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Sol-gel routes towards microporous titania and zirconia membranes on tubular supports

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Sol-gel routes towards microporous titania and zirconia membranes on tubular supports

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Oral presentation

Industrial separation processes consume around 40% of the total energy use in the (petro)chemical industry. For the separation of many liquid or gaseous mixtures molecular separation using membranes is a much more efficient option [1, 2]. To achieve this, industrial demands of (long term) stability, pressure resistance, and permeance should be met. Unlike most polymeric membranes, ceramic membranes such as microporous titania and zirconia membranes are potentially stable at temperatures over 100°C. Moreover, careful design of the ceramic support system ensures mechanical stability and high permeance of the membrane layer. Most of the reported titania and zirconia membranes have pore sizes over 1 nm and are very limited in surface area. Therefore, industrial application of these membranes in molecular separations has not yet been demonstrated.

We will show sol-gel routes towards microporous ceramic membranes on tubular supports. By tailoring the particle size of the sol, the pore size of the resulting membrane is tuned. The resulting pore size distributions are narrow and range in mean size from 0.4-1.0 nm. Defect control on these membranes will also be discussed. To arrive at a mechanically and chemically stable support system, a tubular multilayer support was selected. The application of these membranes in pervaporation and their long-term behaviour is presented.

[1] Van Veen, H.M.; van Delft, Y.C.; Engelen, C.W.R.; Pex, P.P.A.C. *Separation and Purification Technology* **2001,** *22-23* 361-366.

[2] Campaniello, J.; Engelen, C.W.R.; Haije, W.G.; Pex, P.P.A.C.; Vente, J.F. *Chem. Commun.* **2004,** 834.

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Sol-gel routes towards microporous zirconia and titania membranes on tubular supports

Rob Kreiter

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- Non-governmental, non-profit institute
- One of the leading European institutes in energy research
- Develops and implements high-level knowledge and technology for the transition to a sustainable energy system
- Bridges the gap between fundamental research and industrial application

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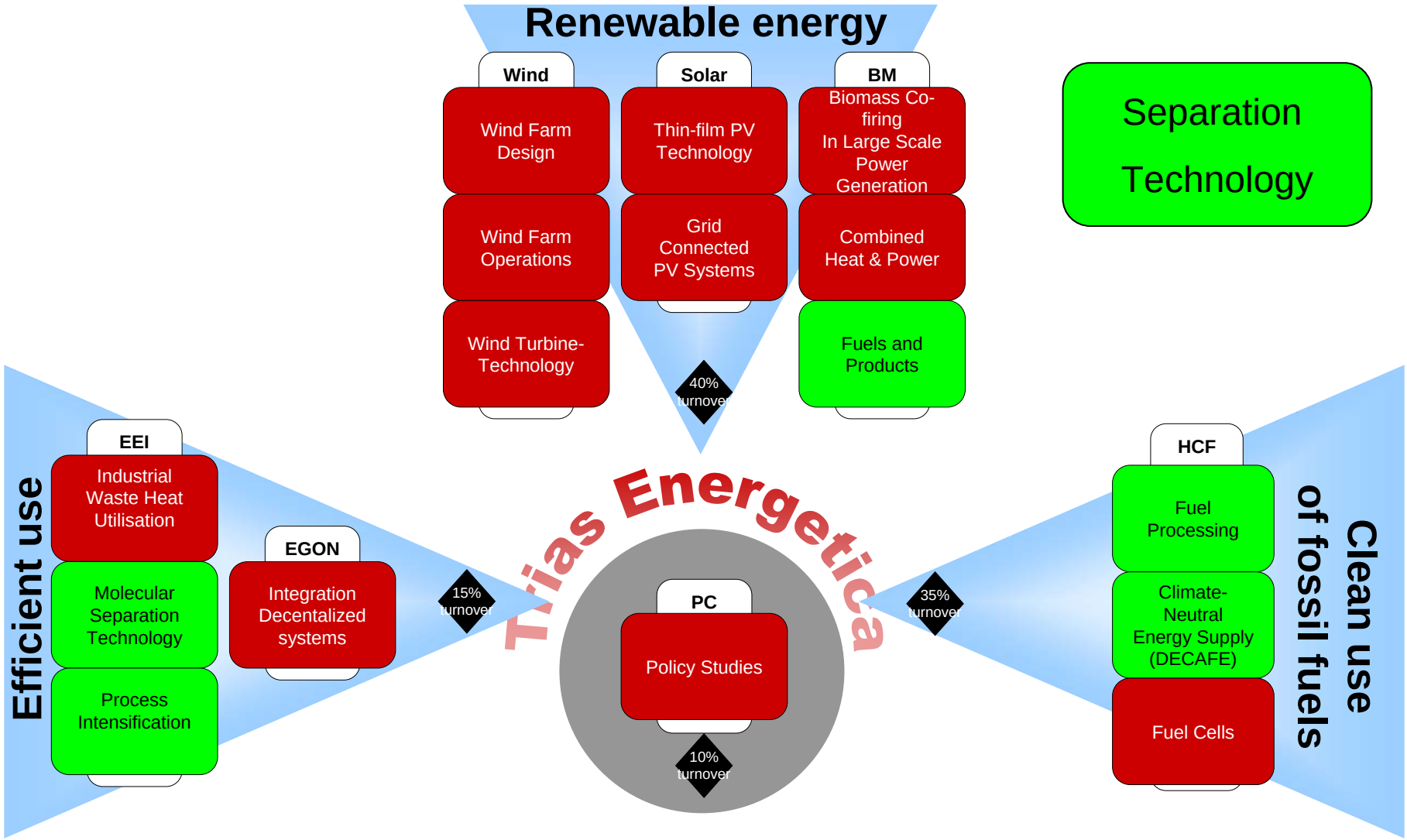
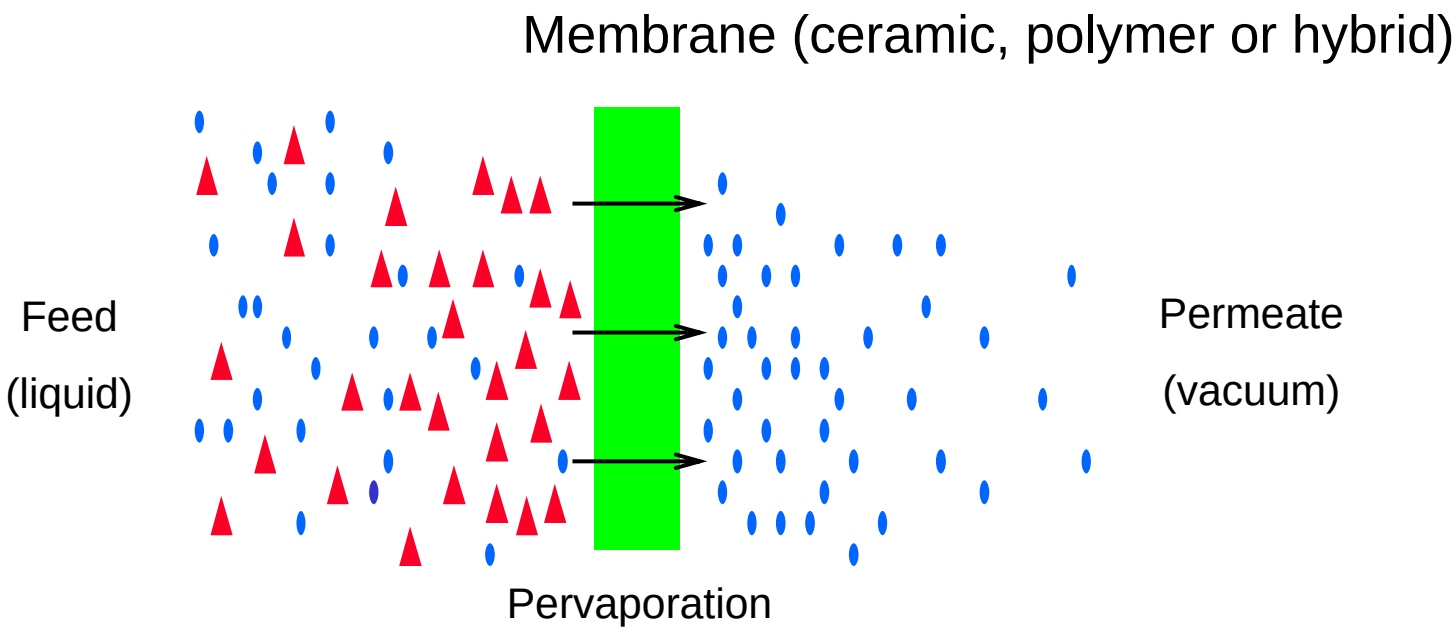

Renewable energy
Wind
Wind Farm Design
Wind Farm Operations
Wind Turbine-Technology
Solar
Thin-film PV Technology
Grid Connected PV Systems
BM
Biomass Co-firing In Large Scale Power Generation
Combined Heat & Power
Fuels and Products
40% turnover
Separation Technology
Efficient use
EEI
Industrial Waste Heat Utilisation
Molecular Separation Technology
Process Intensification
EGON
Integration Decentalized systems
15% turnover
Trias Energetica
PC
Policy Studies
10% turnover
35% turnover
HCF
Fuel Processing
Climate-Neutral Energy Supply (DECAFE)
Fuel Cells
Clean use of fossil fuels

Industrial application of membranes

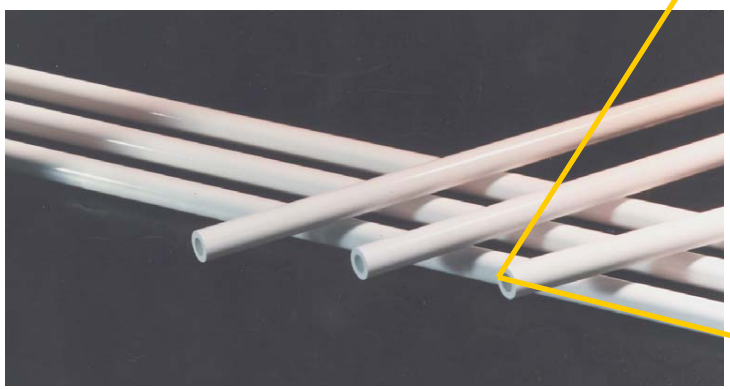
- **Pervaporation**
  - Dewatering of organics, methanol from MTBE or toluene
- **NH_3 separation**
  - Ammonia from synthesis loop
- **Hydrogen separation**
  - Dehydrogenation, steam reforming, water gas shift, recycle loops
- **Oxygen separation**
  - Oxygen production, syngas, partial oxidation of hydrocarbons
- **Hydrocarbon separation**
  - Natural gas processing (CO_2/CH_4), close boilers, olefines/paraffines
- **Nanofiltration**
  - Dyes, macromolecules, catalysts

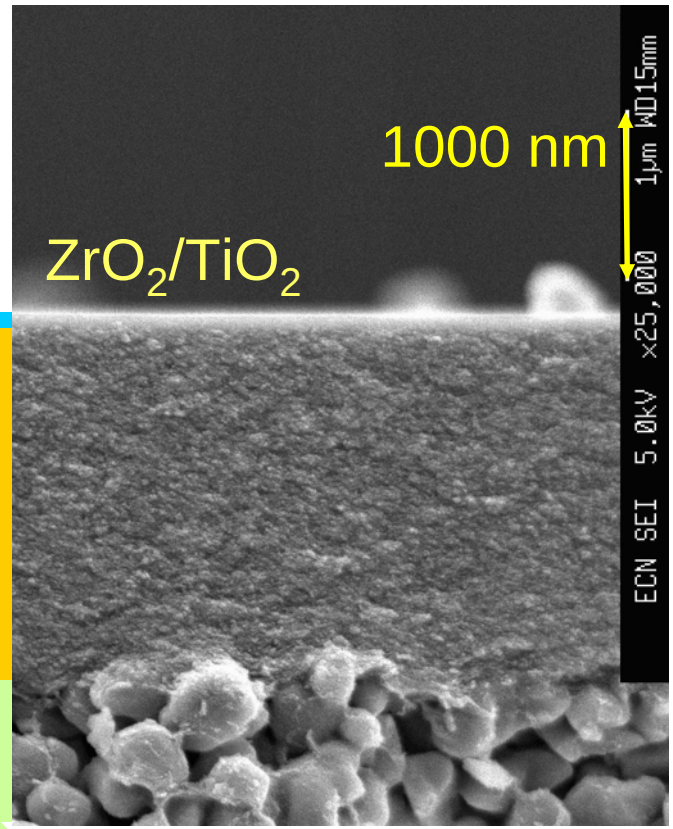
Pervaporation

- Combination of permeation and evaporation
- Selective evaporation of liquids via a membrane
- Much more energy efficient than distillation



Tubular microporous membranes



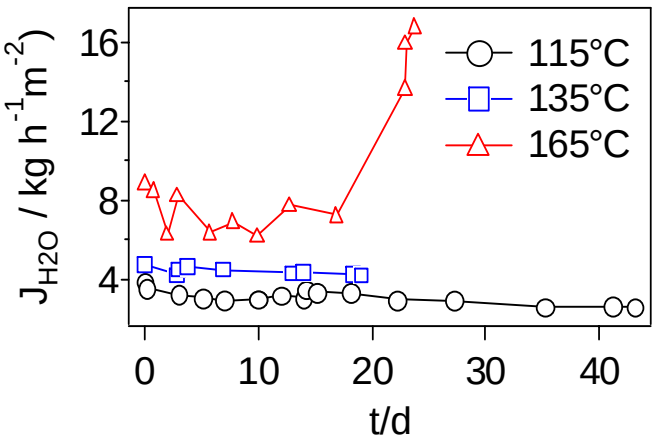


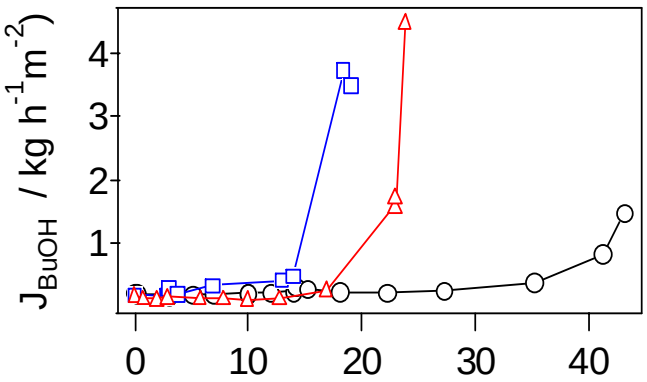
Industrial performance demands

Standard ECN tests: 5 wt.% water in butanol

- Fluxes 3-5 kg/m^{2}h
- Selectivity > 220 (>95% H_2O in permeate)
- Life-time 2 - 3 years
- Conditions: pH of 2-10, T of 100-150°C

Results for Me-SiO_2: not stable





Chem.Commun. 2004, 834-835

Alternative materials

Zirconia and titania should meet the required demands

- Via sol-gel: *e.g.* $Zr(PrO)_4 + 2\ H_2O \rightarrow ZrO_2 + PrOH$
  - Very fast kinetics
  - Uncontrolled particle growth
  - Low reproducibility

Solutions:

- Ligand-modified precursors (AcAc, diethanolamine)

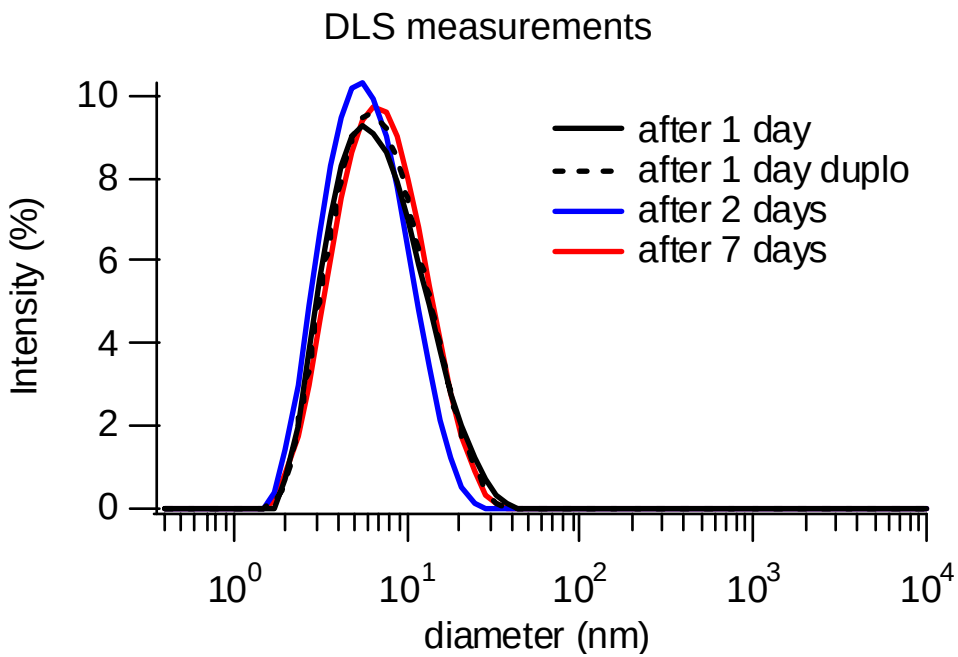
  Spijksma, Bouwmeester, Blank - Twente University
  Kessler - Uppsala
- Micro-emulsions

  Focus of ECN (Based on Smith et al. J.Coll.Int.Sci. 1977)

This presentation

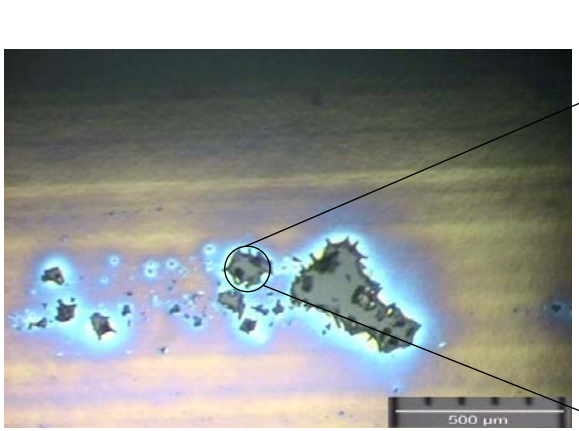
Zirconia sol preparation

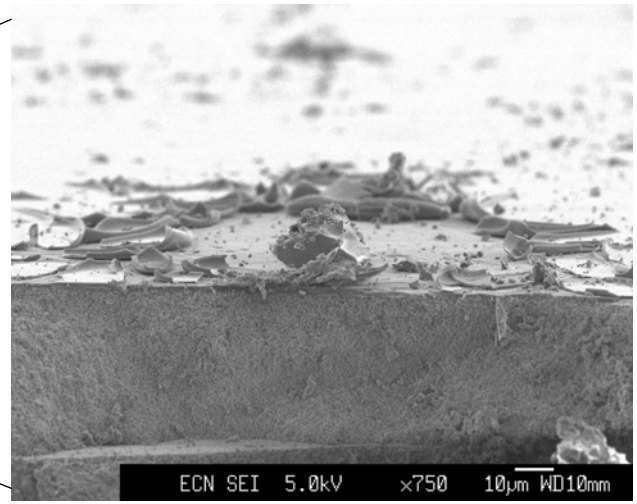
- Premixing of H_2O, hexanol, cyclohexane
- Slow addition of to zirconium n-propoxide in cyclohexane
- Addition of HAc as dispersant



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

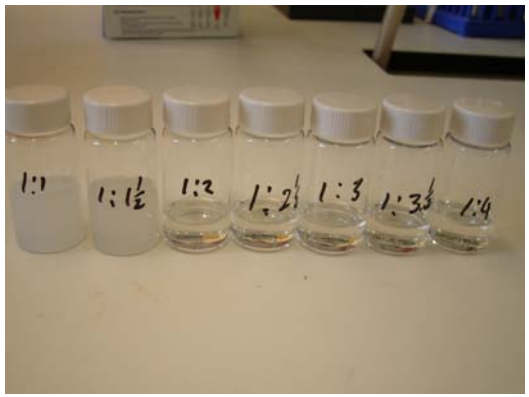
Defect analysis of ZrO_2 membranes

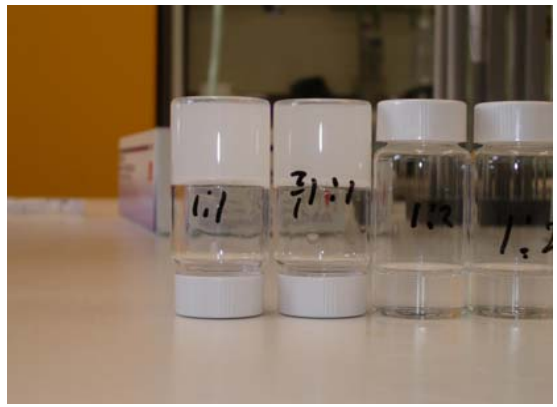


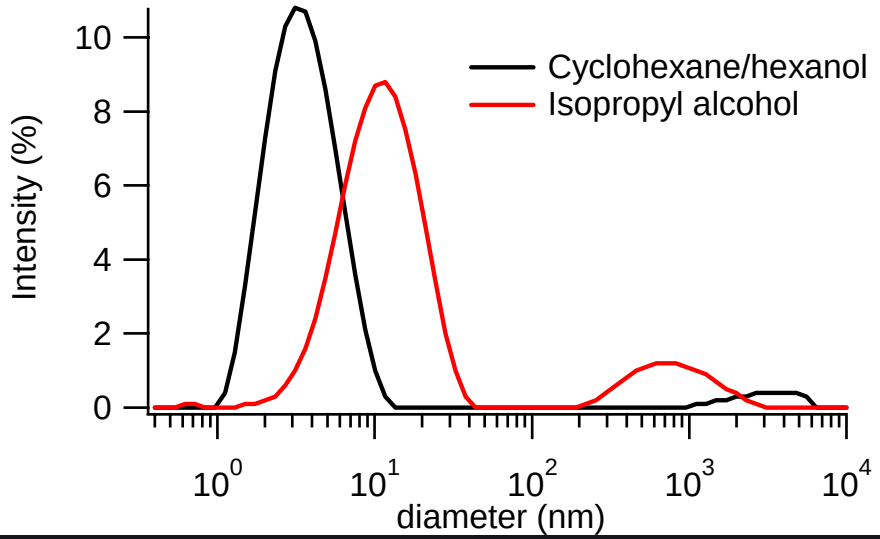


- Delaminated spots
  - sol-support interaction
- Small cracks
  - film thickness

Modification of zirconia sol

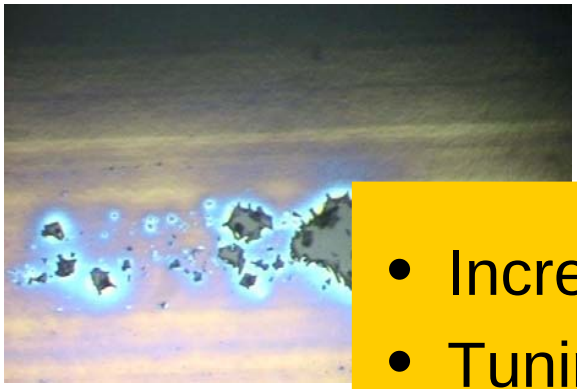


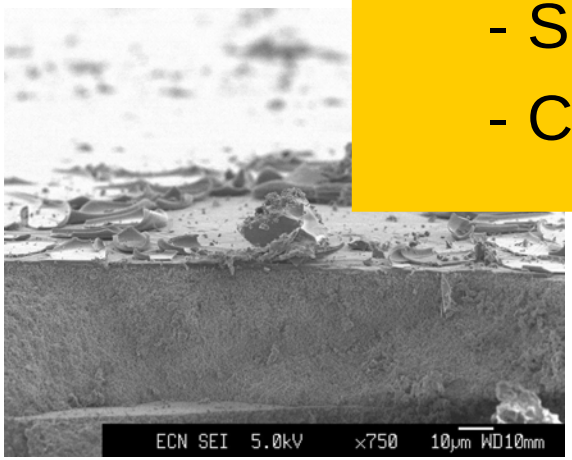




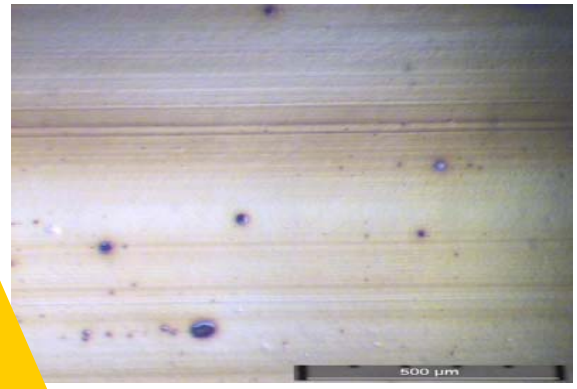
- Increasing amount of HAc
  - [HAc]/[Zr] > 2 needed
  - Improved coating
- Change of solvent by dialysis
  - In IPA larger particles
  - Improved coating (slightly)

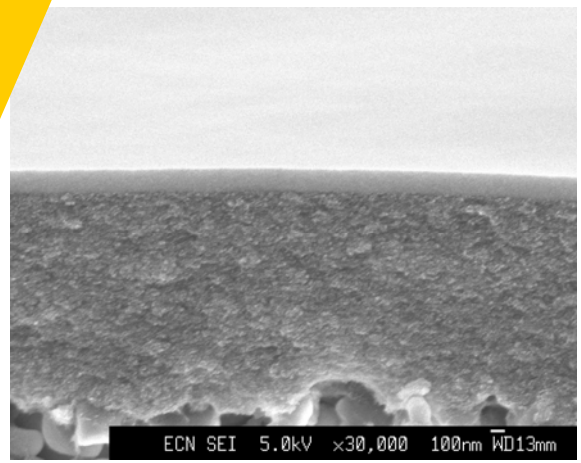
Improvement of ZrO_2 membranes





- Increasing [HAc]/[Zr]
- Tuning of
  - Sol concentration
  - Coating speed

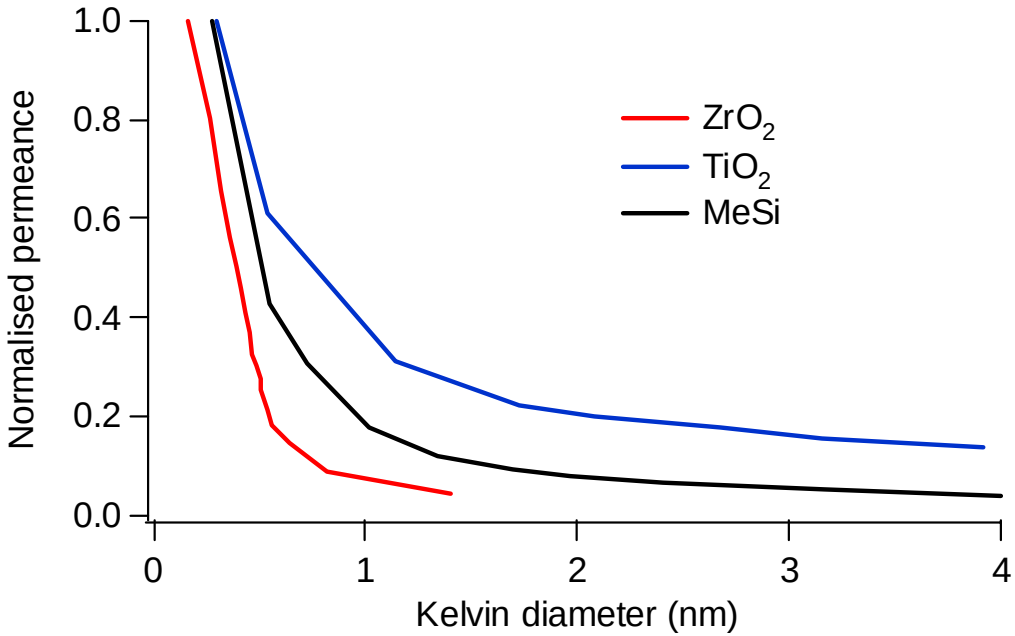




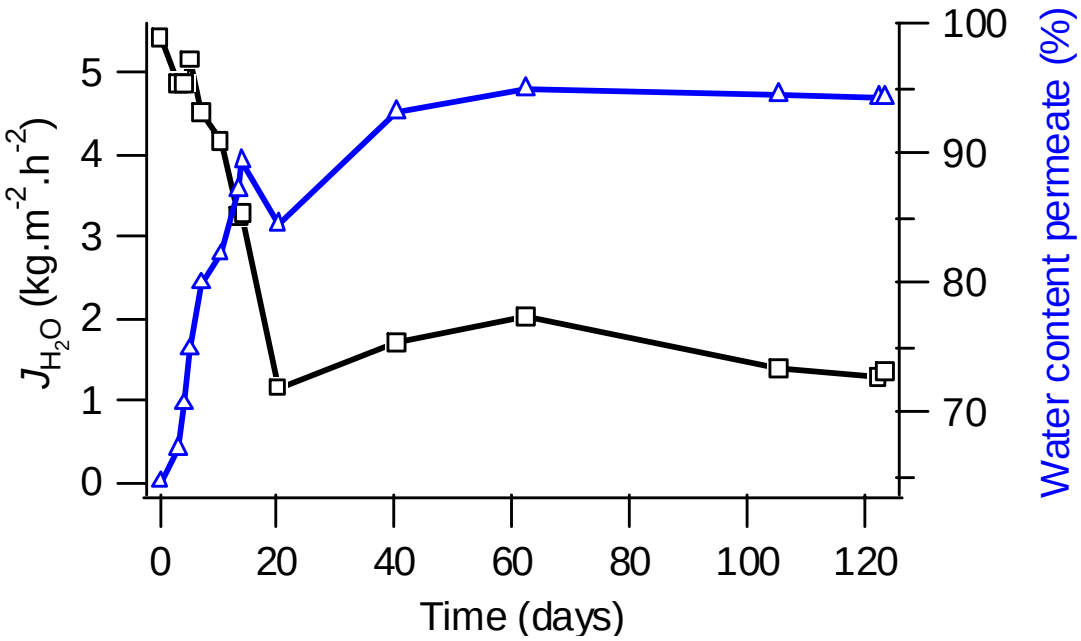
Pore size distribution

- Permporometry with H_2O
  - Suitable for thin toplayers (N_2 and Hg porosimetry are not!)

All 3 types have similar pore size distributions



Pervaporation with zirconia membrane



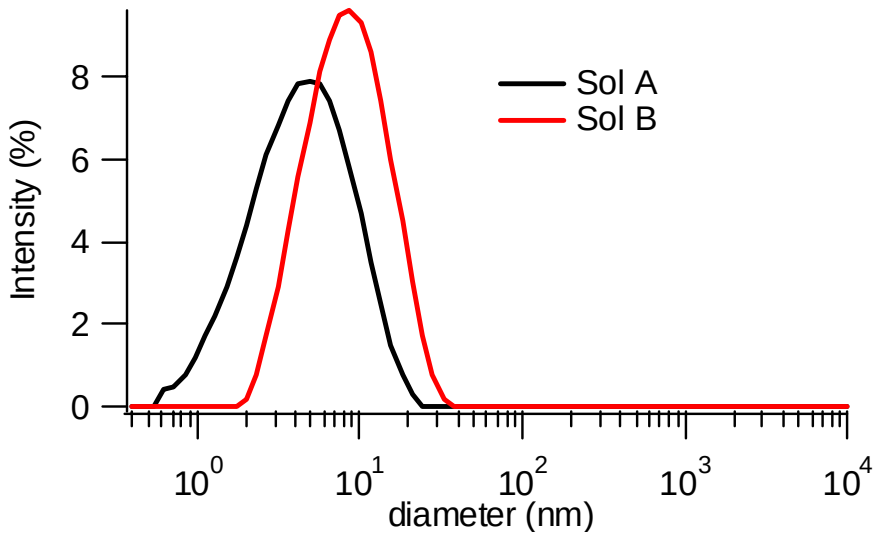
- 95°C, n-butanol/H_2O (95/5%)
- Flux decline, but stable after 20 days
- Operating for at least 120 days

Preparation of TiO_2 sols

- Spin off of our nano-filtration activities
- Various modifiers: HNO_3, HAc, AcAc
- Based on $Ti(O^iPr)_4$, isopropyl alcohol

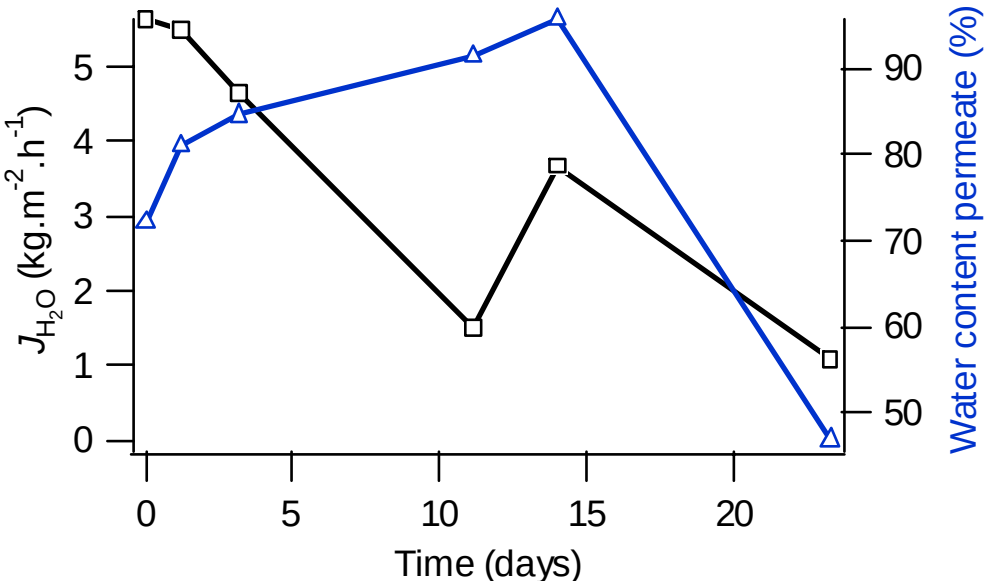
$[H_2O]/[Ti] < 2$ leads to nanoparticle sols

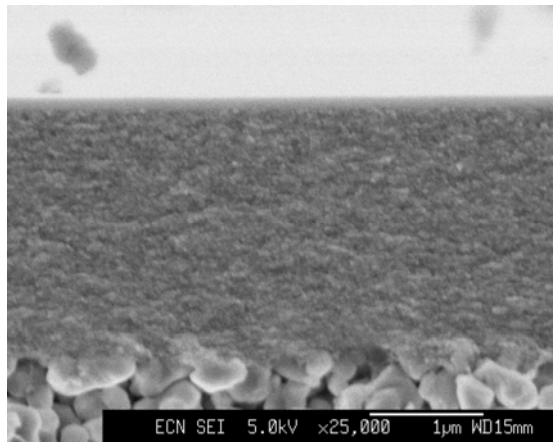
$[H_2O]_A < [H_2O]_B$



Titania membranes

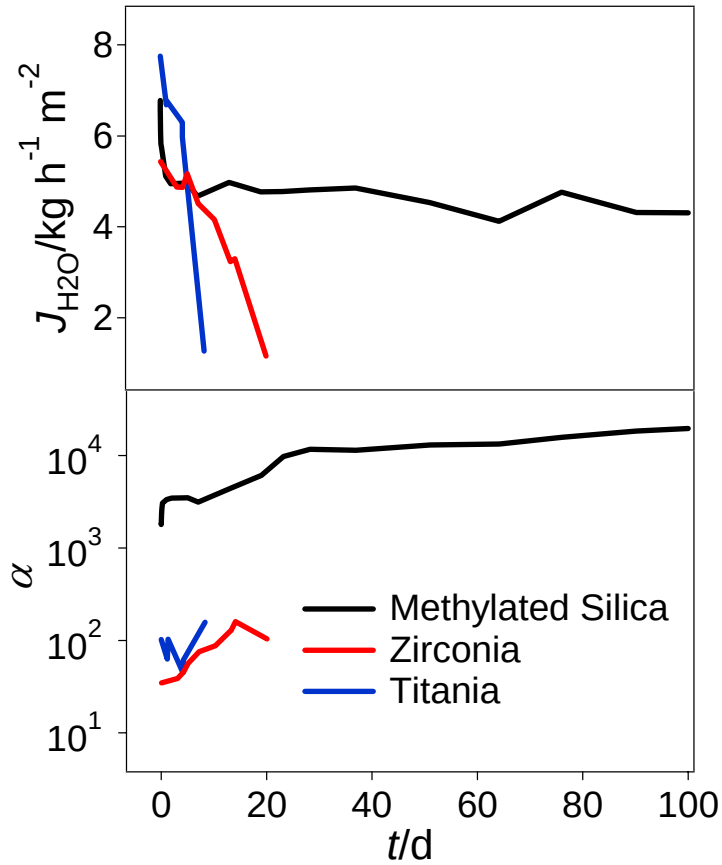
- Different pore size distributions, including pervaporation membranes.
- Stronger flux decline and faster breakdown





Conclusions

- Nanoparticle ZrO_2 and TiO_2 sols highly reproducible
- Successful preparation of tubular microporous ZrO_2 and TiO_2 membranes
- Defect control improved
- Long-term pervaporation promising
- Post test analysis will be done



Acknowledgements

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