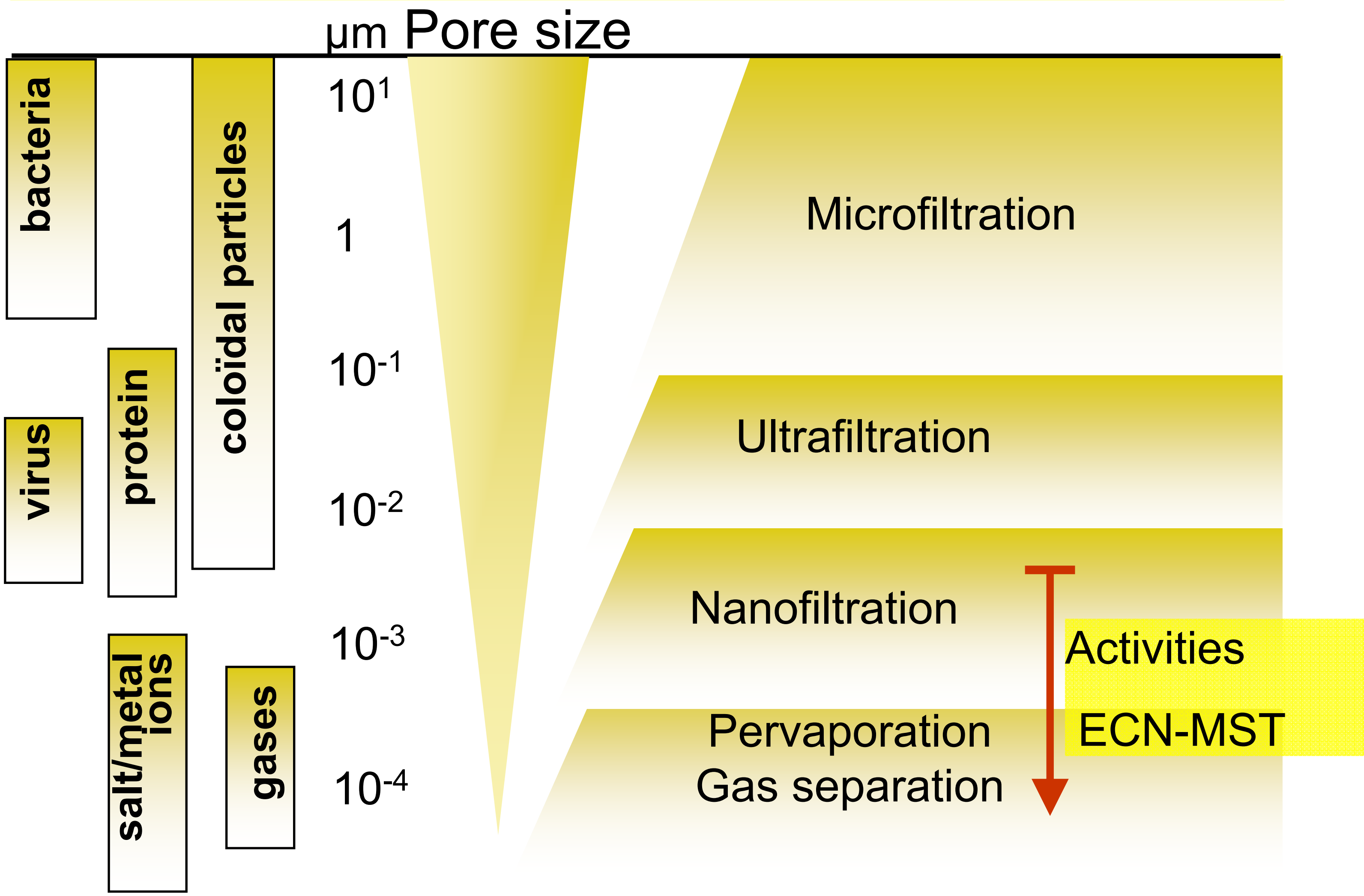


1m² pervaporation unit

SULZER CHEMTECH

Membrane Systems

Porous Membranes



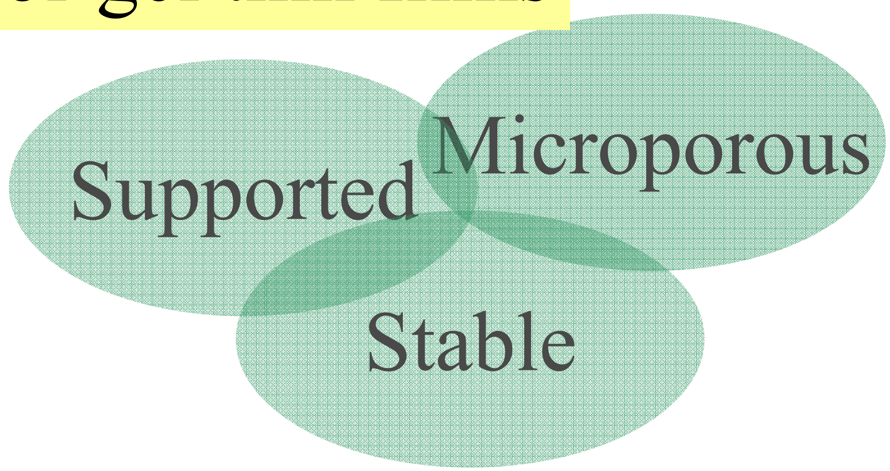
ECN Energy Efficiency in Industry

Molecular Separation Technology

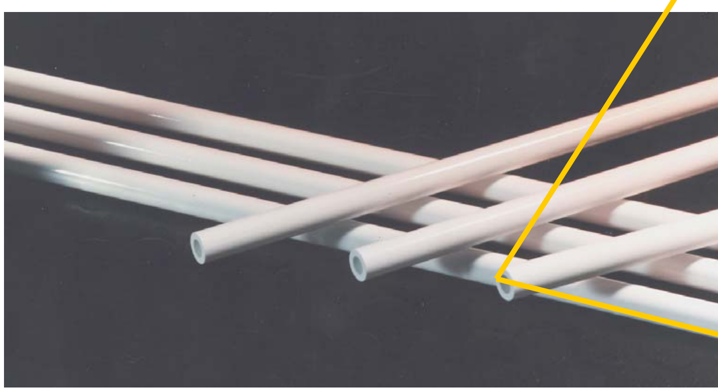
- Materials development
- Separation processes
- Systems development

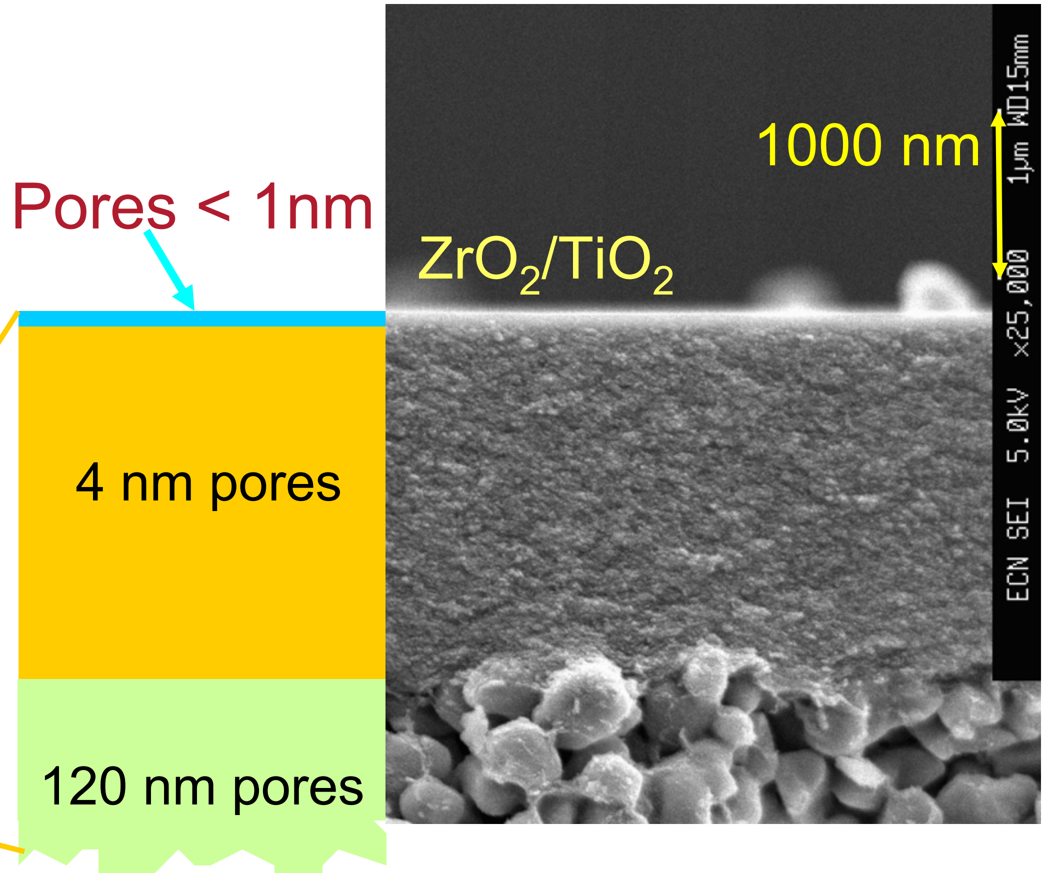
Ceramic membrane preparation

Inorganic sol-gel thin films

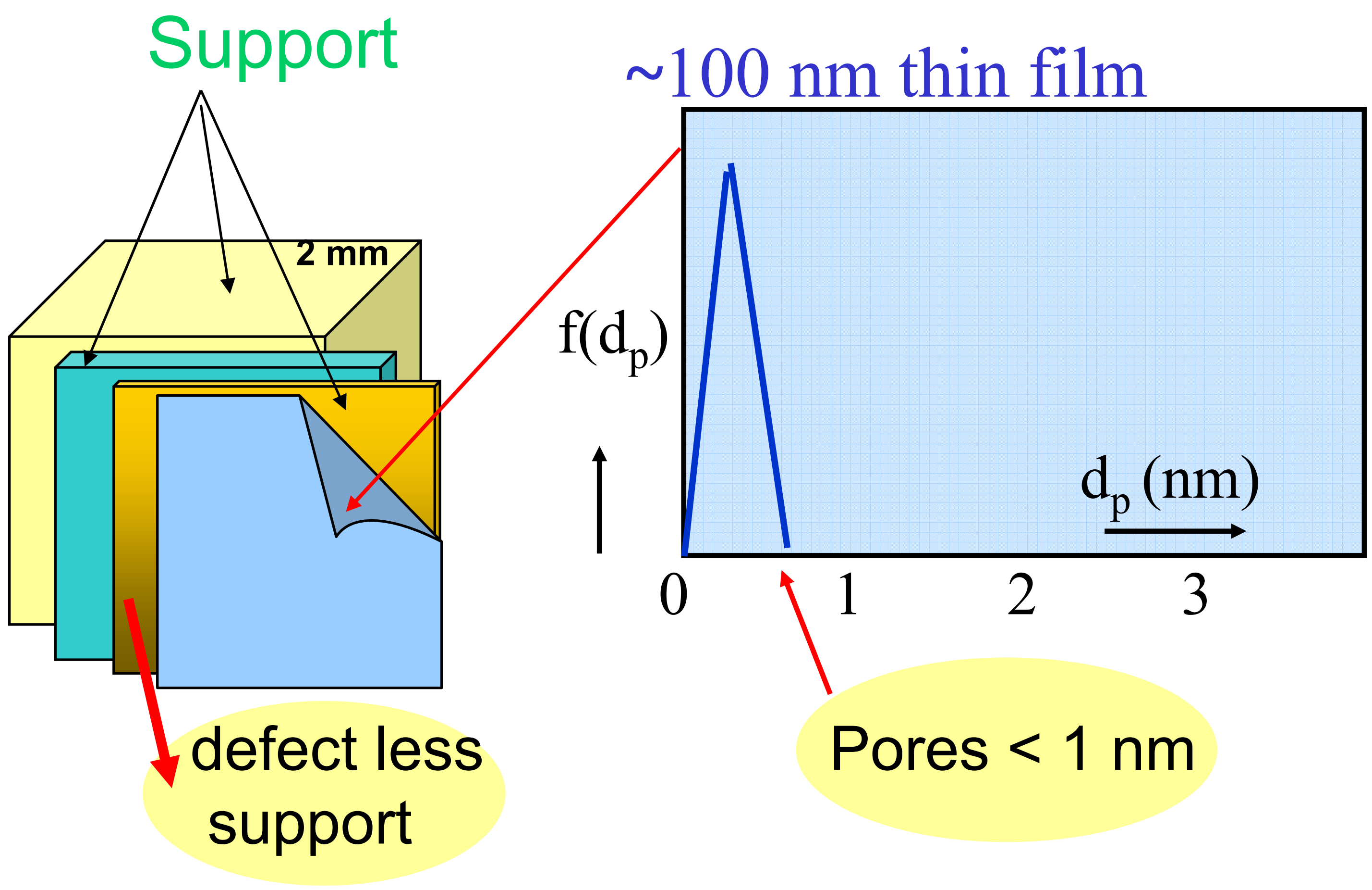


Tubular microporous membranes



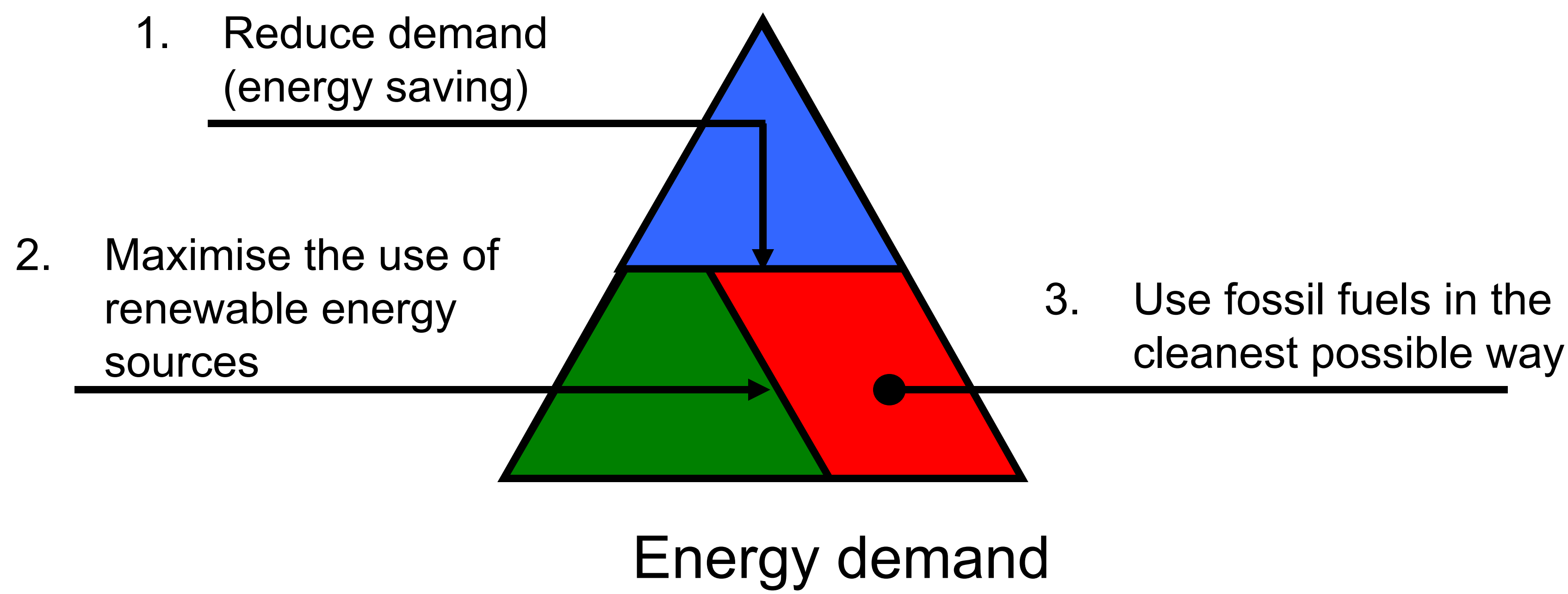


Sol-Gel Thin Film on Porous Support

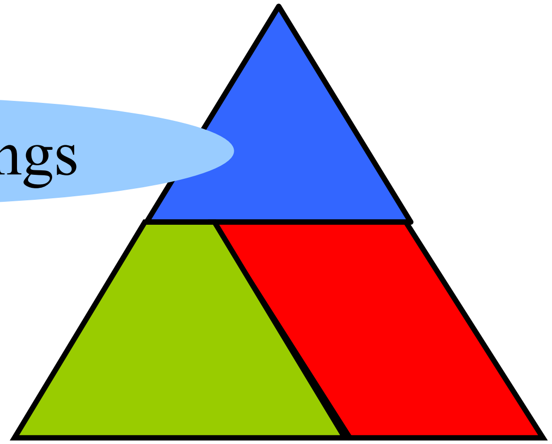


Why ?

Trias Energetica: Pathway to sustainable energy system



Energy savings



Efficient separation processes

Molecular separation with membranes

ECN

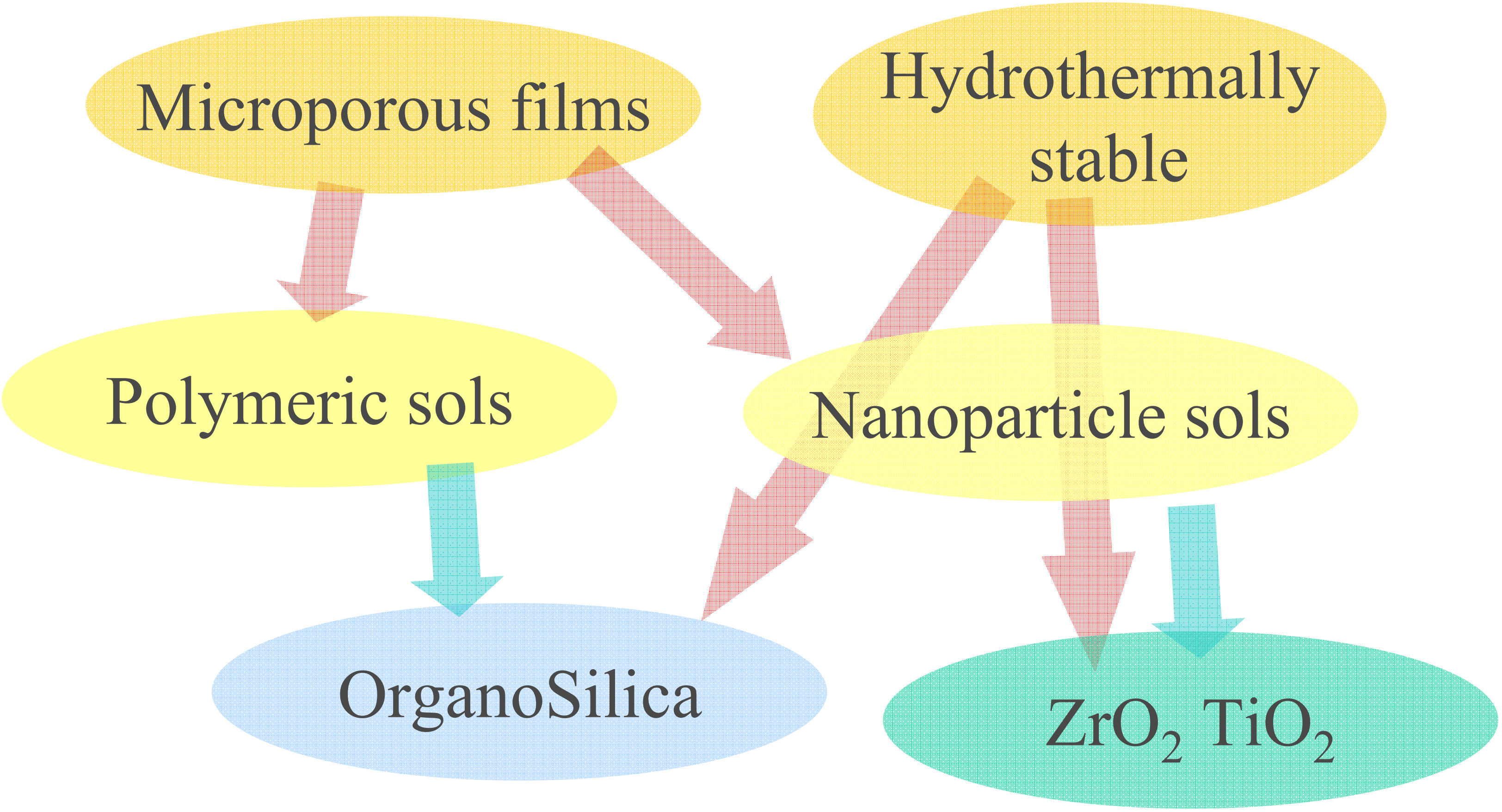
How ?

Sol-Gel Thin Films

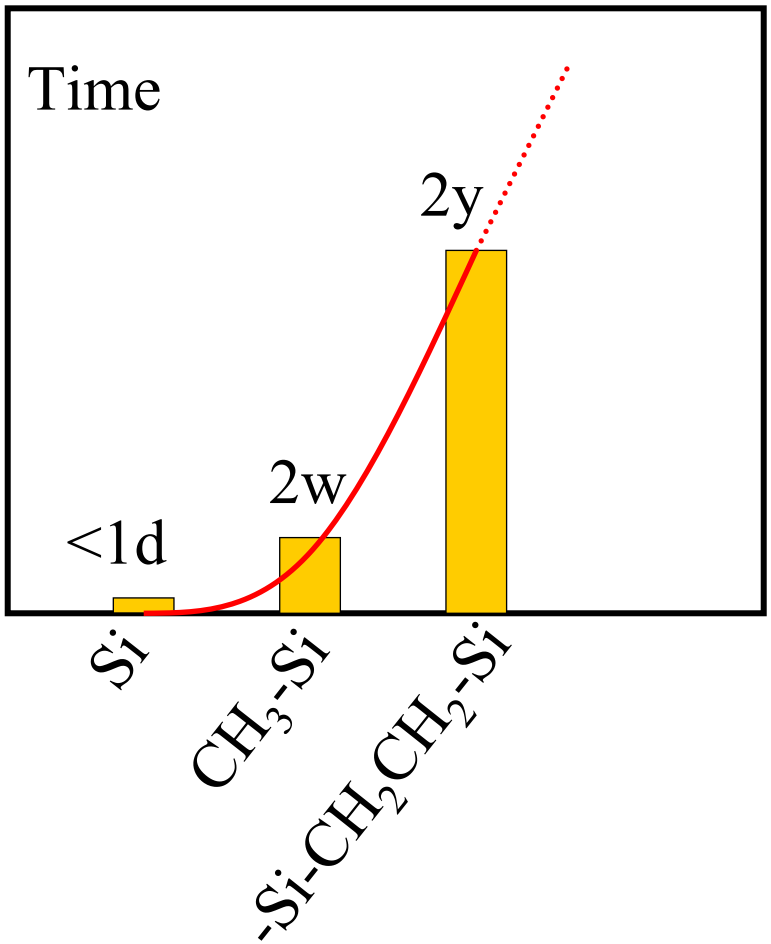
Sol-Gel Technology

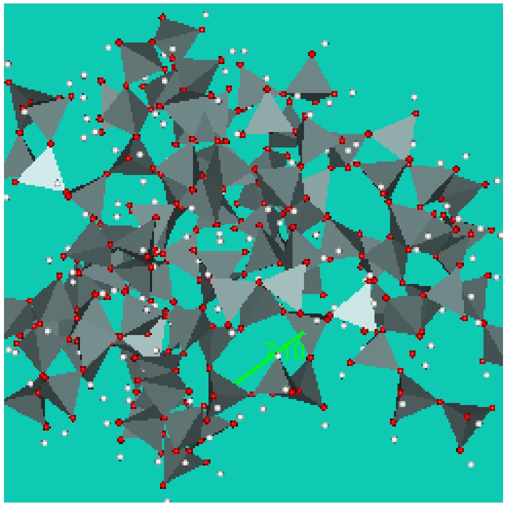
- Sol synthesis
- Substrate preparation
- Thin film coating
- Reducing defect density
- Hydrothermal stability

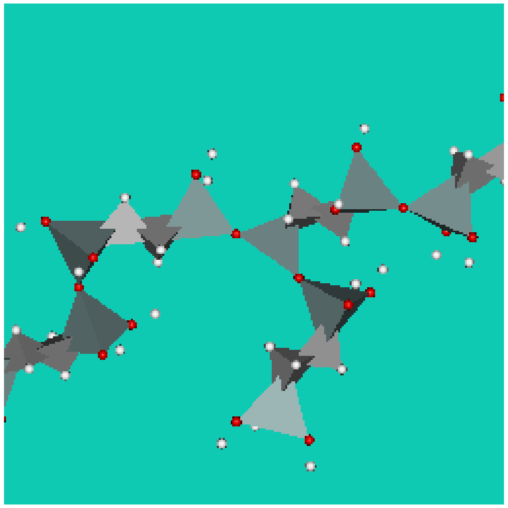
Sol-Gel Thin Films



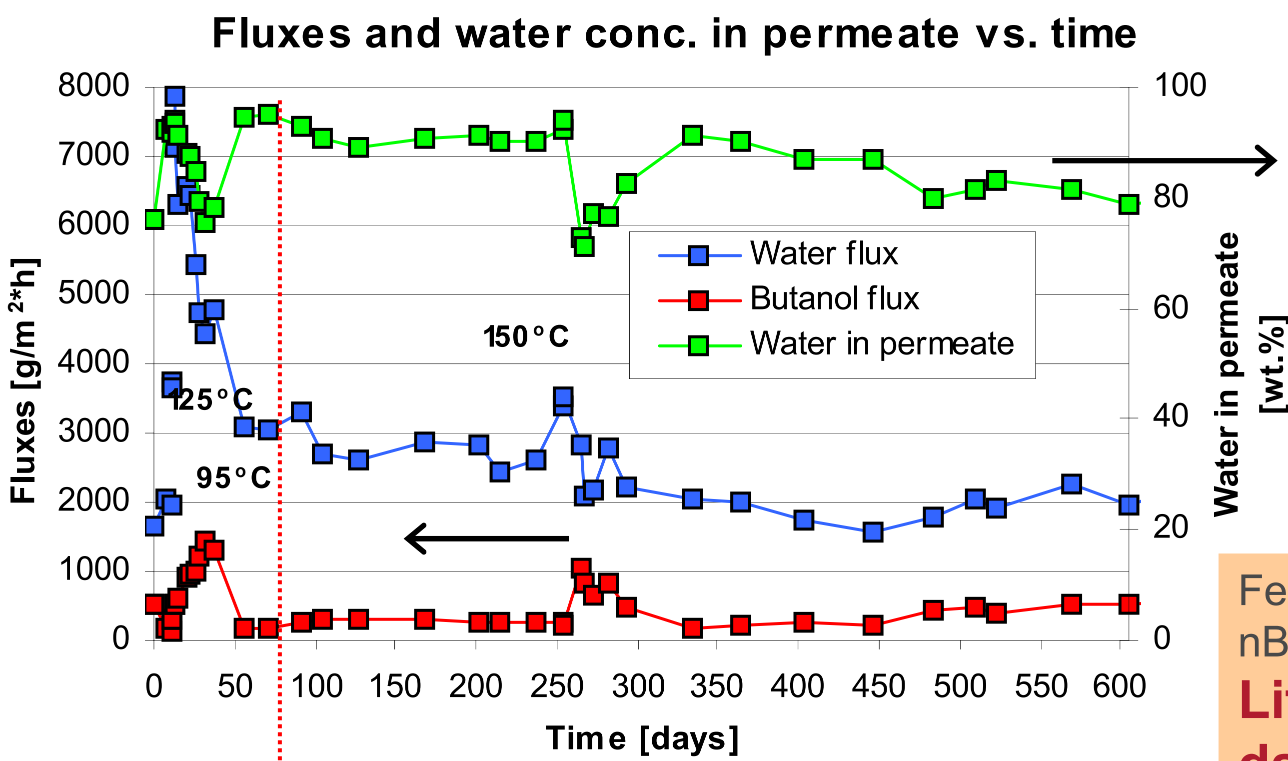
Hydrothermal stability at 150 ^{0}C







Performance hybrid membranes, 150°C



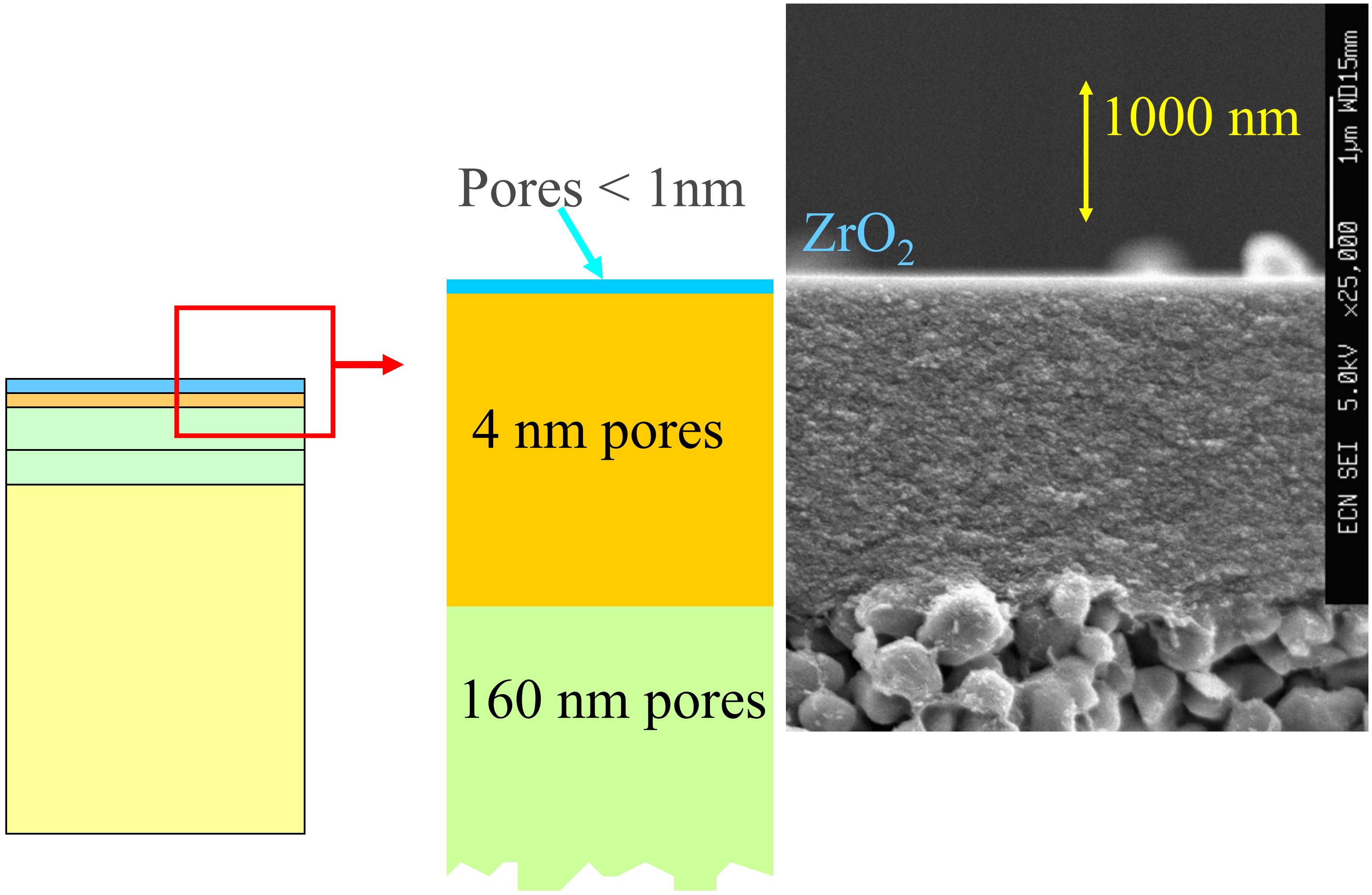
Feed = 5 wt.% water in nBuOH

Lifetime > 650 days

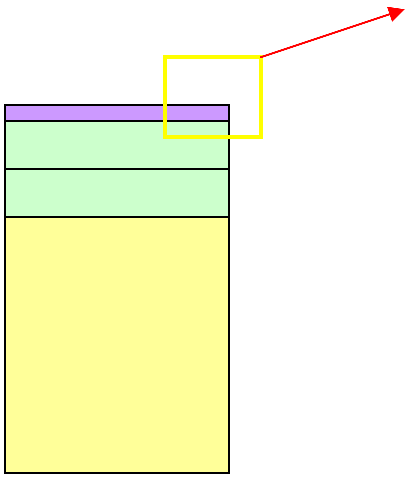
Life time state of the art methylated silica

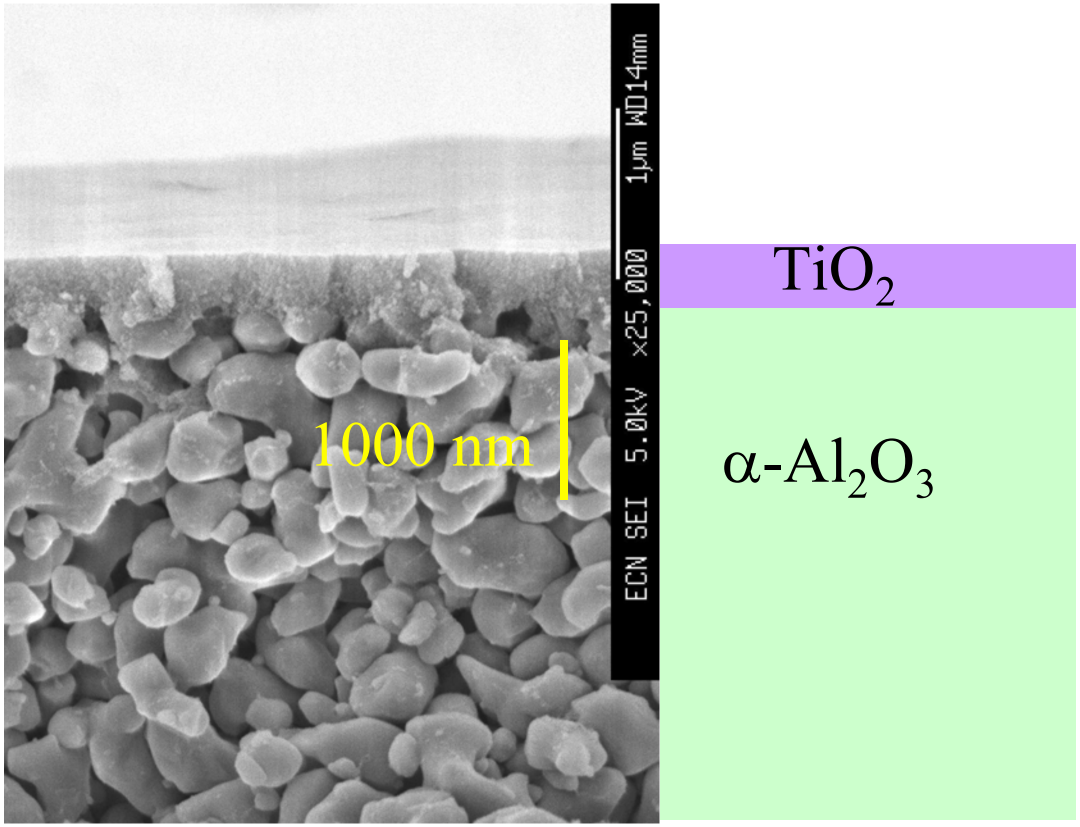
J. Mater. Chem. 2008, 18, 2150-2158

Microporous ZrO_2 on multilayer porous support

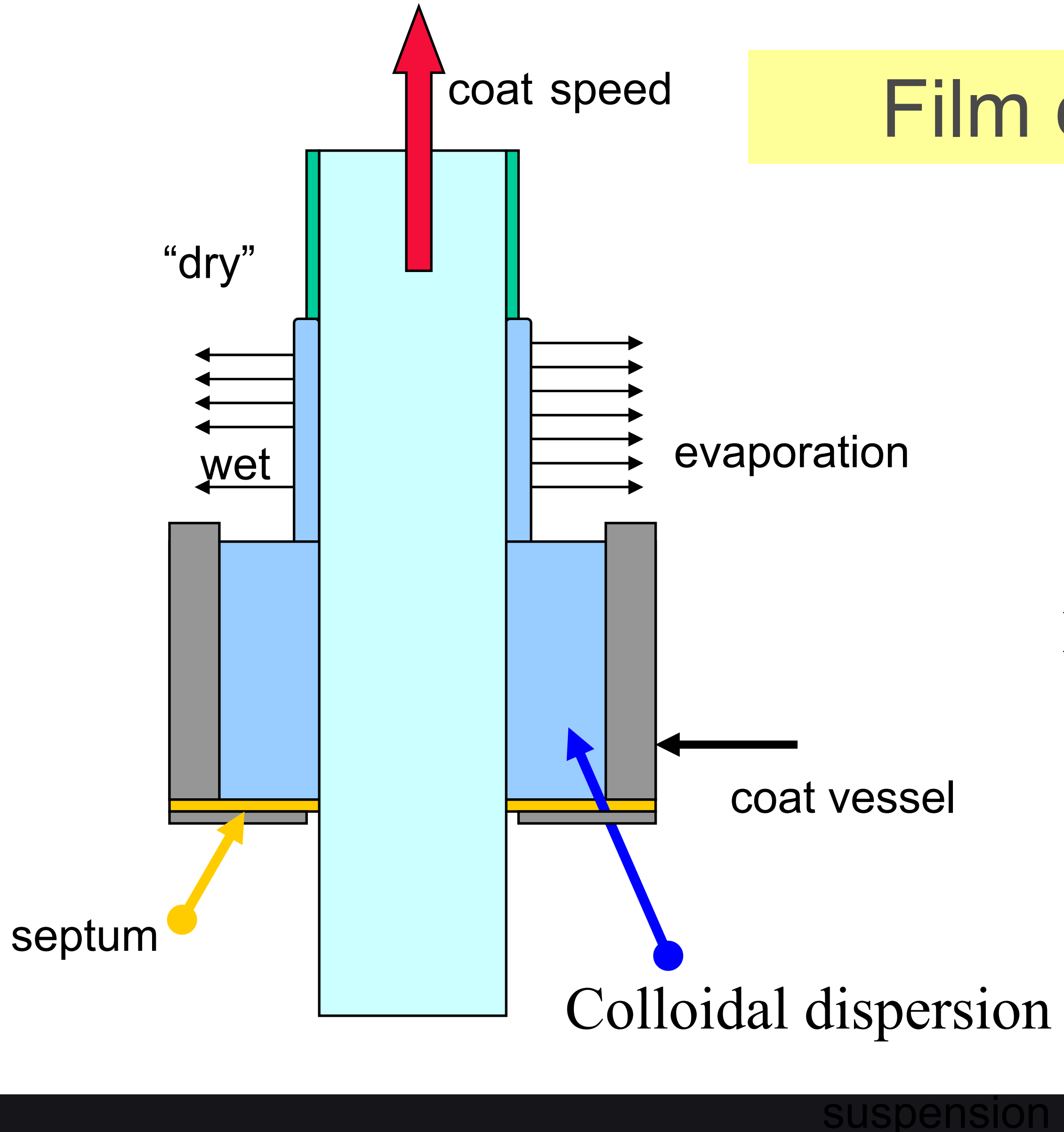


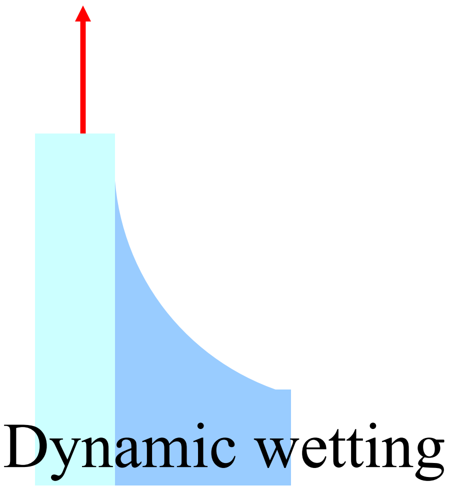
Mesoporous TiO_2 on Multilayer porous support



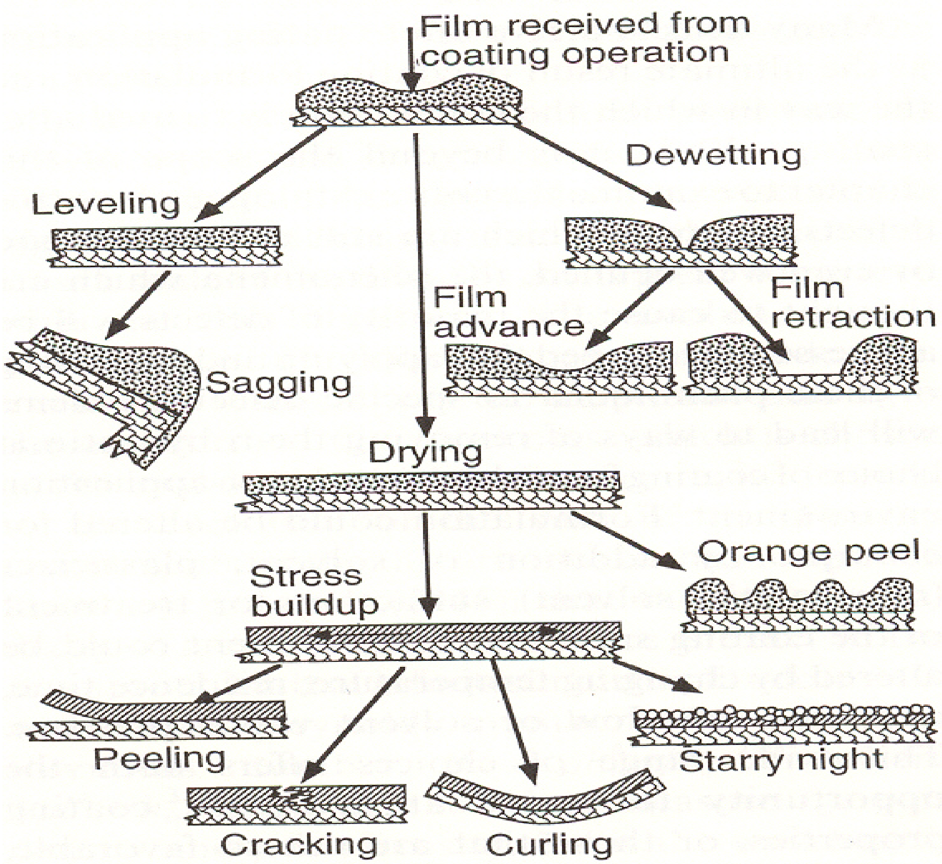


Film coating





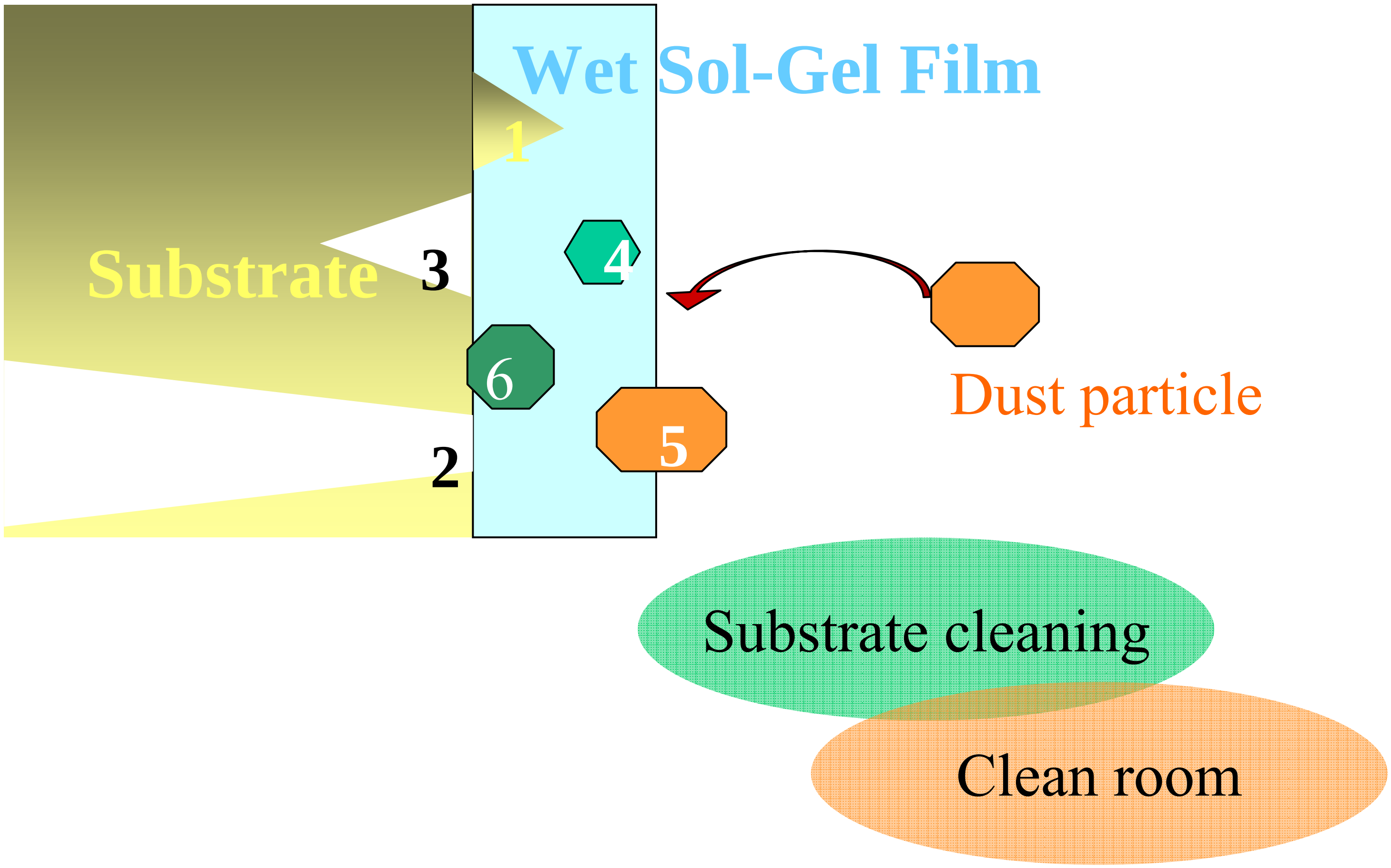
Sol-Gel Thin Film Stability



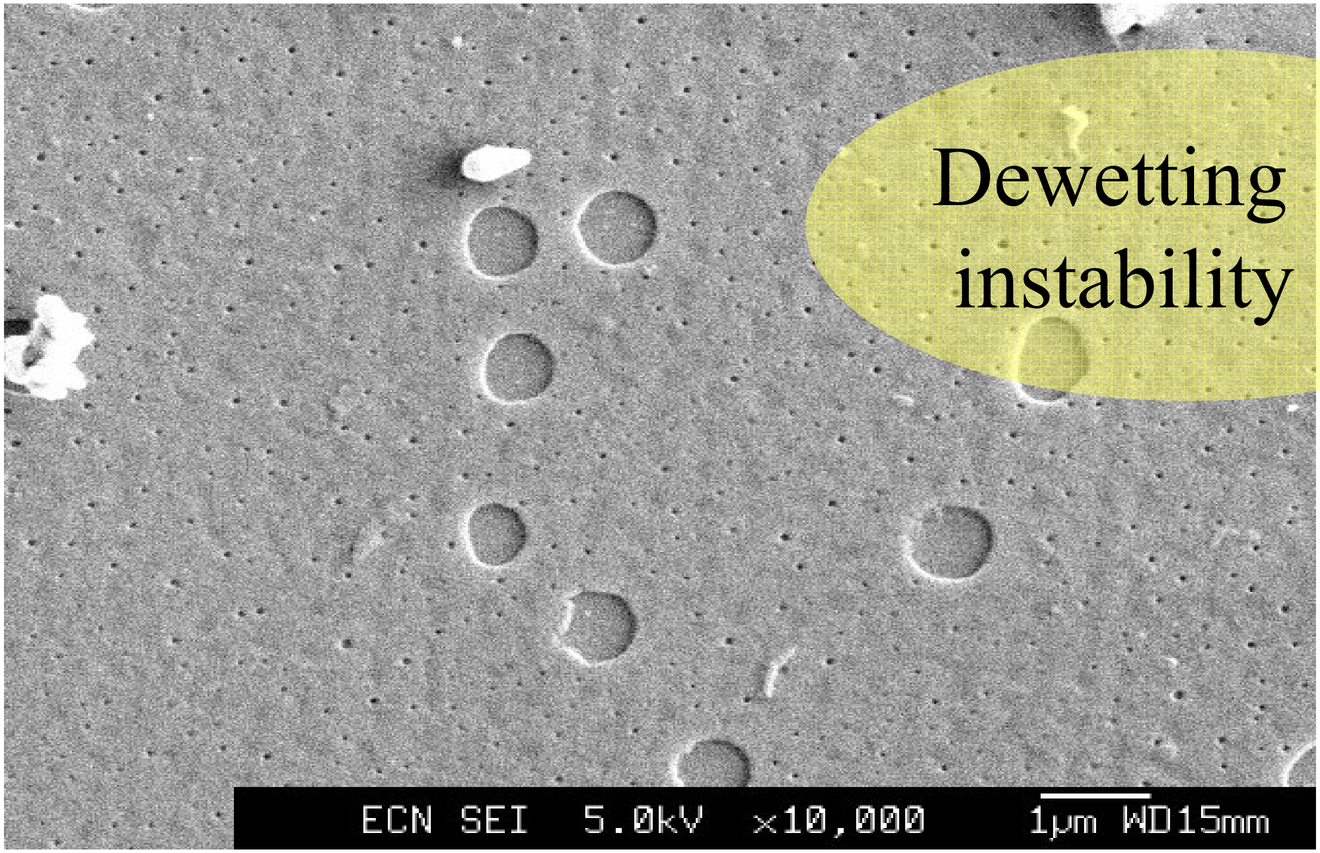
What can happen with a sol-gel coating during and after liquid film coating ?

From Kheshgi (1997) Chapter 6 in “Liquid Film Coating”, Eds Kistler & Schweizer.

Sources of Defects



Methylated Silica coating

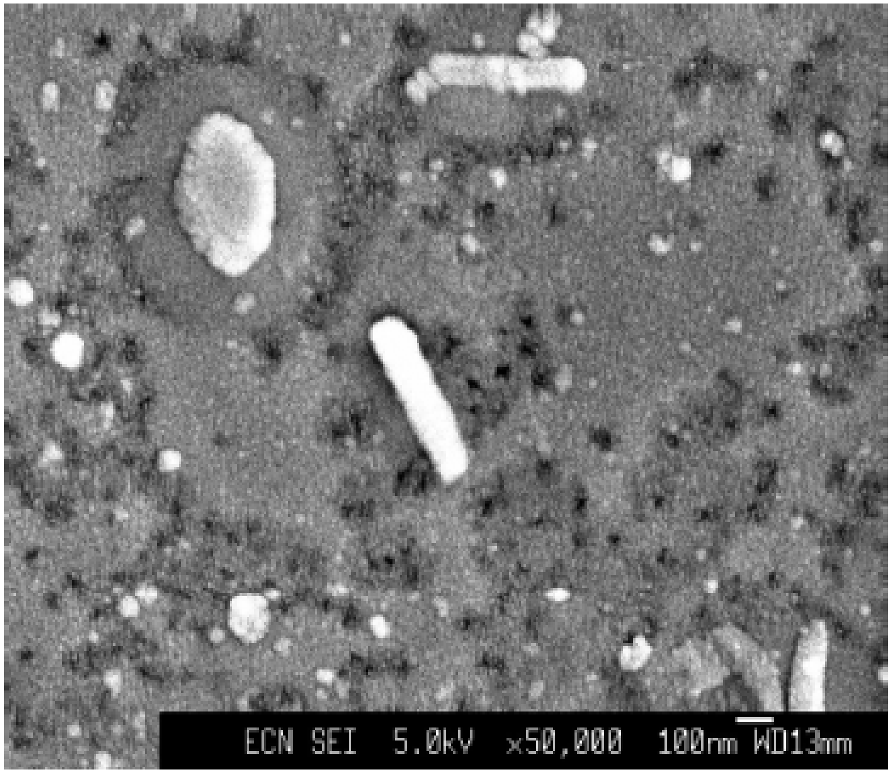


Dewetting instability

Membrane surface after testing (Me-SiO_2)

- Severely damaged
- Dense white particles
- Many pinholes

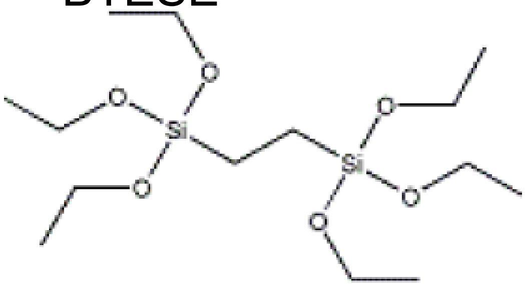
- Illustrative example (Me-SiO_2, 135°C, 7 days)



Sols

New membrane materials: Hybrid membranes

- BTESE



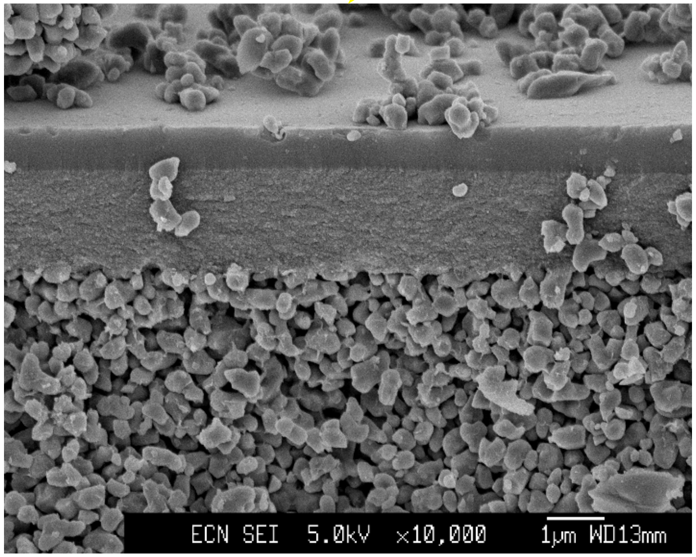
- Water, HNO_3 , EtOH

- Reflux at 60ºC, 3 hrs

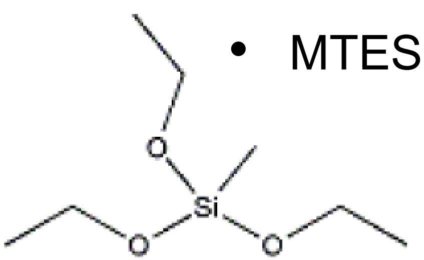
- Mix

- Coating and calcination

- Mix in EtOH

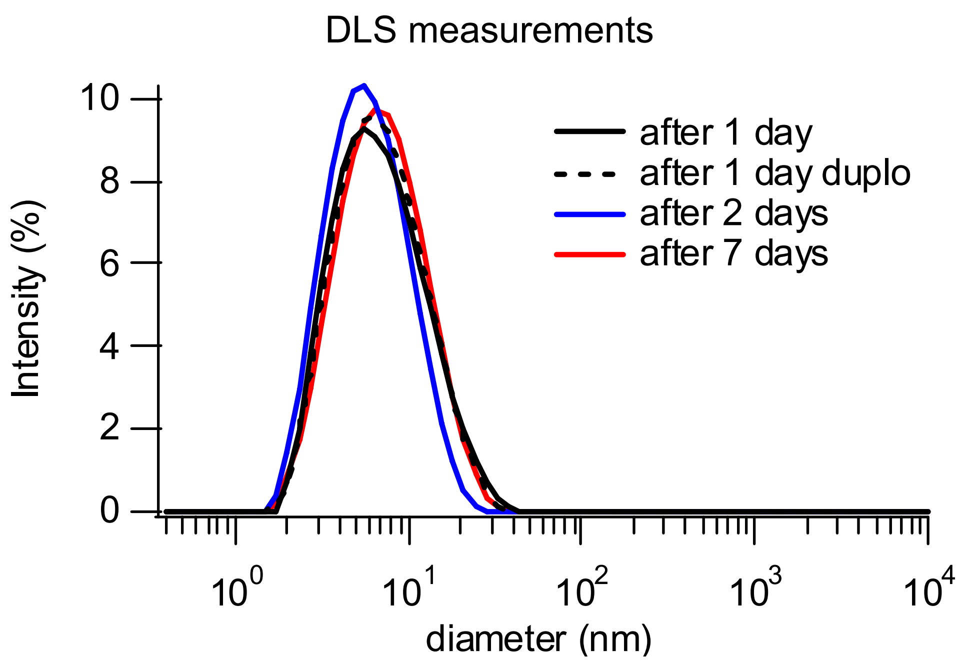


- MTES



Zirconia sol preparation

- Premixing of H_2O, hexanol, cyclohexane
- Slow addition of to zirconium n-propoxide in cyclohexane
- Addition of HAc as dispersant



- Stable nano-particle sols (4-5 nm)
- Highly reproducible

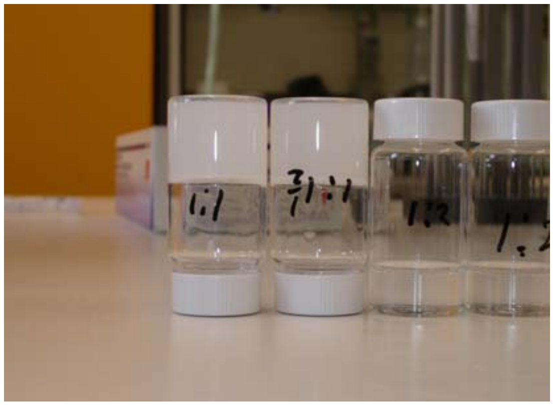
Particle size measurement

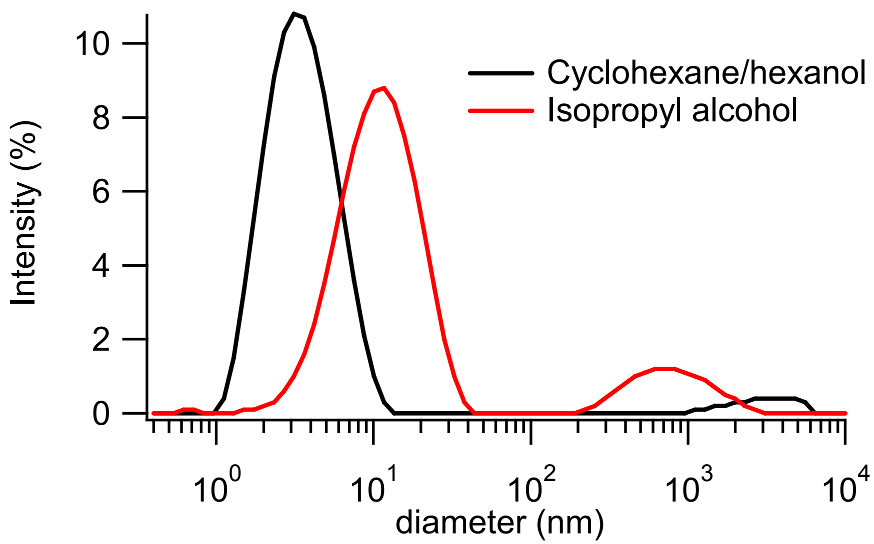
Sol viscosity

Dynamic Light Scattering

Rheometry

Modification of zirconia sol



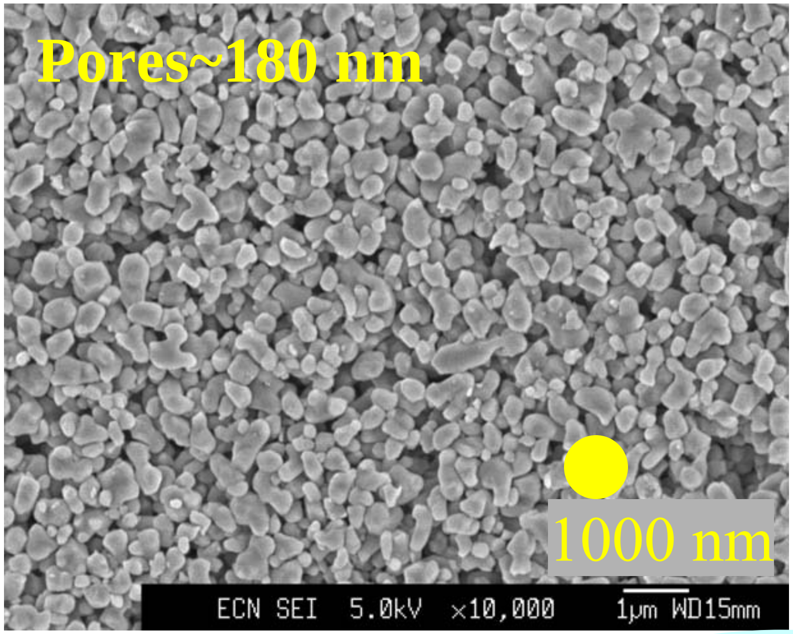


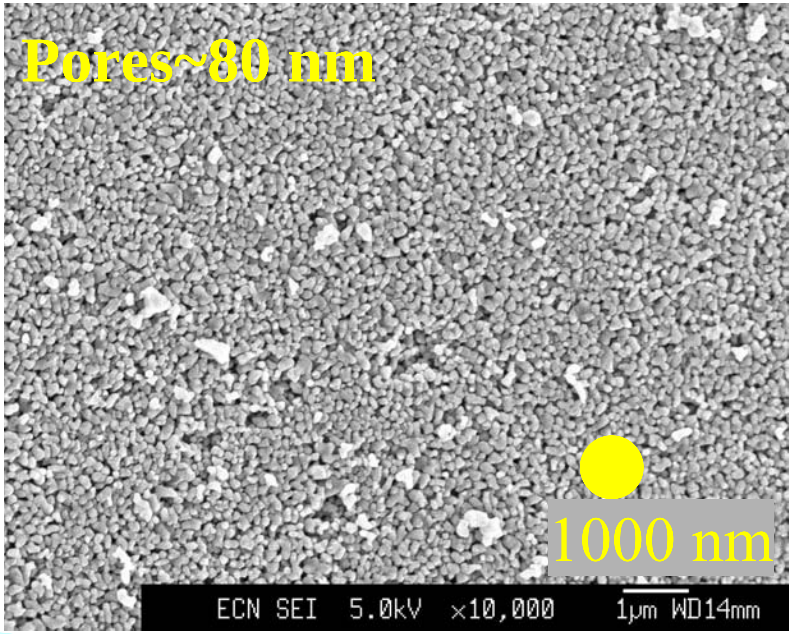
- Increasing amount of HAc
  - [HAc]/[Zr] > 2 needed
  - Improved coating

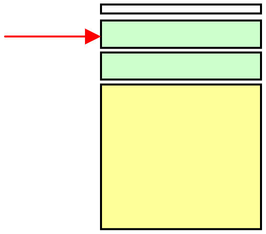
- Change of solvent by dialysis
  - In IPA larger particles
  - Improved coating (slightly)

Supports

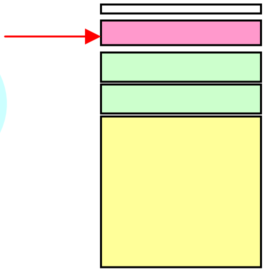
Porous α-Alumina Sol-Gel substrates





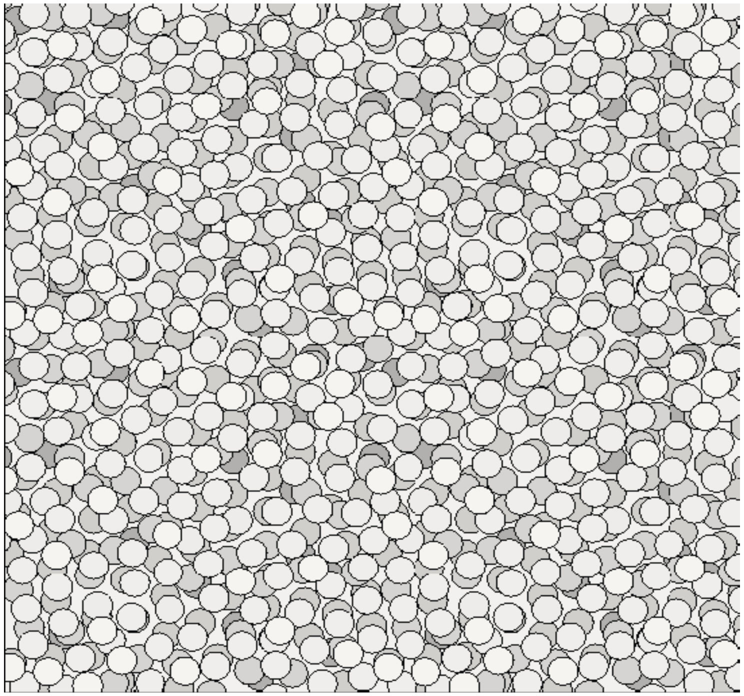


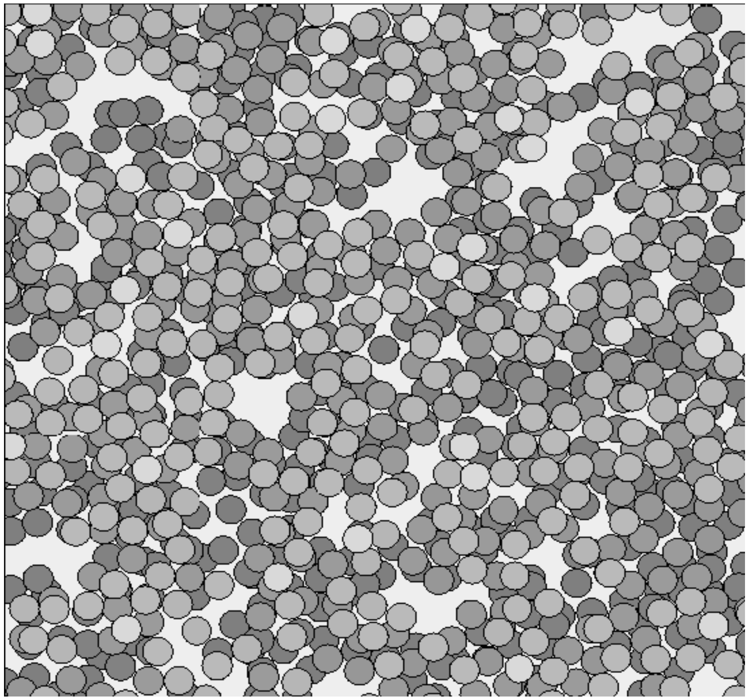
Scanning Electron Microscopy



Suspension structure

stable

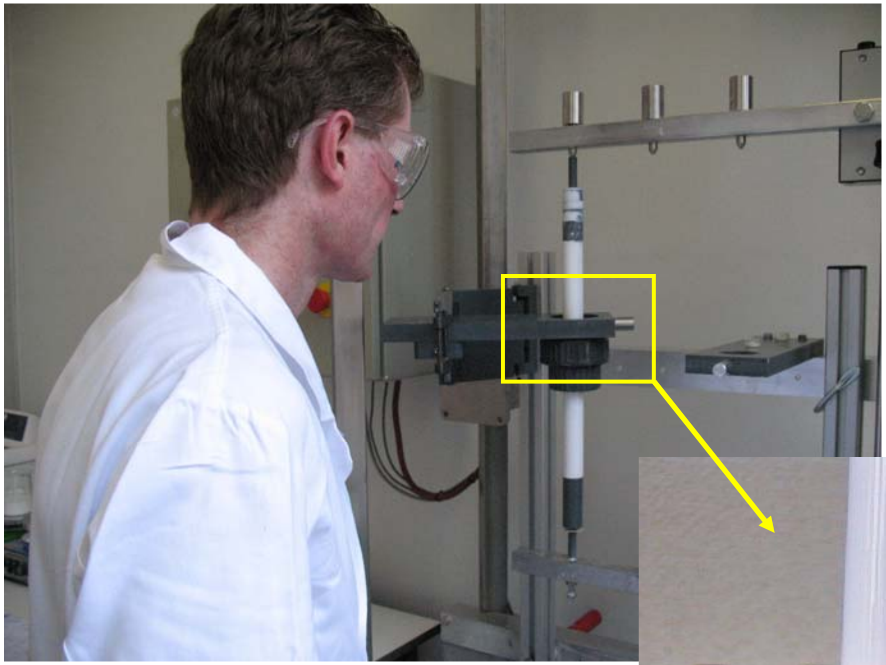


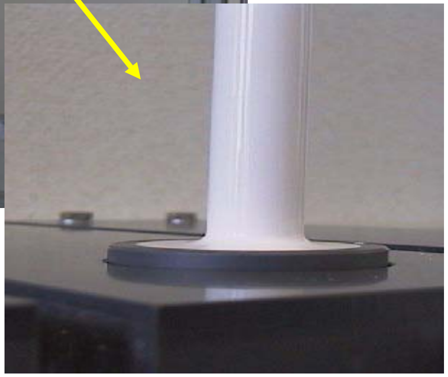


$\Phi = 0.4$

(from Wyss, JACerS *88* p2337(2003))

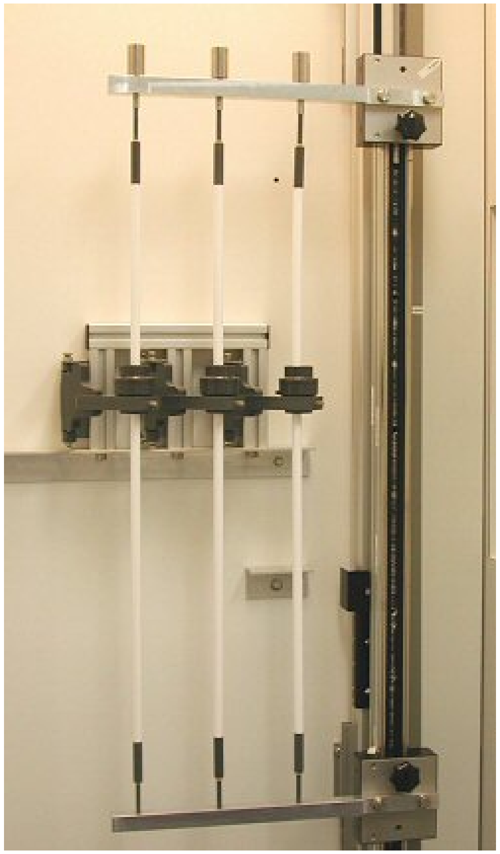
Dispersion coating

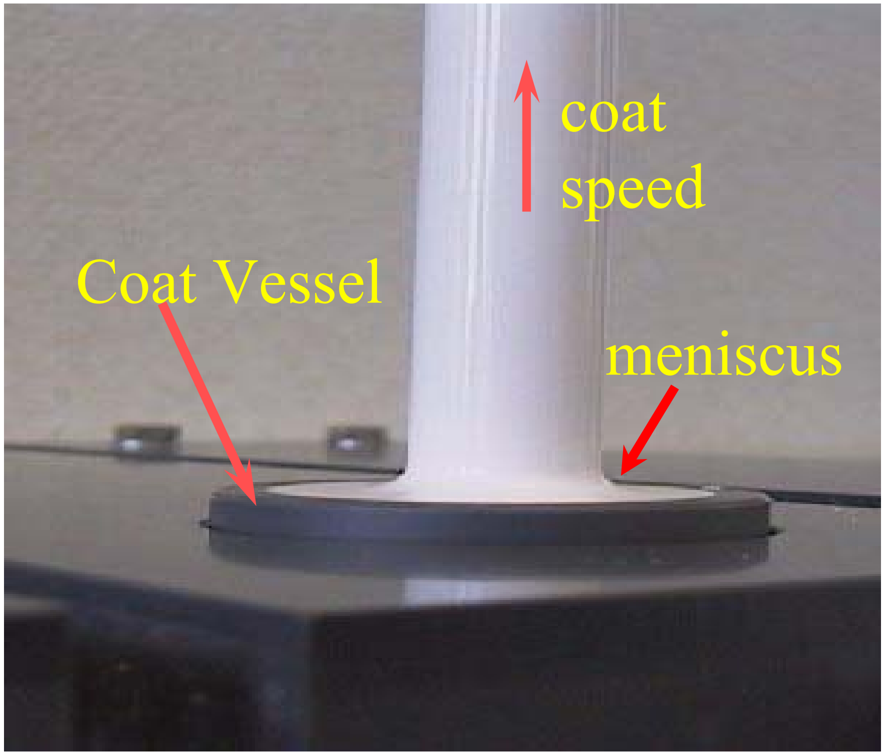




Film Coating

100 cm



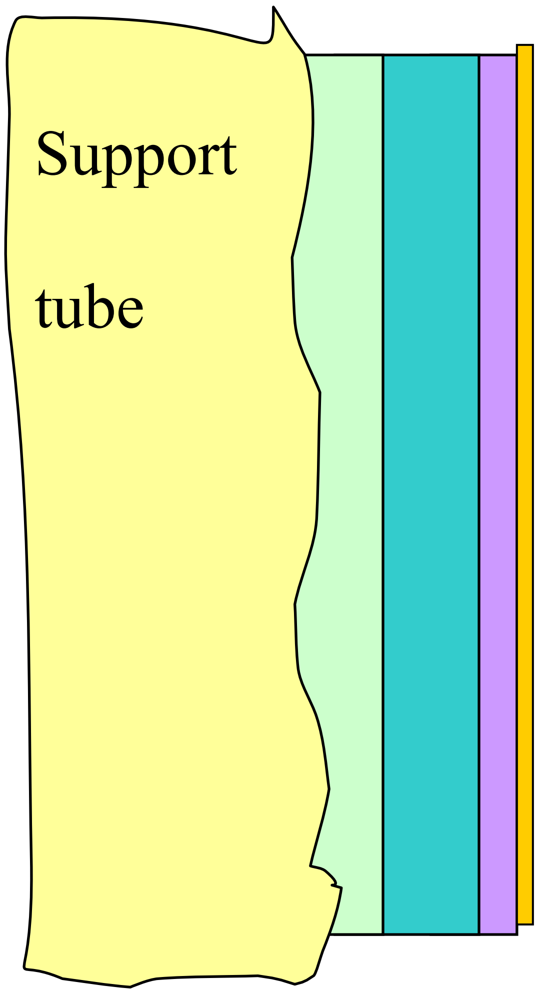


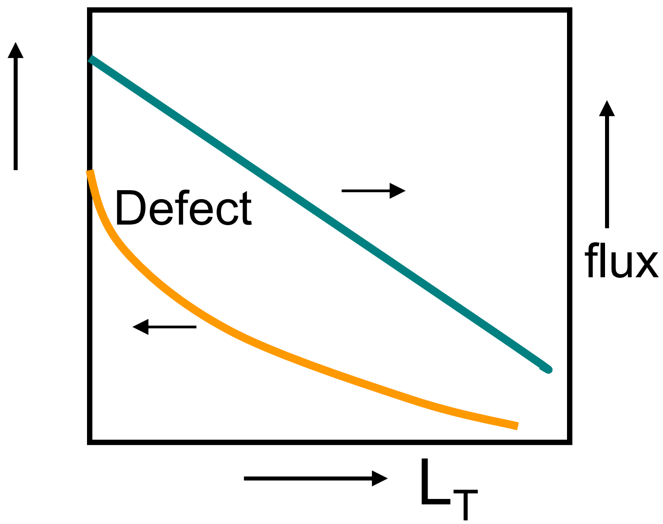
Design of Experiments

Stacking of layers

Minimum defect density

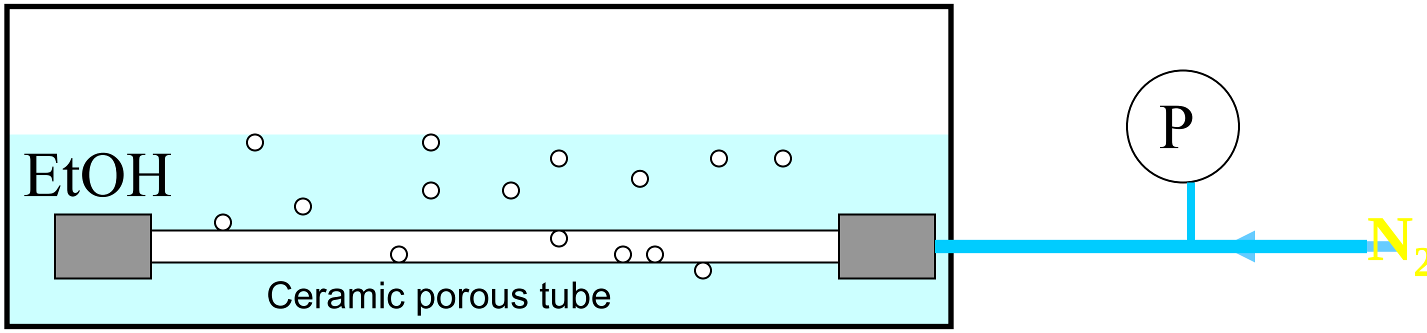
$L_T = L_1 + L_2 + \ldots ?$

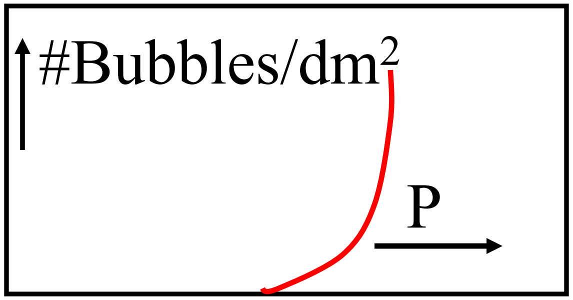




High Troughput experiments

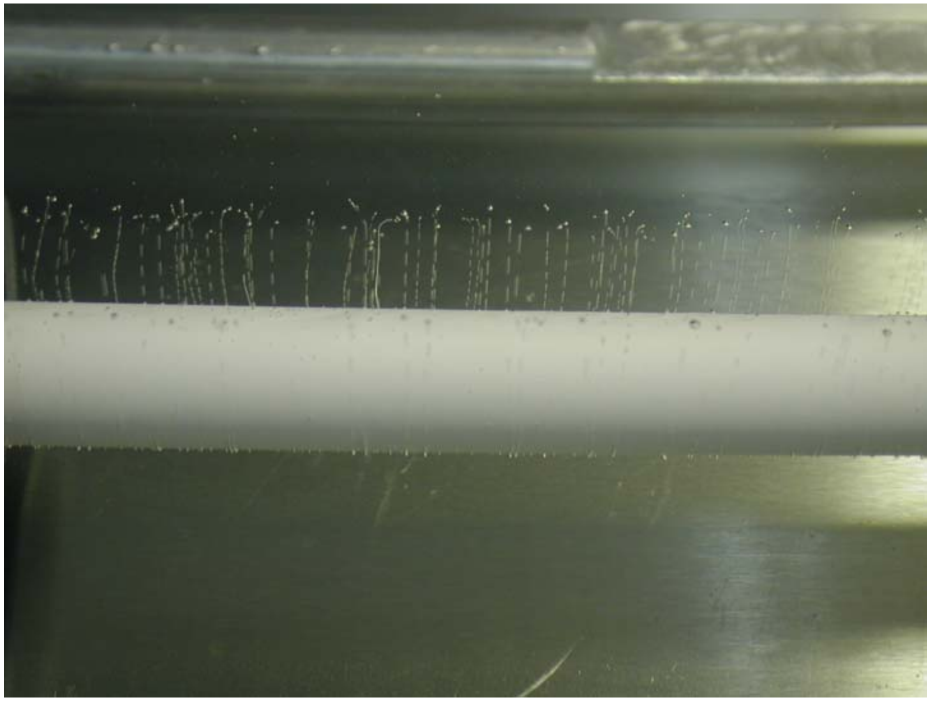
Bubble porometry



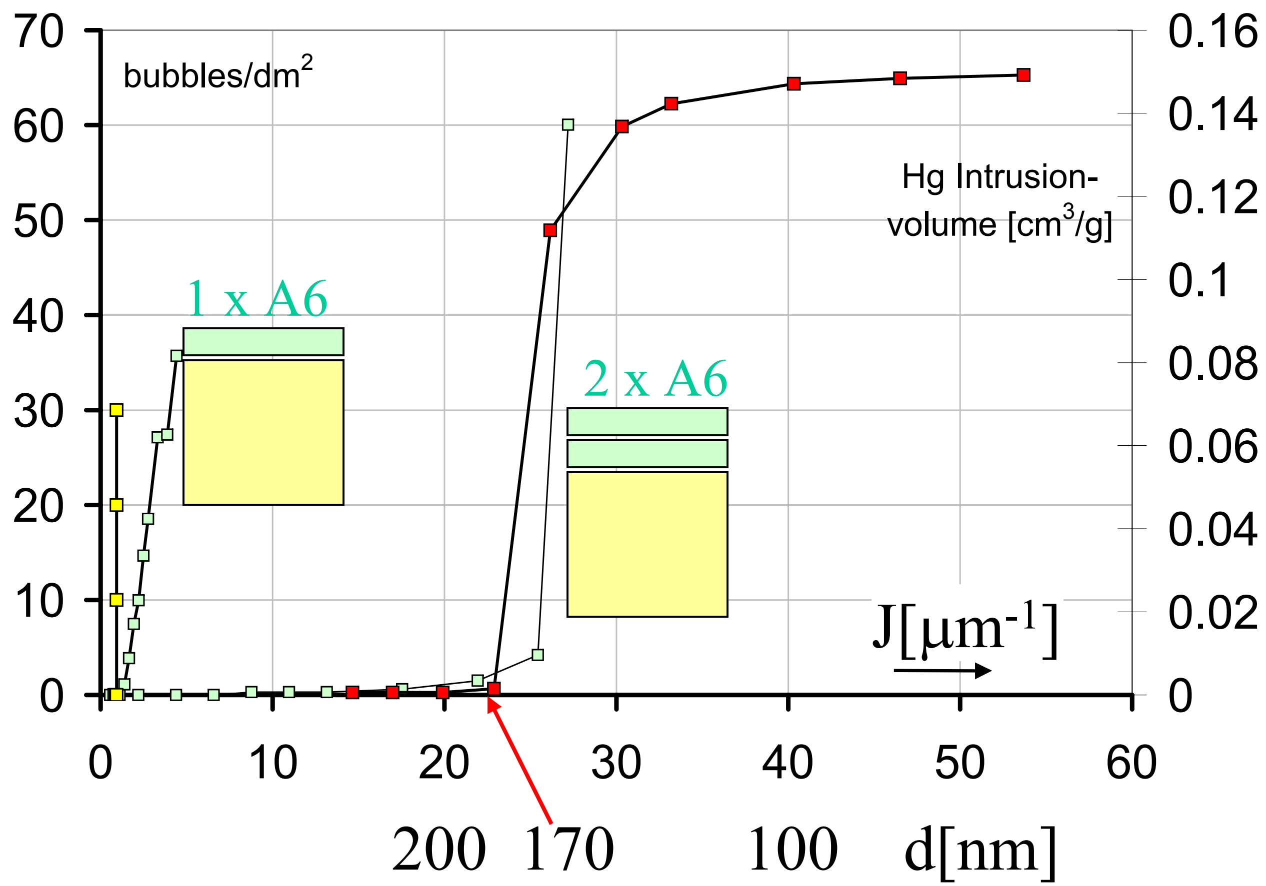


$$\Delta P = \frac{4\gamma}{d}$$

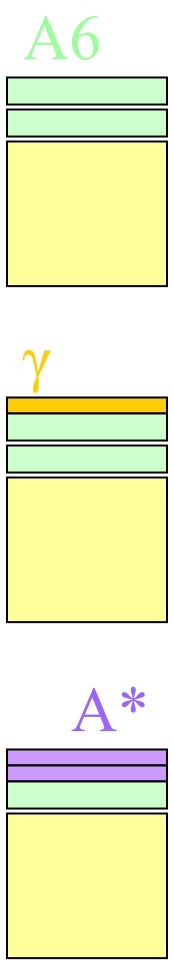
Bubble porometry

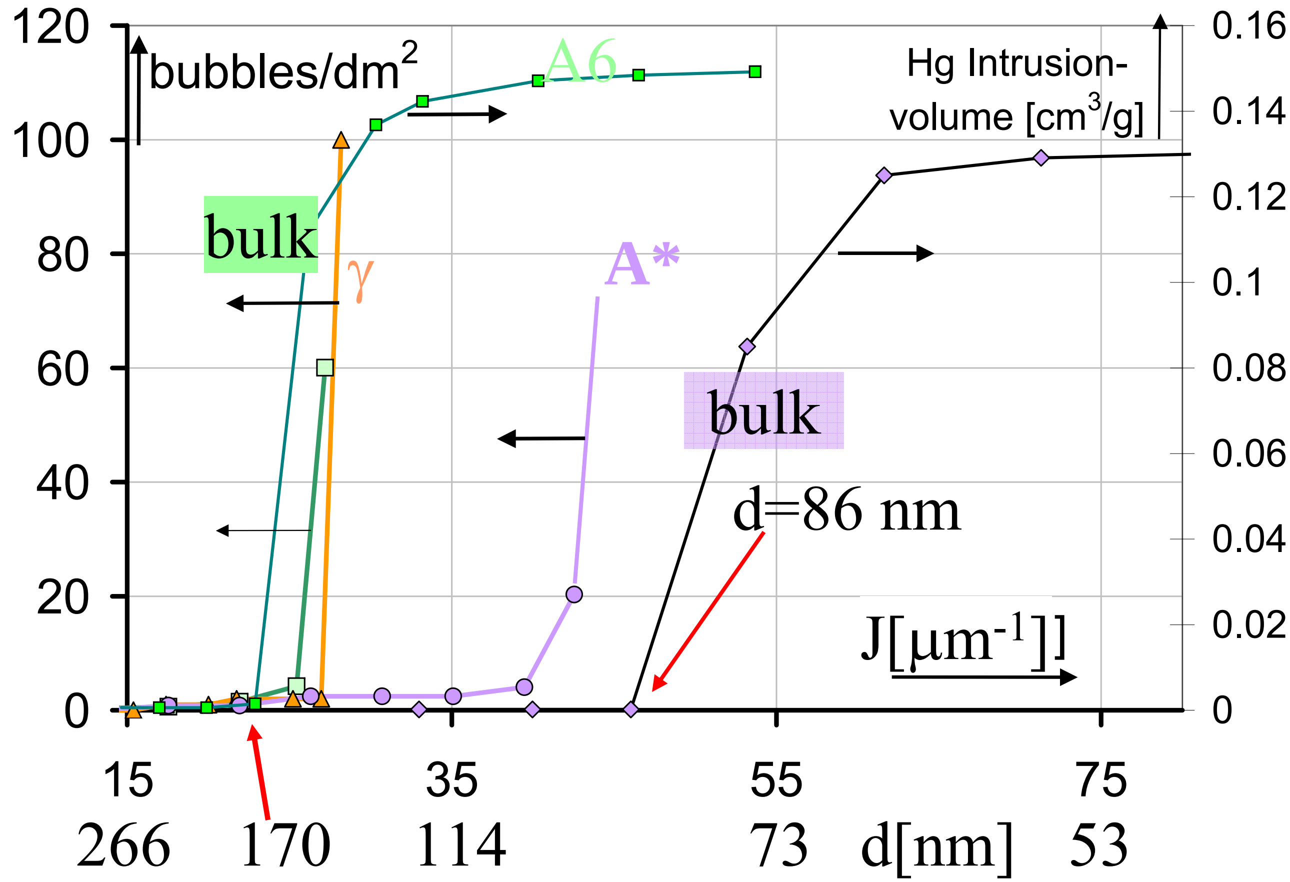


Porometry double A6 support coating



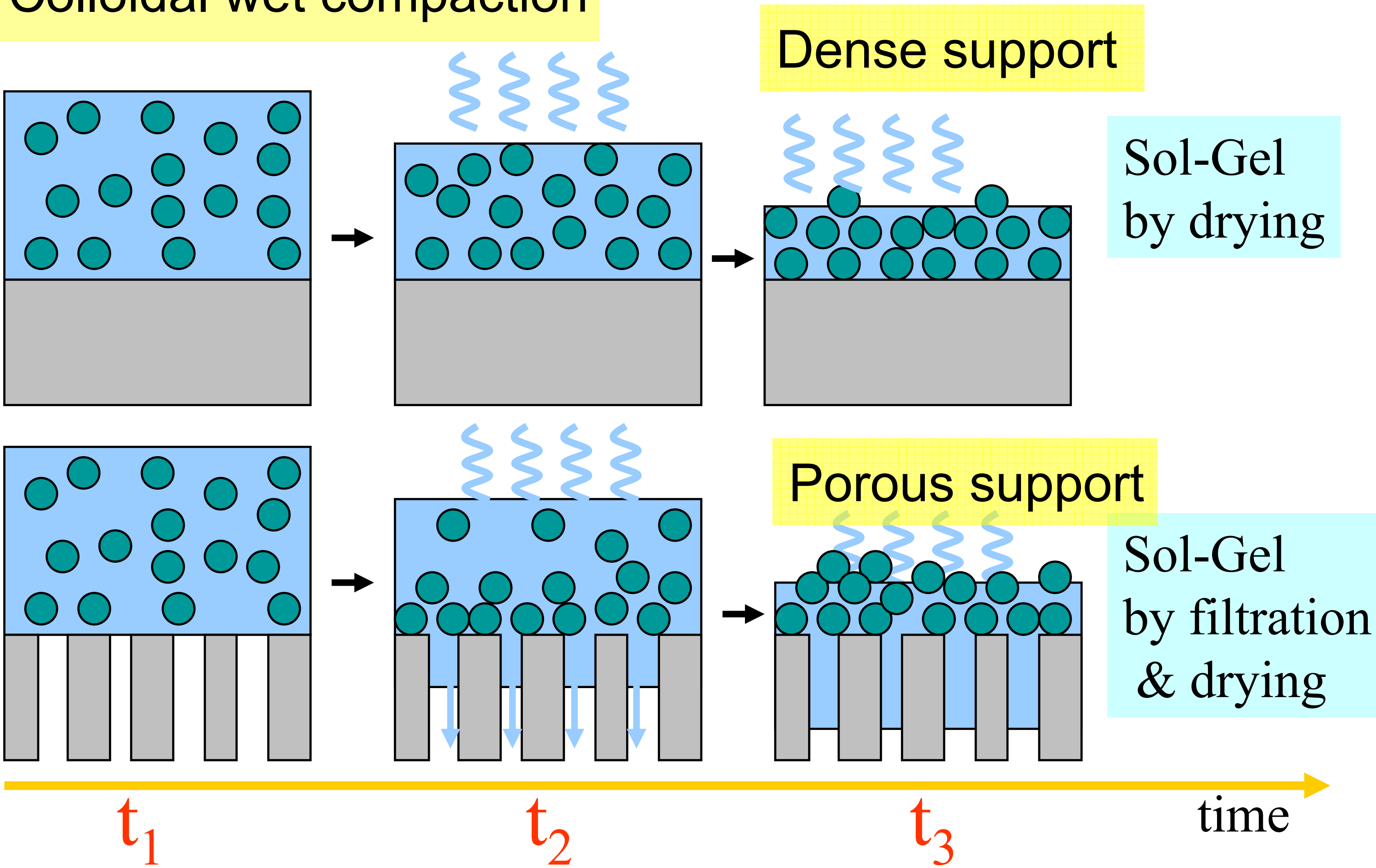
Porometry A6 and A* coatings



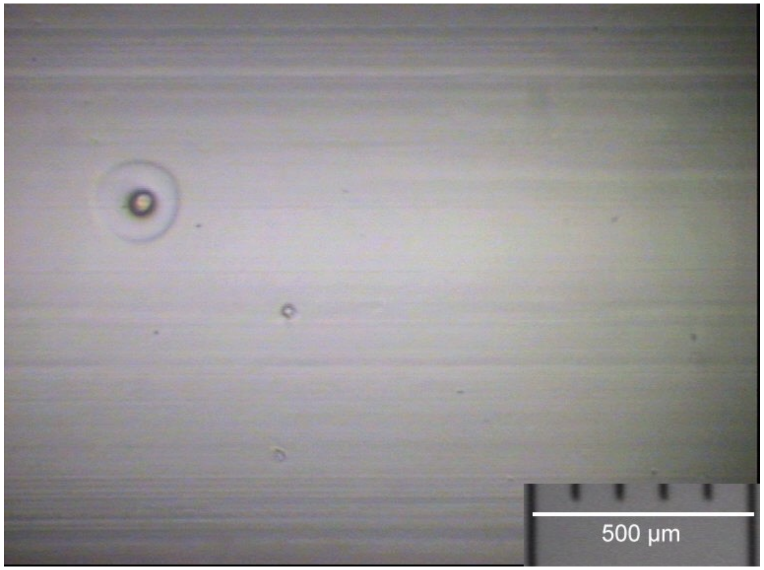


Sol-Gel Thin Film Forming

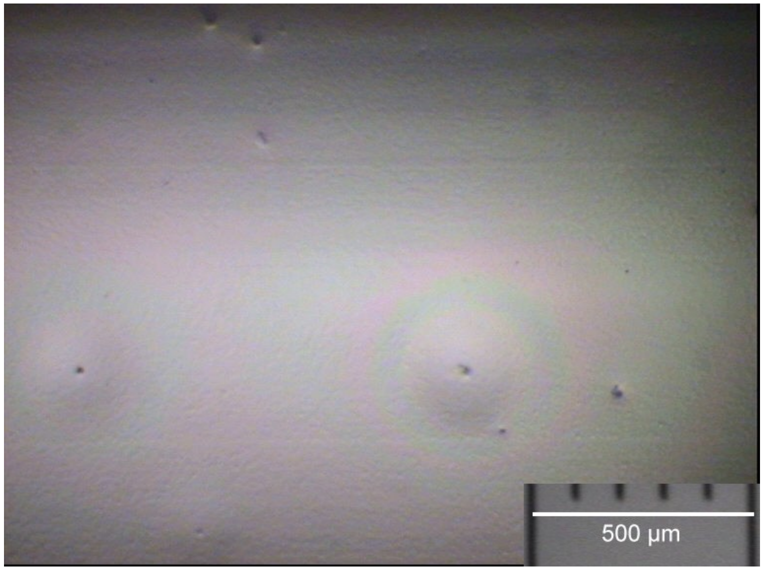
Colloidal wet compaction



Optical microscopy

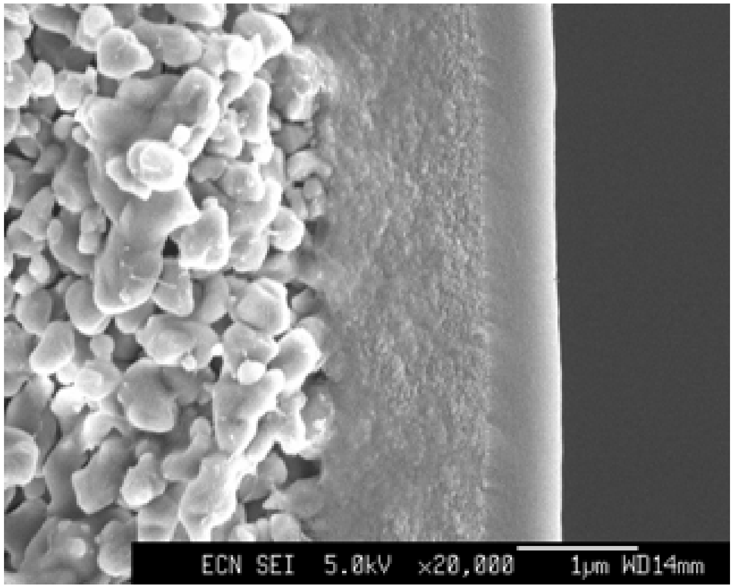


Calcined mesoporous alumina film

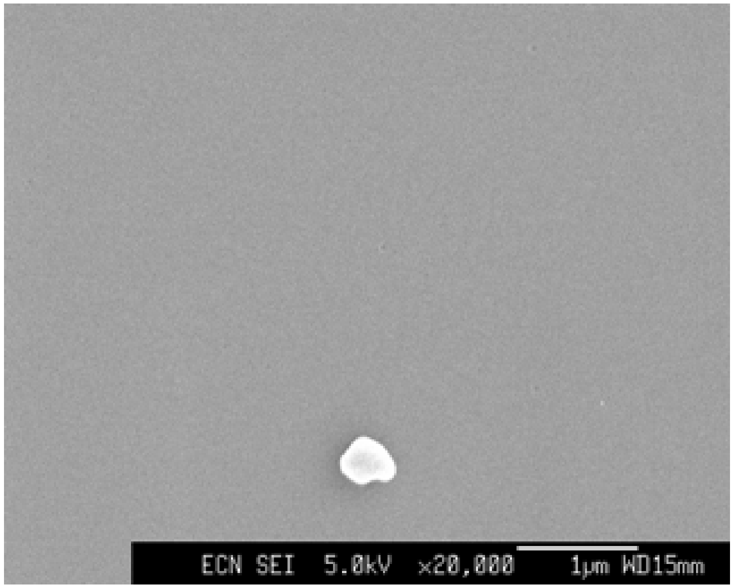


Calcined microporous hybrid organosilica film

SEM

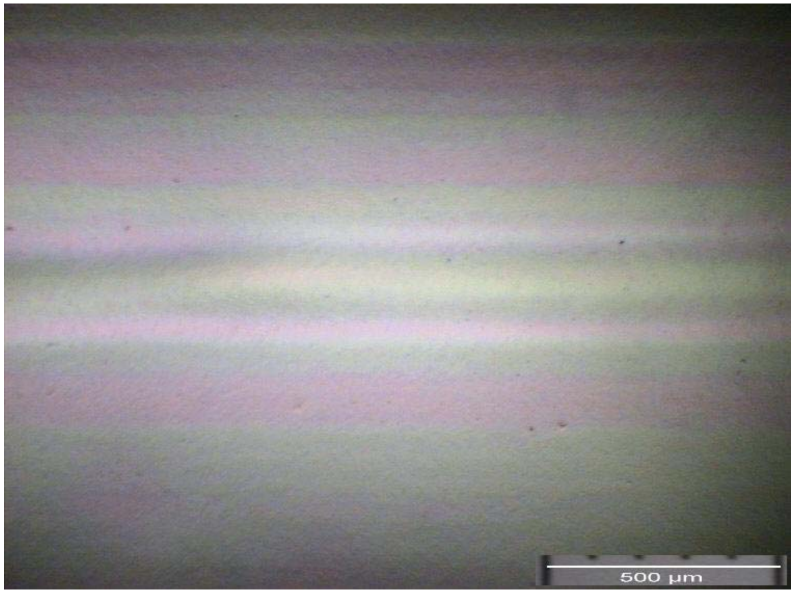


Calcined microporous hybrid silica film; fracture surface

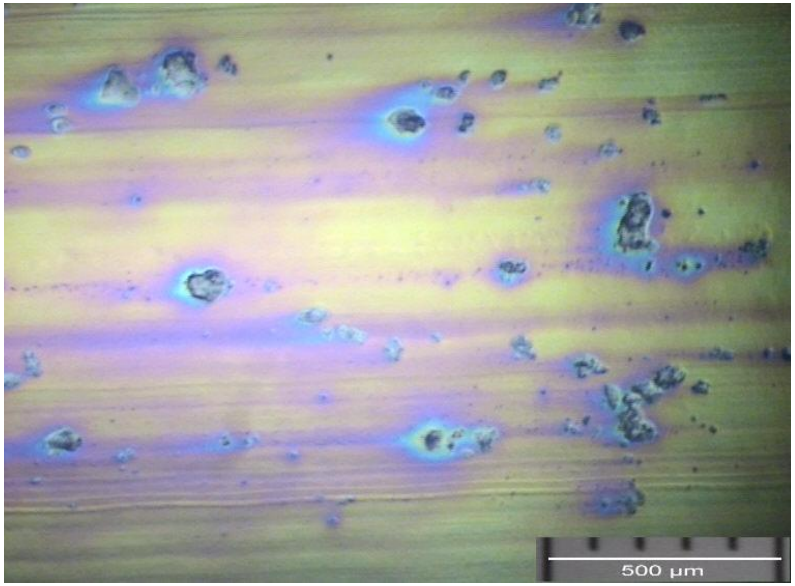


Calcined microporous hybrid silica film; surface

Optical microscopy

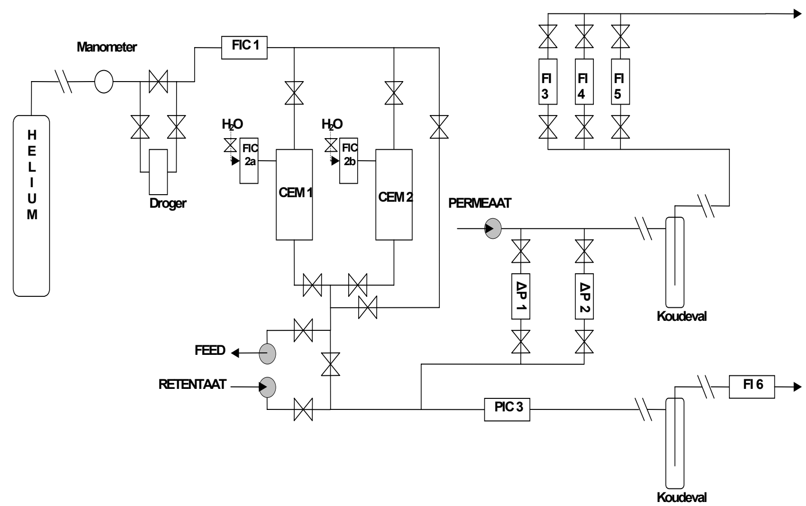


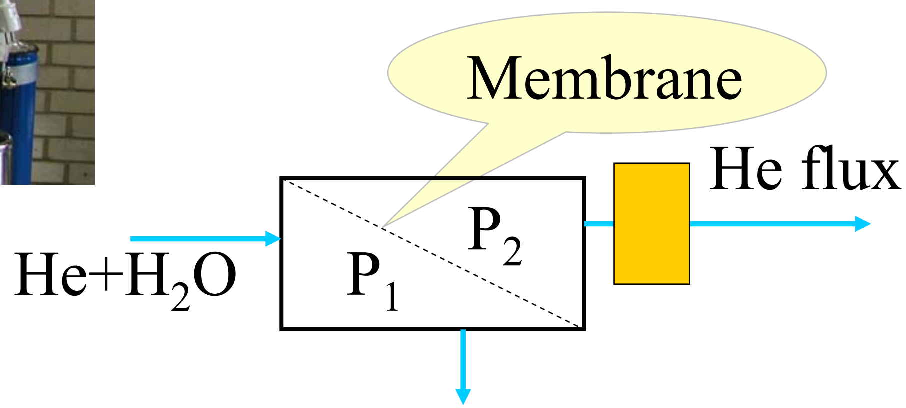
Dried mesoporous titania film



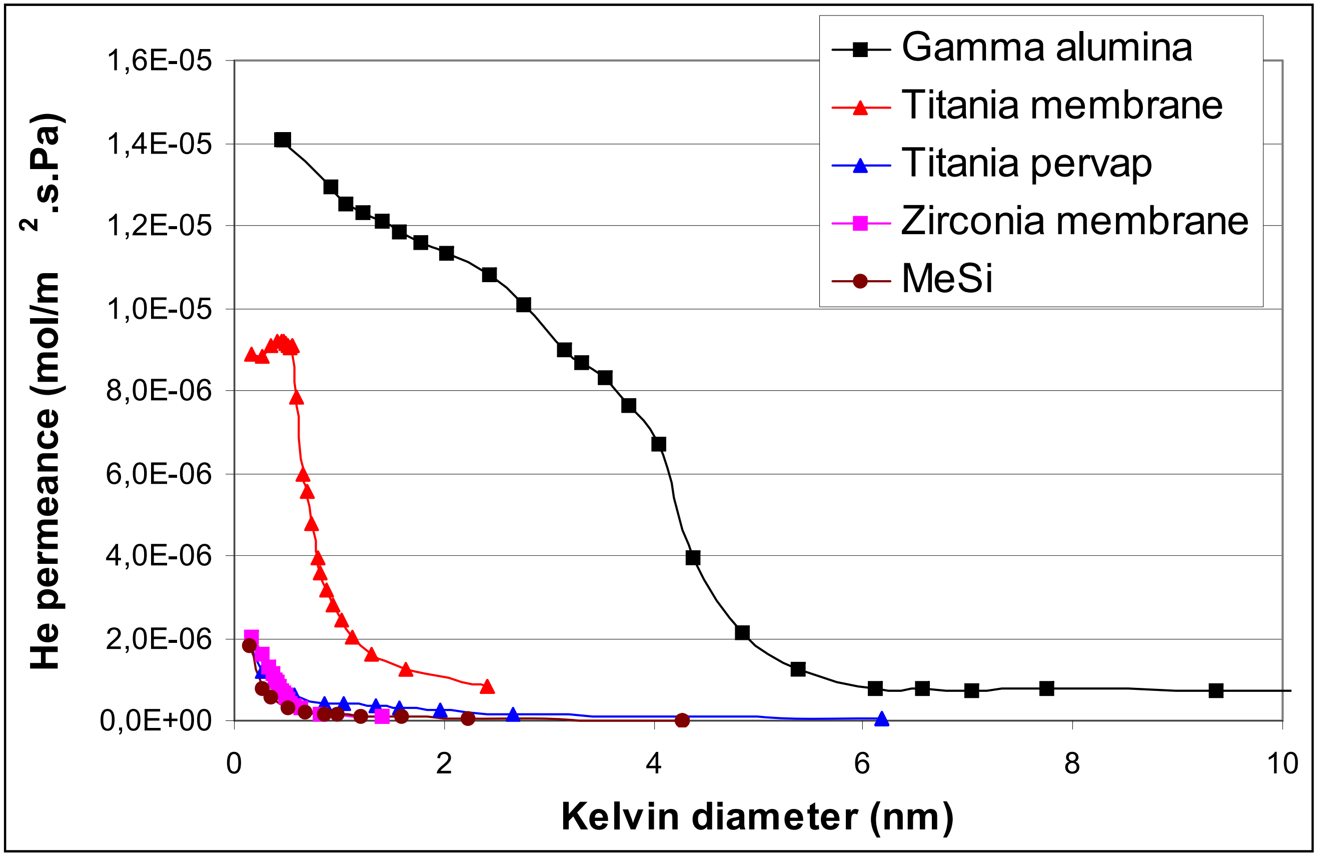
Dried microporous titania film

Permporometry





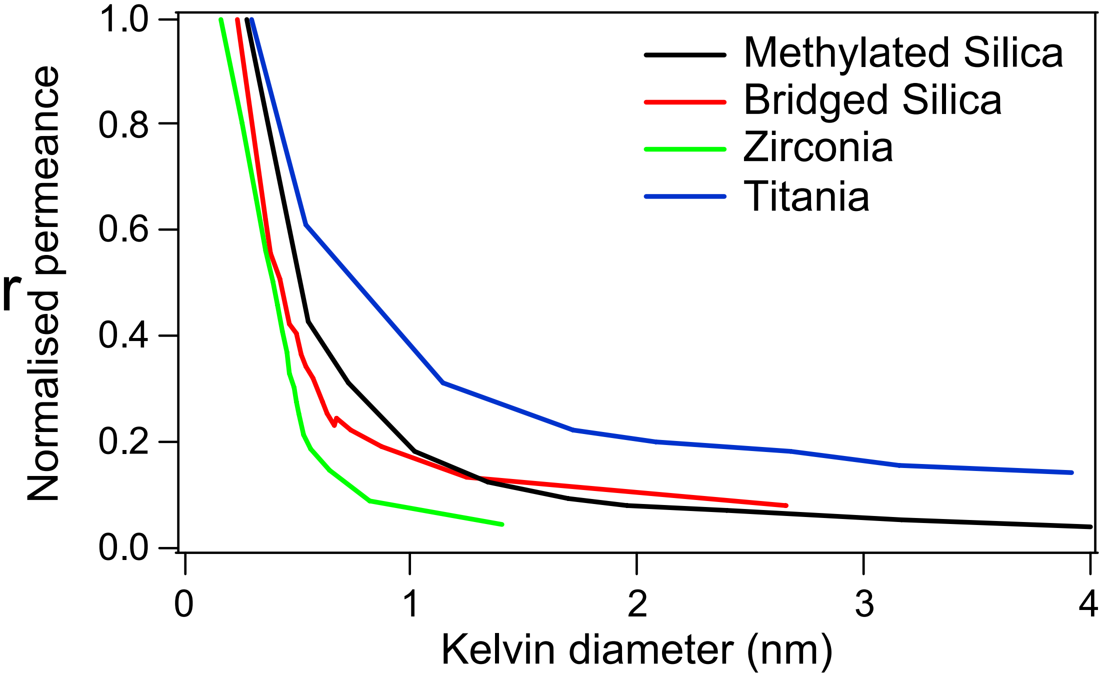
Thin Film Permporometry Overview



ECN

Permporometry microporous membranes

- Permporometry with H_2O
- Suitable for thin toplayers
- All membranes similar
- N_2 and mercury adsorption methods are for bulk material, not for thin layers!



Concluding remarks

Conclusions

- Highly reproducible organosilica sols and nanoparticle ZrO_2 and TiO_2 sols.
- Successful large surface area thin film preparation
- Control over defect density and size
- Long term hydrothermal stability
- High performance microporous organosilica, ZrO_2 and TiO_2 sol-gel thin films on large tubes

Acknowledgements

The MST group at ECN

Questions ?

Contact: bonekamp@ecn.nl

ECN

Additional

Introduction

BUT

Pervaporation membrane stability is limited with respect to:

- (Hydro) thermal conditions
- Solvent resistance
- Acids

Pervaporation membrane materials: goals set

- Test conditions dehydration of organics by pervaporation:

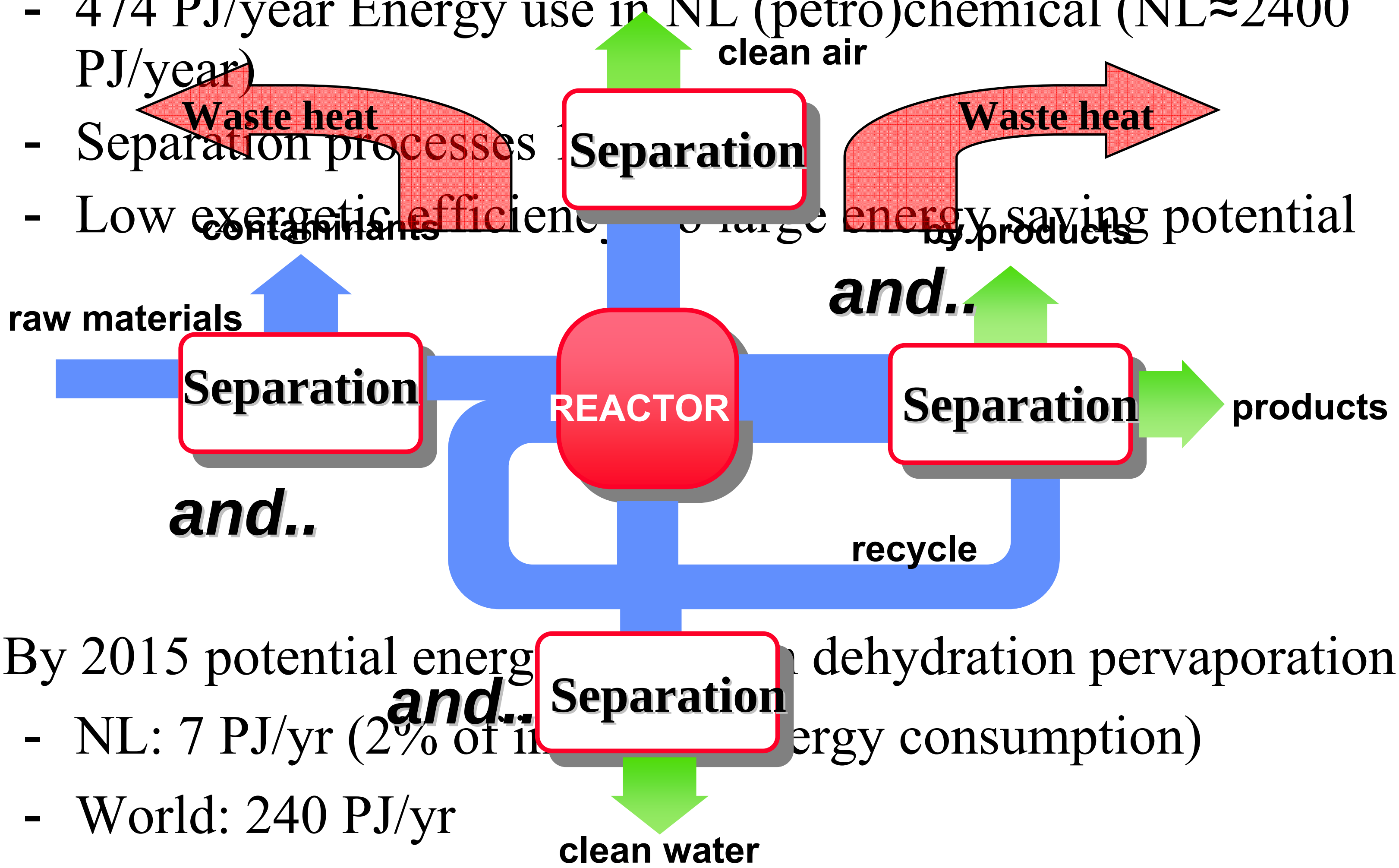
1. Temperature: 150°C.
2. Mixture 5 wt.% water in n-butanol.
3. Acidity: pH 2-10.
4. Pressures and pressure differences up to 30 bar

- and the membrane process should meet the following industrial demands:

1. Water flux of 5 kg/m^{2}h.
2. Selectivity of at least 360 (feed 5 wt.% water → permeate 95 wt.% water).
3. Run time of 3 years = average maintenance time of a process.
4. Change of flux and selectivity of less than 10% per year.

Introduction

- 474 PJ/year Energy use in NL (petro)chemical (NL≈2400 PJ/year)
- Separation processes …
- Low exergetic efficienc… large energy saving potential



- By 2015 potential energ… dehydration pervaporation:
  - NL: 7 PJ/yr (2% of i… ergy consumption)
  - World: 240 PJ/yr