Investigation of fuel cell components and degradation by AFM

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Application of AFM for Fuel Cells

Investigation with AFM techniques of

Surface morphology and surface properties:

- adhesion force, dissipation energy (deformation), peak force,
- elasticity, electronic and ionic conductivity

for characterization, and analysis of ageing processes on

- Electrolyte membranes
- Electrodes
- Gas diffusion layers /microporous layers
- Bipolar plates
AFM Technique

Invented for topography measurement – sensing of tip-sample forces
Nowadays analytic tool for a variety of surface and sub surface physical and chemical properties

Vibration of tip at resonance frequency

Damping of vibration due to energy loss – phase shift and decrease of amplitude

Detection of different materials by their phase shift

Energy loss due to total force acting on tip i.e. no discern of adhesion, deformation, or friction

Evaluation of force-distance curve \( F(x) \)
Analysis of $F(x)$ curve

- Peak Force
- Adhesion Force
- Stiffness: $\frac{\Delta F}{\Delta x}$
- Dissipation Energy
Reconstruction of F(x) curve

Spectrum of excited vibrations of cantilever

Adding up all higher harmonic waves

Force vs. bending

HarmoniX mode (Veeco Instr.): reconstruction of force-distance-distance-curve by Fourier-synthesis of higher harmonic vibrations of cantilever at every image point.

Evaluation of adhesion force, phase shift, stiffness, maximal force, and dissipation energy simultaneous to topography for the whole image.
Example: MPL Surface Properties

Microporous layer (MPL) surface of gas diffusion layer (GDL):

Quantitative evaluation at every image point of:

- Topography
- Phase shift
- Adhesion
- Dissipation energy
- Stiffness (elasticity)
- Peak force
Surface Properties MPL

Statistical evaluation of mean properties of all image points

Adhesion force

Dissipation energy

Measurement of reference samples and MPL before and after fuel cell operation

evaluation of peaks values for further analysis
Microporous Layer
Ageing of GDL/MPLs

Comparison of surface properties of microporous layers (MPL)

• Teflon sheet (and carbon powder) as reference

• GDL/MPL before fuel cell operation and after operation at cathode and anode

  GDL 1: Failure after 12 h of operation
  GDL 2: - 650 h of operation
  GDL 3: - Artificial aging with H₂O₂
MPL - Dissipation after 12 h of Operation

AFM measurement of energy dissipation on MPL at ambient (~dry) conditions

before operation          after operation

Anode                       Cathode

Z-Range: 768 meV            Z-Range: 768 meV

1 μm  200nm

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Comparison of GDL 1 (650 h) and GDL 2 (12 h) - Ambient Humidity

**Adhesion**
- Overall decrease, larger at cathode
- Larger decrease of GDL 2 (12 h) compared to GDL 1 (650 h): hole in MEA leads to very large degradation
- GDL 3: artificial ageing with H₂O₂ for 1 h
- Adhesion of new solid PTFE highest

**Dissipation**
- Overall decrease, larger at cathode
- Dissipation of unused comparable to PTFE

**Adhesion at wet surface compared to ambient condition**
- Small increase at anode - large increase at cathode
- More water adsorption at cathode

More loss of PTFE at cathode than at anode
Segmented Cell-Analyzed Segments

H₂ In

H₂ out

1  2  3  4
5  6  7  8
9 10 11 12
13 14 15 16
Analysis

**Analysis of segments with**
- Infrared spectroscopy (A. Haug/DLR)
- Adhesion forces from AFM
- Energy dissipation from AFM

**Information depth of**
- IR - about 100 nm
- AFM adhesion force - very surface
- AFM dissipation energy – about 10 nm
- V(i) curve – all components of segment

Separation of components by careful manual disassembly
Comparison of IR & AFM Analysis: Electrodes

Content of PTFE from quantitative analysis of C-F vibrational intensities
Voltage loss and IR in parallel – almost similar to AFM adhesion/dissipation – different information depth

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Electrodes

<table>
<thead>
<tr>
<th>Topography</th>
<th>Energy dissipation</th>
<th>Stiffness</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>From statistical evaluation of stiffness images</td>
</tr>
<tr>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>Pt/C 40 wt %</td>
</tr>
<tr>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>no Nafion &amp; Teflon</td>
</tr>
<tr>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>surface evaluation</td>
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<tr>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td>41% Pt in 59 % carbon</td>
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<tr>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td>70 % (Pt/C 40 wt %)</td>
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<tr>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td>30 % Teflon</td>
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<tr>
<td><img src="image15.png" alt="Image" /></td>
<td><img src="image16.png" alt="Image" /></td>
<td>no Nafion</td>
</tr>
<tr>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
<td>surface evaluation</td>
</tr>
<tr>
<td><img src="image19.png" alt="Image" /></td>
<td><img src="image20.png" alt="Image" /></td>
<td>80 % Pt/C 20 % PTFE</td>
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<tr>
<td><img src="image21.png" alt="Image" /></td>
<td><img src="image22.png" alt="Image" /></td>
<td>70 % (Pt/C 60 %)</td>
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<tr>
<td><img src="image23.png" alt="Image" /></td>
<td><img src="image24.png" alt="Image" /></td>
<td>30 % Nafion</td>
</tr>
<tr>
<td><img src="image25.png" alt="Image" /></td>
<td><img src="image26.png" alt="Image" /></td>
<td>no Teflon</td>
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<td><img src="image27.png" alt="Image" /></td>
<td><img src="image28.png" alt="Image" /></td>
<td>surface evaluation</td>
</tr>
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<td><img src="image29.png" alt="Image" /></td>
<td><img src="image30.png" alt="Image" /></td>
<td>71 % Pt/C 29 % Nafion</td>
</tr>
</tbody>
</table>
Conductivity

Electronic conductivity

Ionic conductivity
Low Conductive State of Membrane

after preparation - lamellar conductive structure

Nr. 4 23.6.09
scan rate 1.49 Hz
I = 10 pA
U= 1.82 V
rh 61 %

Low conductivity state with currents about 10 pA

after electrode fabrication by dry spraying of catalyst and subsequent hot pressing quite smooth conductivity

Nr. 5 29.6.09
scan rate 1.49 Hz
I = 10 pA
U= 1.85 V
rh 69 %

after 4 h current flow without liquid water - still large areas with homogeneous conductivity

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Ionic Conductivity

Current distribution on Nafion 112 membrane at RT
AFM image measured at 70 % rh

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(a) formation of inverted micelles in a continuous semi-crystalline PTFE-phase, water filled, mean diameter 2.4 nm
(b) micelles are clustering together
(c) side view on water filled nanochannels

Calculated @ 20 vol % water (95 % rh) from SAXS data
Conductive Nanostructure

Bright spots are highly conductive
• attributed to single inverted micelles of about 2 nm
• inverted micelles cluster together
• surrounded by non-conductive regions, probable PTFE–backbone

Conductive clusters with 10 - 50 nm

Comparison of measured conductive nanostructure (left side) with model predictions of clustered inverted micelles (right side).

Current distribution on Nafion 112 membrane measured at 68 % rh, V =1.4 V
Nafion NR 212

Distribution of conductive channels on Nafion 112 (small scattered channels) different from recast Nafion NR212 (large conductive assemblies).

Ion Power
- Temperature 30 °C
- RH 75 %
- U=1.2 V
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Nafion NR 212

Surface properties measured by HarmoniX-Mode

Identification of ionic and PTFE rich structures

Phase shift

Dissipation

Adhesion

PeakForce

DMt/ Elasticity

Nafion NR 212 from IonPower
Bipolar Plates
Bipolar Plate

Topography

The standard deviation of the mean roughness value is given by:

$$R_q = \sqrt{\frac{\sum_{i=1}^{N} (Z_i - Z_{ave})^2}{N}}$$
Summary

Analysis of ageing processes at GDL/MPL by AFM & Infrared

– measurement of surface properties like adhesion and energy dissipation by AFM

– Change of surface properties (relative to reference samples) as a measure for PTFE losses and ageing

– Comparable results from IR and AFM analysis

– PTFE reduction parallel to voltage loss during operation

– AFM suitable for investigation of MPL, electrodes, membranes, and bipolar plates
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Segmented Cell

\[
\begin{align*}
T_{\text{Zelle}} &= 80 \, ^\circ\text{C} \\
T_{\text{H}_2 \text{ Befeuchter}} &= 70 \, ^\circ\text{C} \\
T_{\text{Luft Befeuchter}} &= 70 \, ^\circ\text{C} \\
\rho_{\text{H}_2} &= 500 \, \text{mbar Überdruck} \\
\rho_{\text{Luft}} &= 500 \, \text{mbar Überdruck} \\
I &= 0.6 \, \text{A/Segm.} \sim 384 \, \text{mA/cm}^2 \\
V_{\text{H}_2} &= 157.5 \, \text{ml/min} \\
V_{\text{Luft}} &= 525 \, \text{ml/min} \\
\text{CCM:} &= \text{ION-Power} \\
\text{Anode:} &= \text{ETEK Single Sided} \\
\text{Kathode:} &= \text{SGL 25 BC}
\end{align*}
\]
Electrodes

Segment 16: **small change** in performance and surface properties

Segment 13: **large change** in performance and surface properties