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

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Acknowledgement

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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
**New Materials for HT-PEMFCs**

**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 microscopy (TEM) and related techniques
TEM AND RELATED TECHNIQUES

Chemical composition and distribution maps via EDX

Bonding states via EELS

HRTEM > 0.1 nm

HRSTEM > 0.1 nm

Diffraction

Monochromated electron gun

3-condenser system

C₃-probe corrector

Sample holder

1 of 4 SDD-EDX detectors

Annular STEM detector

High resolution, high speed energy filter

1 of 4 SDD-EDX detectors
NEW MATERIALS FOR HT-PEMFCs

\[ \text{Cathode} \quad \text{Pt catalyst NP on amorphous carbon} \]

\[ \text{Anode}^{5,6} \quad \text{Pt catalyst on tungsten suboxide} \]

\[ \text{Membrane}^{1-4} \quad \text{Polybenzimidazole (PBI)} \]

\[ \begin{align*}
\text{H}_2 & \quad \text{H}_2 \text{O} \\
\text{O}_2 & \quad \text{H}_2 \text{O} \\
\end{align*} \]

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 CO₂
  → possible replacement by WC or WO₃-x based systems (as anode material)

• Benefits of using WO₃-x as anode material
  □ WO₃ is an electrical insulator while WO₃-x is a semiconductor (band gap 2.6 – 2.8 eV)
  □ melting temperature > 1700 °C
  □ corrosion resistant
  □ CO-tolerant
  □ H+-conductivity

WO₃-x catalyst support

Tungsten materials as durable catalyst supports for fuel cell electrodes
M. Perchthaler, T. Ossiander, V. Juhart, J. Mitzel, C. Heinzl, C. Scheu, V. Hacker
Pt loaded Anode

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

4 MEAs – 3 different operation modes and times

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

Unintended shutdowns of stack

DEGRADATION BEHAVIOR OF HT-PEMFCs(1)

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

SEM Image:
- Anode
- Cathode
- Membrane
- W-L: Tungsten suboxide
- O-K
- Pt-L

STEM Image:
- Hole due to FIB cutting
- Pt on WO$_{3-x}$
- Membrane
- Hole due to FIB cutting

References:
Comparison of **PLATINUM** networks

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

Comparison of $\text{WO}_3-x$ based areas

Facetted and rounded $\leftrightarrow$ Randomly arranged $\text{WO}_3-x$ grains

- Platinum only between randomly arranged $\text{WO}_3-x$ grains
- Single crystalline grains; sizes up to 1 µm
- EELS: no change of oxidation state in the bulk material

Comparison of CARBON based areas

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

- **Pt: elongated crystals**
  - 7.3 ± 1.5 nm
- **Pt: individual, spherical shaped nanoparticles**
  - 10.0 ± 3.4 nm
- **Pt diffusion into carbon based areas**
  - 12.5 ± 3.8 nm
  - 7.1 ± 1.9 nm

- **Pt near WO$_{3-x}$ grains**

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Comparison of **MEMBRANE** based areas

<table>
<thead>
<tr>
<th>Reference</th>
<th>650 h</th>
<th>2000 h</th>
<th>Start-stop cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PBI</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>Pt in PBI</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
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<tr>
<td>Membrane</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td>5.4 ± 0.7 nm</td>
<td>2.9 ± 0.5 nm</td>
<td>3.7 ± 0.5 nm</td>
<td></td>
</tr>
</tbody>
</table>

**Highest stress on Pt catalyst**

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Degradation during FC operation:

- No changes of bulk $\text{WO}_{3-x}$
- Pt structures become dense
- Pt diffuses into membrane
• Development of new membrane
  □ to improve proton conductivity → chemical modification, doping,…
  □ to improve mechanical stability → addition of SiO₂ nanoparticles

Pure PBI based membrane

Modified PBI based membrane

PBI: Polybenzimidazole
TEOS: tetraethoxysilane
• 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

- Modified membranes obtained with different tetraethoxysilane (TEOS) contents
  - best performance obtained for membranes with 40% TEOS

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

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

C. Heinzl, T. Ossiander, S. Gleich, and C. Scheu
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 incorporating larger particles, but performance is lower

C. Heinzl, T. Ossiander, S. Gleich, and C. Scheu
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
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