Transmission electron microscopy – a versatile tool to study the microstructure of HT-PEMFC

Max-Planck-Institut für Eisenforschung GmbH
Düsseldorf, Germany

Christina Scheu

Acknowledgement

K. Hengge, S. Gleich
Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

C. Heinzl, T. Ossiander, M. Welsch, M. Perchthaler
Elcore GmbH, Munich, Germany

V. Hacker
Graz University of Technology, Graz, Austria

Motivation



Need for „green“ energy



GEOTHERMAL ENERGY



WATER





WIND



SUN

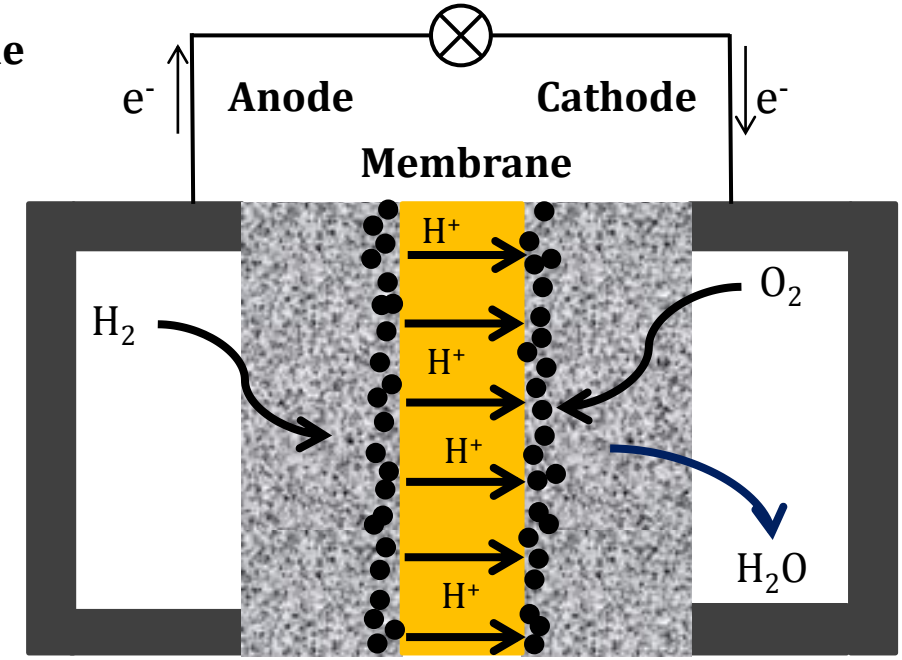




- BUT: seasonal conditions, daytime, over- and underproduction, energy peaks…
- Energy needs to be stored
- One possibility: hydrogen fuel
- Use at any time in fuel cells (FC) possible

High-Temperature Polymer-Electrolyte-Membrane Fuel Cell (HT-PEMFC) stack





Membran-Electrode-Assembly (MEA)

AIM of the work:

- Develop new materials for HT-PEMFCs
- Link microstructure and properties
- Discover degradation mechanisms

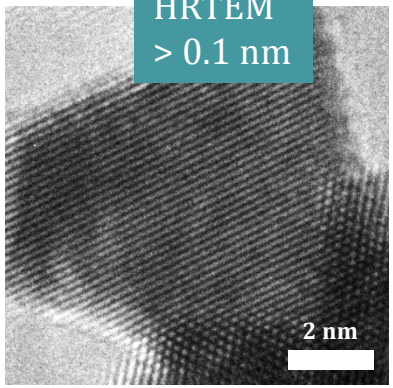
- Microstructural features of interest are on the nanometer scale
- High spatial resolution techniques are required

In our work:

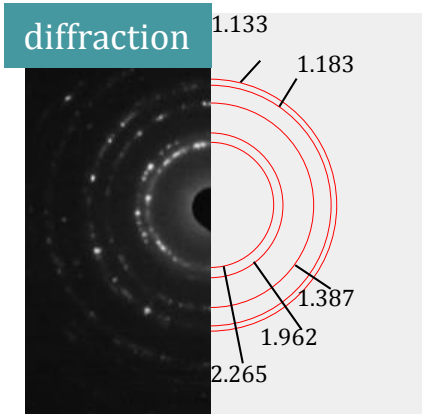
- Scanning electron microscopy (SEM)
- Focussed ion beam sectioning (FIB)
- Transmission electron microcopy (TEM) and related techniques

TEM AND RELATED TECHNIQUES

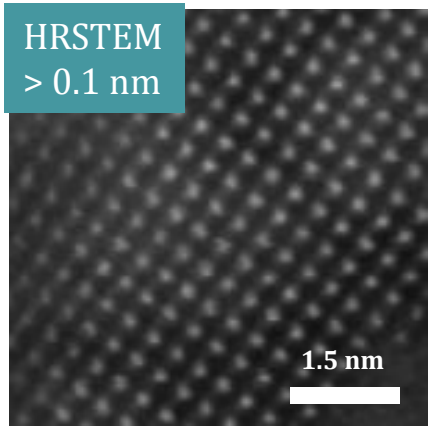
HRTEM
> 0.1 nm

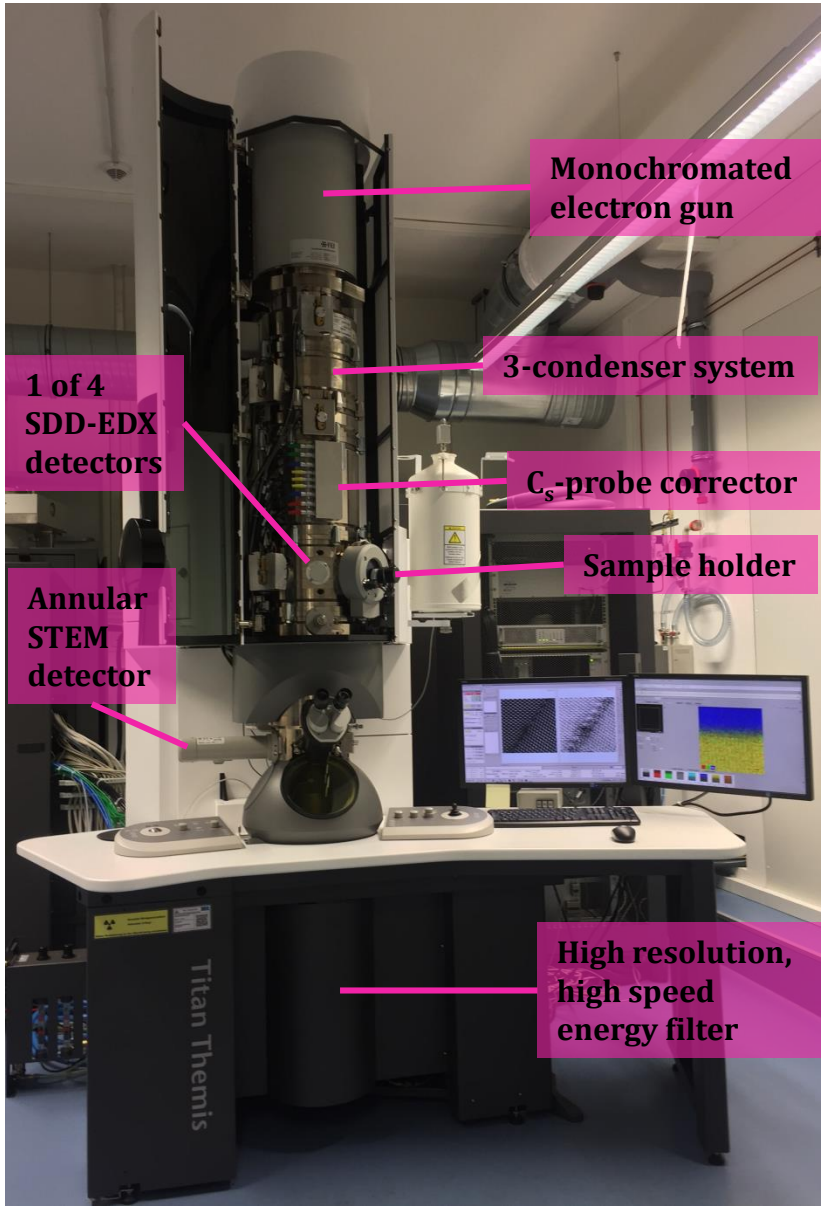


diffraction

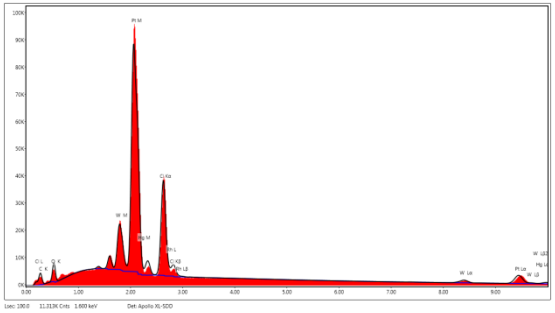


HRSTEM
> 0.1 nm

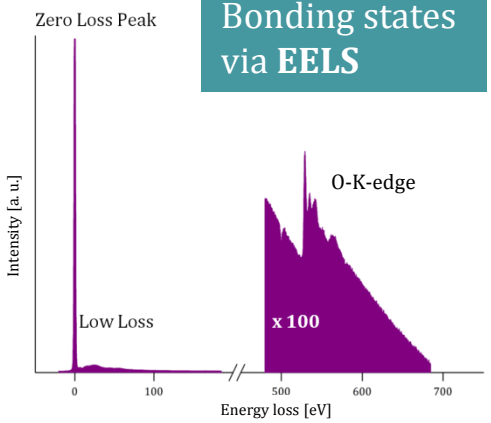




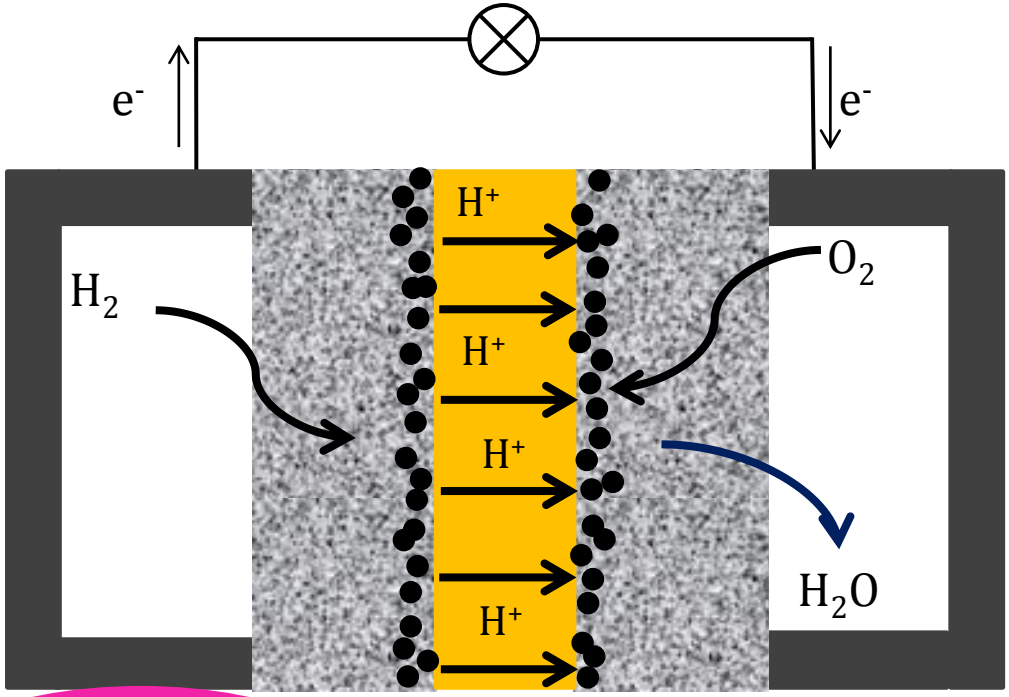
Chemical composition and distribution maps via **EDX**



Bonding states via **EELS**



New materials for HT-PEMFCs



Anode[5,6]
Pt catalyst on tungsten **sub**oxide

Membrane[1-4]
Polybenz-imidazole (PBI)

Cathode
Pt catalyst NP on amorphous carbon

(1) Heinzl, C.; Ossiander, T.; Gleich, S.; Scheu, C. *J Membrane Sci* **2015**, *478*, 65.
(2) Ossiander, T.; Heinzl, C.; Gleich, S.; Schönberger, F.; Völk, P.; Welsch, M.; Scheu, C. *J Membrane Sci* **2014**, *454*, 12.
(3) Ossiander, T.; Perchthaler, M.; Heinzl, C.; Scheu, C. *Journal of Power Sources* **2014**, *267*, 323.
(4) Ossiander, T.; Perchthaler, M.; Heinzl, C.; Schönberger, F.; Völk, P.; Welsch, M.; Chromik, A.; Hacker, V.; Scheu, C. *J Membrane Sci* **2016**, *509*, 27.
(5) Perchthaler, M.; Ossiander, T.; Juhart, V.; Mitzel, J.; Heinzl, C.; Scheu, C.; Hacker, V. *Journal of Power Sources* **2013**, *243*, 472.
(6) Heinzl, C.; Hengge, K. A.; Perchthaler, M.; Hacker, V.; Scheu, C. *Journal of The Electrochemical Society* **2015**, *162*, F280.

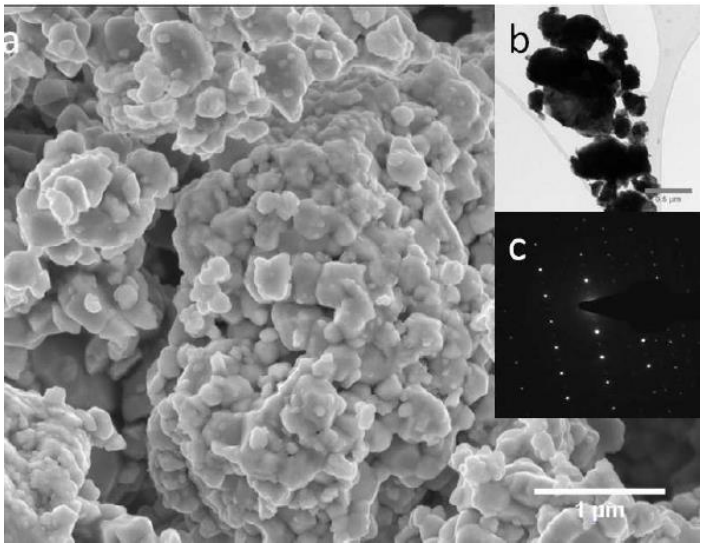
HT-PEM Electrodes

- **Development of new electrodes for HTPEM-FC**

□ usually high surface area carbon (HSAC) is used as catalyst support

□ due to high potentials and temperatures this carbon catalyst support oxidizes to CO_2

→ possible replacement by WC or WO_{3-x} based systems (as anode material)



WO_{3-x} catalyst support

- **Benefits of using WO_{3-x} as anode material**

□ WO_3 is an electrical insulator while WO_{3-x} is a semiconductor (band gap 2.6 –2.8 eV)

□ melting temperature > 1700 °C

□ corrosion resistant

□ CO-tolerant

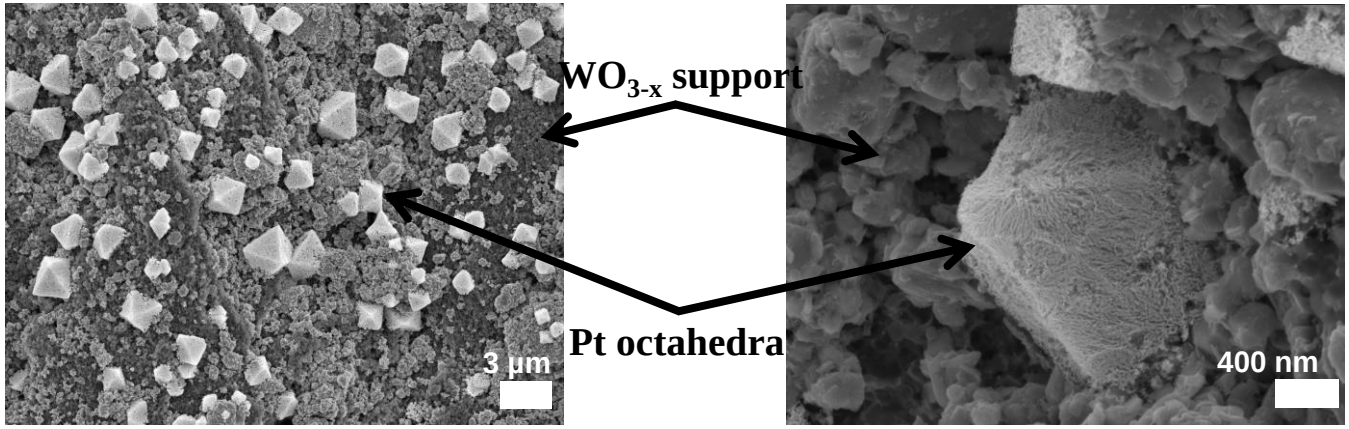
□ H+-conductivity

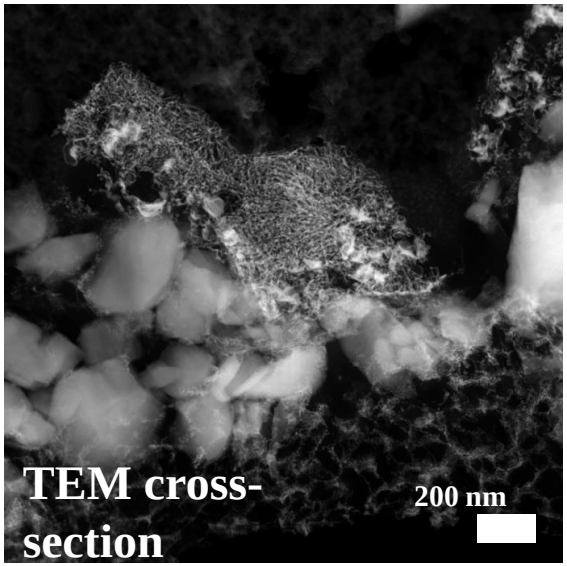
Tungsten materials as durable catalyst supports for fuel cell electrodes
M. Perchthaler, T. Ossiander, V. Juhart, J. Mitzel, C. Heinzl, C. Scheu, V. Hacker
Journal of Power Sources, 243, 472–480 (2013)

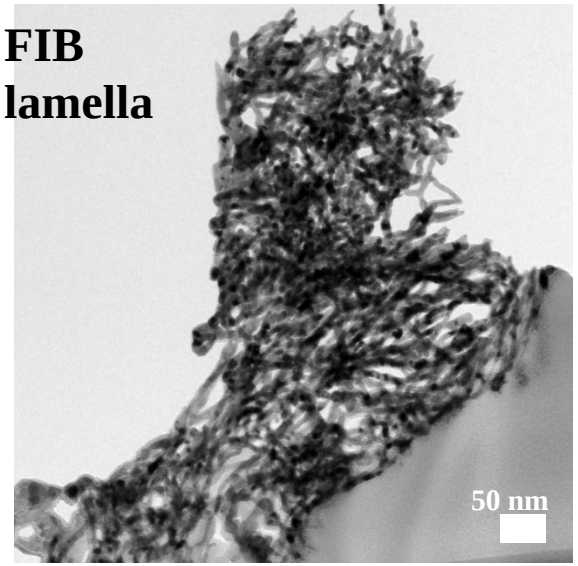
Pt loaded Anode

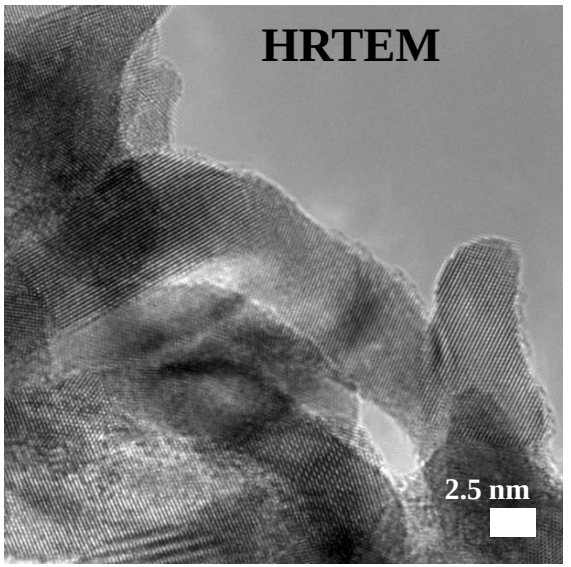
- **Pt loaded WO_{3-x} prior application as an anode**

SEM



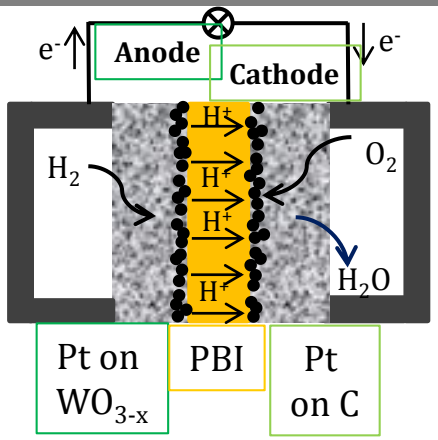






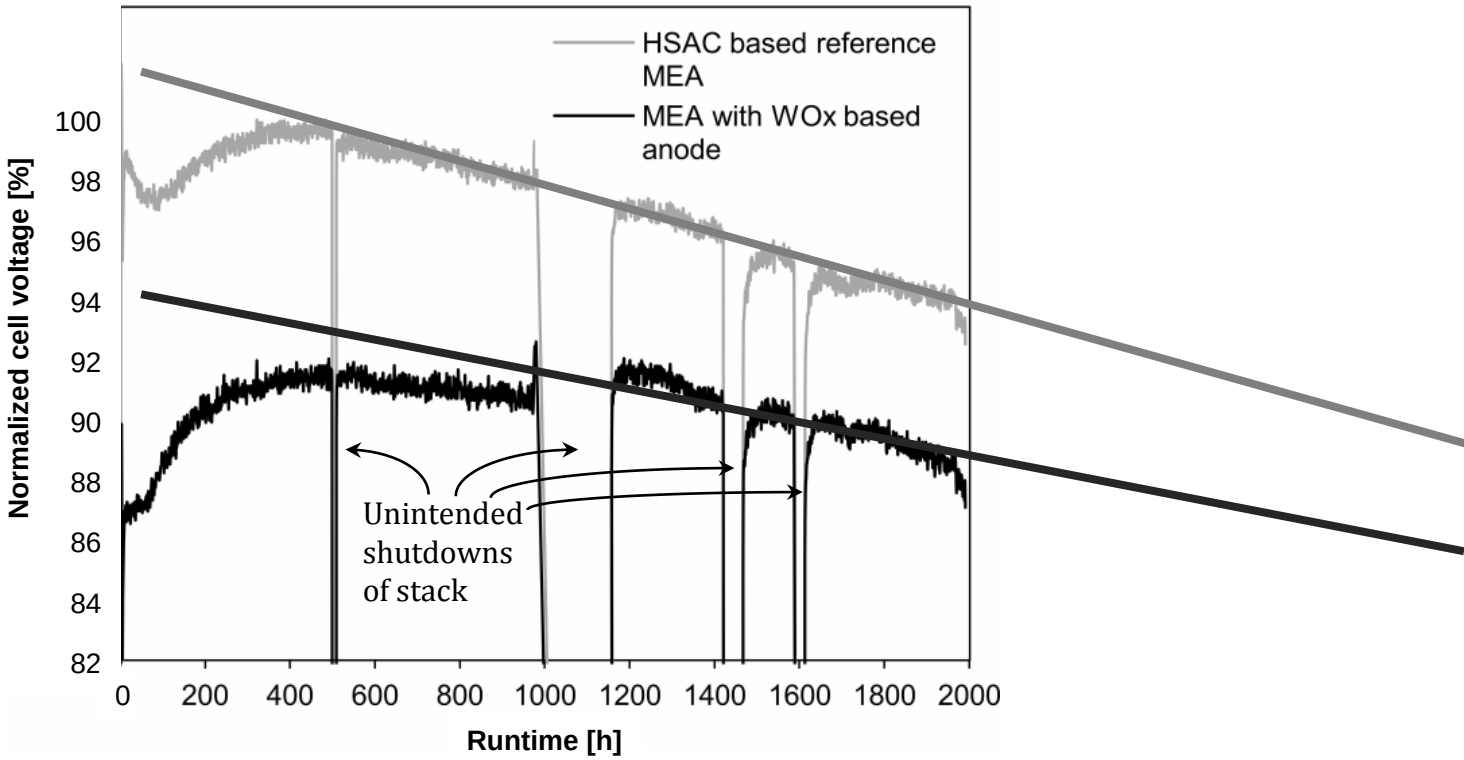
C. Heinzl, K. A. Hengge, M. Perchthaler, V. Hacker, and C. Scheu , *J. Electrochem*. Soc., 162, 3, F280-F290, (2015)

DEGRADATION BEHAVIOR OF HT-PEMFCS(1)



4 MEAs – 3 different operation modes and times

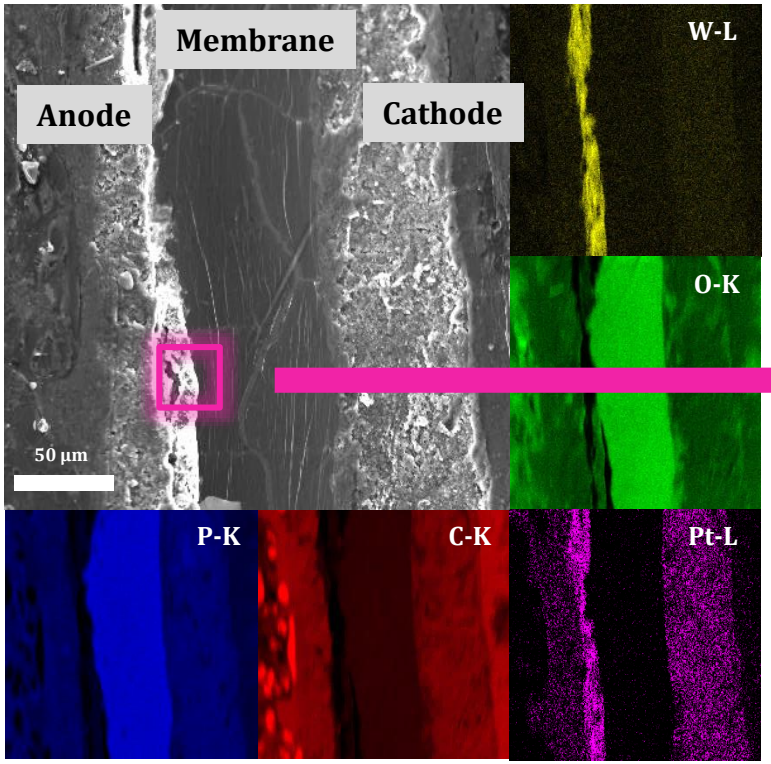
- Ready to use
- 650 h of continuous operation
- 2000 h of continuous operation
- Start-stop cycles

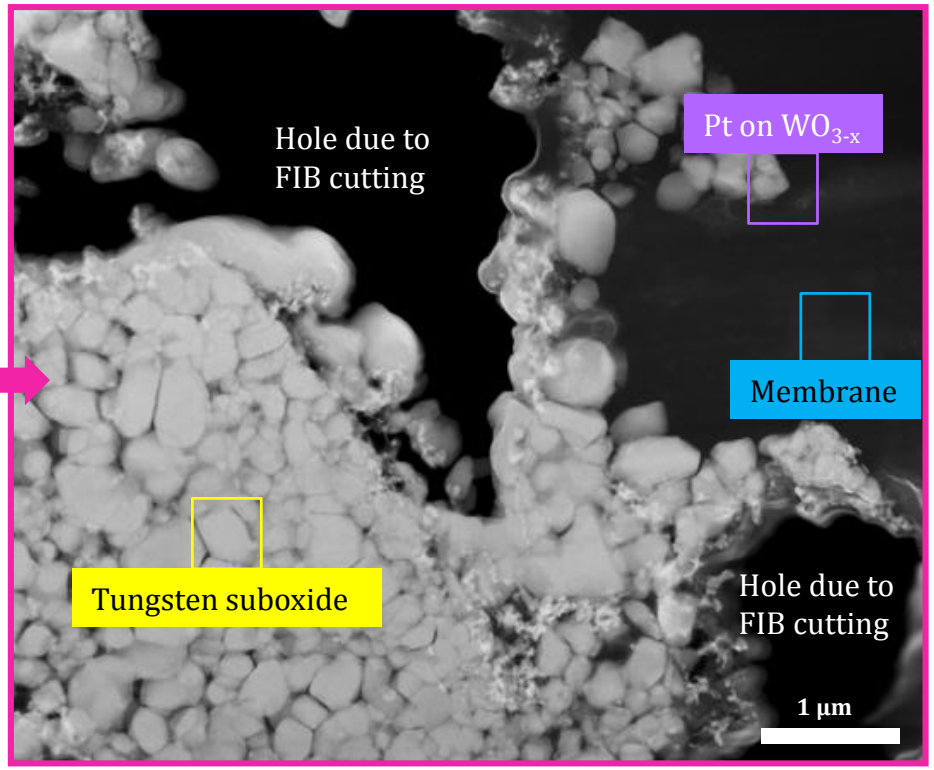


2000 h of continuous operation – insights via SEM and TEM:

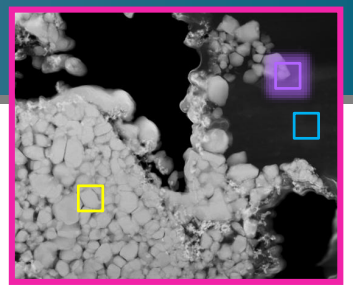
SEM
EDX Map shows elemental distribution

STEM
Interface between anode and membrane
➢ **TEM investigation of highlighted areas**



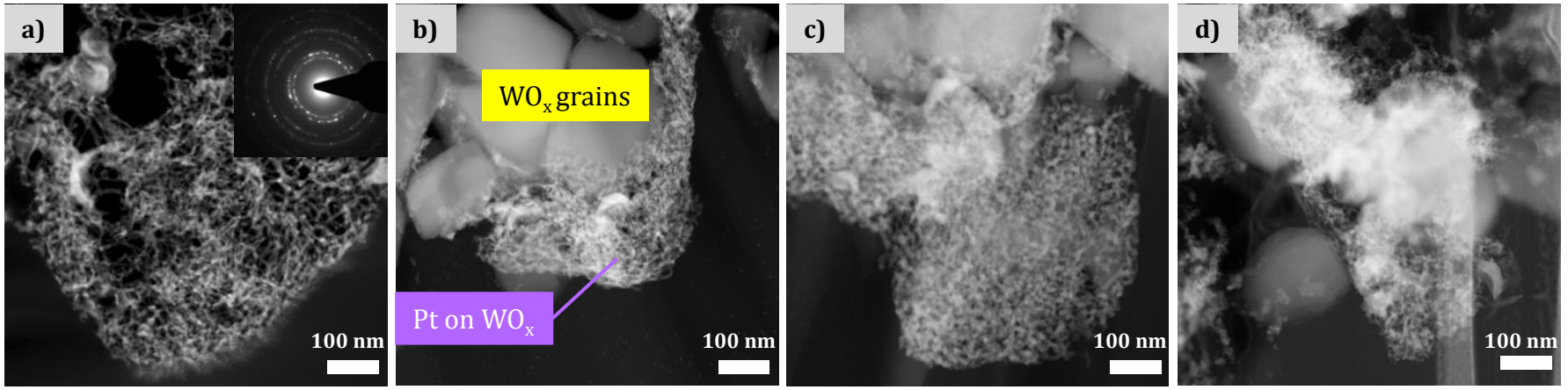


DEGRADATION BEHAVIOR OF HT-PEMFCS[1]



Comparison of PLATINUM networks

Reference	650 h	2000 h	Start-stop cycles

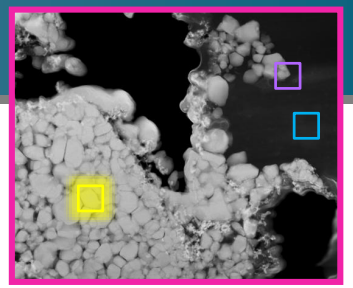


Well defined network ⟷ Pt networks become deformed

Many pores ⟷ Number of pores decreased

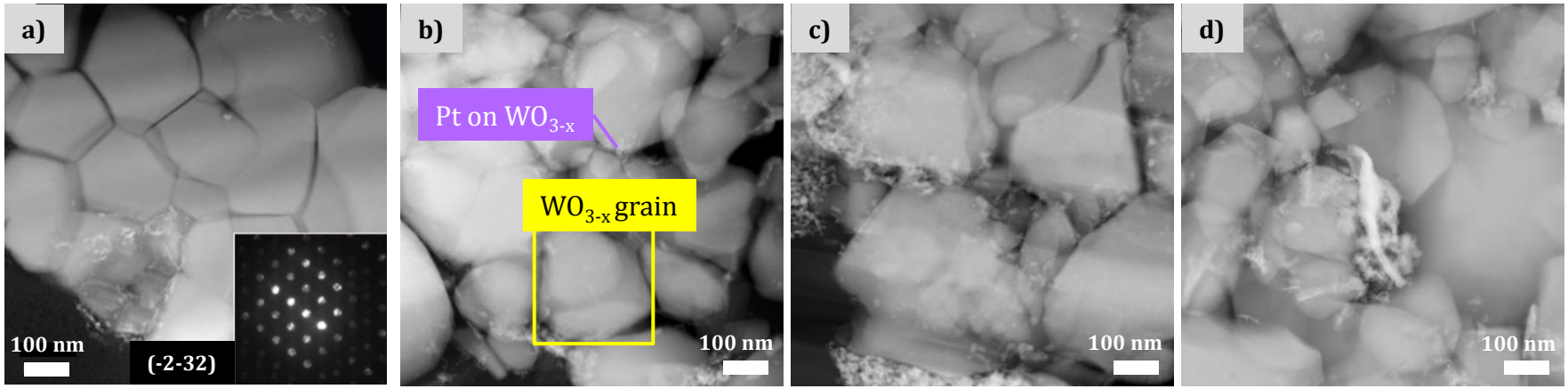
- Only present on WO_{3-x} grains
- Located at the interface between anode and membrane

Degradation behavior of HT-PEMFCs[1]



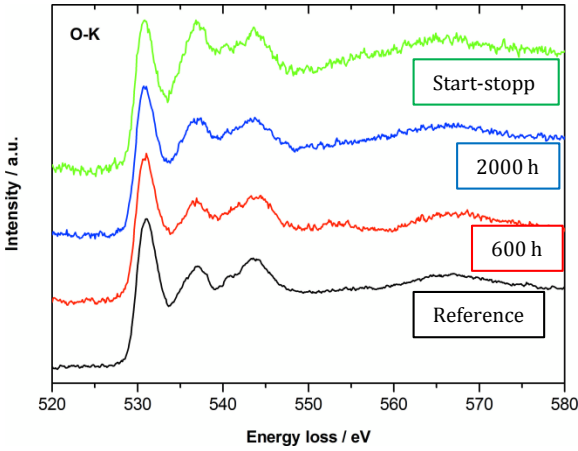
Comparison of WO_{3-x} based areas

Reference | **650 h** | **2000 h** | **Start-stop cycles**



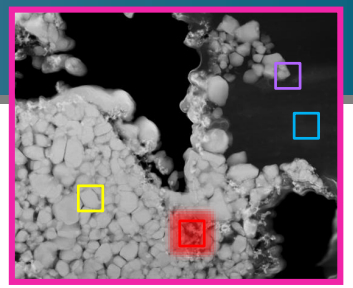
Facetted and rounded ⟷ Randomly arranged WO_{3-x} grains

- Platinum only between randomly arranged WO_{3-x} grains
- Single crystalline grains; sizes up to 1 µm
- **EELS**: no change of oxidation state in the bulk material



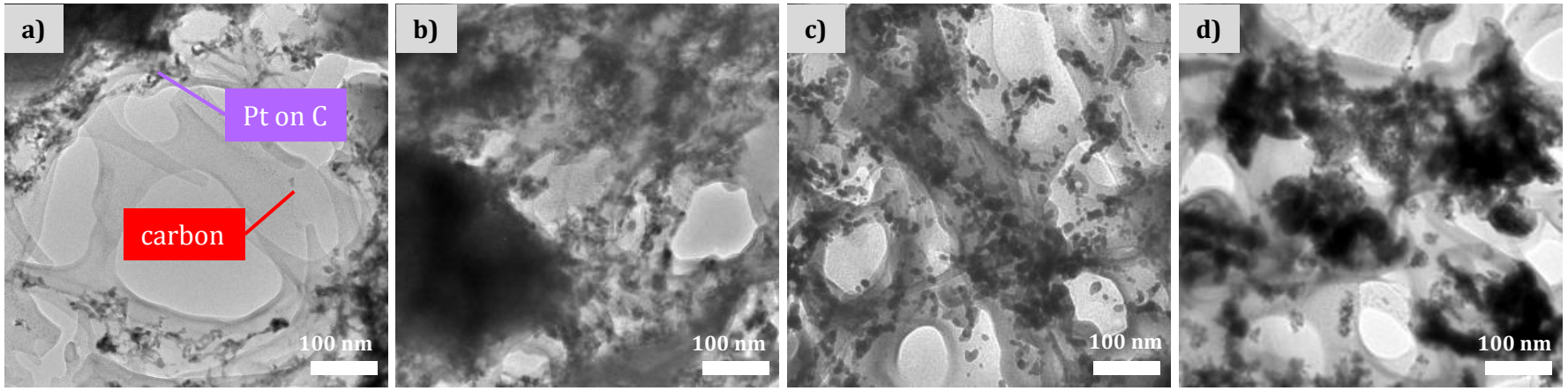
(1) Heinzl, C.; Hengge, K. A.; Perchthaler, M.; Hacker, V.; Scheu, C. *Journal of The Electrochemical Society* **2015**, *162*, F280.

DEGRADATION BEHAVIOR OF HTPEM FCs(1)



Comparison of CARBON based areas

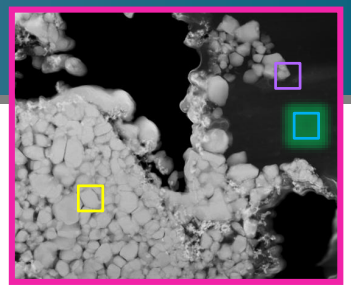
Reference | **600 h** | **2000 h** | **Start-stopp cycles**



- Pt: elongated crystals ⟷ Pt: individual, spherical shaped nanoparticles

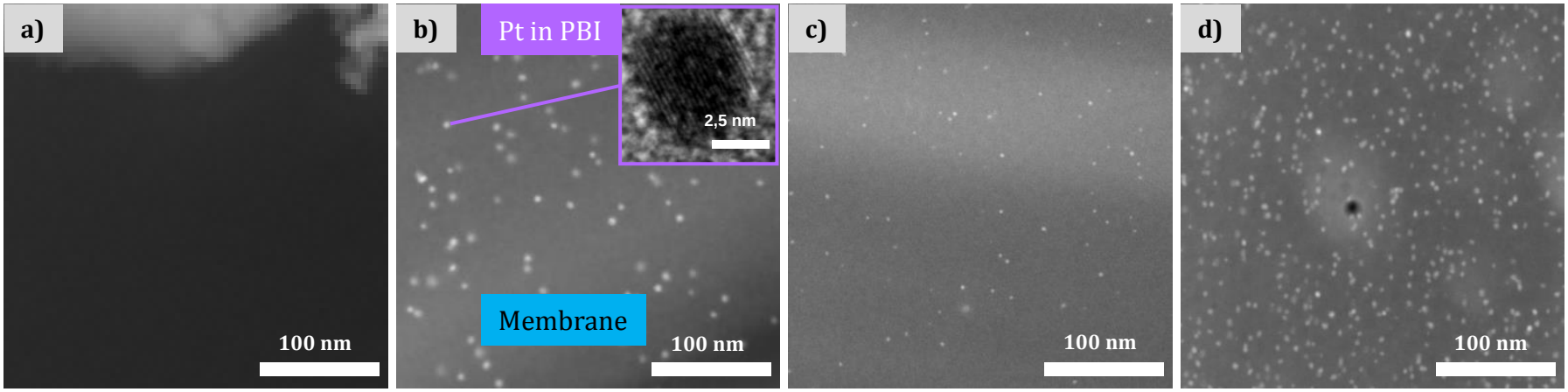
  7.3 ± 1.5 nm 10.0 ± 3.4 nm 12.5 ± 3.8 nm 7.1 ± 1.9 nm

- Pt near WO_{3-x} grains ⟷ Pt diffusion into carbon based areas



Comparison of MEMBRANE based areas

Reference | **650 h** | **2000 h** | **Start-stop cycles**

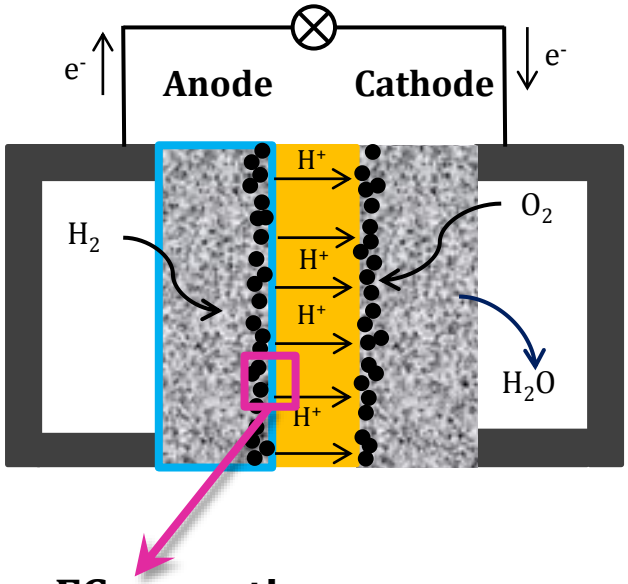


Pure PBI ⟷ Pt particles in the membrane material

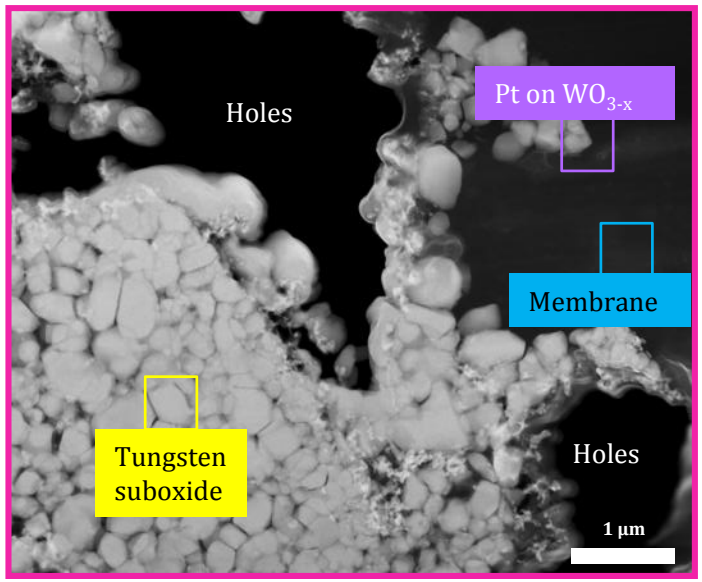
5.4 ± 0.7 nm | 2.9 ± 0.5 nm | 3.7 ± 0.5 nm

highest stress on Pt catalyst

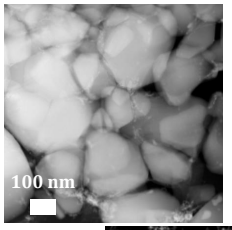
Summary – New Electrode Materials



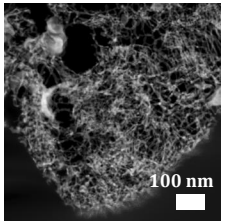
Degradation during FC operation:

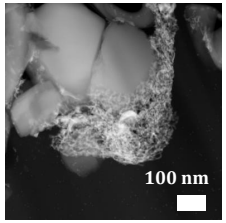


- No changes of bulk WO_{3-x}

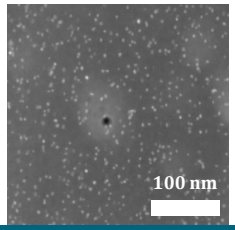


- Pt structures become dense



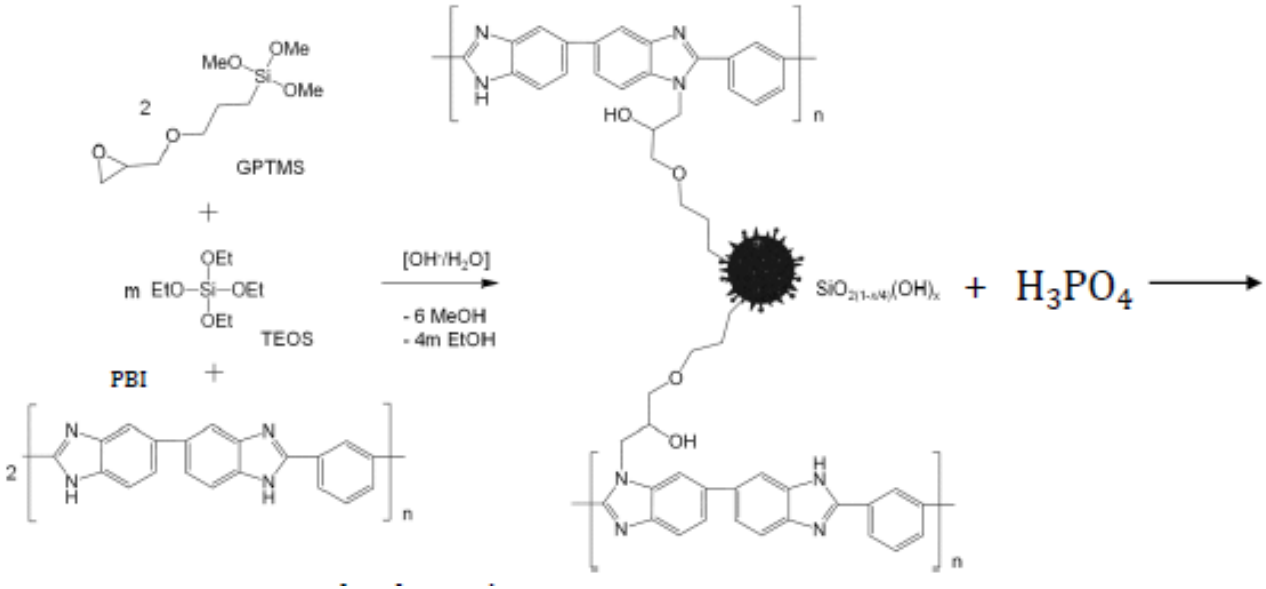


- Pt diffuses into membrane

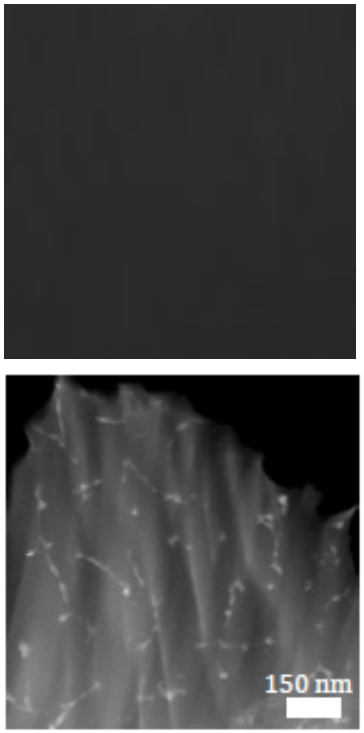


HT-PEMFC Membrane

- **Development of new membrane**
  - □ to improve proton conductivity → chemical modification, doping,…
  - □ to improve mechanical stability → addition of SiO_2 nanoparticles



Pure PBI based membrane

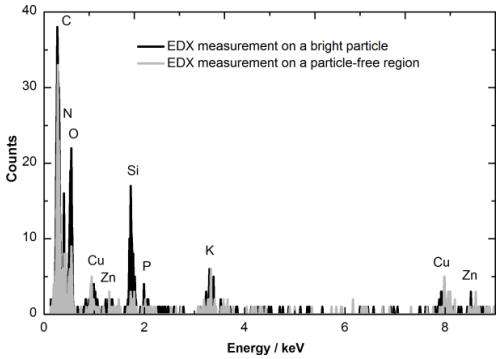


Modified PBI based membrane

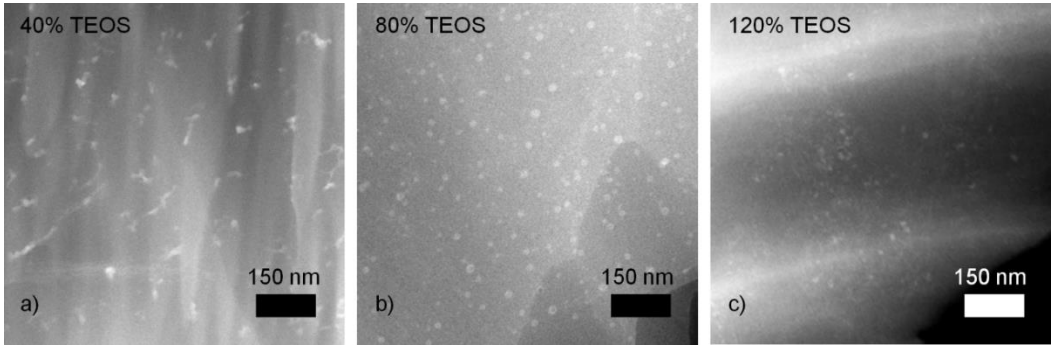
PBI: Polybenzimidazole
TEOS: tetraethoxysilane

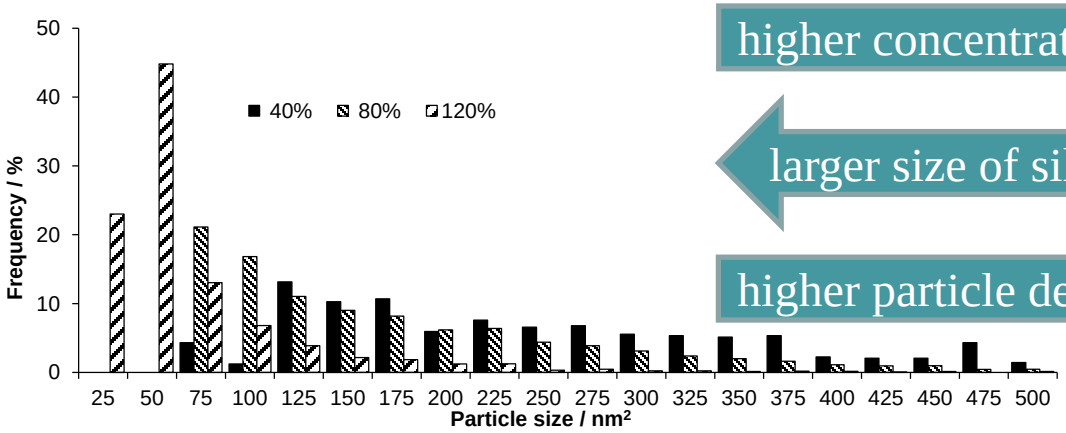
HT-PEMFC Membrane

- **Modified membranes obtained with different tetraethoxysilane (TEOS) contents**



EDS measurements on particles and particle free regions





higher concentration of tetraethoxysilane (TEOS)

larger size of silica nanoparticles

higher particle density in the membrane

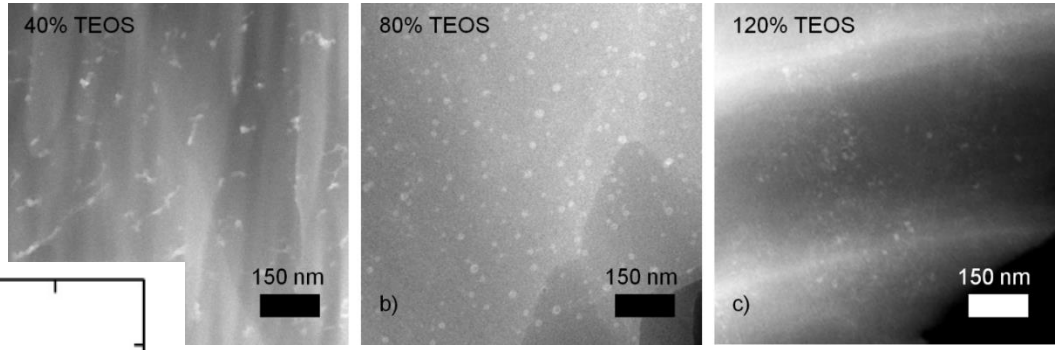
T. Ossiander*, C. Heinzl*, S. Gleich, F. Schönberger, P. Völk, M. Welsch, C. Scheu, J. Membr. Sci. **2014**, 454, 12-19

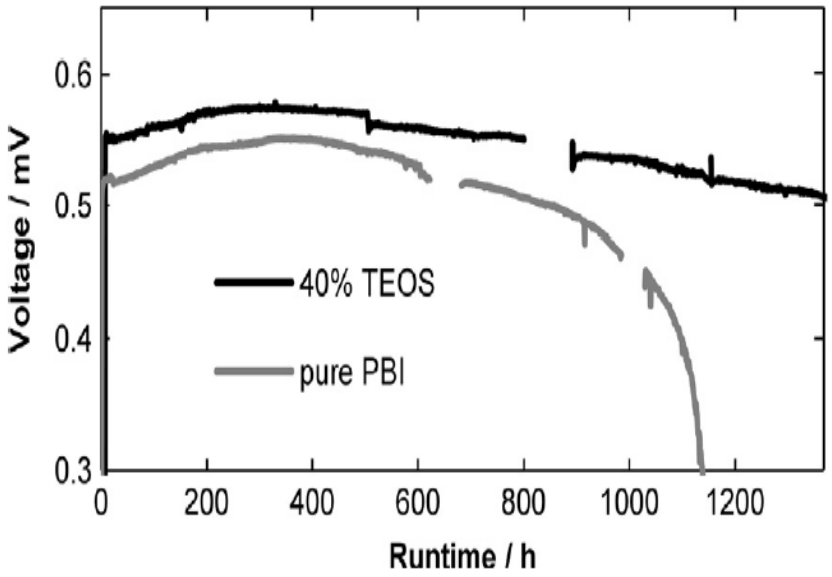
T. Ossiander, M. Perchthaler, C. Heinzl, C. Scheu. Journal of Power Sources **2014**, 267, 323 - 328

Performance

- **Modified membranes obtained with different tetraethoxysilane (TEOS) contents**

□ best performance obtained for membranes with 40% TEOS



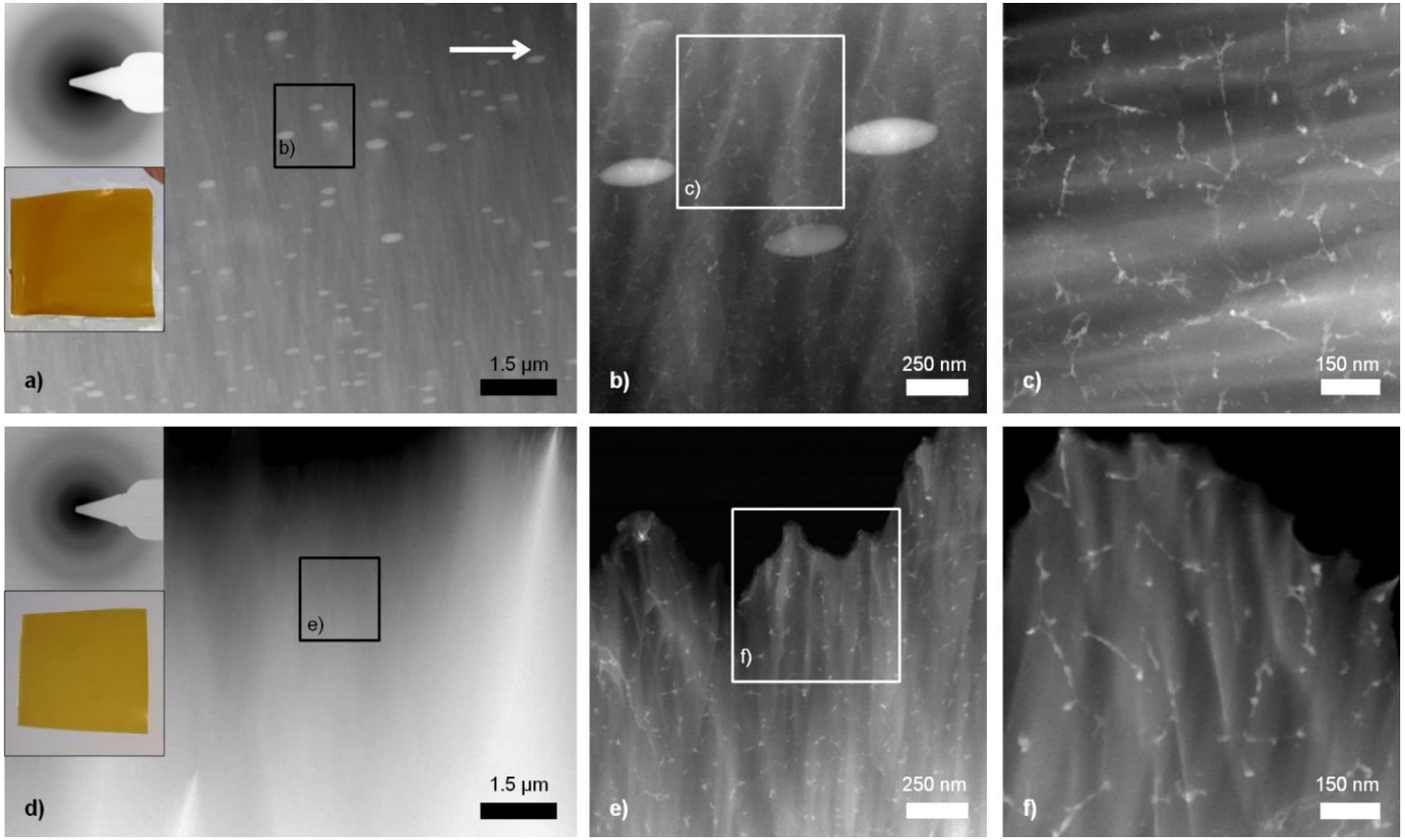


High performance in stack tests and low degration rate!
Good mechanical properties.

T. Ossiander, C. Heinzl*, S. Gleich, F. Schönberger, P. Völk, M. Welsch, C. Scheu, J. Membr. Sci.* ***2014****, 454, 12-19.*

HT-PEMFC Membrane

Membranes fabricated with 40% TEOS, one has a further thermal treatment (at 70 °C):



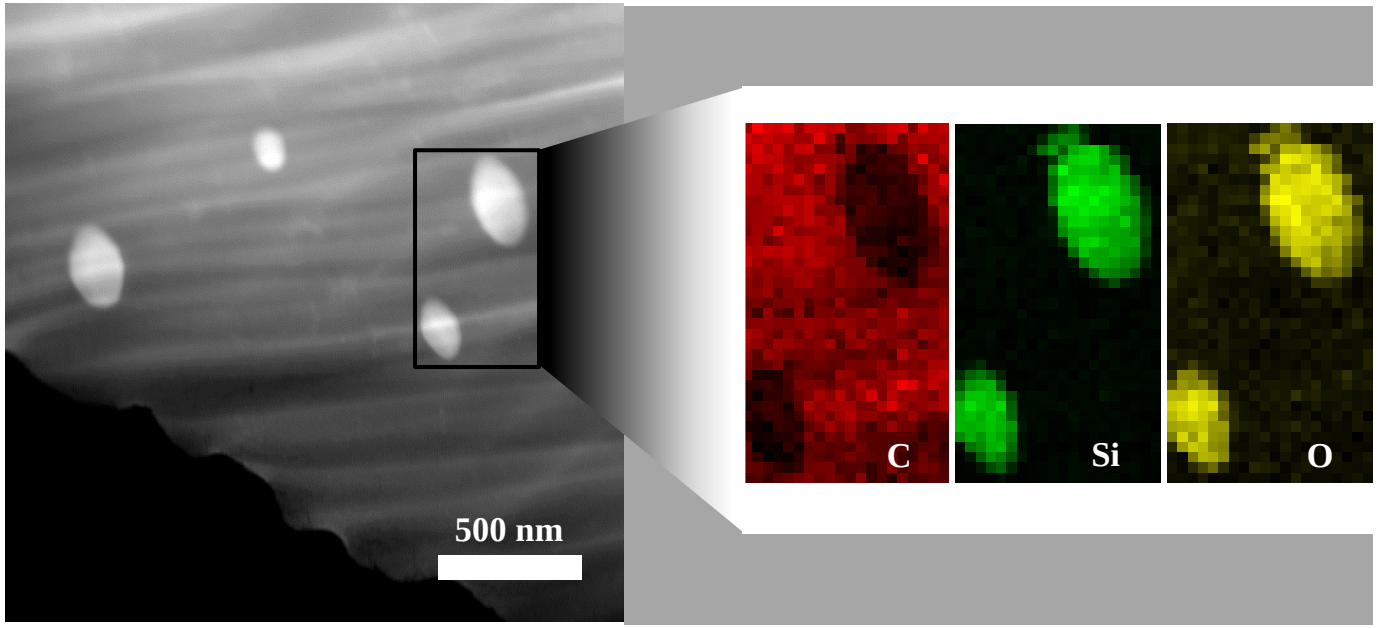
M1
70 °C

M2
RT

C. Heinzl, T. Ossiander, S. Gleich, and C. Scheu
Journal of Membrane Science, 478, 65–74 (2015)

HT-PEMFC Membrane

Further thermal treatment (at 70 °C) leads to additional large SiO_2 particles:



detected elements:

C, **N** (PBI)

Si, **O** (silica)

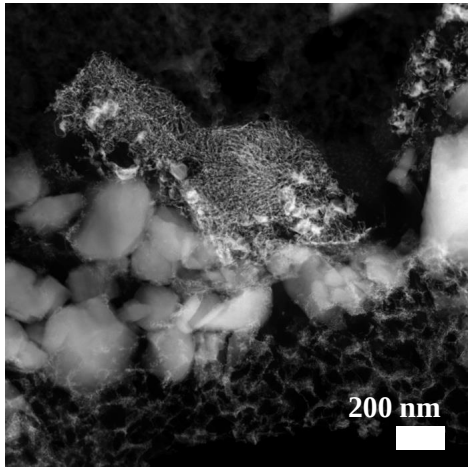
P, **K** (additives)

Good mechanical properties achieved by incorperating larger particles, but performance is lower

C. Heinzl, T. Ossiander, S. Gleich, and C. Scheu
Journal of Membrane Science, 478, 65–74 (2015)

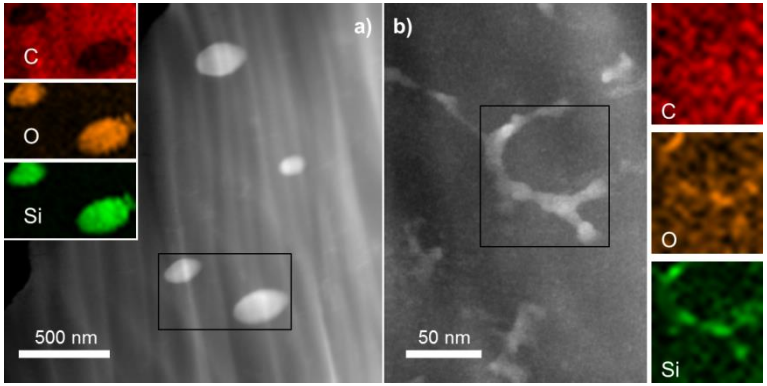
New Materials for HT-PEMFC

Tungsten oxide as promising electrode material:
- slightly reduced performance
- better degradation behavior
- different parts of anode show different degradation mechanisms



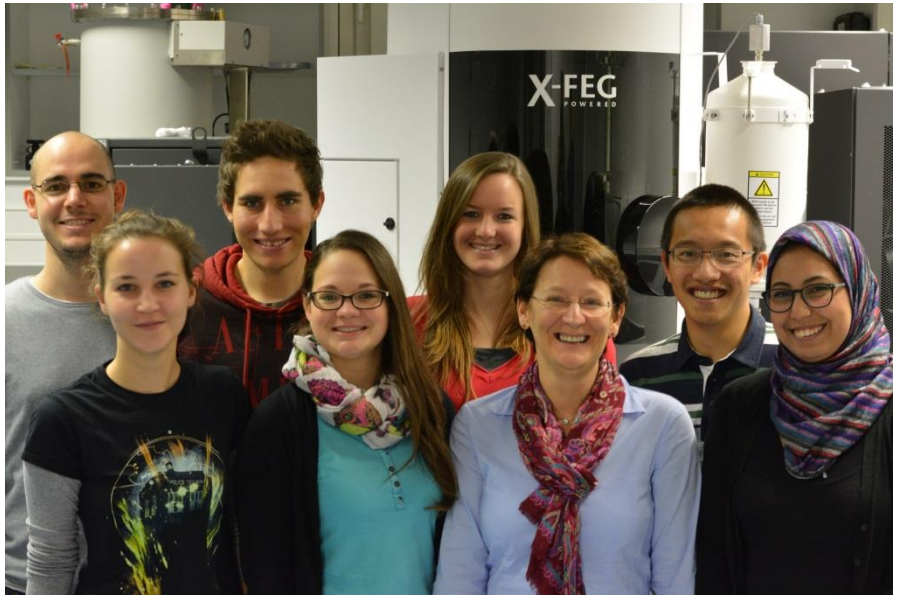
Incorporation of silica particles (40% TEOS) in PBI based membranes leads to increase in:
- mechanical stability (compared to PBI
- lifetime
- performance

Increase of temperature during synthesis:
- additional large silica particles
- increased mechanical stability
- slightly lower performance



Thanks to…

Katharina Hengge
Stephan Gleich
Christoph Heinzl
Markus Perchthaler
Marina Welsch
Tanja Ossiander
Viktor Hacker



Gefördert durch:
Bundesministerium für Wirtschaft und Technologie
aufgrund eines Beschlusses des Deutschen Bundestages

elcore

Thank you for your Attention!