Materials research for sustainable energy production

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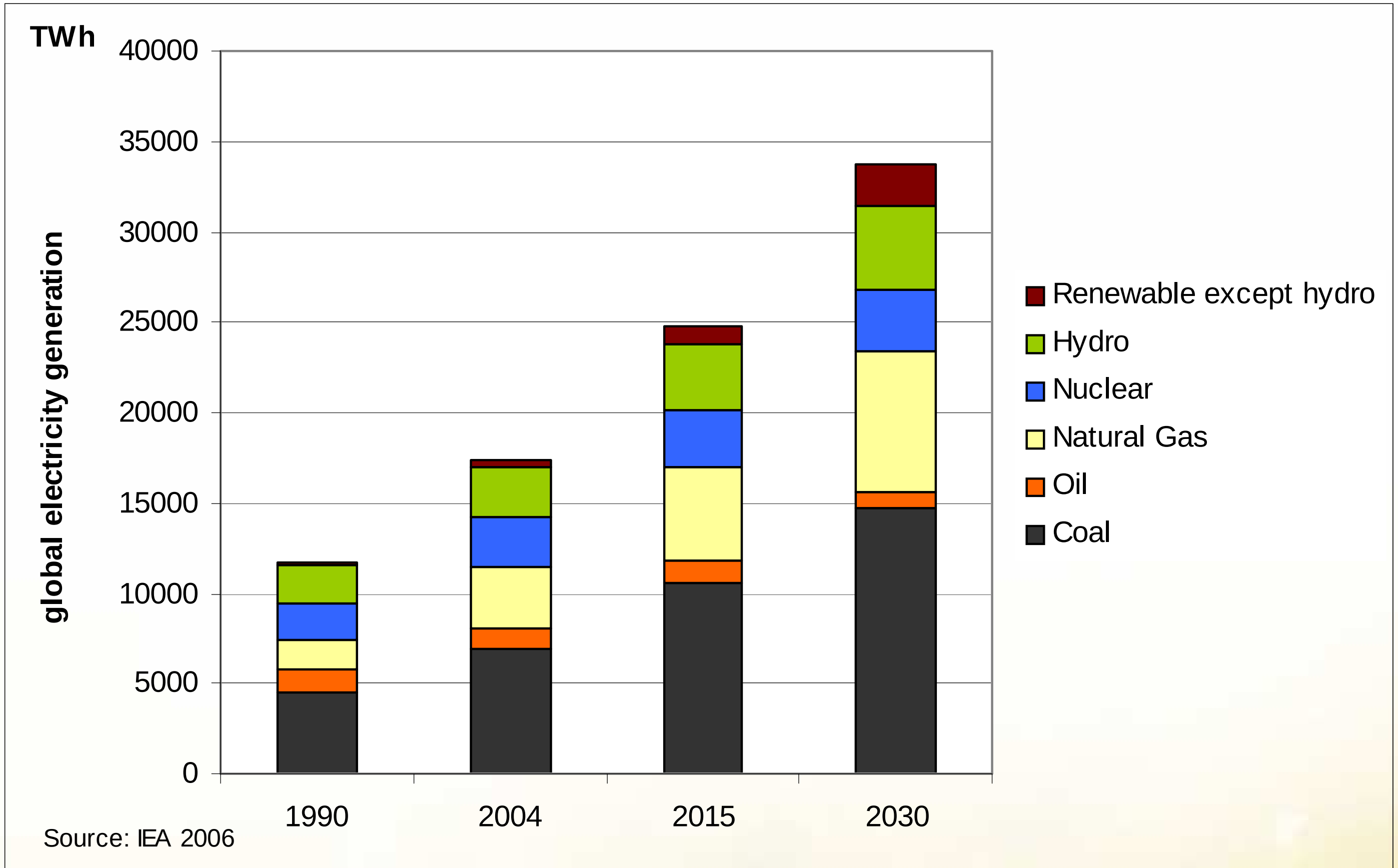
Expected evolution of electricity generation

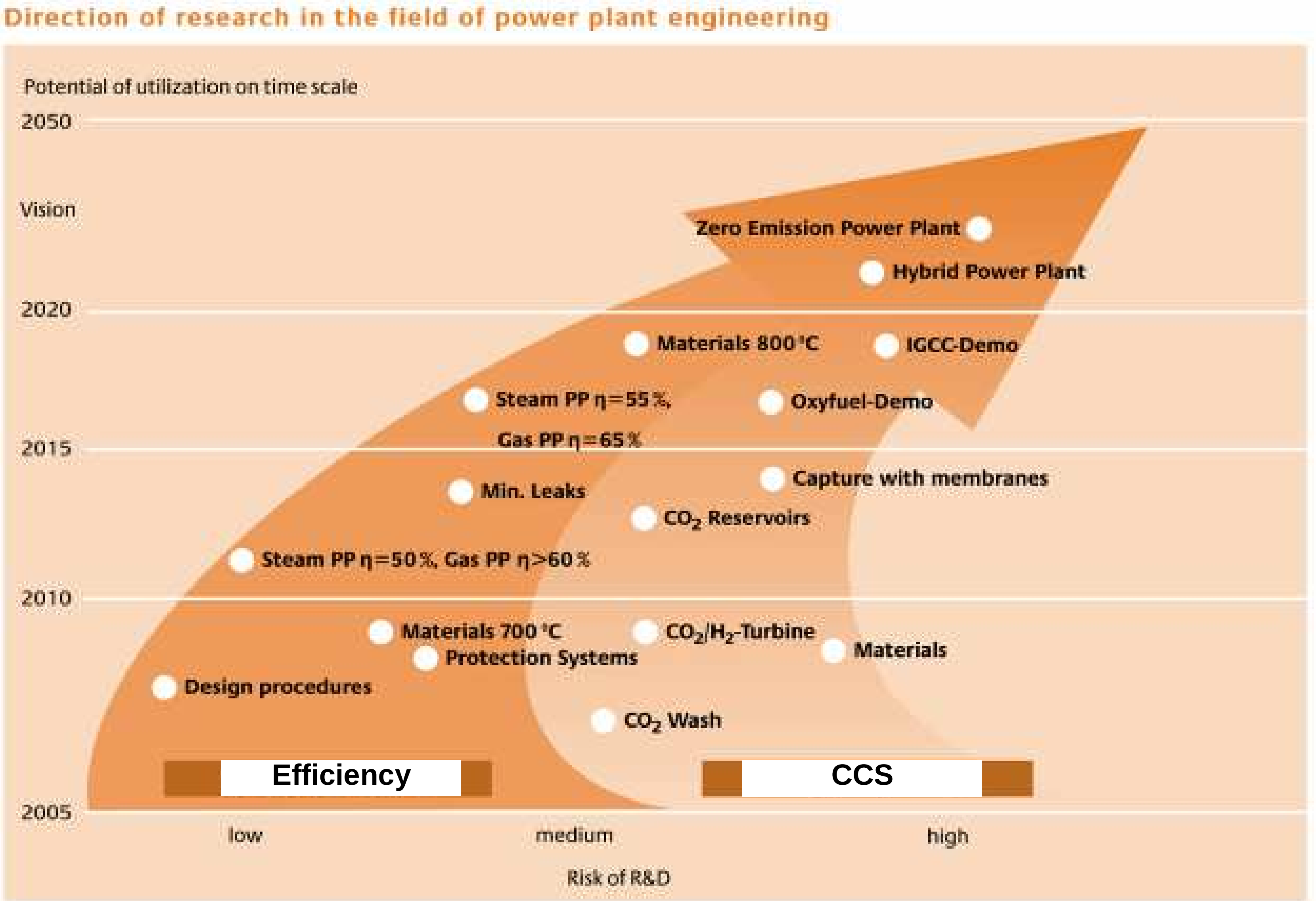


- CO_2 emission levels are expected to increase
- emissions (all sources) are estimated to grow by 36% in 2010 and by 76% in 2020 (projection by World Energy Council, ref. = 2000).

Natural gas 2004 – 2030: + 128%, Coal 2004 – 2030: + 112%

Data source : World Energy Outlook 2006

Approaches to reduction of CO_2 emission

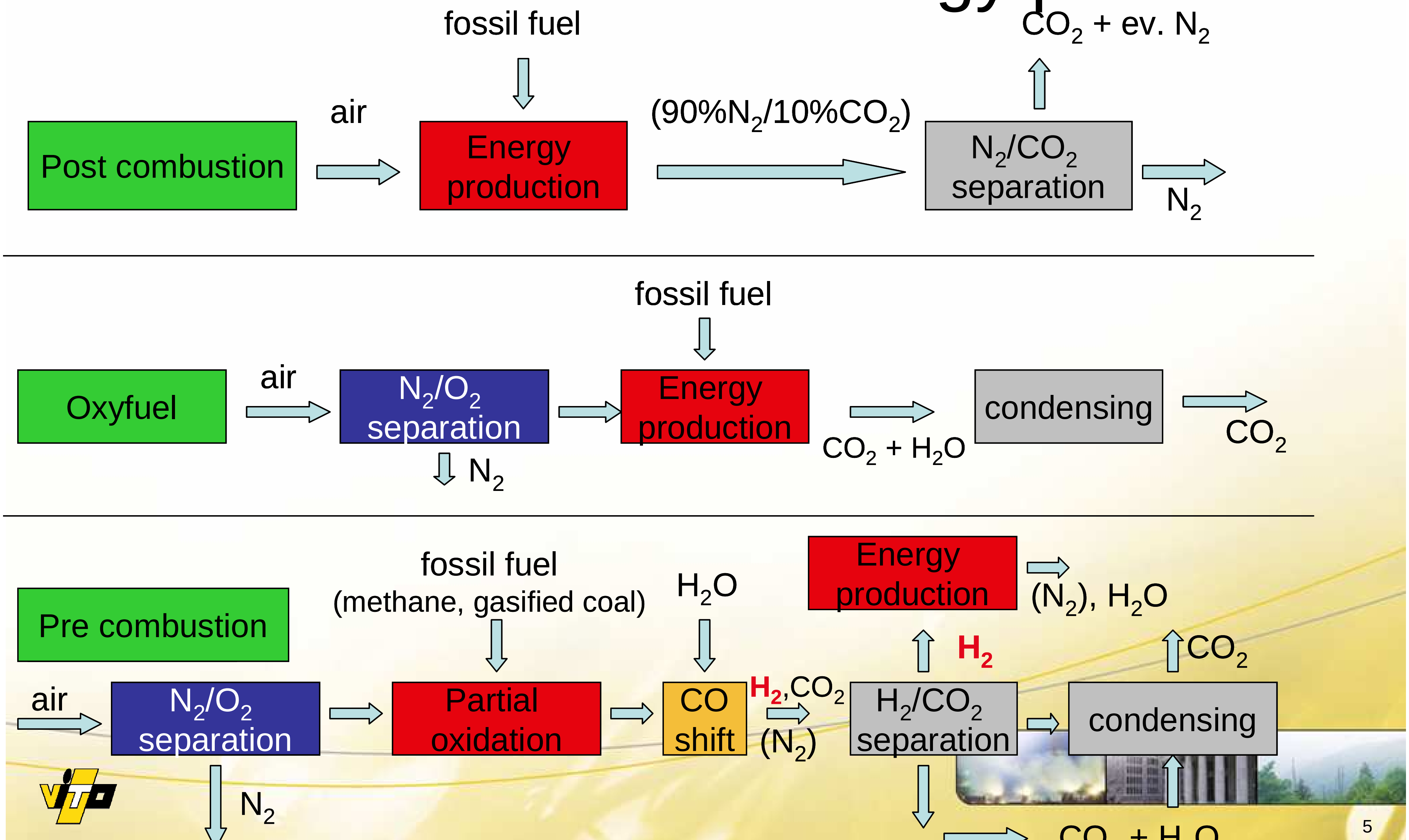


Data source : German COORETEC initiative

Outline

- Introduction: energy needs and CO_2-emission
- Energy production routes
- State-of-the-art
- Technologies under development
  - Zeolite membranes
  - Chemical looping combustion
  - Hollow fiber gas separation membranes
- Summary & conclusions

Routes for sustainable energy production



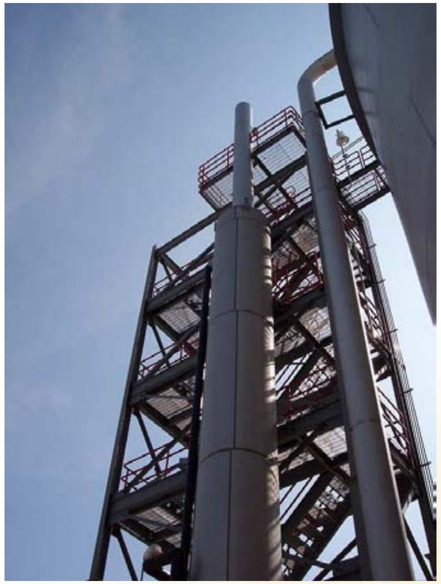
State of the art - Membrane technology

	Post-combustion	Oxy-fuel	Pre-combustion
N_2/CO_2 separation	Liquid absorption • polymer • organo-mineral • Zeolite	-	-
N_2/O_2 separation	-	Cryogenic destillation • polymer • ceramic O^{2-}-conductors	Cryogenic destillation • polymer • ceramic O^{2-}-conductors
H_2/CO_2 separation	-	-	Pressure swing adsorption (PSA) • microporous ceramic • Pd-based membranes • ceramic H^+-conductors

Energy technologies under development

	Post-combustion	Oxy-fuel	Pre-combustion
N_2/CO_2	**BIT:** • **integrated gasification combined cycle (IGCC)** • **polymer, organo-mineral or zeolite membranes**	-	-
N_2/O_2	-	**AZEP:** • membrane reactor: separation annex combustion • **ceramic O^{2-} conductors** **CLC:** • Coupled fluidised bed reactors • **ceramic catalyst**	**SMR:** **POM:** • integration of separation + SMR using membrane reactor with reformer catalyst • OTM, ITM • **ceramic O^{2-} conductors**
H_2/CO_2	- ■ = CCP-choice	-	**SE-WGS** **M-WGS (ceramic H^+-conductors)** **HMR: Hydrogen Membrane reforming (ceramic H^+-conductors)**

N_2/CO_2 separation (post-combustion)

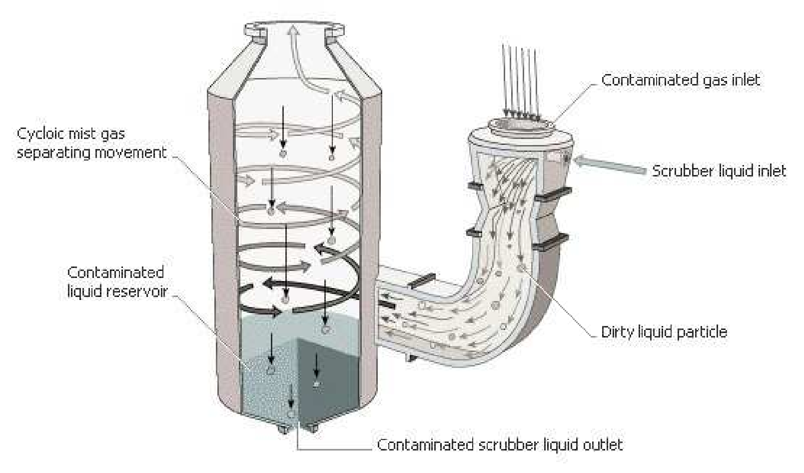


State-of-the art: CO_2 scrubbing

- Absorption by liquid ethylamines (MEA/DEA)
- Mature technology in chemical process industry
- Technology not proven in power plants
- Huge installations with efficiency losses of 10 to 25%
- Dust, soot and SO_2 have to be removed beforehand, max. 30% O_2
- Cost of retrofitting: too high for existing plants, acceptable for new plants; price for CO_2 capture: 20 à 50 Euro/ton CO_2

1. Improved CO_2 scrubber:

- Use of membrane contactors
  - 10x smaller installations, less efficiency losses
- BIT = Best Integrated Technology
  - extensive integration in Integrated Gasification Combined Cycle (or IGCC-) plant
- Diluted emission: ~4% CO_2



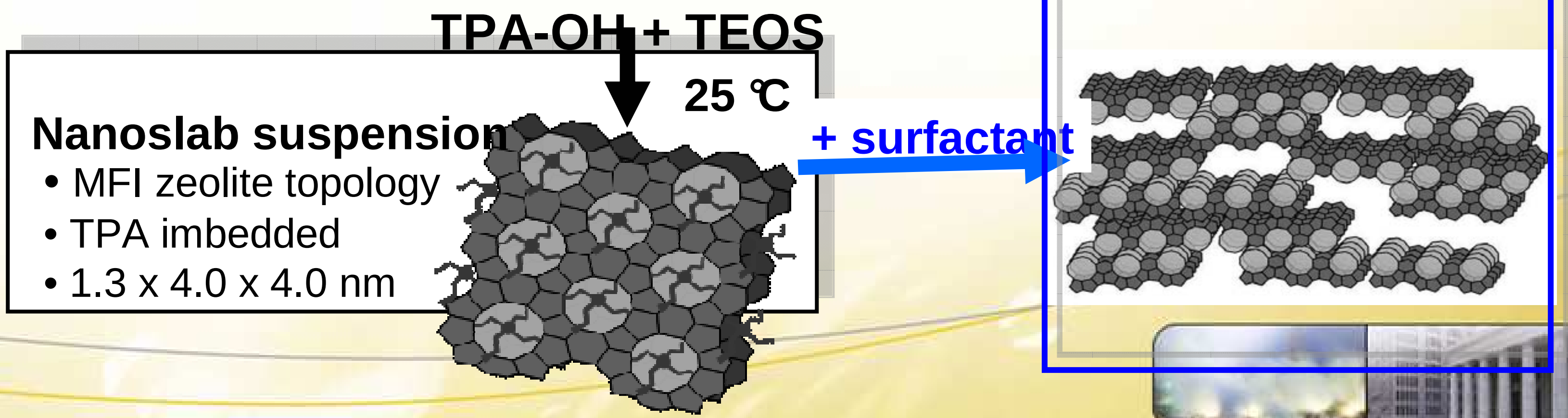
N_2/CO_2 separation by membranes

2. Alternative: gas separation membranes

- Economic if CO_2/N_2 > 200, flux > 0.2-1 m^3/m^2hbar
- State-of-the-art:

Membrane type	CO_2/N_2 ratio	CO_2 flux (m^3/m^2hbar)
Commercial polymers (CO_2/CH_4)	*30*	*0.2*
Zeolite membranes (FAU X,Y)	30 - 50	3 - 20
Block-copolymer membranes (PEO)	50	2
Mixed matrix membranes	40	0.2 - 2
Facilitated transport membranes	100	0.02

- VITO: zeolite-like membranes from nano building blocks



N_2/CO_2 separation by zeolite membranes

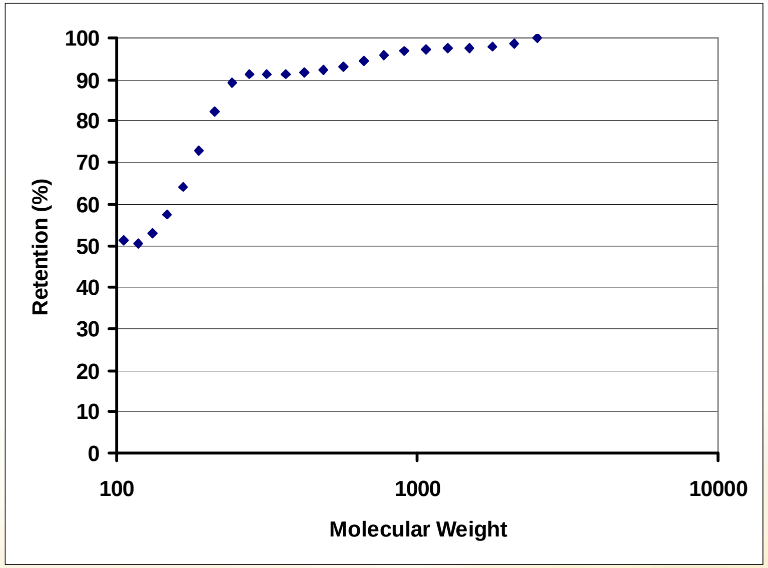
VITO: CO_2-adsorption by 'zeogrid' on support

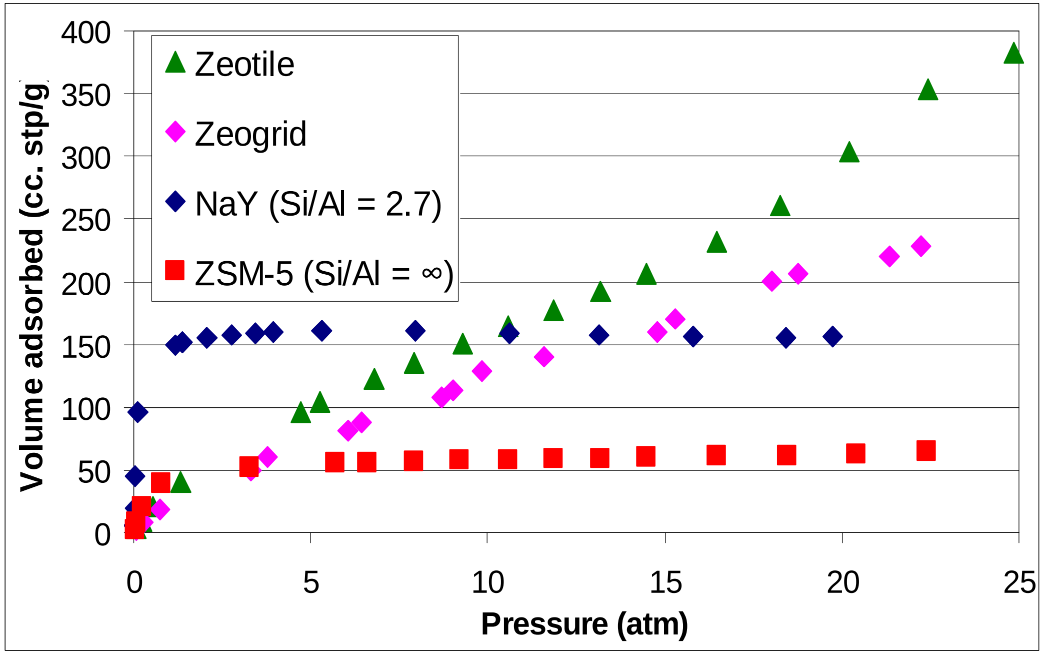
> FAU Y = Na Y

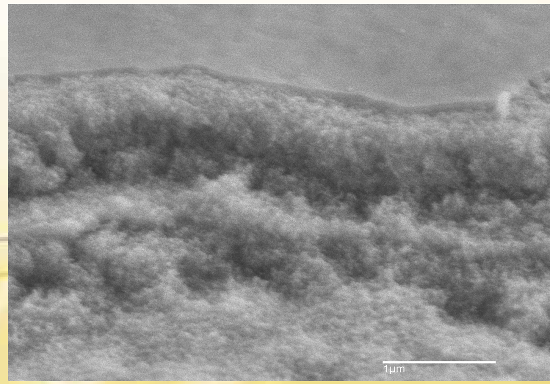
>> adsorption N_2

↓

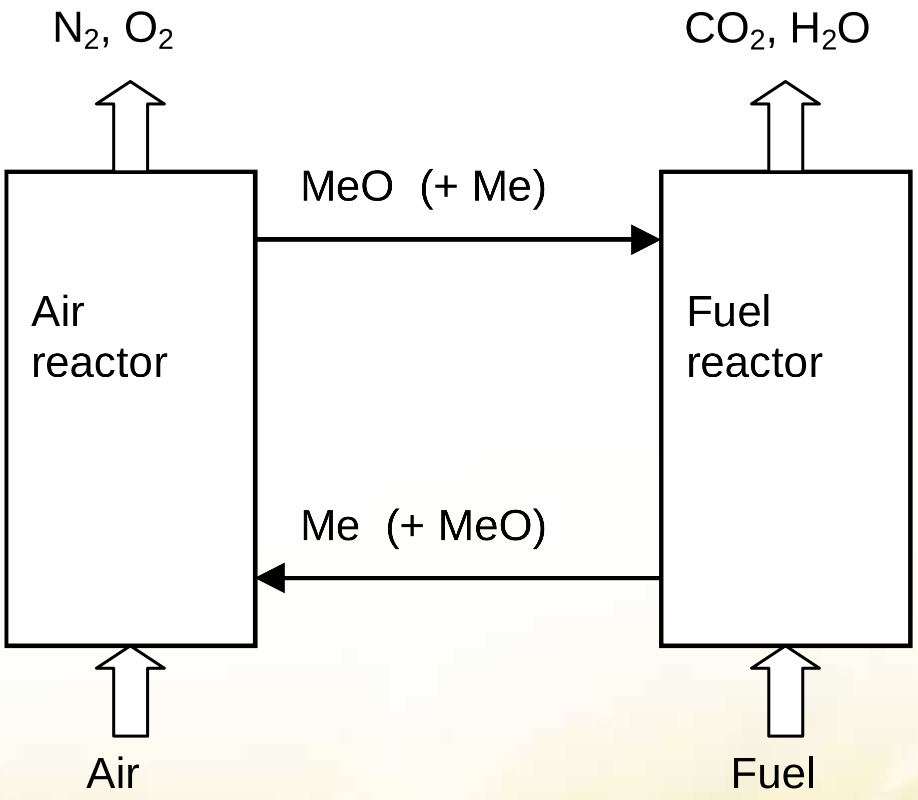
Zeogrid-membranes show high potential wrt CO_2/N_2 -separation







Chemical Looping Combustion (oxy-fuel)



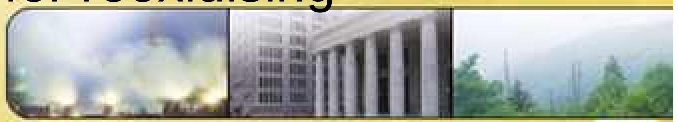
Alternative to gas separation membranes

Principle:

Coupled air and fuel reactor (eg. fluidised bed reactors, good contact between gas and solids).

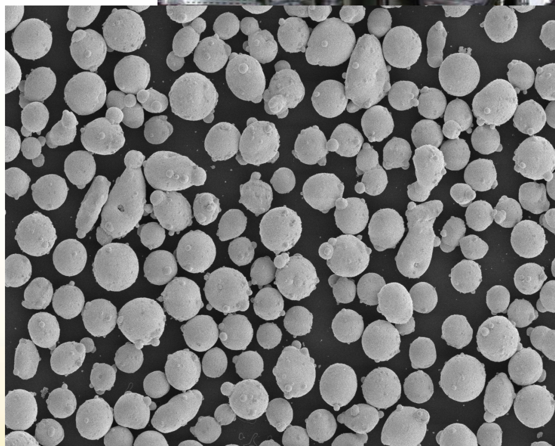
- **fuel reactor, endothermic:**
  $$(2n+m)MeO + C_nH_{2m} \rightarrow (2n+m)Me + mH_2O + nCO_2$$
- **air reactor, exothermal:**
  $$Me + \tfrac{1}{2}O_2 \rightarrow MeO$$

Reduced metaloxide Me, is transfered to the air reactor for reoxidising



Chemical looping combustion

- Expected time-to-market: ~2012 (CCP)
- Expected cost reduction for CO_2 removal: ~40%
- Development ao in CLC GASPOWER (6FP, Alstom, TU Chalmers, Shell (CCP))
- Fabrication of MeO catalyst particles by spray drying and subsequent sintering



E. Jerndal, F. Snijkers, I. Thijs, T. Mattisson, A. Lyngfelt, 'Investigation of MeO carriers for CLC produced by spray-drying, submitted for GHGT-9, 2008

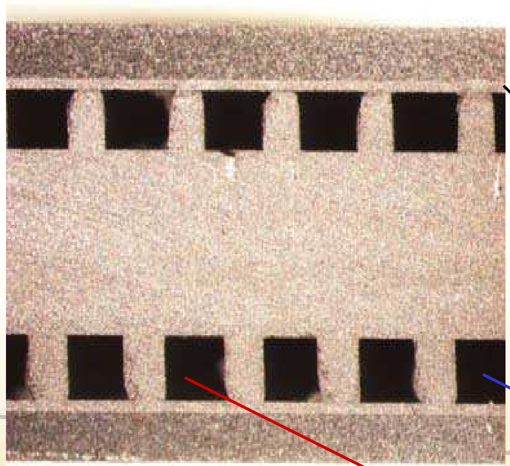
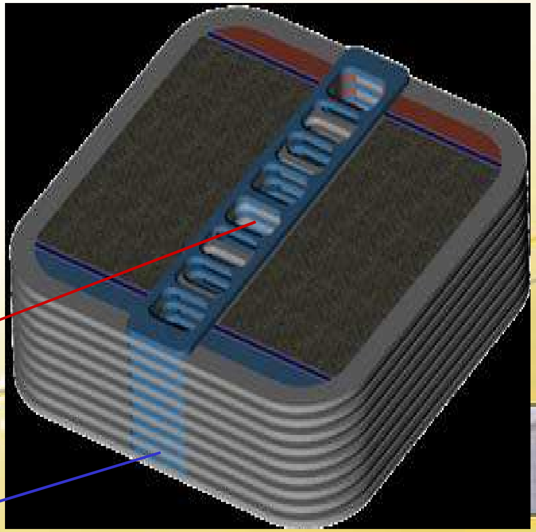
T. Mattisson, F. Snijkers, A. Lyngfelt et al., Chemical-looping combustion CO_2 Ready Gas Power, submitted for GHGT-9, 2008

N_2/O_2 separation
(oxy-fuel & pre-combustion)

State-of-the-art: cryogenic destillation	Alternative: gas separation membranes
• ~100 year old, mature technology for O_2 production in power plants • High cost and energy consumption (250 kWh/ton O_2) • For syngas plants, up to 40% costs are related to the cryogenic oxygen generation units •Efficiency loss: 10 to 20% •Low-T process: integration in energy generation from fossil fuel combustion difficult •No cost reduction, nor efficiency improvements to be expected.	***polymer membranes*** ✓Commercially available, but low O_2 purity ✓Less interesting for large capacity, e.g. for energy generation from fossil fuels ✓Stable at low temperatures only: hampers integration in energy generation from fossil fuel combustion ***dense ceramic membranes*** ✓100% pure O_2 and stable at high temperatures: advantageous for integration in energy production

N_2/O_2 separation (pre-combustion)

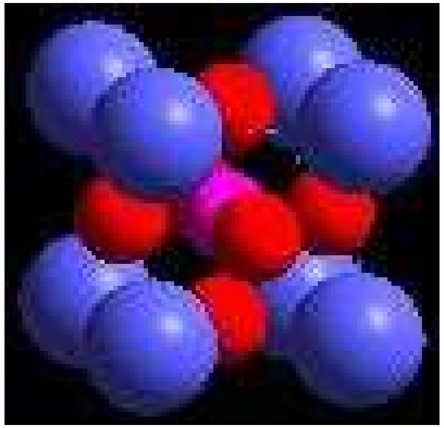
- Harsch conditions: severe requirements to membrane material (ΔP, ΔP_{O2}, T ~850℃); reformer catalyst incorporated in membrane
- Economical if flux > 6 m^3/m^2hbar
- Parties
  - Praxair (Oxygen Transport Membrane, OTM);
  - Air Products (Ion Transport Membrane, ITM);

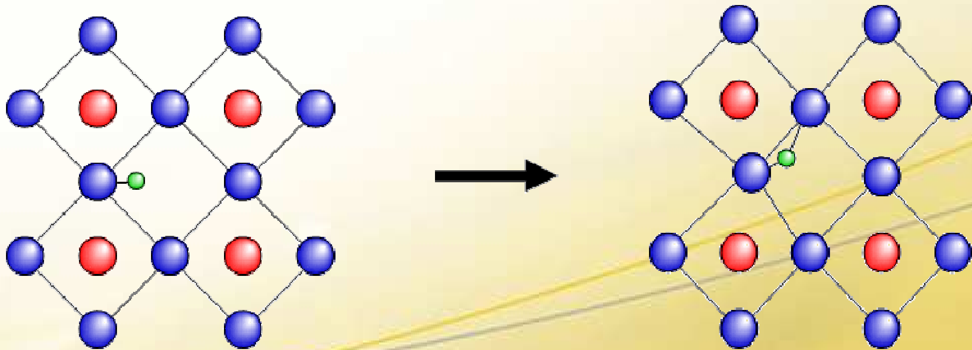



(Mixed) ion conducting ceramics

Ceramic membrane materials:

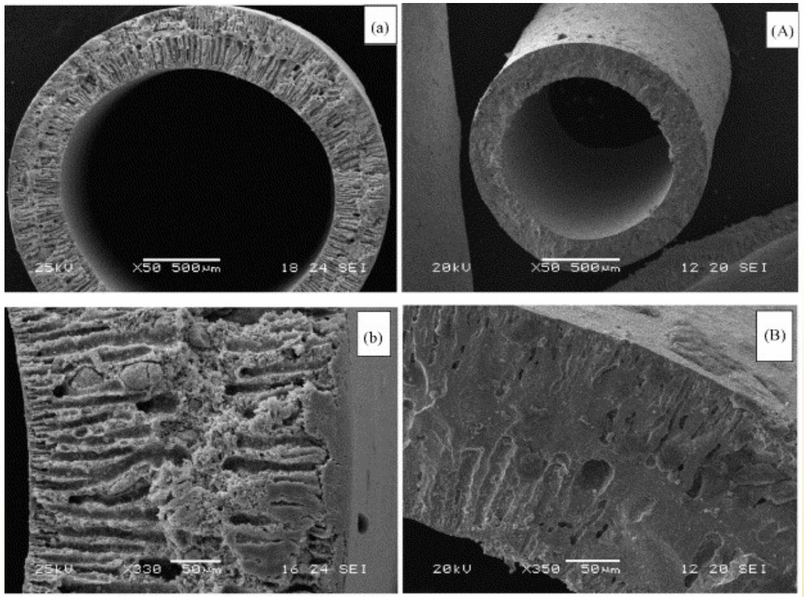
- H^+- or O^{2-}-ion conductor or (preferred) mixed H^+- or O^{2-}-ion electron conductor
- ABO_3 (perovskite) or $A_2B_2O_5$ (brownmillerite) structure
- Mixed conductor: ‘hopping’ of ions, simultaneous transport of electrons in the opposite direction: no external circuit
- Conduction at high temperatures (> 600℃)





Hollow fibers

- Maximize specific surface area to volume ratio (500-9000 m^2/m^3) → minimizes the volume of the membrane module and enhances membrane fluxes
- The ideal asymmetric membrane structure could be obtained with the phase-inversion spinning technique
- Macrovoids due to instantaneous liquid-liquid demixing (phase separation):
  - Polymer-rich phase delays the diffusion solvent/non-solvent in the polymer arme fase
  - Nuclei in low-polymer phase (~stable compositione) grow due to slow diffusion solvent/niet-solvent till high polymeer concentration is obtained
- → weak spots: to be avoided

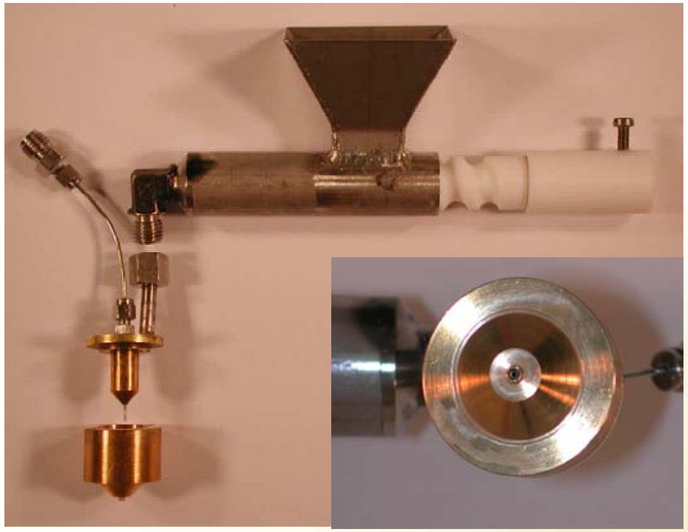


J. Luyten, A. Buekenhoudt, et al., Preparation of LaSrCoFeO3-x membranes, Ceramic Trans., vol 109.

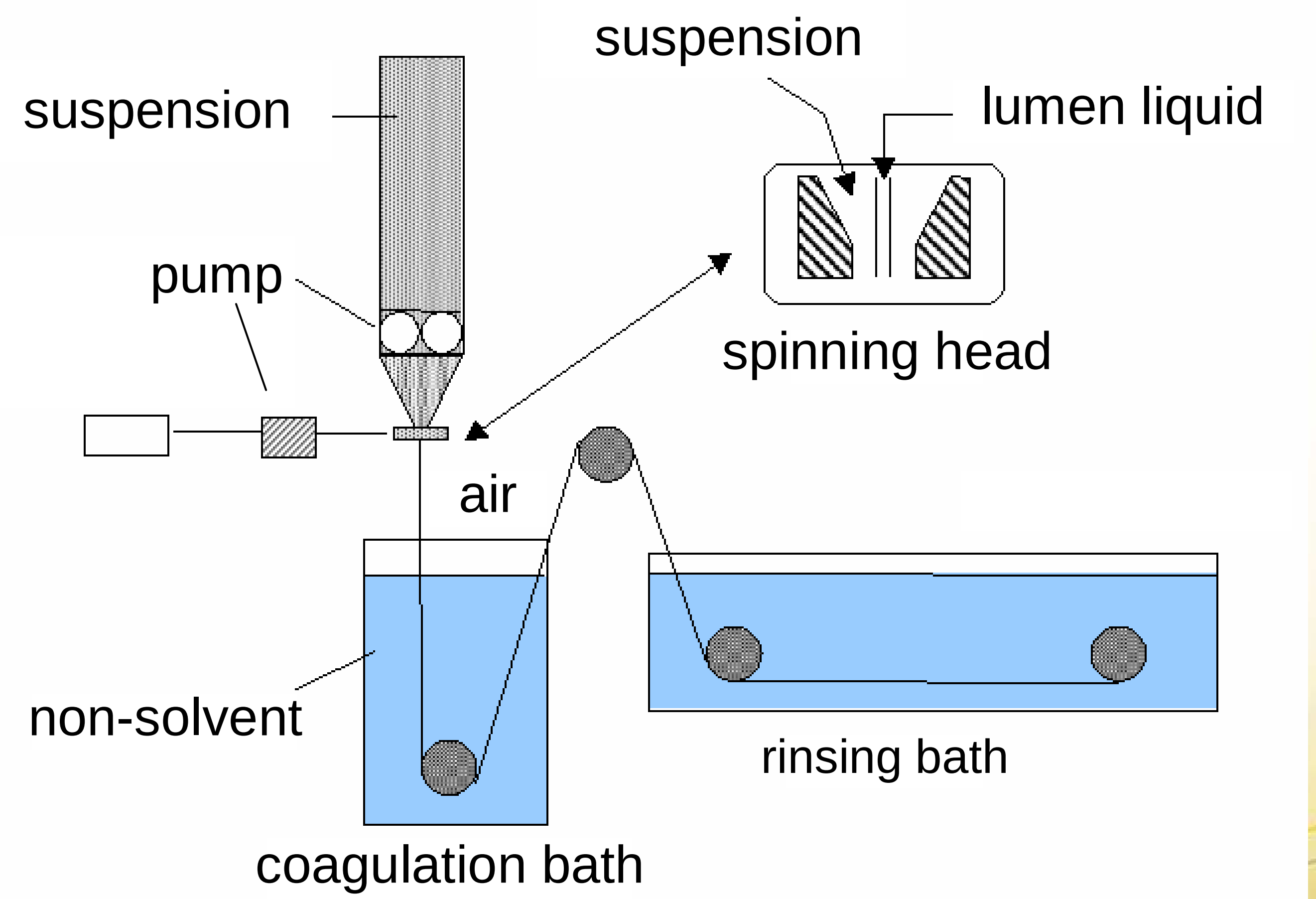
'MEM-BRAIN'-project (FZJ, Helmholtz-institutes, VITO,..)

Spinning with phase-inversion

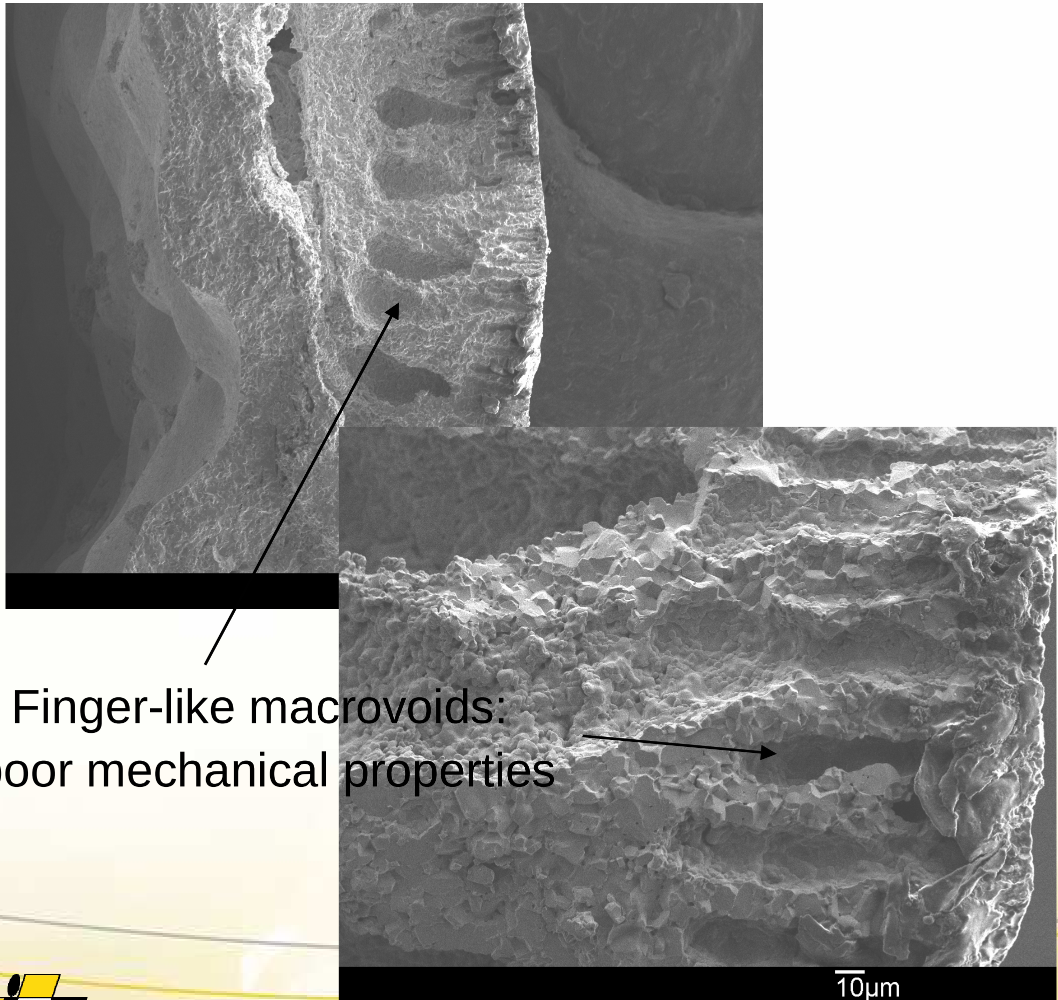
- Suspension:
  - Ceramic powder (60-70%)
  - Binder (5-7%)
  - Solvent (25-30%)
- Lumen liquid
- Coagulation bath with non-solvent
- After drying: calcining and sintering



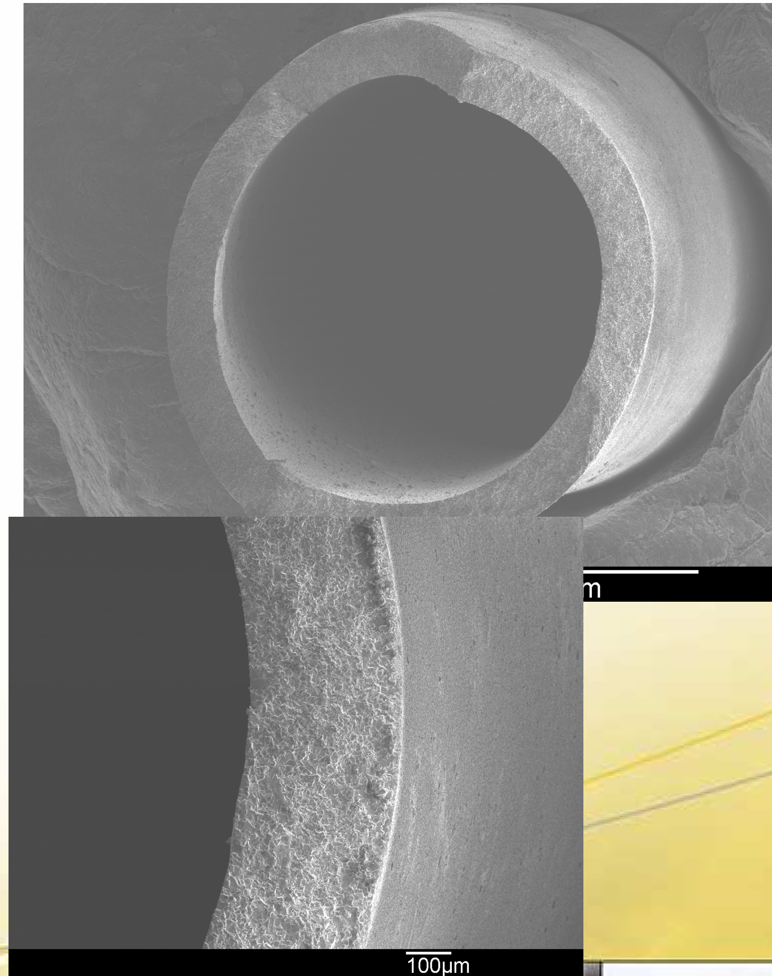
Phase-inversion spinning technique



Improved macrostructure



Finger-like macrovoids:
poor mechanical properties



Conclusions

- Energy technologies under development rely strongly on materials R&D
- Membranes can have large added value to sustainable energy production; significant efforts are being spend worldwide
- Membranes and membrane materials must meet considerable requirements; in this respect (mixed) ion conducting ceramics are an important class of materials with high potential.
- Hollow fibers with improved macrostructure by the phase inversion spinning technique are an interesting option for membrane modules with high surface area to volume ratio