Innovation for Sustainable Production – i-SUP 2008
Congrescentrum Oud Sint-Jan, Brugge
21. – 24. April 2008

MANUFACTURING OF MICROPOROUS CERAMIC MEMBRANES FOR ENVIRONMENTAL APPLICATIONS

I. CO_2-free power plants

II. Fuel cells

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Membrane research topics in IEF-1

Focus on energy-related applications :

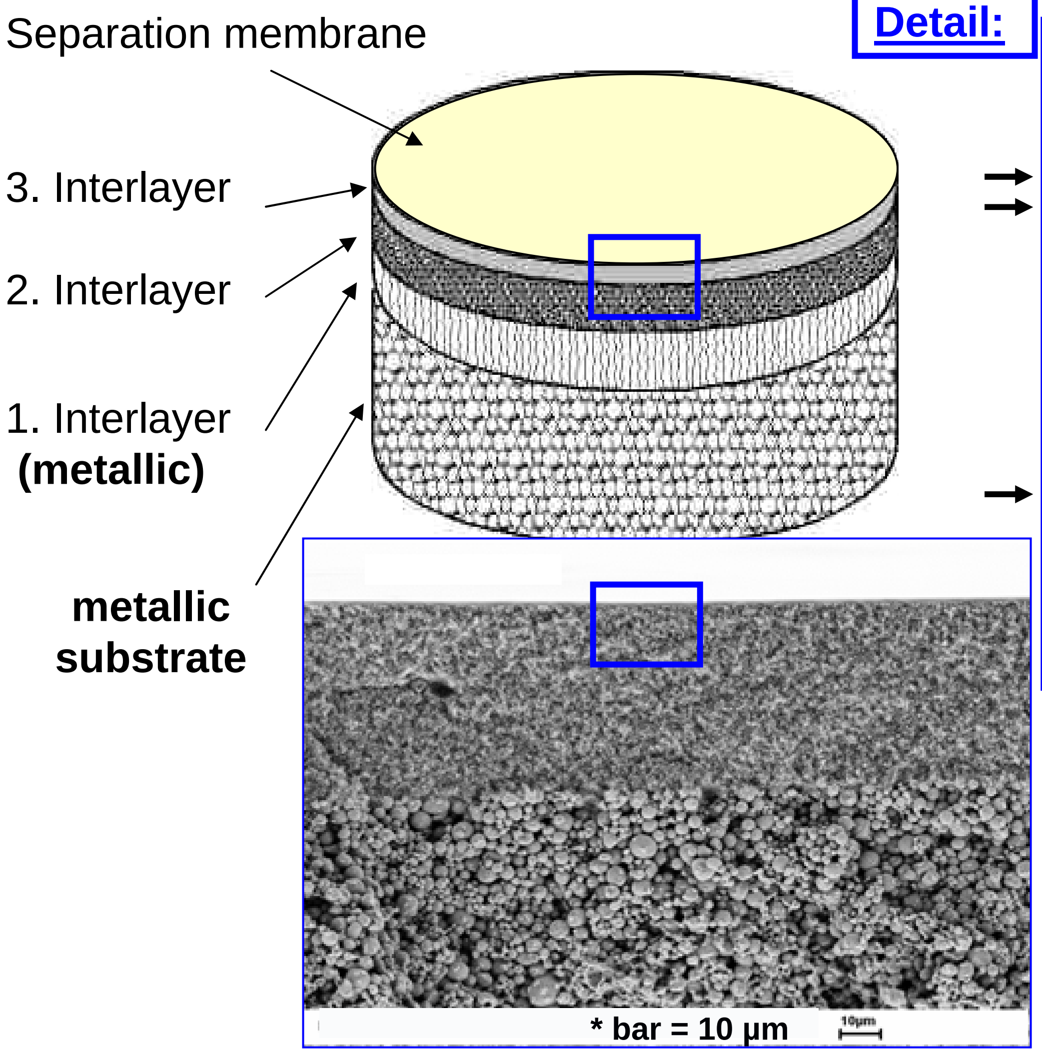
1. **Development of porous and dense membranes for application in CO_2-free power plants**
   - **dense membranes for O_2/N_2 separation**
   - **microporous membranes for CO_2/H_2 separation** ✓

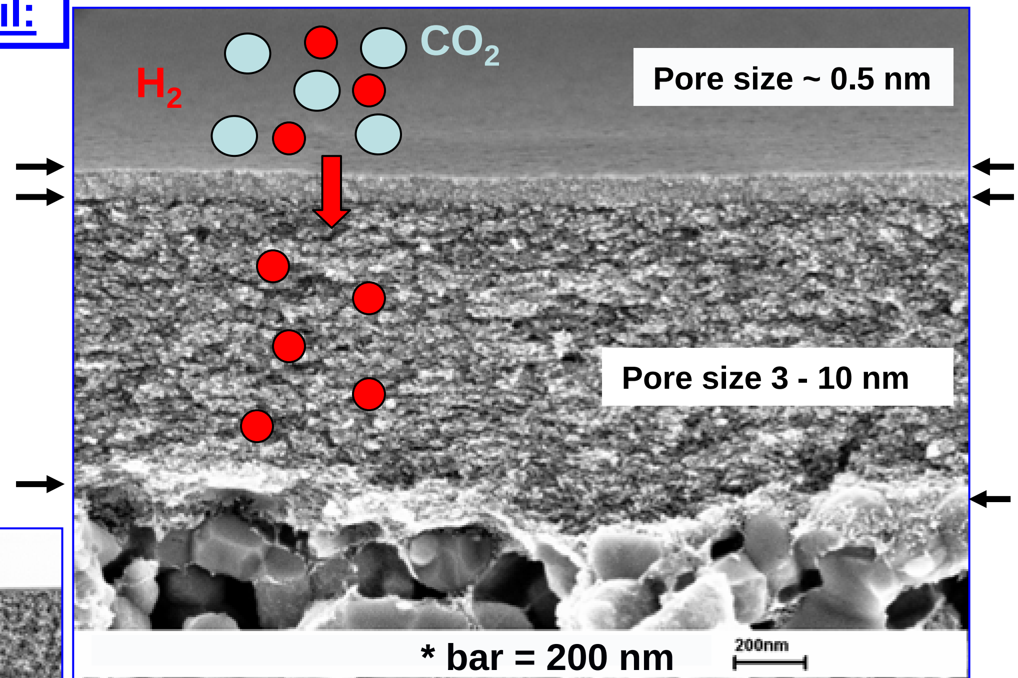
2. **Development of porous and dense membranes for application in advanced Solid Oxide Fuel Cells (SOFC´s)**
   - **porous anode and cathode layers**
   - **dense electrolyte membrane** ✓

Microporous membranes for CO_2 separation

Example: *Metal-supported Membranes for H_2/CO_2-Separation*

Detail:





Gas Molecule	H_2	CO_2	N_2
d_{kin} in nm	0,29	0,33	0,36

Microporous membranes for CO_2 separation

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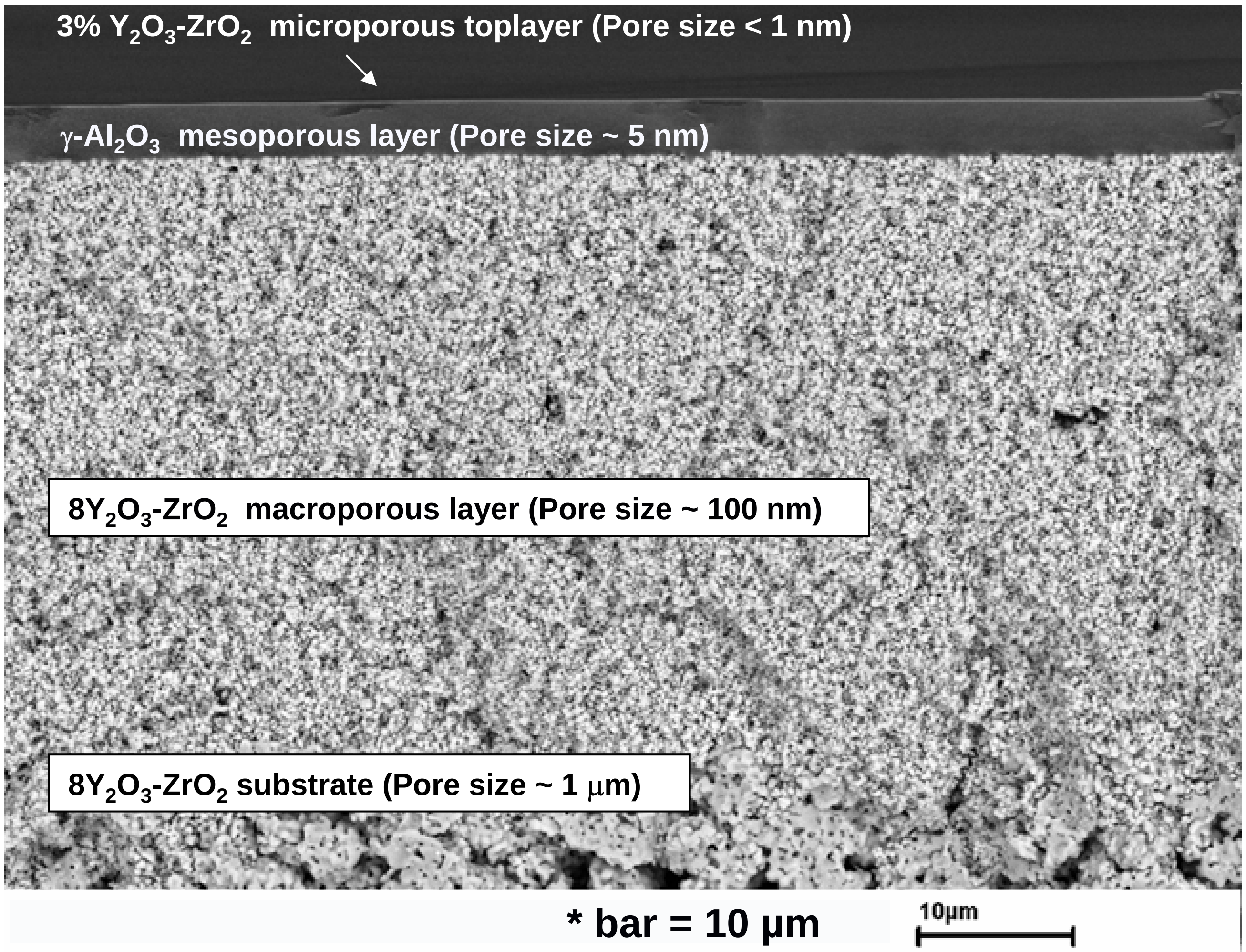
Example: *Multilayer-Membrane on ceramic ZrO_2 substrate*



Sol-Gel Method:
Nano-Particle sol
Particle size ~ 6 nm

Sol-Gel Method:
Colloidal Particle Sol
Particle size ~ 30 nm

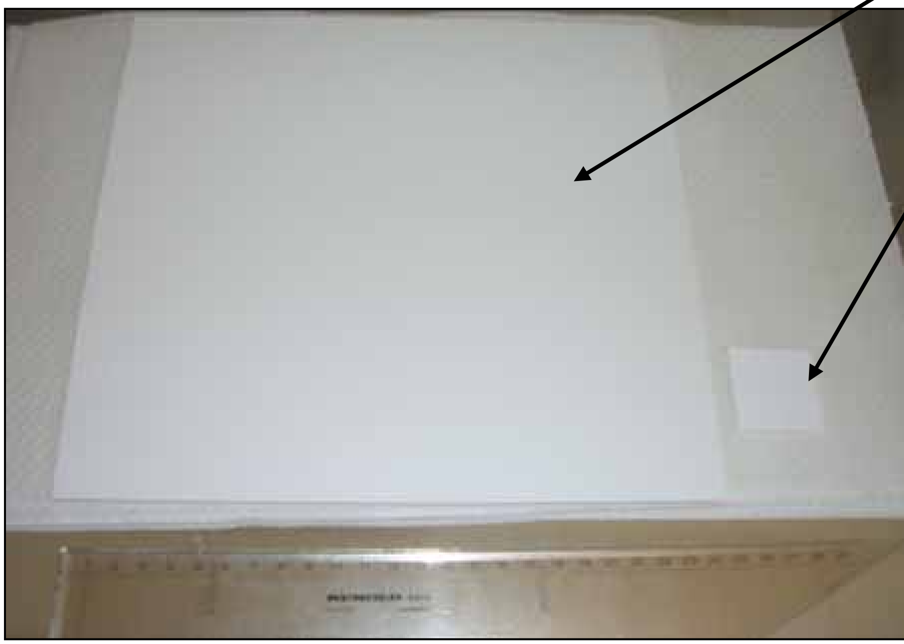
Suspension Method:
Particle size ~ 350 nm
- Vacuum slip-casting
- Dip-coating
- Screen-printing

Powder Method:
Warm-pressing

Microporous membranes for CO_2 separation

Substrate preparation - Warmpressing

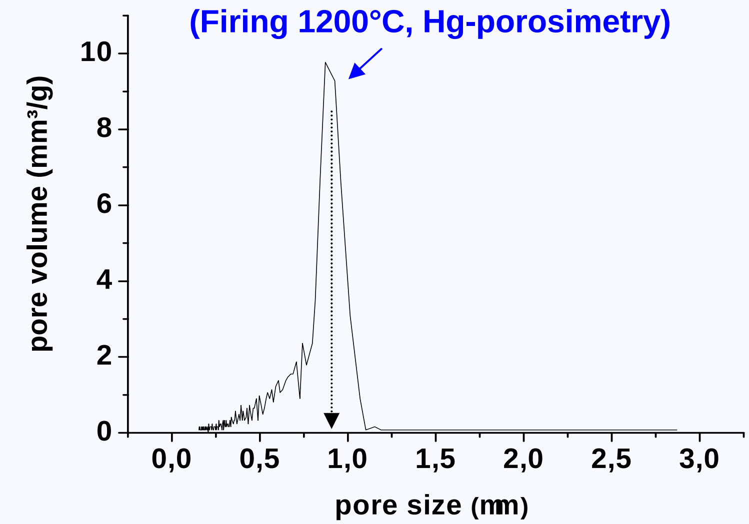
Warmpressing $8Y_2O_3$-ZrO_2 Substrate + Sintering (1200 ºC)



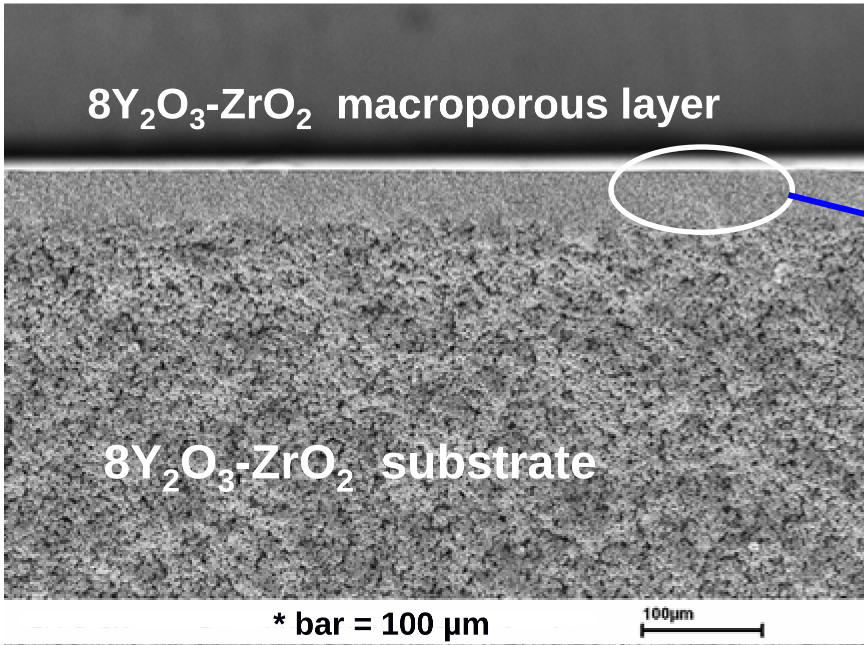
Particle size: ~ 3 - 5 µm
Average Pore size: ~ 1 µm

Large-scale Support: **Preparation with Standard IEF-1 Technology for Solid Oxide Fuel Cells SOFC's (25 x 25 cm)**

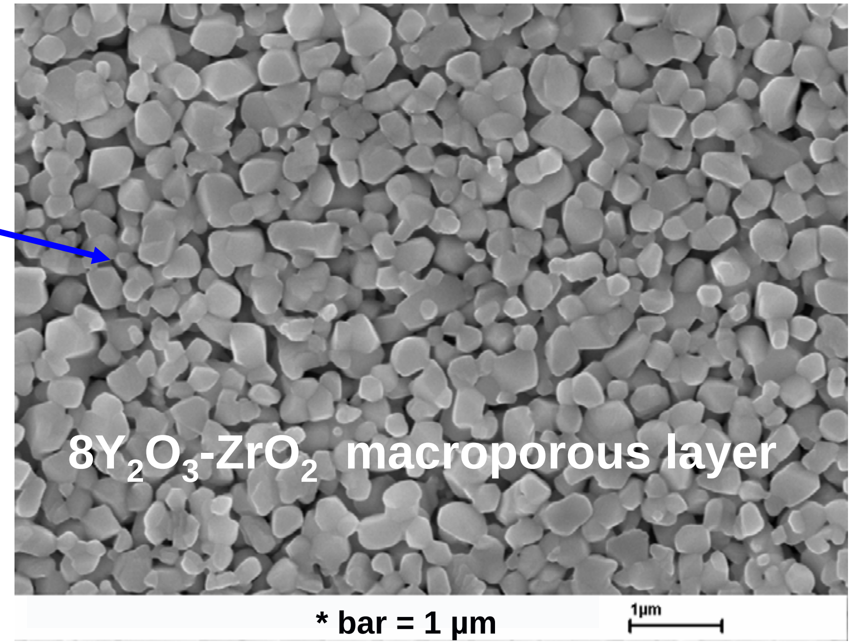
Lab-scale Support for R & D: **Polishing with diamant particles for improving Surface roughness (4 x 4 cm)**



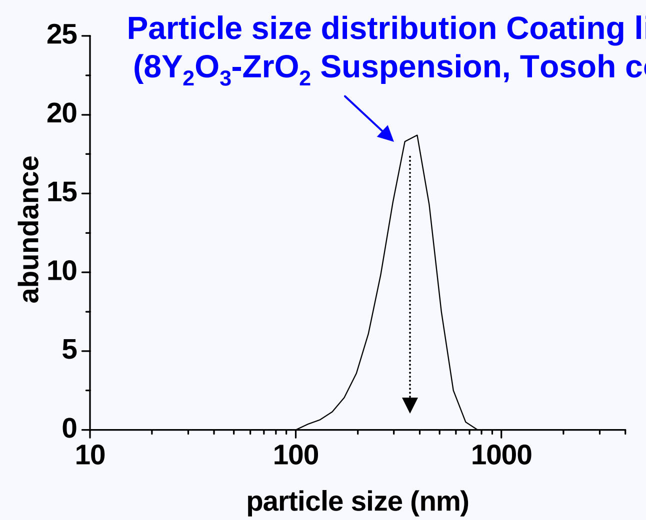
Macroporous Interlayer – Suspension coating



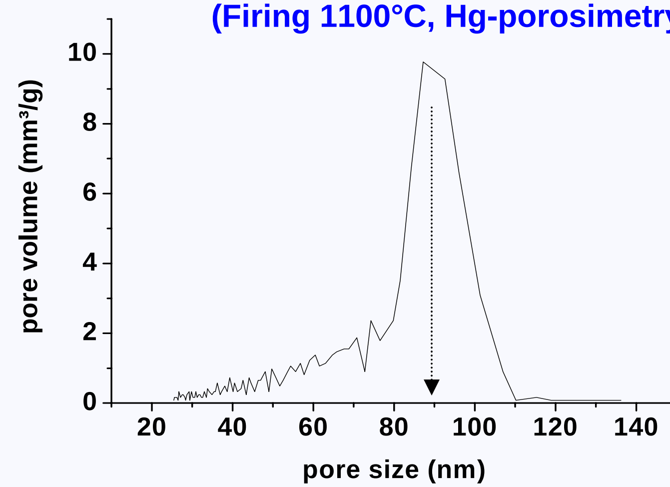
* bar = 100 µm



* bar = 1 µm

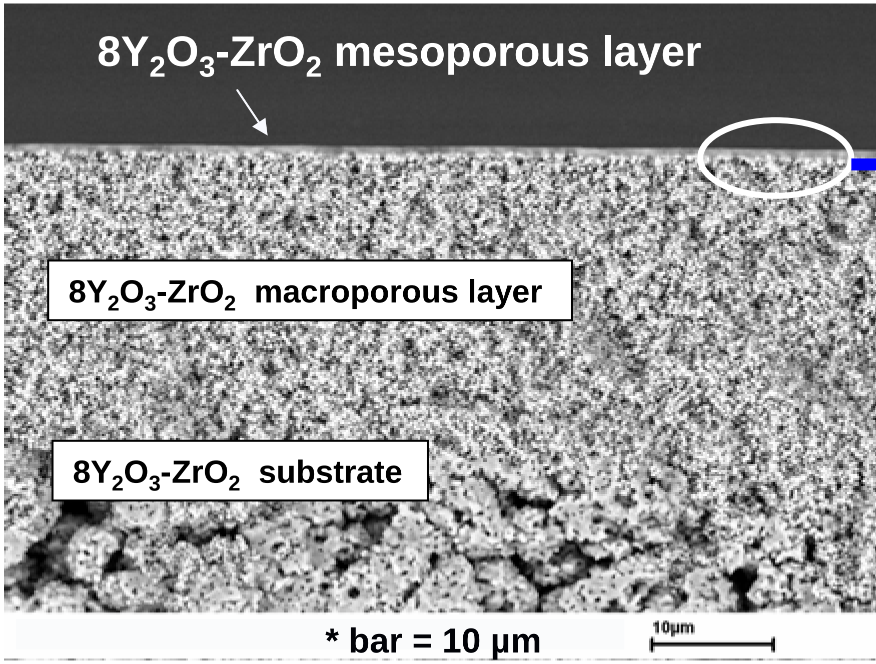


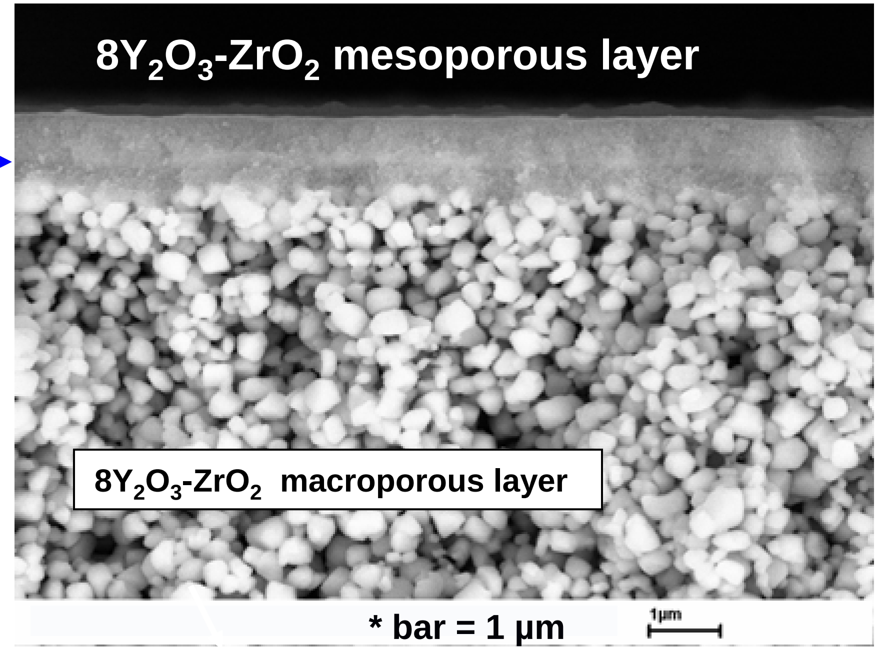
Particle size distribution Coating liquid ($8Y_2O_3$-ZrO_2 Suspension, Tosoh corp.)

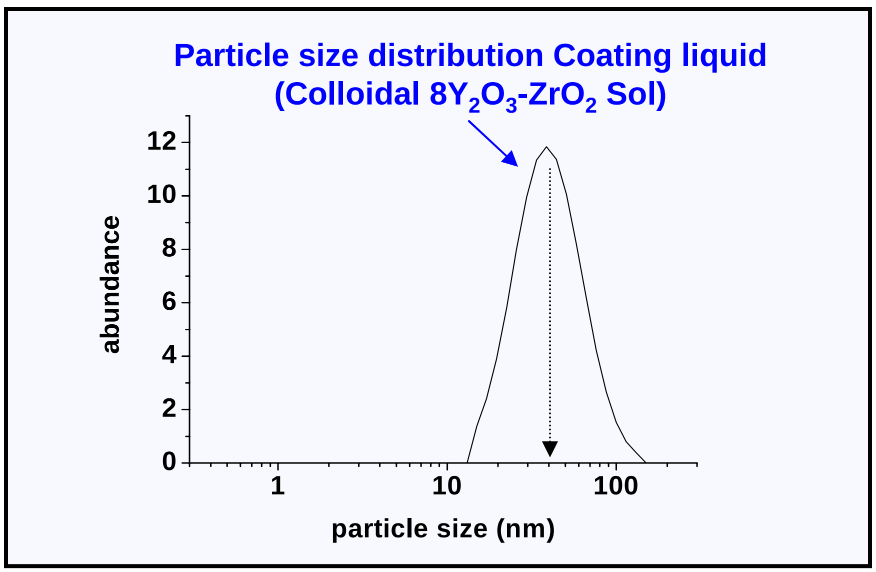


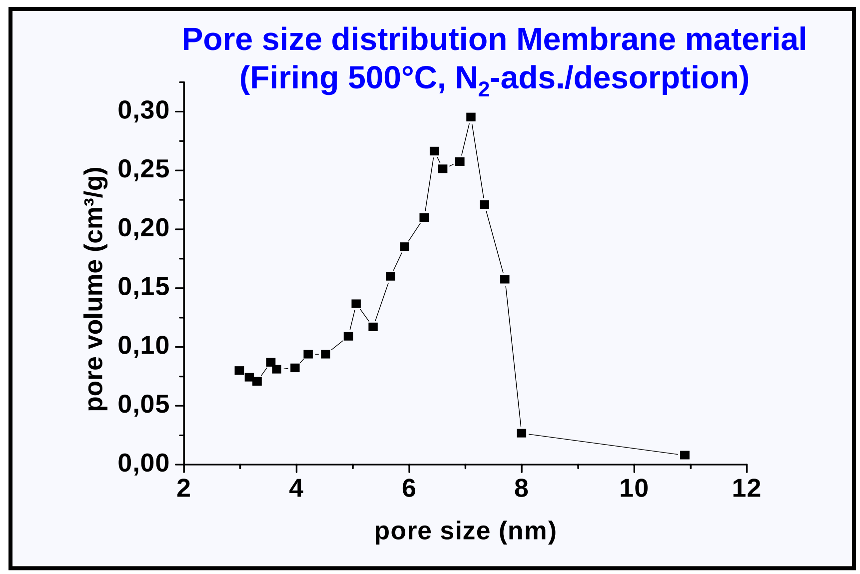
Pore size distribution Membrane material (Firing 1100°C, Hg-porosimetry)

Mesoporous interlayer – Sol-gel coating

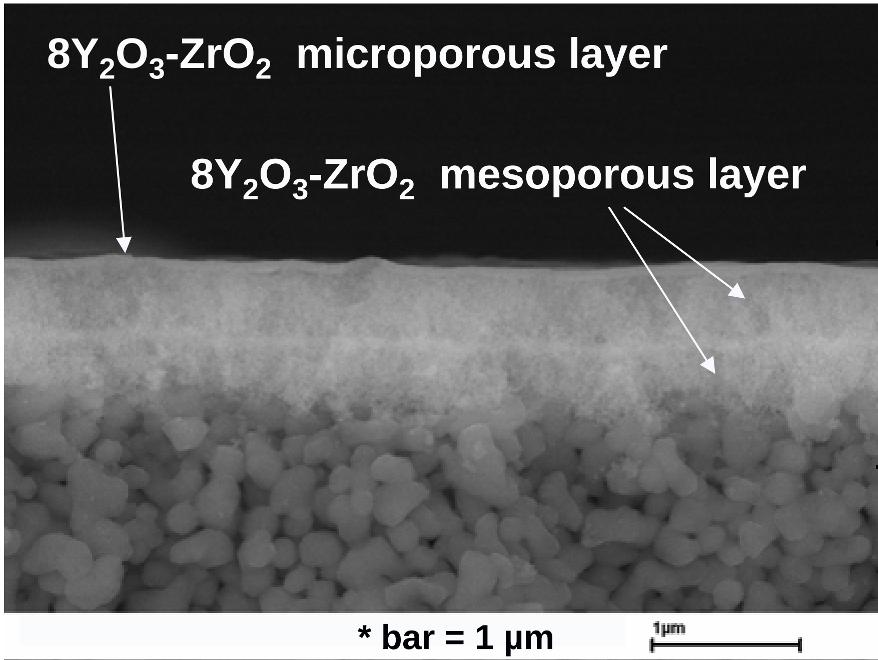


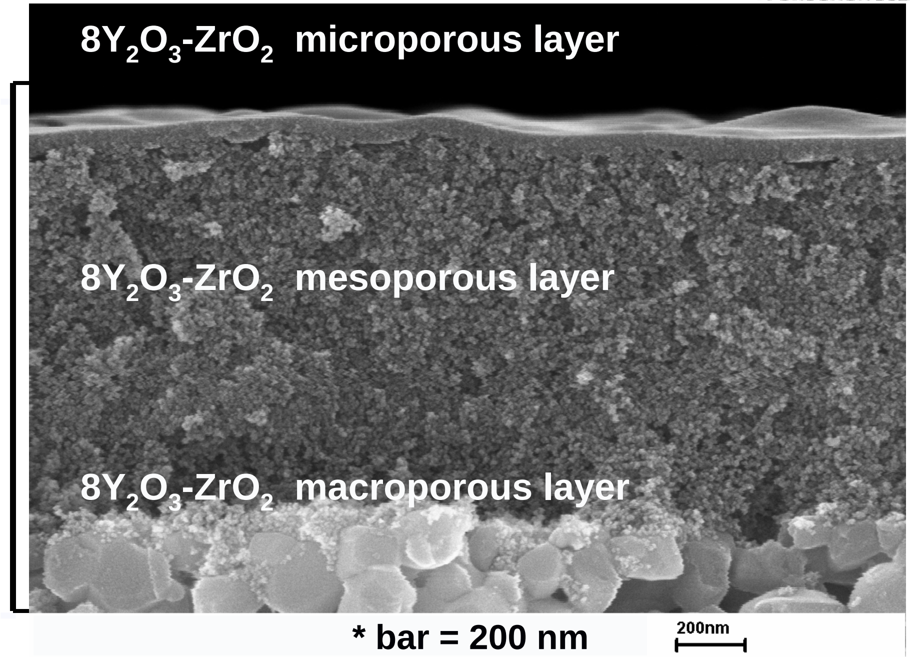


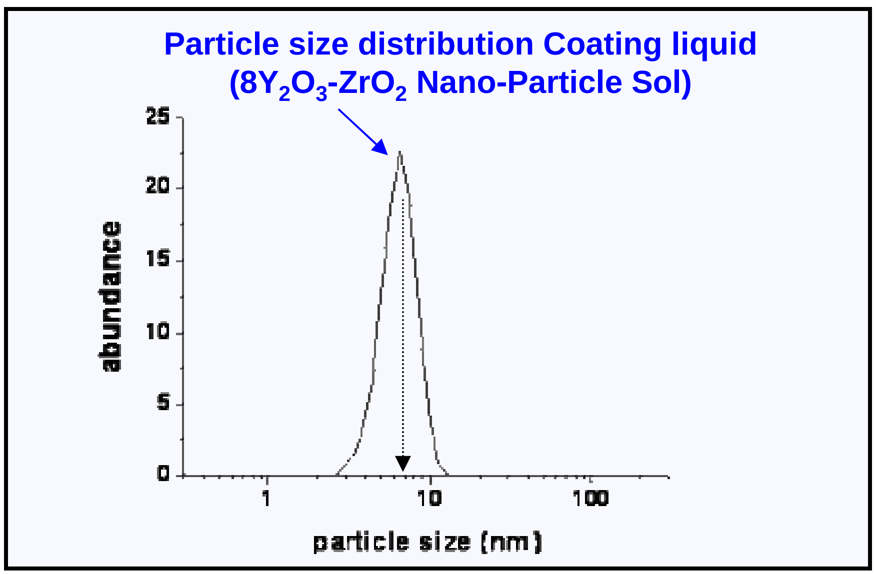


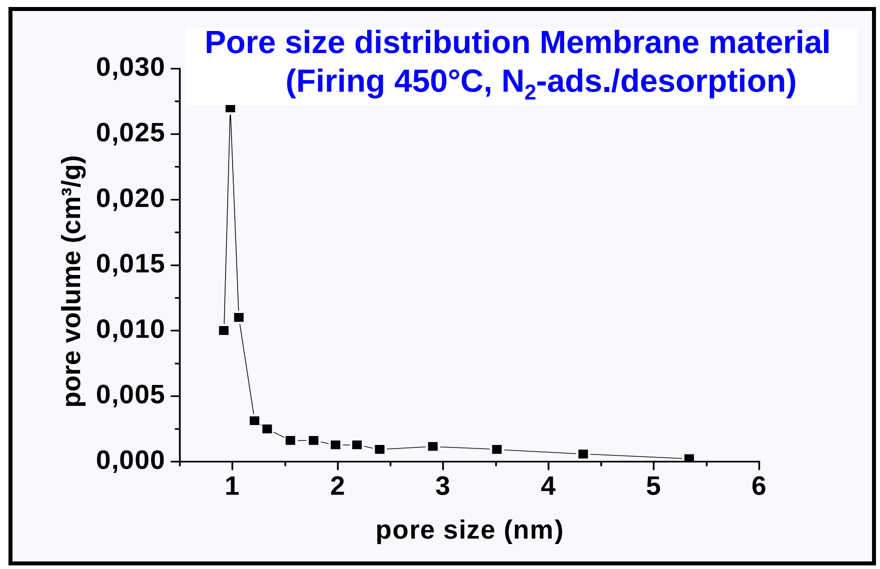


Microporous toplayer – Sol-Gel Coating









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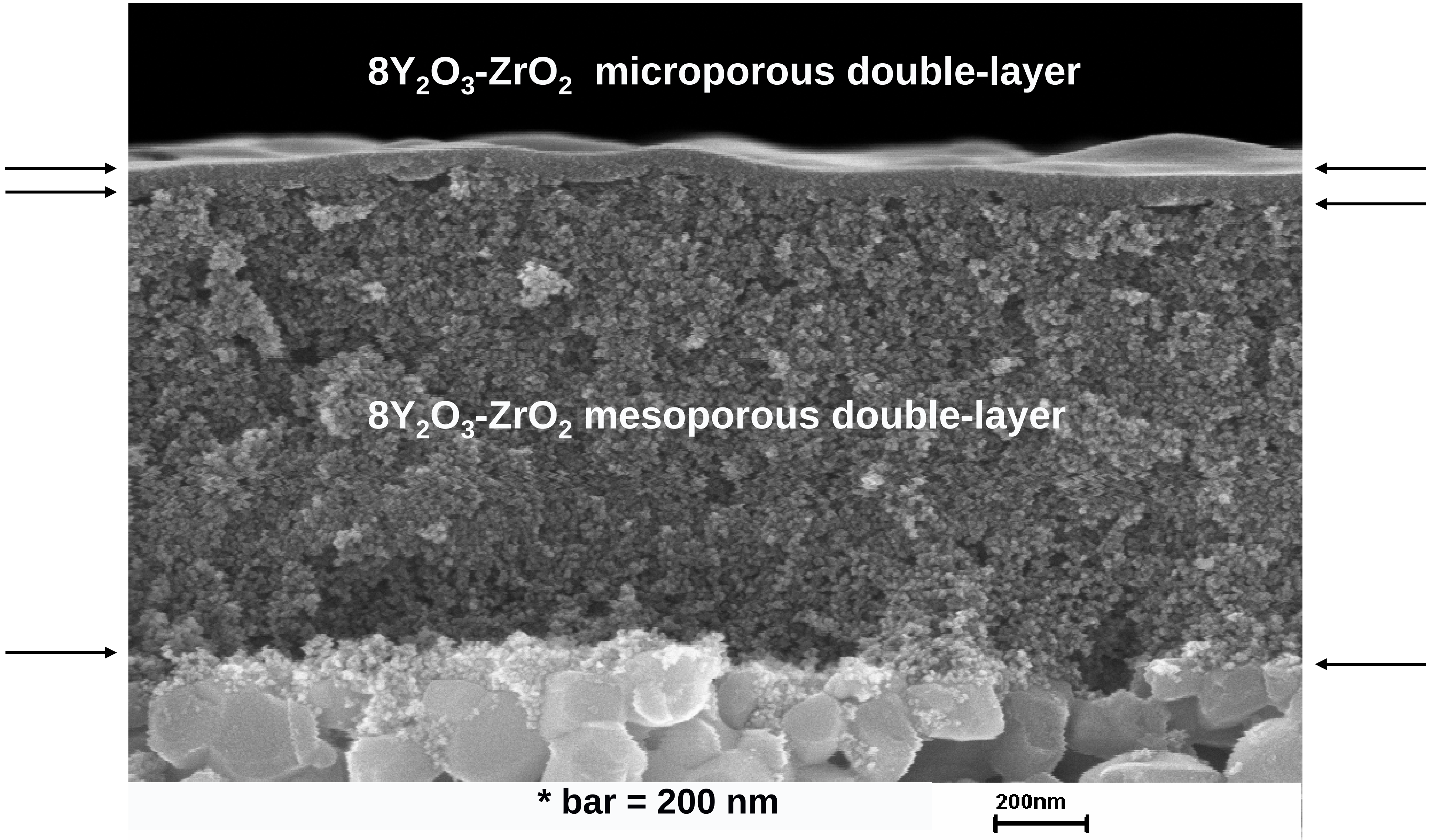
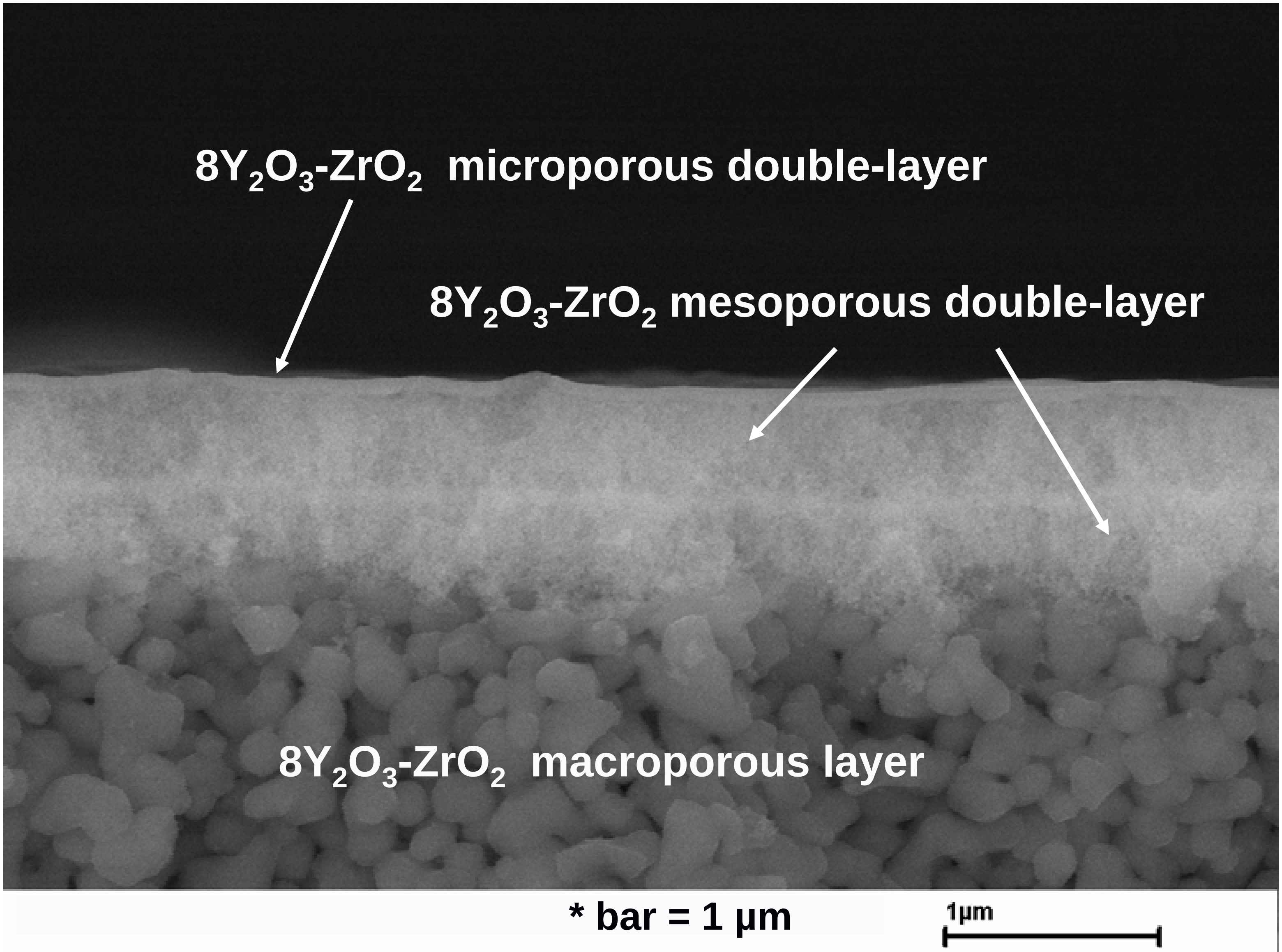


Microporous toplayer – Sol-Gel Coating



* bar = 1 µm

Overview subsequent membrane coating steps

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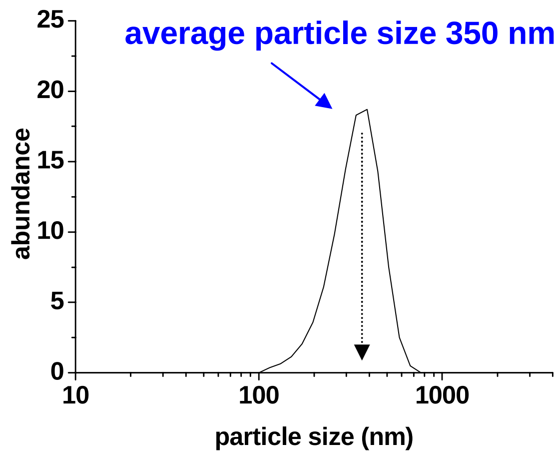
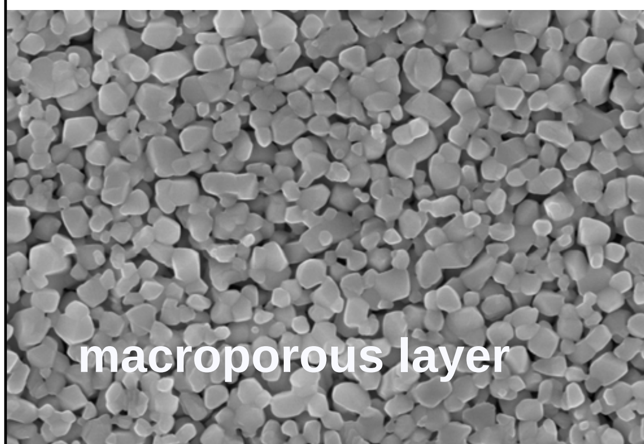
Particle size $8Y_2O_3$-ZrO_2 Suspension

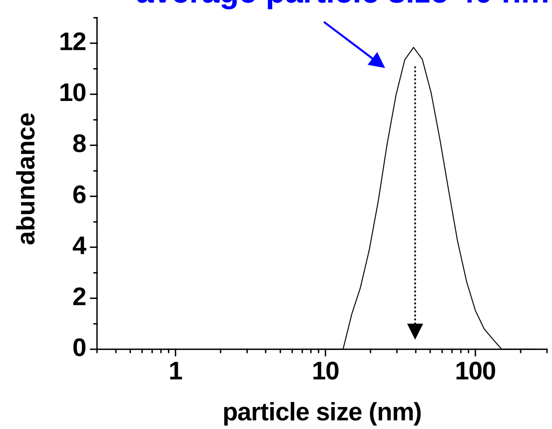


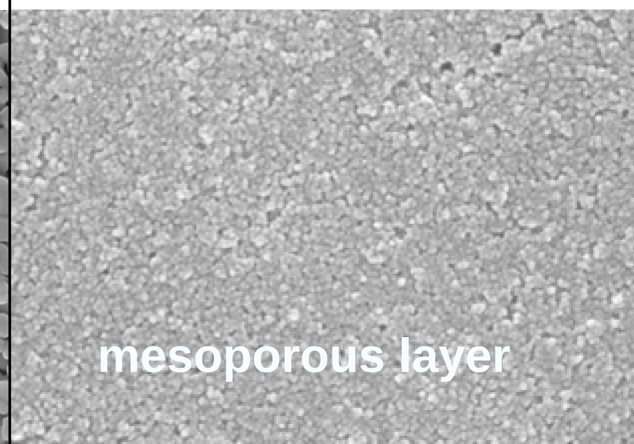


* bar = 1 µm

Pore size ~ 90 nm (1200ºC)
Phase structure: Cubic-ZrO_2

Particle size ´Colloidal´ $8Y_2O_3$-ZrO_2 Sol

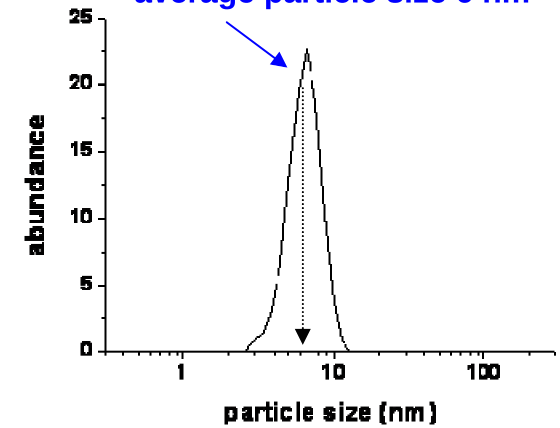


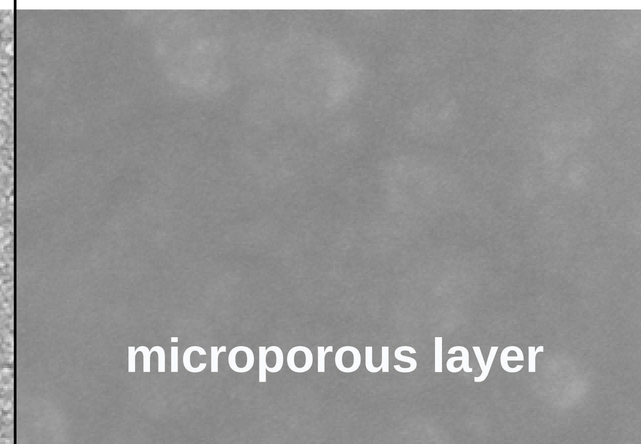


* bar = 200 nm

Pore size ~ 6 - 7 nm (500ºC)
Phase structure: Cubic-ZrO_2

Particle size ´Polymeric´ $8Y_2O_3$-ZrO_2 Nano-Sol





* bar = 200 nm

Pore size ~ 1 nm (450ºC)
Phase structure: Cubic-ZrO_2

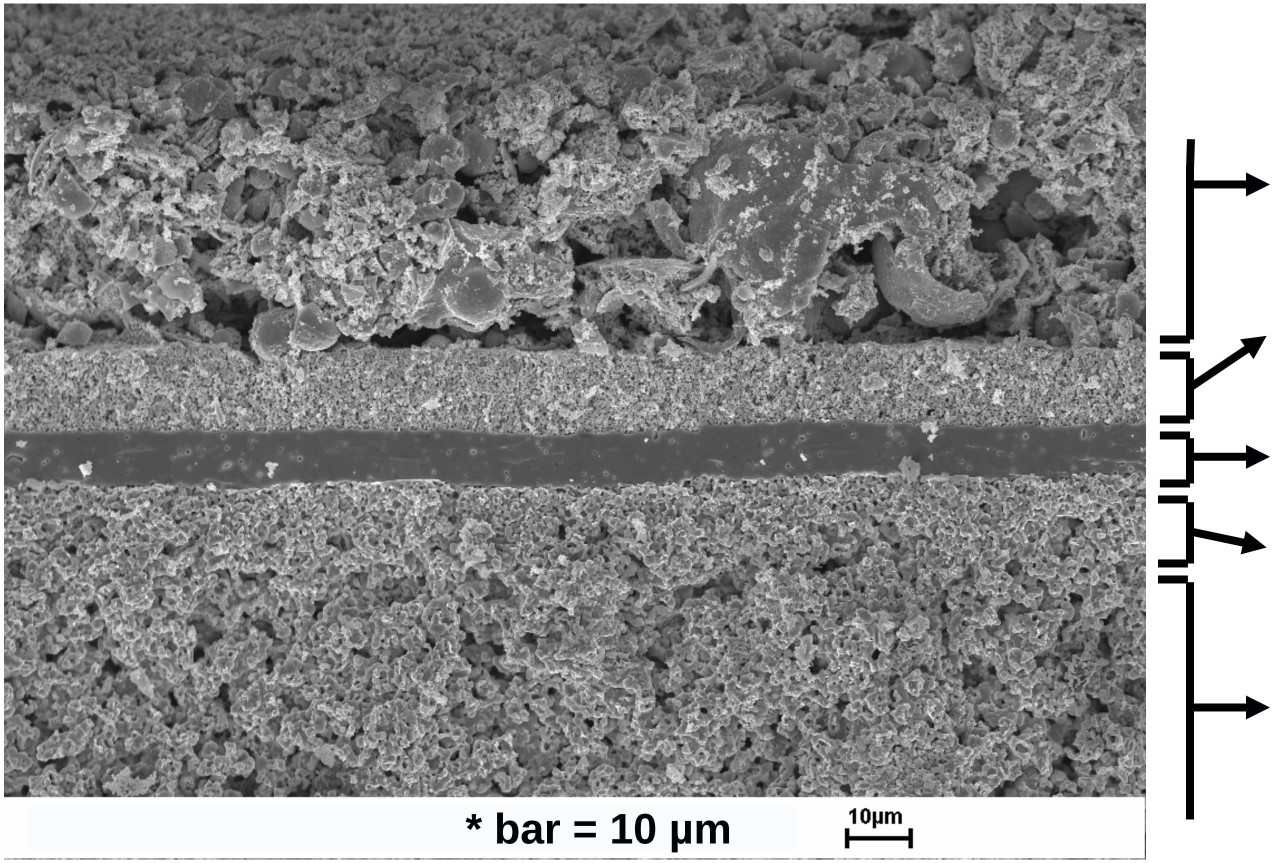
Membrane research topics in IEF-1

Focus on energy-related applications :

1. **Development of porous and dense membranes for application in CO_2-free power plants**
   - **dense membranes for O_2/N_2 separation**
   - **microporous membranes for CO_2/H_2 separation** ✓

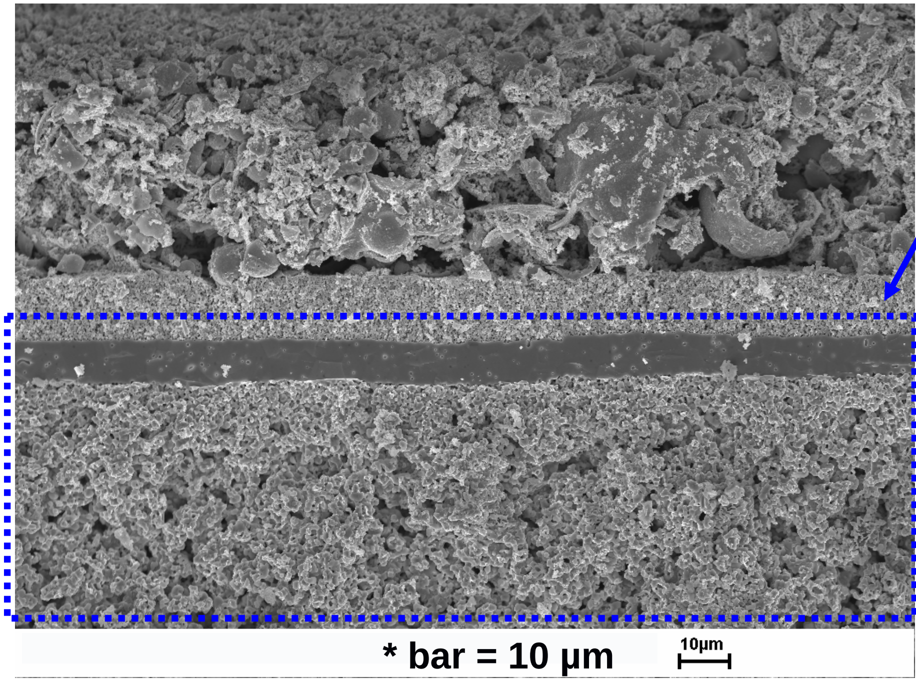
2. **Development of porous and dense membranes for application in advanced Solid Oxide Fuel Cells (SOFC´s)**
   - **porous anode and cathode layers**
   - **dense electrolyte membrane** ✓

Standard FZ-Jülich SOFC



- **Planar configuration (→ 20 cm x 20 cm)**
- **Anode supported concept with thin-film electrolyte**
- **I = ~ 1.5 A/cm² at 800ºC and 0.7 V (single cell); ~ 1.1 A/cm² (stack)**
- **Demonstrated 60-cell stack with 13 kW; in progress 20 kW system**

Novel membranes for advanced SOFC´s



* bar = 10 µm

dense $8Y_2O_3$-ZrO_2 electrolyte membrane on porous NiO/$8Y_2O_3$-ZrO_2 substrate

Conventional preparation method:

(1) Deposition of macroporous membrane starting from ZrO_2 powder suspension

(2) Sintering of macroporous membrane at high temperature (1400°C, 5h)

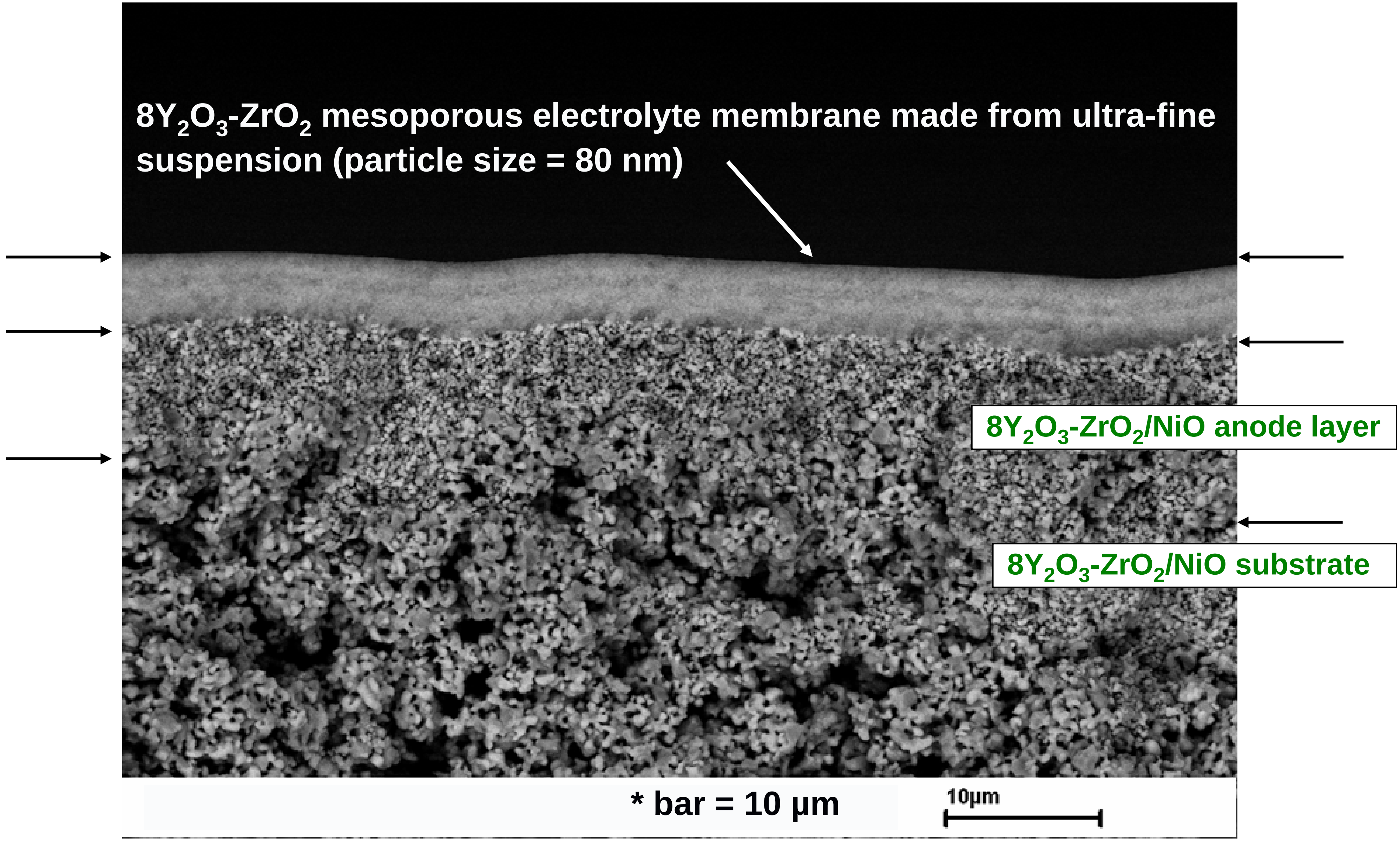
Proposed alternative preparation method:

(1) Deposition of membrane starting from ZrO_2 nano-particles (e.g. Coating with ultra-fine suspension or sol)

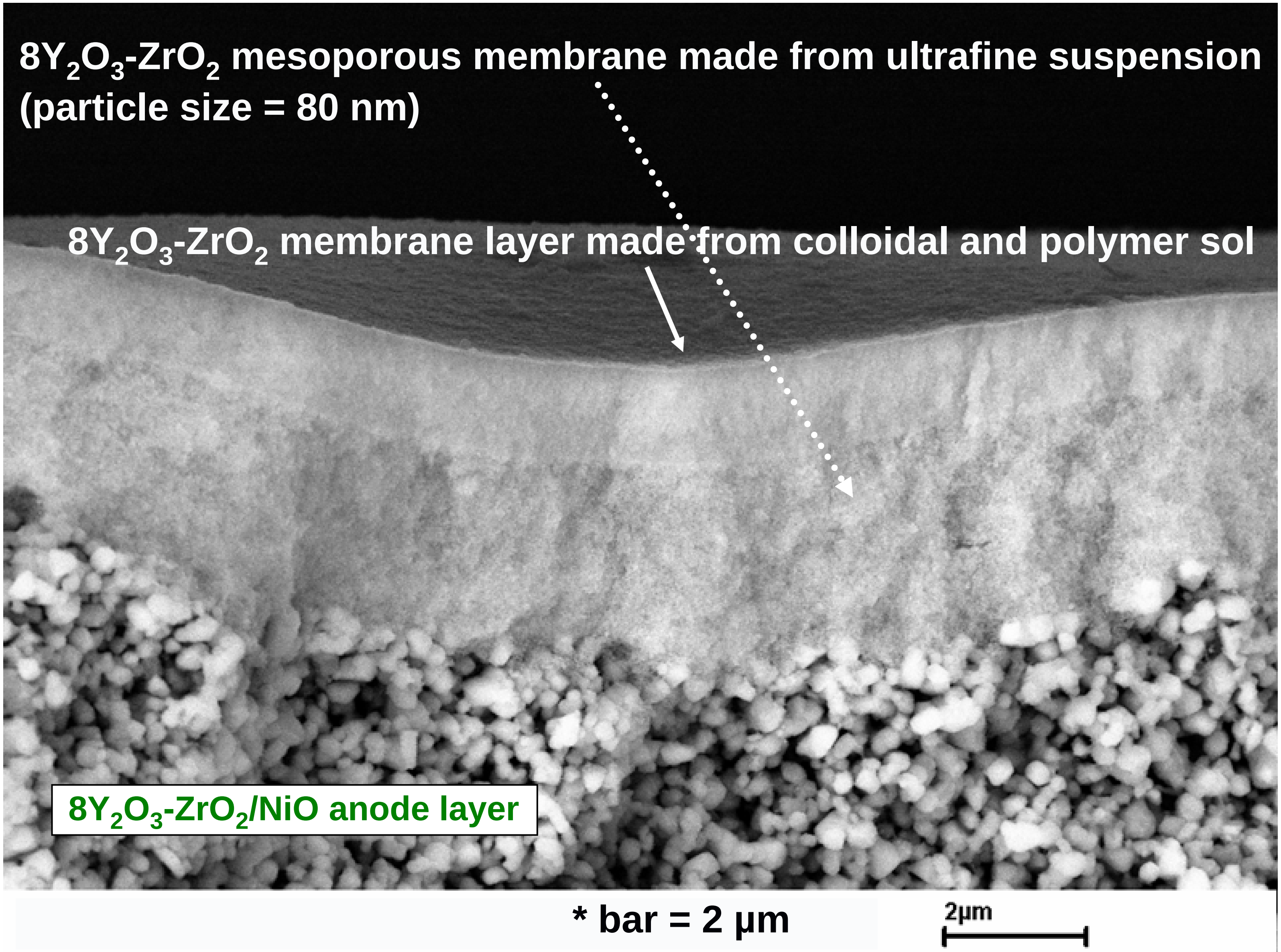
(2) Sintering at lower temperature (objective < 1100°C)

(3) Possibility to apply steel substrate, reduction of production cost

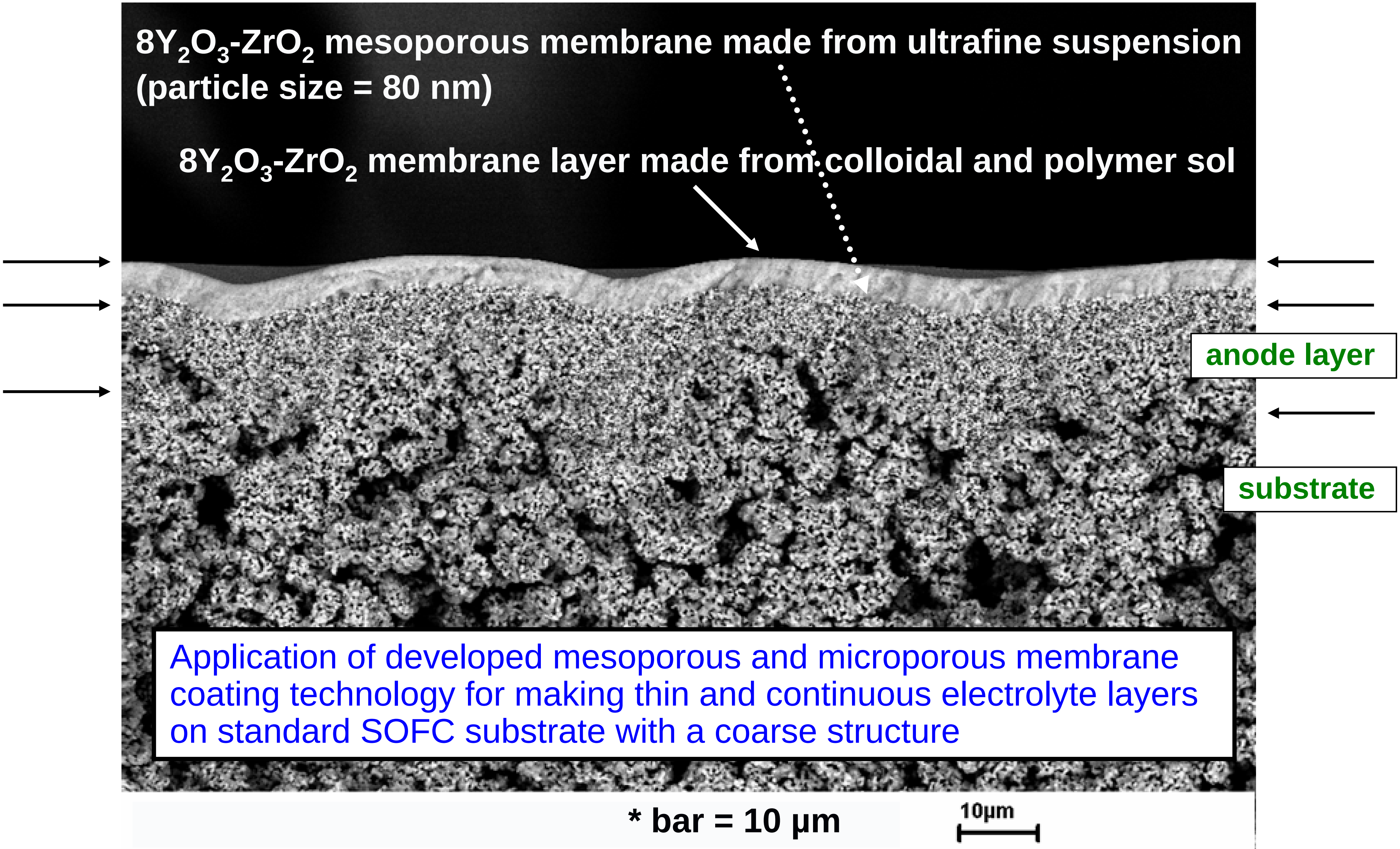
Novel membranes for advanced SOFC´s



Novel membranes for advanced SOFC´s



Novel membranes for advanced SOFC´s



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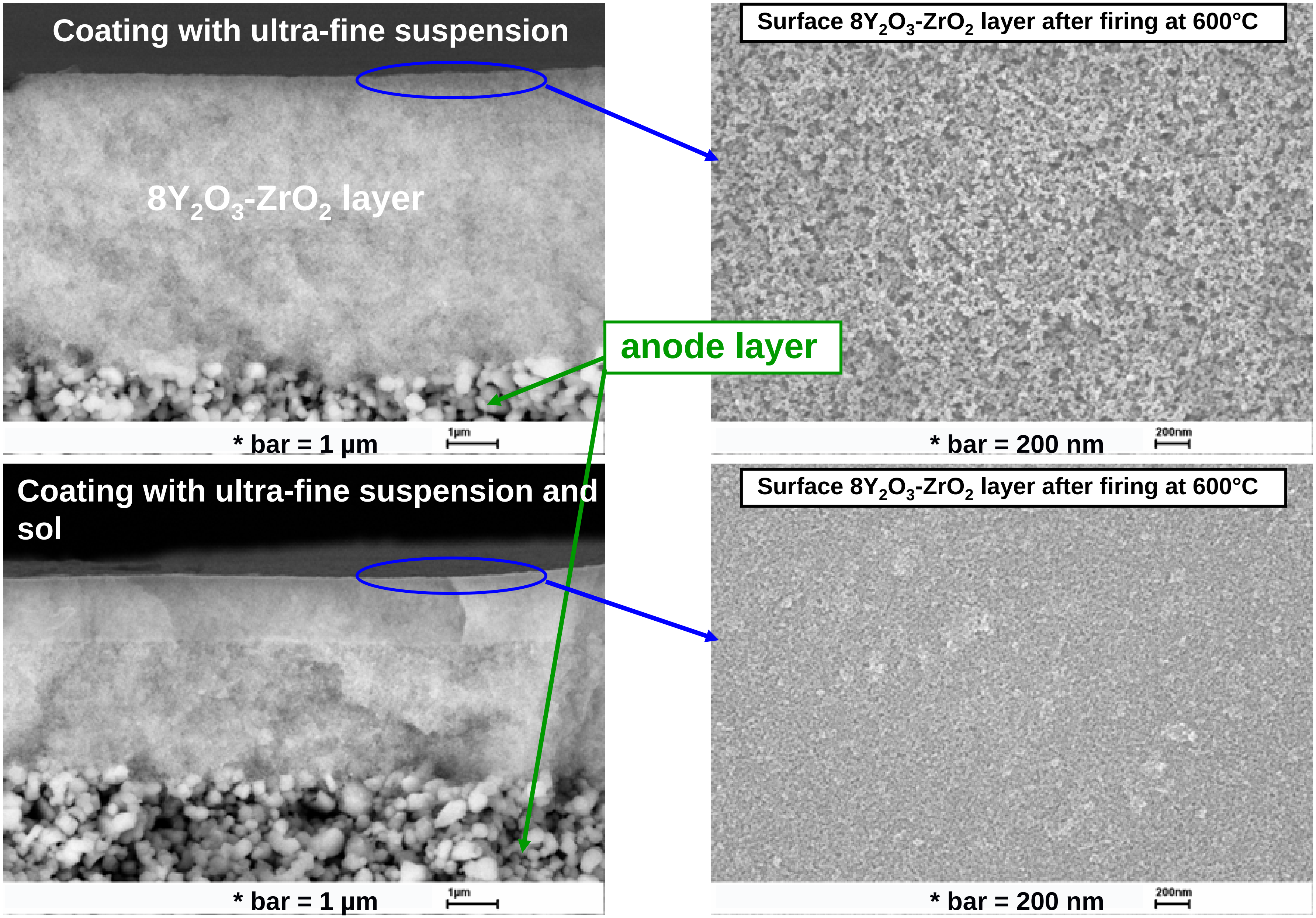
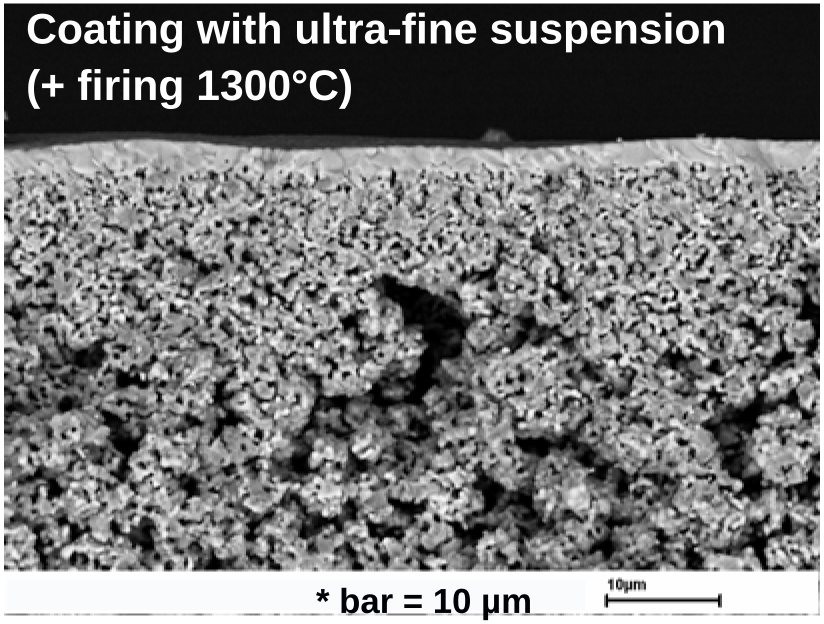
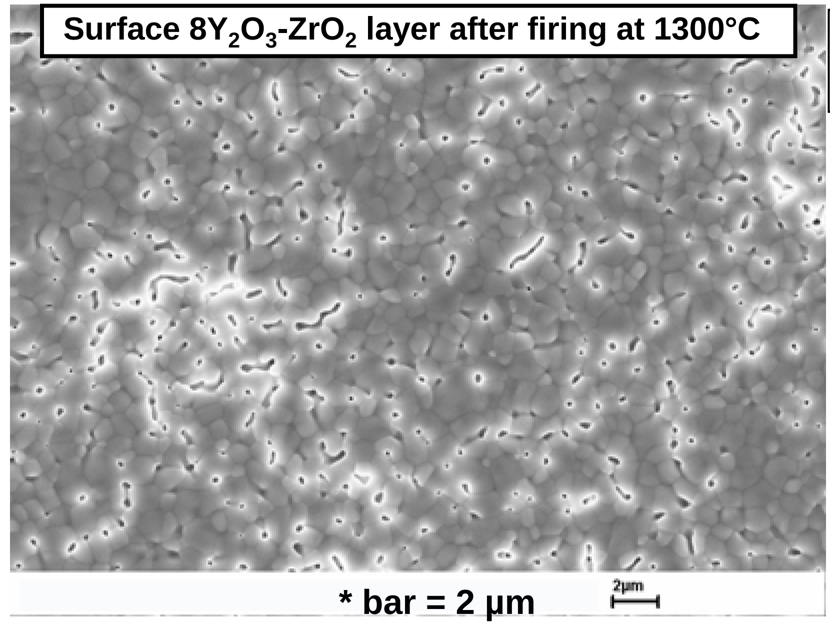
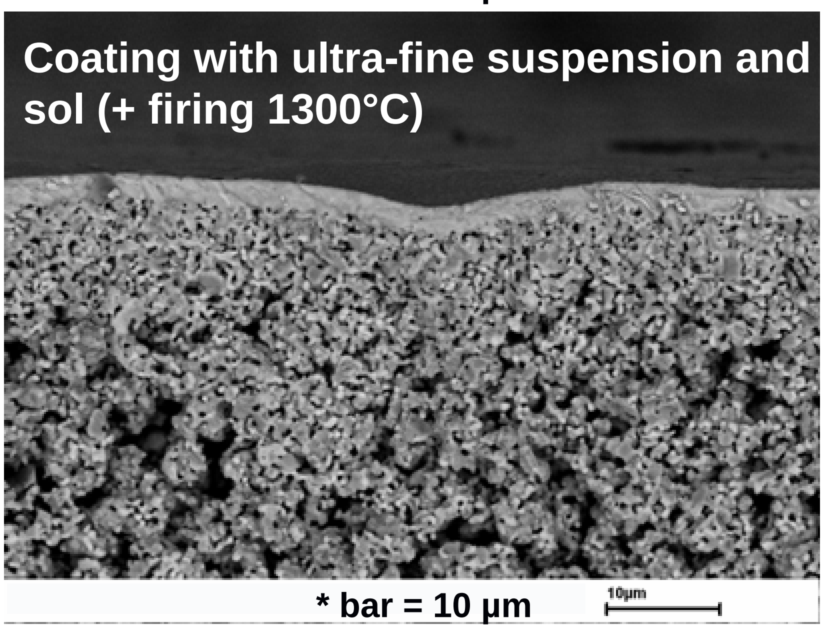


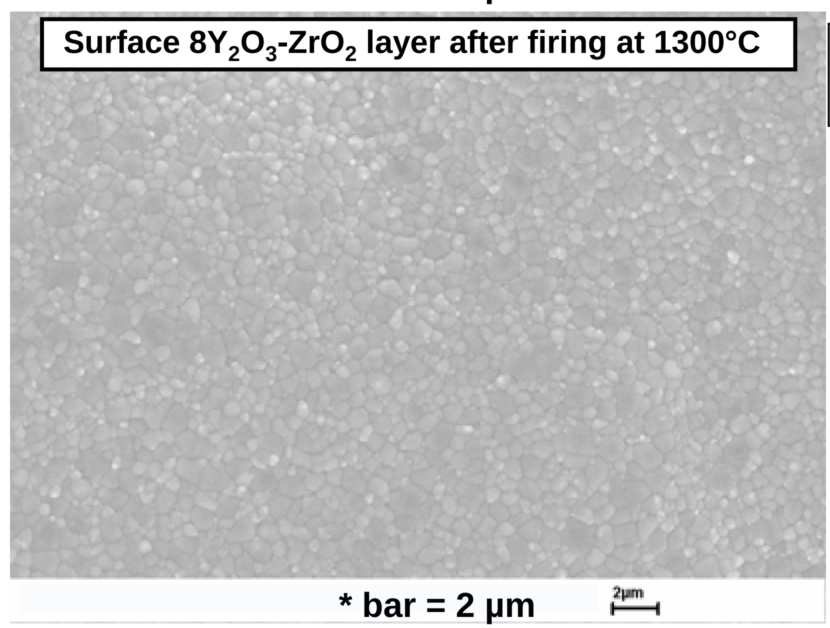
Novel membranes for advanced SOFC´s





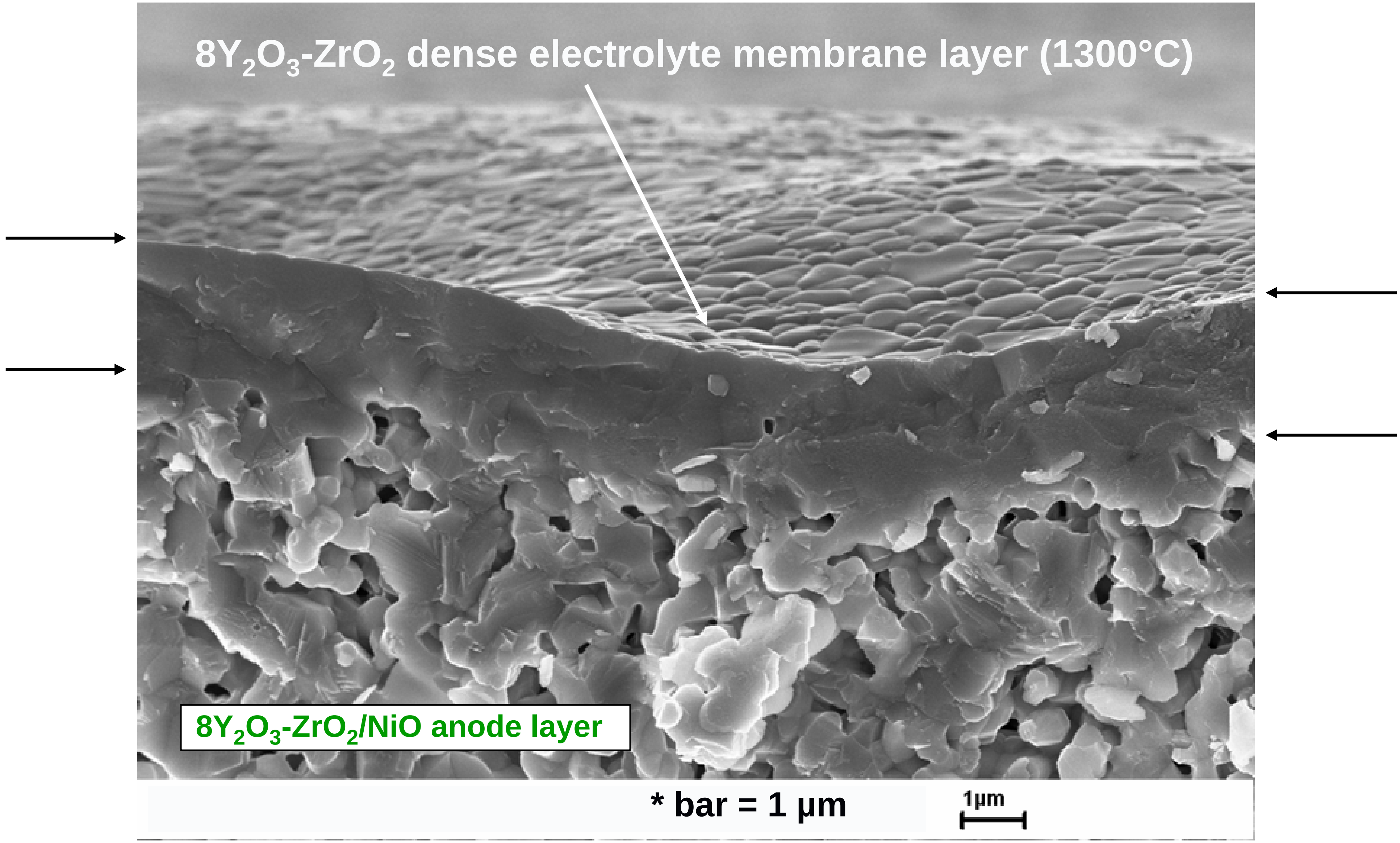
Standard 1400°C



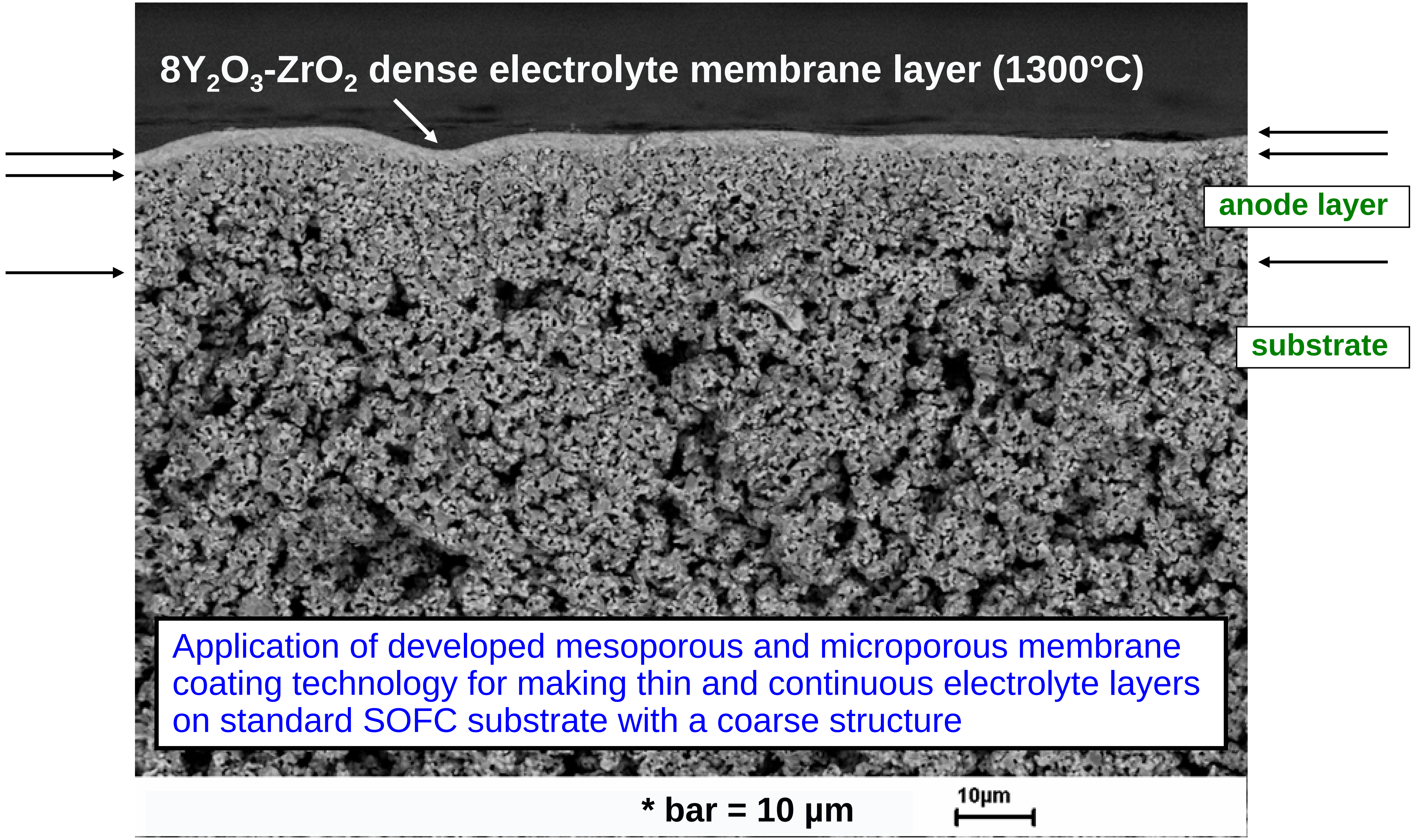


Standard 1400°C

Novel membranes for advanced SOFC´s

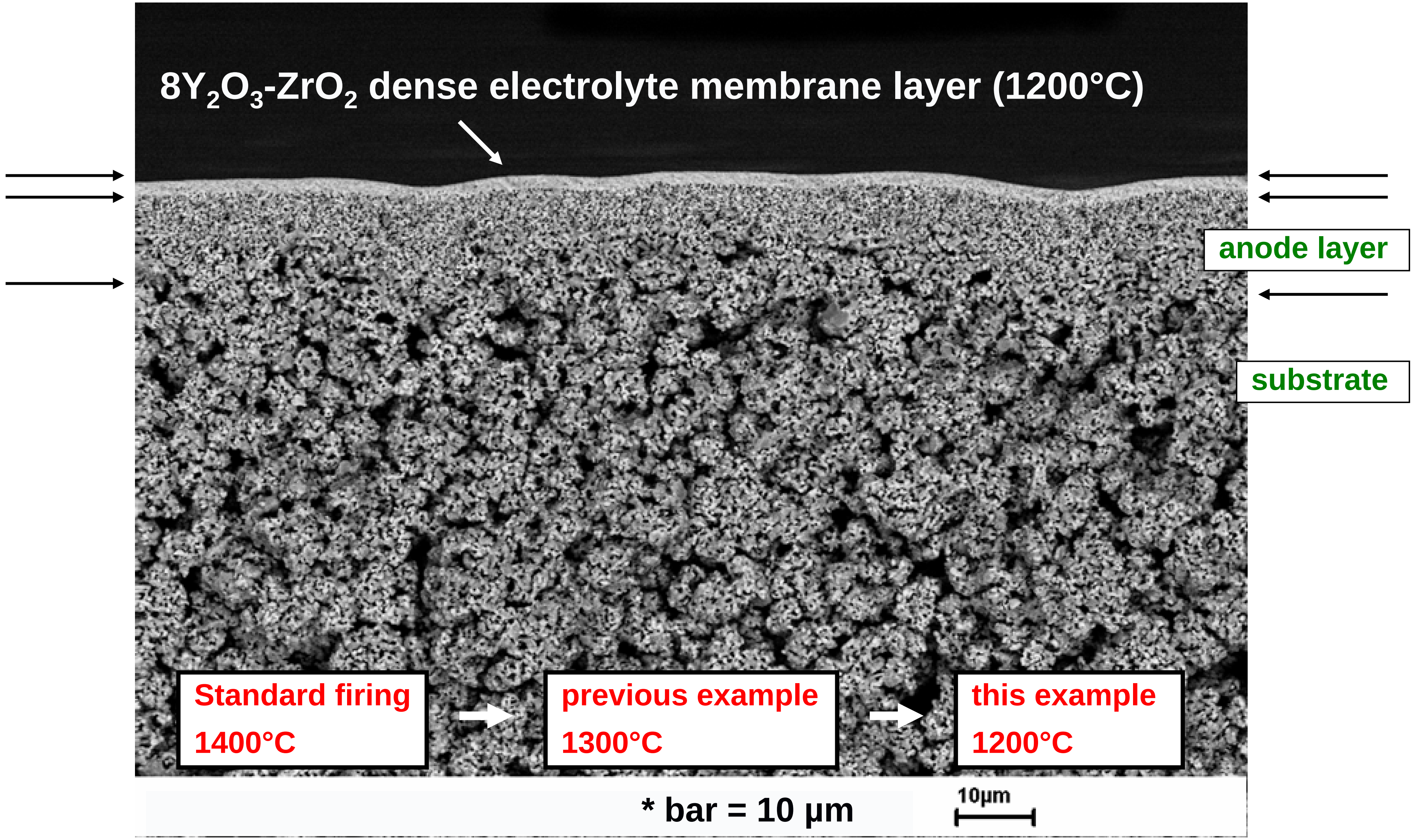


Novel membranes for advanced SOFC´s

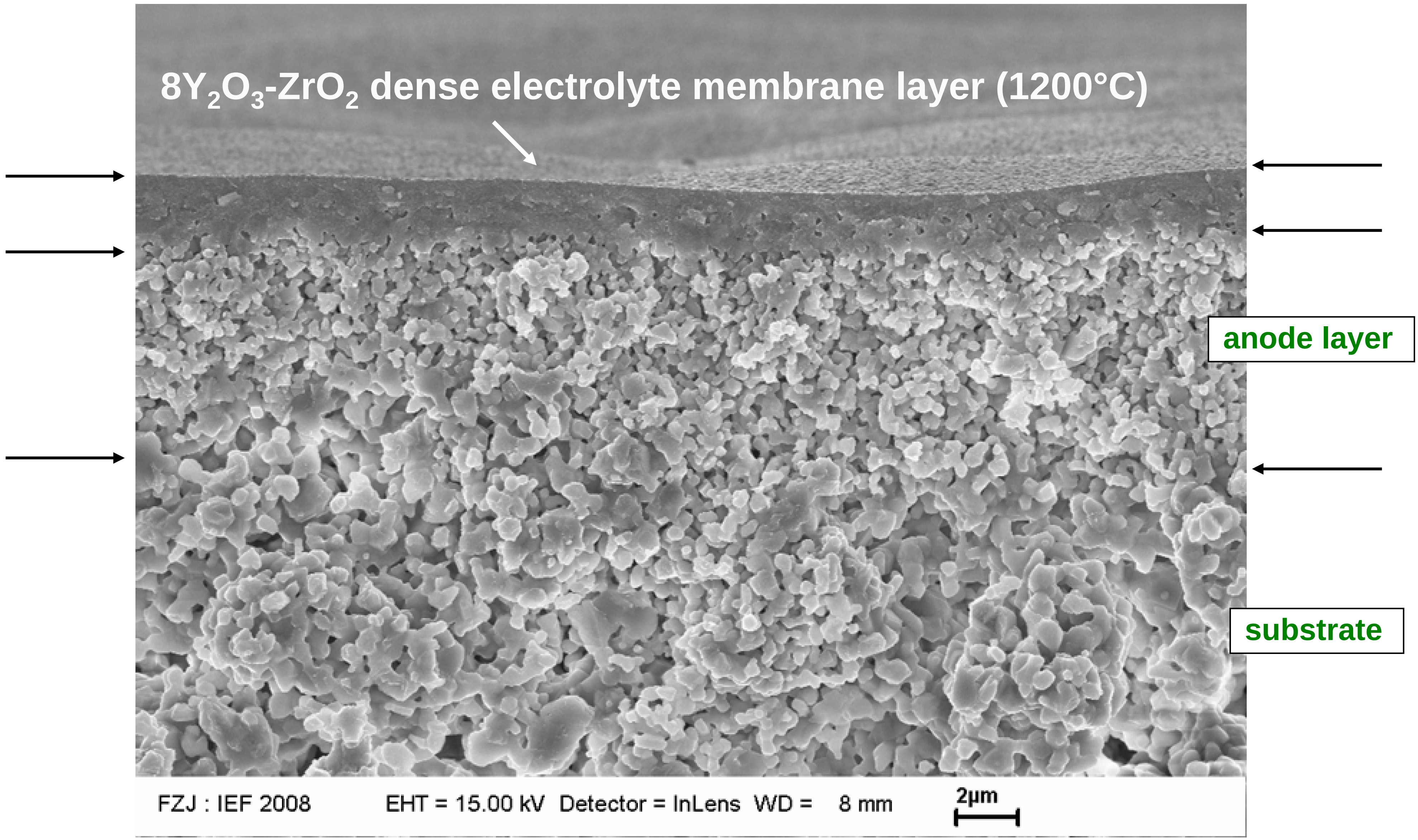


Application of developed mesoporous and microporous membrane coating technology for making thin and continuous electrolyte layers on standard SOFC substrate with a coarse structure

Novel membranes for advanced SOFC´s

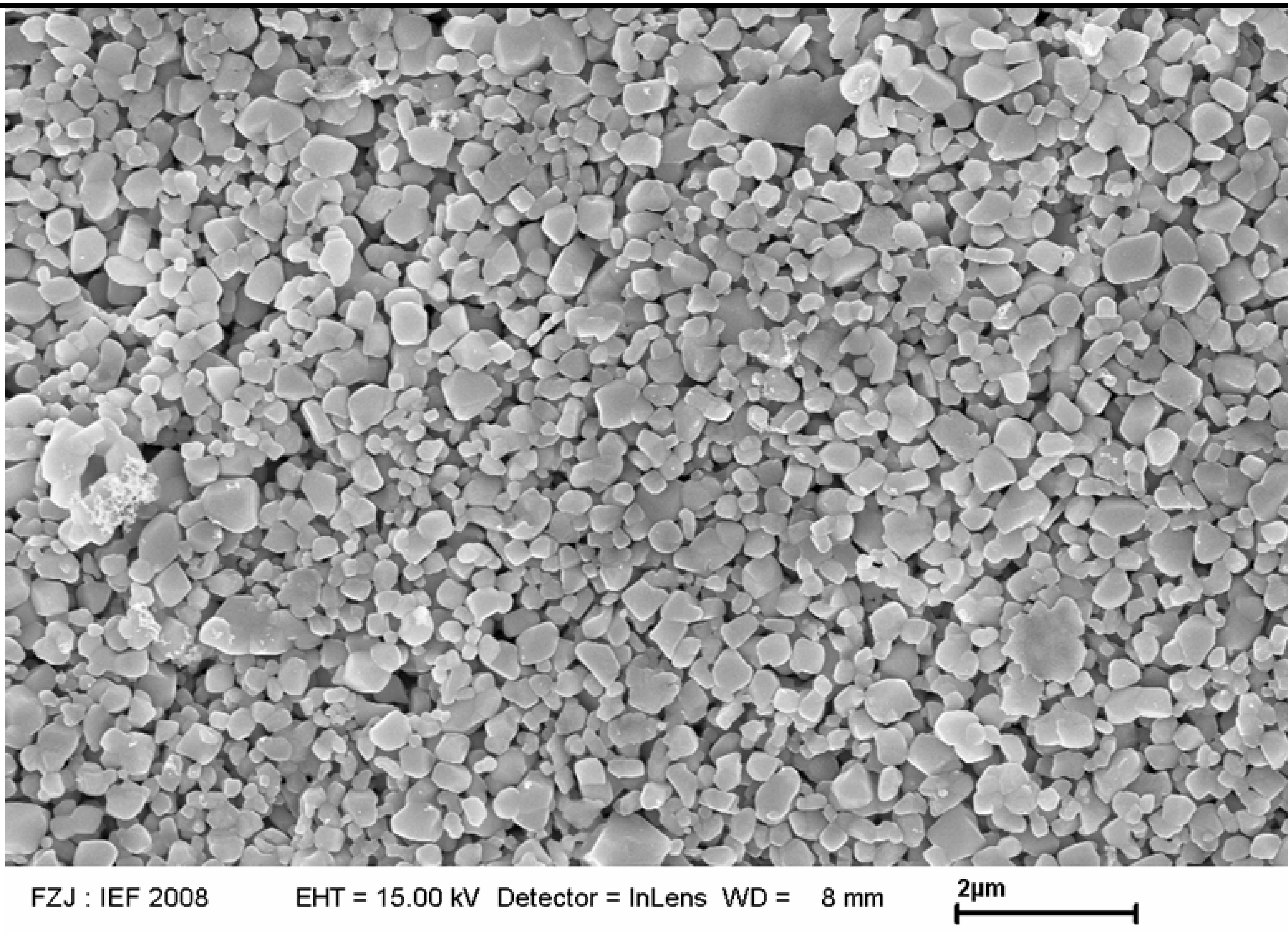


Novel membranes for advanced SOFC´s



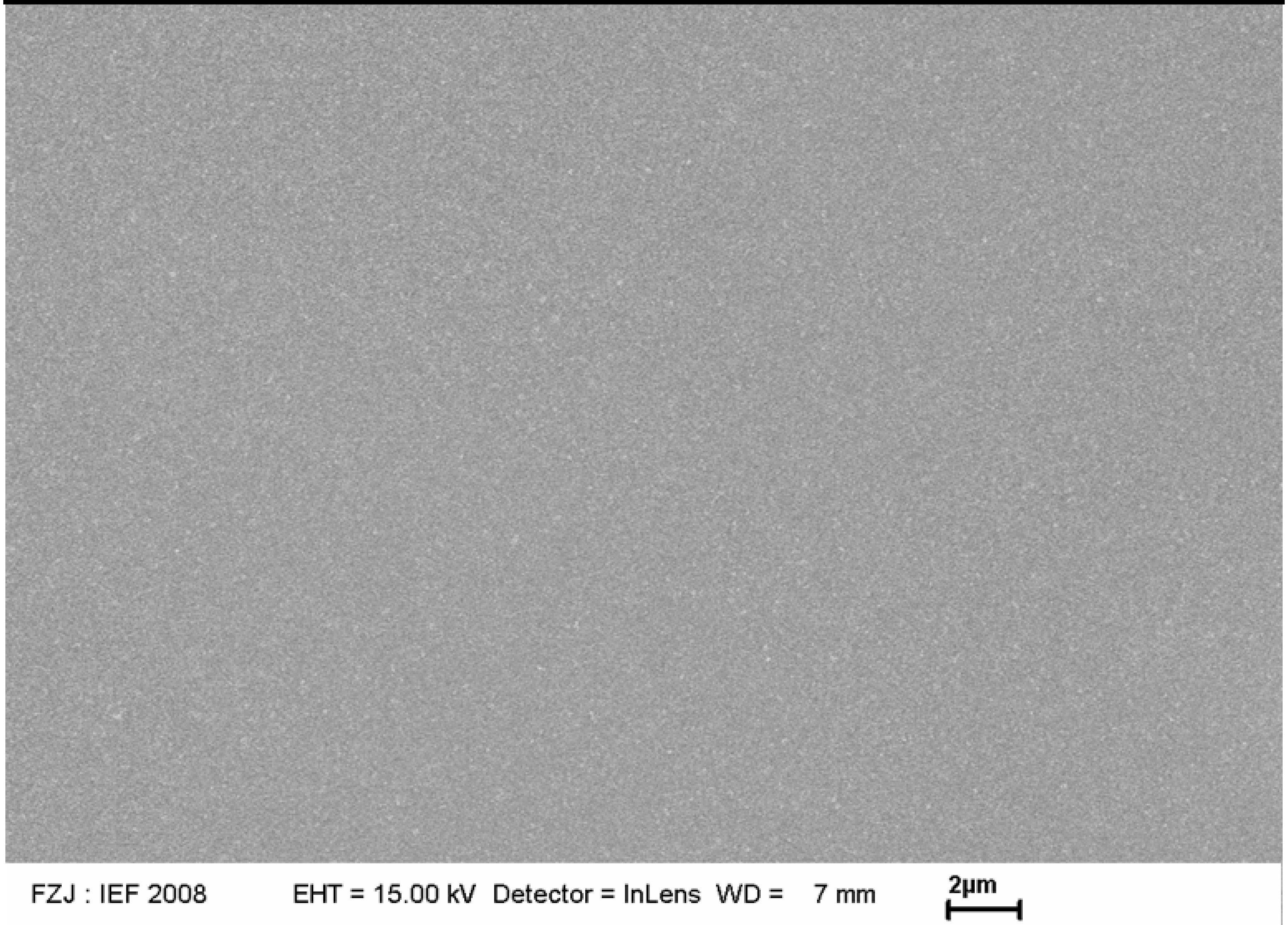
Novel membranes for advanced SOFC´s

Surface $8Y_2O_3$-ZrO_2/NiO anode layer (on standard SOFC substrate)



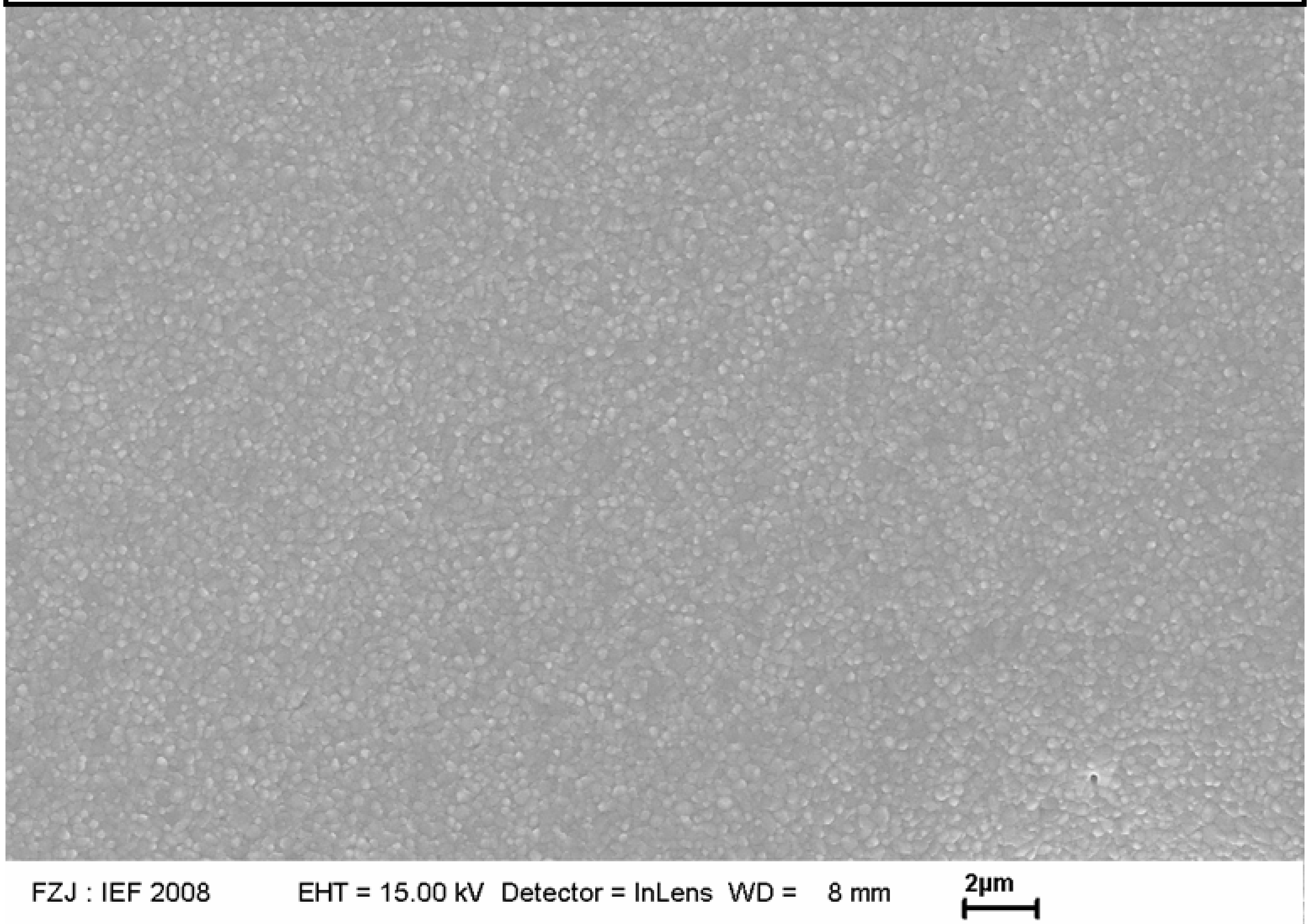
Novel membranes for advanced SOFC´s

Surface $8Y_2O_3$-ZrO_2 porous membrane after firing at 600°C



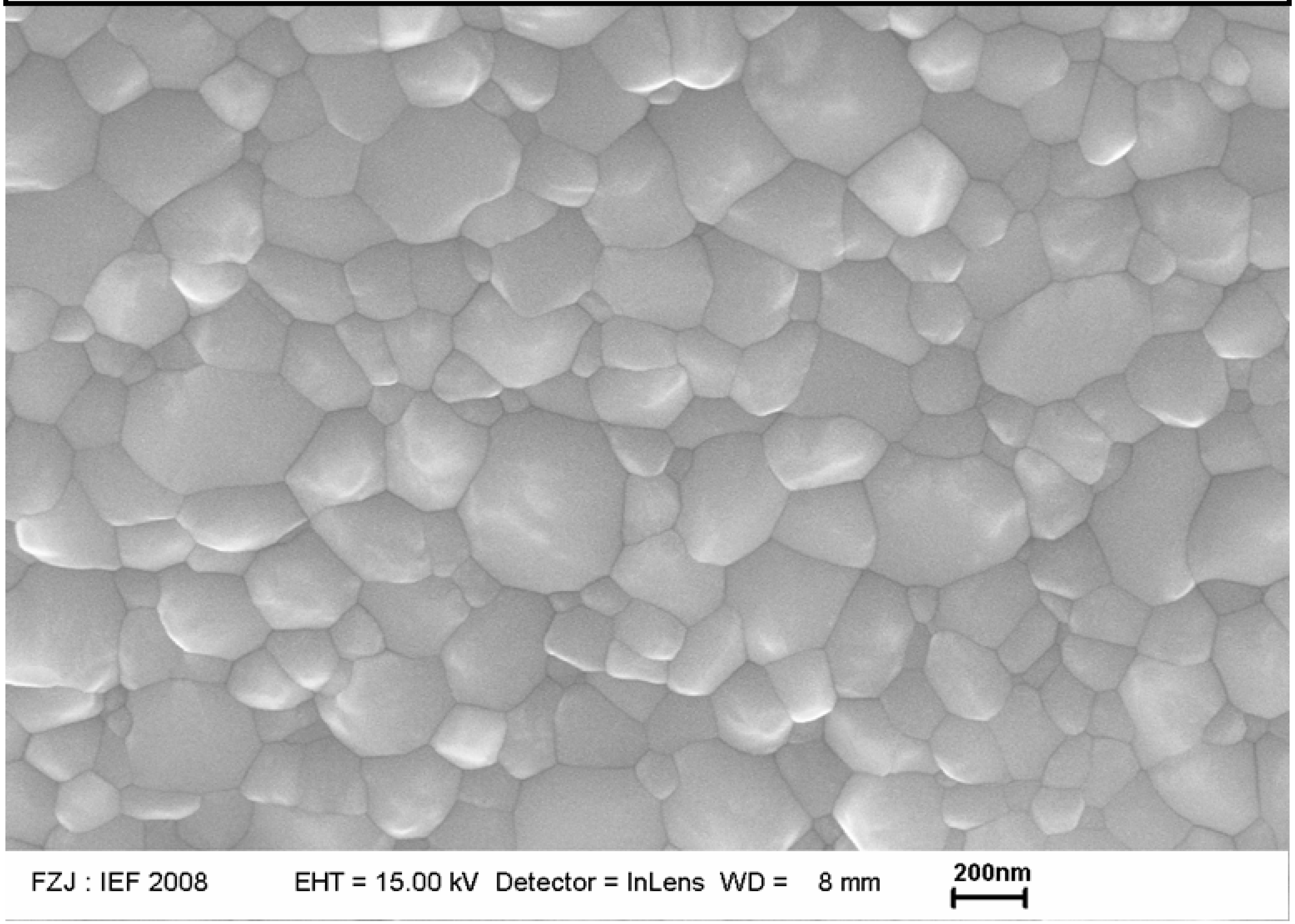
Novel membranes for advanced SOFC´s

Surface $8Y_2O_3$-ZrO_2 membrane after firing at 1200°C



Novel membranes for advanced SOFC´s

Detail $8Y_2O_3$-ZrO_2 membrane after firing at 1200°C



State of the art - Conclusion

☞ **Current gas separation membranes** are made of SiO_2 materials, having an insufficient (hydro)thermal stability for application in power plant streams

☞ **Current solid oxide fuel cells** are made by unwanted high-temperature sinter treatments

In this work :

✦ Manufacturing of novel nano-structured ZrO_2 membranes

✦ Widely accepted material for long-term operation in gas separation

✦ Densification material at a lower temperature for SOFC manufacturing

In progress :

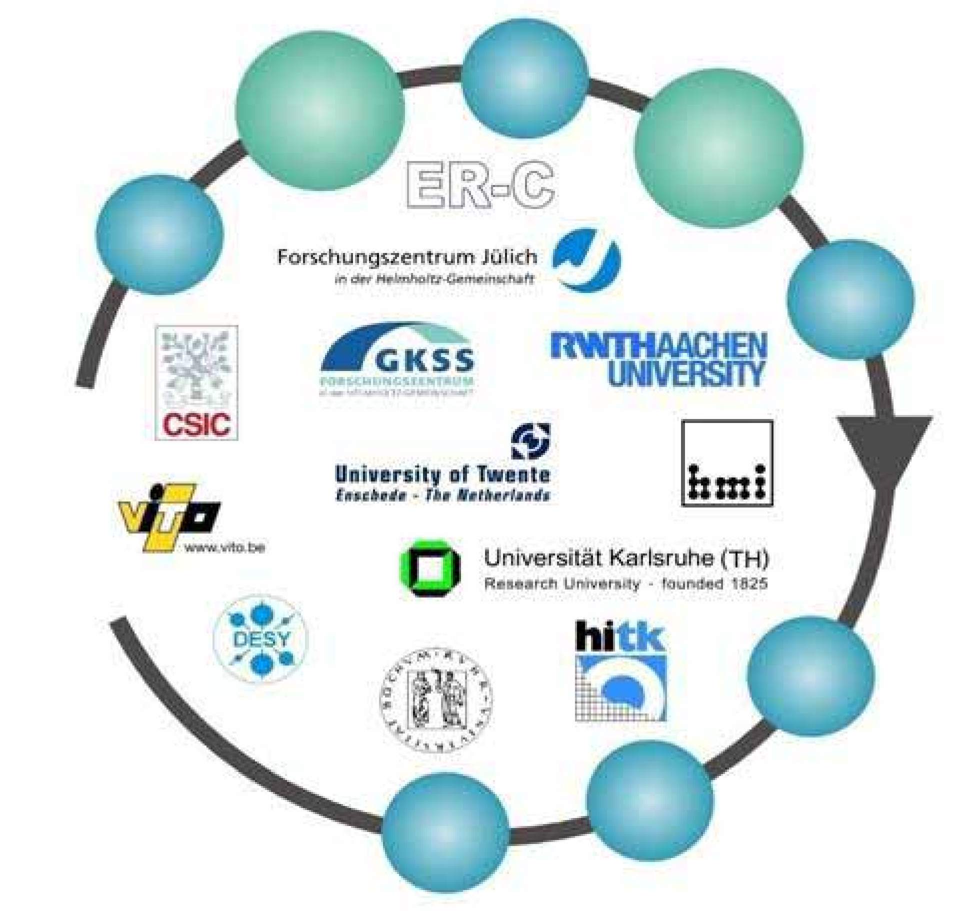
✦ Optimization of the membrane pore size (target: high H_2/CO_2 selectivity)

✦ Manufacturing SOFC's for current density characterization

Acknowledgement :

Funding by Helmholtz Association of German Research Centers

Helmholtz Alliance MEM-BRAIN



SEM images made by

Dr. Doris Sebold

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