Preparation and characterisation of carbon nanotube supported Pt catalysts for the application in hydrogen fuel cells

Synthesis and characterisation of carbon supported platinum and platinum alloy catalysts

Norwegian University of Science and Technology
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1. Hydrogen Institute of Applied Technologies gGmbH at a glance

2. Preparation of Pt catalysts based on MWCNT

3. Preparation of Catalyst Coated Membranes (CCMs), screen printing

4. Test bench, test cell, test equipment

5. Benchmark with Johnson Matthey HiSPEC catalysts / LT-PEFC

6. Benchmark with Johnson Matthey HiSPEC catalysts / HT-PEFC

7. Results, HIAT catalysts

8. Summary and Conclusions

9. Outlook
1. The Hydrogen Institute of Applied Technologies gGmbH (short HIAT), was founded in 2002 as a non-profit research institute with the focus on hydrogen and fuel cell technology.

2. Development of electrocatalysts for PEFC and DMFC

3. Electrode development for PEM fuel cells (LT and HT) und PEM water electrolysis

4. Polymer membrane development for DMFC

5. Process engineering for pilot production and quality management of CCMs (produced by screen printing) and membranes

6. Developing of fuel cell-based system solutions for specific power ranges for portable and quasi-stationary applications
Hydrogen Institute of Applied Technologies gGmbH

at a glance

HIAT

Polymer Electrolyte

MEMs / CCMs:
Screen Printing
Ink Jet

Membranes Coating

PEM
Fuel Cells
(PEFC, HT-PEFC, DMFC)

Catalysis

Process Engineering

Pt-Reduction Deposition
What kind of CNT we can use?

1. MWCNT are the cheapest choice

2. Physical, chemical properties and the kind of fuel cell decide which CNT are useful

3. We decided to test different kind of MWCNT and found out:

<table>
<thead>
<tr>
<th>Property</th>
<th>MWCNT(1)</th>
<th>MWCNT(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density / g/cm³</td>
<td>0.14-0.16</td>
<td>2</td>
</tr>
<tr>
<td>Outer diameter / nm</td>
<td>5-20</td>
<td>60 – 150</td>
</tr>
<tr>
<td>Length / µm</td>
<td>10</td>
<td>30 – 100</td>
</tr>
<tr>
<td>BET surface N₂ / m²/g</td>
<td>260</td>
<td>84</td>
</tr>
<tr>
<td>Tensile strength / GPa</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Electrical conductivity / S/cm</td>
<td>10000</td>
<td>18000</td>
</tr>
<tr>
<td>Heat conductivity / W/m³*K</td>
<td>2000</td>
<td>1950</td>
</tr>
</tbody>
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PEFC  DMFC
Surface activation or functionalization of the MWCNT (surface treatment)

1. Electrochemical activation is difficult to control
2. Plasma activation leads only to a middle surface activation
3. Chemical activation in oxidising agents leads to a high surface activation
Plasma activation at room temperature

**Shake reactor diagram:**
- Perforated metal plate
- Adjustment network
- Copper strip
- Glass plate
- Sample table
- Reaction zone
- Oscillation device

**Fluidised bed reactor:**
- Precipitation zone
- Filter
- Plasma source
- Fluidised bed
- Storage container
- Charging screw
- Vacuum pump
- Circulation pump
- Gas supply

**Table:**

<table>
<thead>
<tr>
<th>P_{\text{Plasma}}</th>
<th>O_2/Ar</th>
<th>time</th>
</tr>
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<tbody>
<tr>
<td>80 W</td>
<td>0.1 mbar</td>
<td>5 min</td>
</tr>
<tr>
<td>150 W</td>
<td>1.0 mbar</td>
<td>5 min</td>
</tr>
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</table>

**Microwave plasma at 27.12 MHz**
Chemical activation

Purification, if the purity is less than 95%:
boiling under reflux in HNO₃ + H₂SO₄ for approx. 2 h

Chemical activation:
boiling under reflux in xM HNO₃ (8 h)
x=2-10 mol/L

Washing and filtration under pressure:
with destillated water

Drying under reduced pressure:
for 4 hours at 80°C

activated carbon in water

none activated carbon in water
Chemical precipitation of Pt

Precursor $\text{H}_2\text{PtCl}_6(6\text{H}_2\text{O})$ solved in a mixture of ethylene glycol and hydrazine plus phase mediator: boiling under reflux for 15 – 60 min

Washing and filtration under pressure: with destillated water until free from chloride

Drying under reduced pressure: for 8 hours at 30°C

Catalyst powder is ready for use

Cubo-octahedral Pt particles with (111) and (100) facets
Johnson Matthey HiSPEC 13100
73 wt.% Pt on acetylene black, 4nm

HIAT Pt-MWCNT(1)
40 wt.% Pt, 4nm

HIAT Pt-MWCNT(1)
60 wt.% Pt, 4nm
Screen printing starts with development of the catalyst paste

The catalyst paste must have the right composition, viscosity and rheology

Influencing factors are: 1. catalyst  
2. ionomer content  
3. solvents  
4. membrane

CCMs are produced by directly printing on the membrane, means gap-less contact between the electrodes (<10µm) and membrane.

Advantages:  
1. easy scale up electrode area of screen printing  
2. high and fast reproducibility  
3. homogeneous electrode densities  
4. precise positioning of multilayered electrodes  
5. uniform thicknesses of single- and multilayered electrodes
Preparation of Catalyst Coated Membranes (CCMs), screen printing
Test bench, test cell, test equipment
Test cell with Dynamic Hydrogen Reference Electrode / DHRE (baltic FuelCells GmbH)

quickCONNECT fixture / FC_{25/100}:

Principle of the DHRE:
Test cell with moving piston
(baltic FuelCells GmbH)

quickCONNECT fixture / FC\textsubscript{25/100}:
Benchmark with Johnson Matthey
HiSPEC catalysts / LT-PEFC

Durability HiSPEC 13000 at 0.5A/cm²: LT-PEFC (65°C)

- Ambient $p$, $\lambda_{\text{air}}$: 3.5 (60% r.h.), $\lambda_{\text{H}_2}$: 1.5 (60% r.h.)
- Contact pressure: 1N/mm², GDLs: Freudenberg H2314I3C1,
  Membrane: Fumapem F950
- Cathode: 0.5mg Pt/cm², anode: 0.2mg Pt/cm²

Degradation:
- 53µV/h
- 47µV/h

Voltage / V

Time / h
Benchmark with Johnson Matthey
HiSPEC catalysts / LT-PEFC

UI-plots, BOL vs. EOL, HiSPEC 13000, LT-PEFC (65°C)

Ambient $p_A$, $\lambda_{air}$: 3.5 (60% r.h.), $\lambda_{H_2}$: 1.5 (60% r.h.)

Contact pressure: 1N/mm$^2$, GDLs: Freudenberg H2314I3C1
Membrane: Fumapem F950
Cathode: 0.5mg Pt/cm$^2$, anode: 0.2mg Pt/cm$^2$

scan rate: 0.5A/5s from OCV to short circuit

Voltage BOL after 45h: 660mV
Power density BOL after 45h: 0.52W/cm$^2$
Voltage EOL after 1509h: 624mV
Power density EOL after 1509h: 0.49W/cm$^2$
Benchmark with Johnson Matthey
HiSPEC catalysts / HT-PEFC

Durability at 0.4 A/cm²: HT-PEFC (160°C)
HIAT GDEs
H₃PO₄ doped PBI membrane
Ambient pressure, dry air: λ=2.5, dry hydrogen: λ=1.2
Anode: 0.5mg Pt/cm², cathode: 1mg Pt/cm²

Degradation:
5µV/h
(289.95h - 556.90h)
UI-plots, BOL: LT-PEFC (65°C)

Ambient $p$, $\lambda_{\text{air}}$: 3.5 (60% r.h.), $\lambda_{\text{H}_2}$: 1.5 (60% r.h.)

Contact pressure: 1N/mm², GDLs: Freudenberg H2314/3C1
Membrane: Fumapem F950
Cathode: 0.5mgPt/cm², anode: 0.2mgPt/cm²

at 0.5A/cm²:
- 675mV
- 660mV
- 651mV

Scan rate: 0.5A/5s from OCV to short circuit

Voltage, Anode: CNT Pt60%, Cathode: HiSPEC 13100
Voltage, Anode: HiSPEC 13100, Cathode: CNT Pt60%
Voltage, Anode: HiSPEC 13100, Cathode: HiSPEC 13100
Power density, Anode: CNT Pt60%, Cathode: HiSPEC 13100
Power density, Anode: HiSPEC 13100, Cathode: CNT Pt60%
Power density, Anode: HiSPEC 13100, Cathode: HiSPEC 13100
Durability at 0.5A/cm$^2$: LT-PEFC (65°C)

Ambient $p$, $\lambda_{\text{air}}$: 3.5 (60% r.h.), $\lambda_{\text{H}_2}$: 1.5 (60% r.h.)

Contact pressure: 1N/mm$^2$, GDLs: Freudenberg H2314I3C1, Membrane: Fumapem F950
Cathode: 0.5mg Pt/cm$^2$, anode: 0.2mg Pt/cm$^2$

- Cathode: HiSPEC13100, Anode: HiSPEC13100 / Degradation: 53µV/h
- Cathode: CNT Pt60%, Anode: HiSPEC13100 / Degradation: 89µV/h
- Cathode: HiSPEC13100, Anode: CNT Pt60% / Degradation: 102µV/h
UI-plots, cathode with oxygen: LT-PEFC (80°C)

\[ \lambda_{O_2} : 1.5 \text{ (60\%r.h.)}, \ \lambda_{H_2} : 1.2 \text{ (60\%r.h.)} \]

Contact pressure: 1N/mm², GDLs: Freudenberg H2314I3C1
Membrane: Fumapem F950
Cathode: 0.5mgPt/cm² (HiSPECS13100), anode: 0.2mgPt/cm² (CNT-Pt)

Voltage: ambient media pressure
Voltage: 3bara
Voltage: 5bara
Power density: ambient media pressure
Power density: 3bara
Power density: 5bara

- Voltage: 684mV, 0.5A/cm²
- Voltage: 771mV
- Voltage: 799mV
- Power density: 0.83W/cm²
- Power density: 1.21W/cm²
- Power density: 1.52W/cm²
Results, HIAT catalysts

UI-plots, HiSPEC13000 vs. CNT-Pt: LT-PEFC (65°C)
Ambient \( p \), \( \lambda_{\text{air}} \): 3.5 (60% r.h.), \( \lambda_{\text{H}_2} \): 1.5 (60% r.h.)
Contact pressure: 1N/mm\(^2\), GDLs: Freudenberg H2314\#3C1
Membrane: Fumapem F950, Quick Connect Fixure 25/100
Cathode: 0.5mgPt/cm\(^2\), anode: 0.2mgPt/cm\(^2\)

650mV at 0.5A/cm\(^2\)

Use of the DHRE:

Equivalent circuit for cathode and anode:

- Voltage CNT-Pt
- Voltage HiSPEC 13100

scan rate: 0.5A/5s from OCV to short circuit

Current density / Acm\(^{-2}\)

Voltage / V

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Cathode impedance at 0.6A/cm² / Nyquist plots / 5kHz-100mHz, ZView 2.1b

**HiSPEC 13100**

\[
\begin{align*}
R_{el} & = 0.15 \text{ Ohmcm}^2 \\
R_{ct} & = 0.27 \text{ Ohmcm}^2 \\
W_{N}(R) & = 0.21 \text{ Ohmcm}^2 \\
W_{N}(t) & = 12.9 \text{ ms}
\end{align*}
\]

**MWCNT(1)-Pt**

\[
\begin{align*}
R_{el} & = 0.16 \text{ Ohmcm}^2 \\
R_{ct} & = 0.18 \text{ Ohmcm}^2 \\
W_{N}(R) & = 0.14 \text{ Ohmcm}^2 \\
W_{N}(t) & = 15.0 \text{ ms}
\end{align*}
\]
Results, HIAT catalysts

Anode impedance at 0.6A/cm² / Nyquist plots / 5kHz-100mHz, ZView 2.1b

HiSPEC 13100

= 0.13 Ohmcm²
\( R_{ct} \) = 0.04 Ohmcm²
\( W_N(R) \) = 0.03 Ohmcm²
\( W_N(t) \) = 0.83 s

MWCNT(1)-Pt

= 0.09 Ohmcm²
\( R_{el} \) = 0.06 Ohmcm²
\( W_N(R) \) = 0.02 Ohmcm²
\( W_N(t) \) = 0.12 s
Results, HIAT catalysts

Electrolyte resistance ($R_{el}$) from impedance at different current densities

**Cathode:**

- **HiSPEC 13100**
- **CNT Pt**
Electrolyte resistance ($R_{el}$) from impedance at different current densities

**Anode:**

- **HiSPEC 13100**
  - Graph showing a decrease in electrolyte resistance with increasing current density.

- **CNT Pt**
  - Graph showing a decrease in electrolyte resistance with increasing current density.
1. A degradation rate of approx. 50µV/h was found for a LT-PEFC with commercial catalysts

2. A very low degradation rate of only 5µV/h was found for a HT-PEFC with commercial catalysts

**Liquid water is one main reason for degradation (corrosion) on the cathode side**

3. The MWCNT-catalysts showed excellent starting performances compared to commercial catalysts

4. Unfortunately, the degradation rates of MWCNT-catalysts were high (90µV/h)

5. Measurements with O₂ instead of air showed that an anode made of MWCNT-catalysts generates high power densities up to 1.5W/cm²

6. The electrolyte resistance of a MWCNT-catalyst CCM is lower compared to HiSPEC 13000

**The MWCNT-catalyst prevents the anode to dry out**

**Accumulation of water on the cathode seems to be a problem (corrosion, lower performance to short circuit)**
We compared a commercial catalyst (HiSPEC 13100) with 73wt. % Pt loading on AC01 to a MWCNT-catalyst with only 60wt. % Pt loading.

To prepare thinner cathodes higher loadings on the MWCNT are necessary.

The degradation rates of the MWCNT-catalysts must be reduced.

The different behaviour concerning water needs further investigations.
Thank you for your attention!