Spectroscopic investigation of modified and aged GDLs

M. Schulze[1], I. Biswas[1], P. Gazdzicki[1], M. Tomaš[1,2]

[1]Deutsches Zentrum für Luft- und Raumfahrt, Stuttgart, Germany
[2]Západočeská Univerzita v Plzni, Plzeň, Czech Republic

DLR

Outline

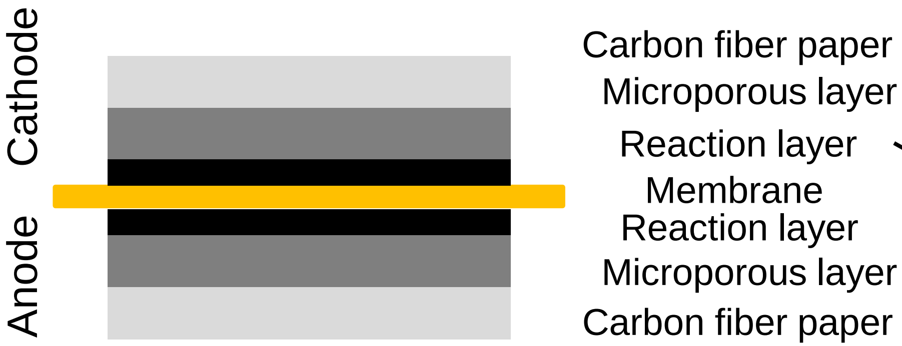
Analytic tools

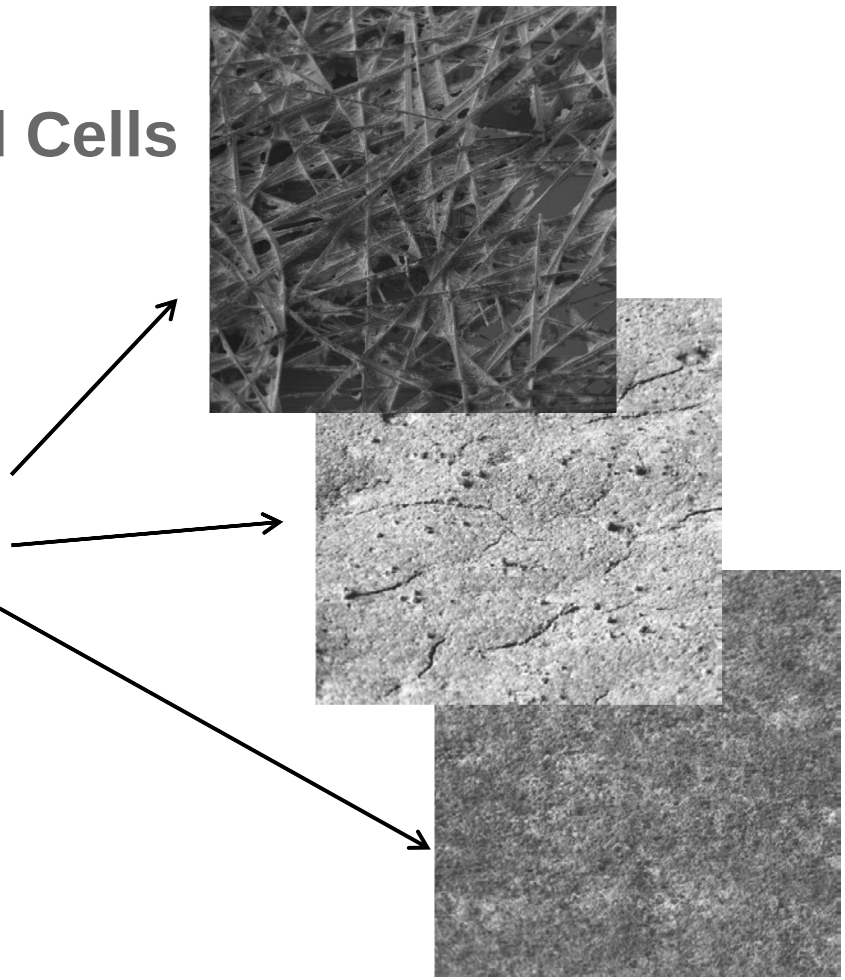
Heterogenous Modification Methods

- X-ray
- Ion beam modification
- Chemical modification
- Laser
- Mechanical stressing/damaging

Feasibility

Polymer Electrolyte Fuel Cells

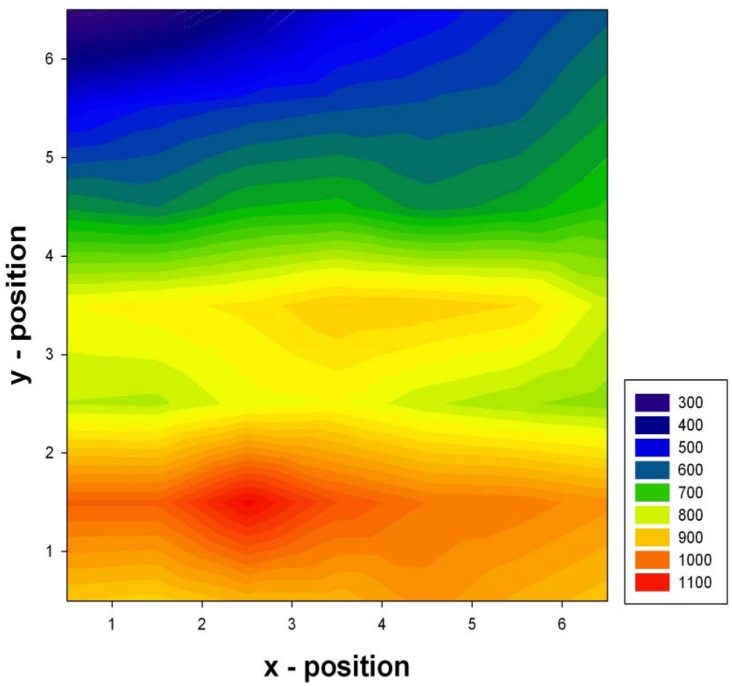


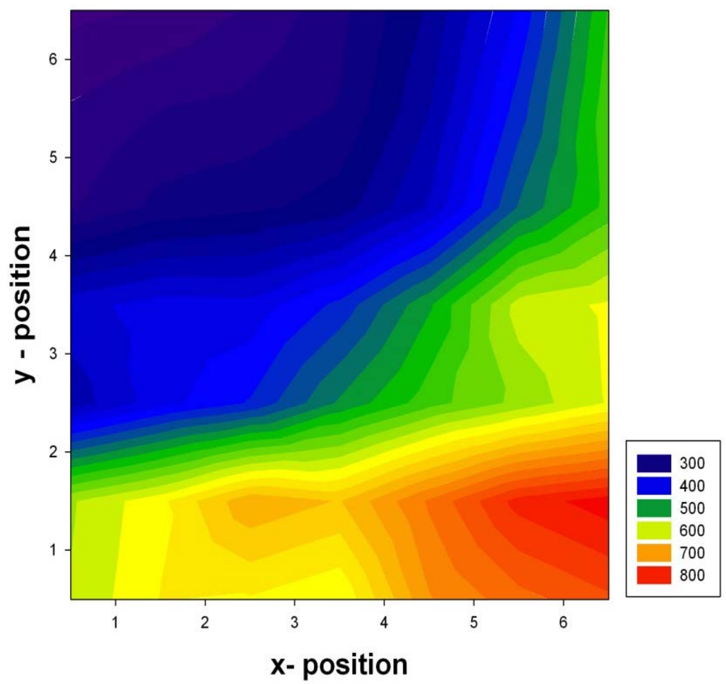


SEM: 3x3 mm

Change of current density due to degradation of the MEA

after 400 h @ 600 mV





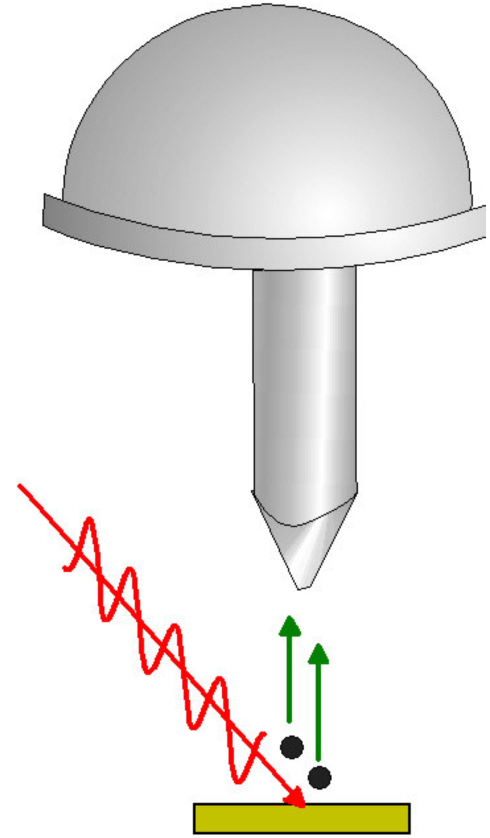
Analytical Methods

Ex-situ diagnostic tools

- X-ray photoelectron spectroscopy (XPS), Scanning Auger electron spectro(mirco-)scopy (SAM), scanninng electron microscopy (SEM)
- XPS, ultra-violet photoelectronspectroscopy (UPS), thermo desorptions spectroscopy (TPD)
- SEM with energy dispersive X-ray spectroscopy (EDX)
- Fourier-transformed infra-red spectrocoy (FTIR) with ATR, transmission and reflection
- Raman spectroscopy
- Atomic force microscopy (AFM)
- X-ray diffraction (XRD)

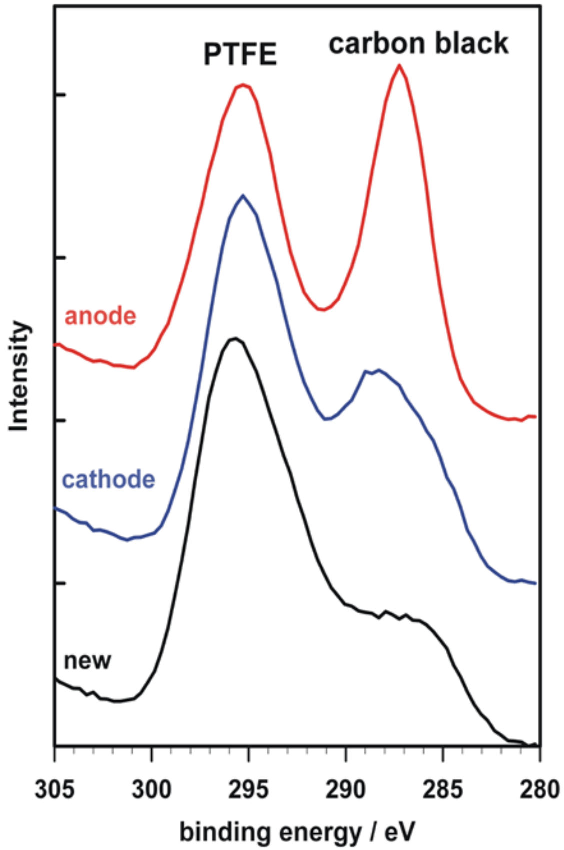
X-Ray Photoemission Spectroscopy

- Excitation of core level electrons with x-rays (~1-1.5 keV)
- Emission core level electrons
- Analysis of excess energy
- Detection of elements
- Detection of chemical state
- Surface sensitivity <10 nm
- Ultra high vacuum necessary
- X-Ray damage possible

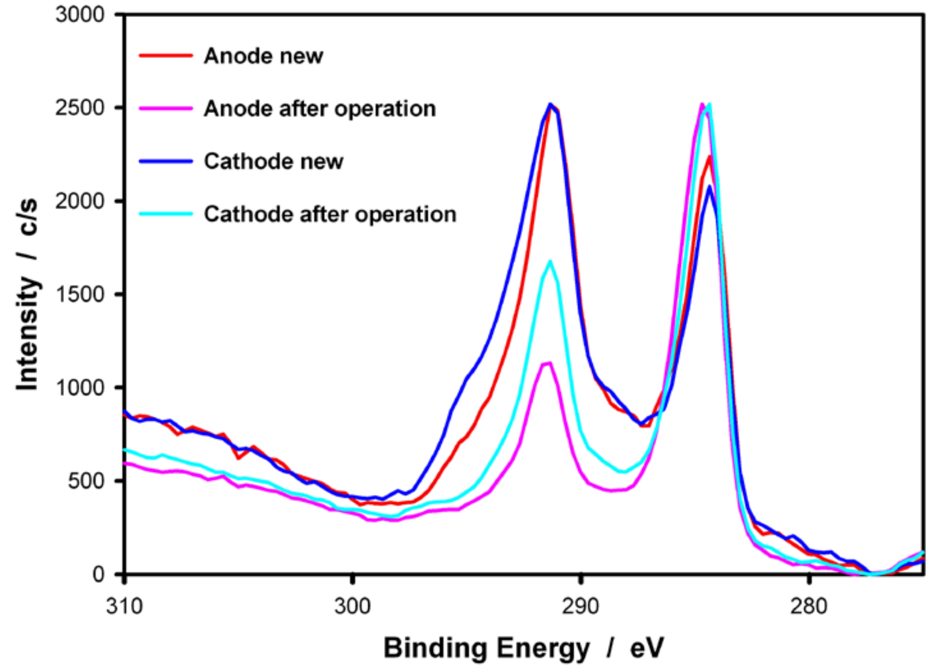


Degradation in PEFC

X-ray photoelectron spectroscopy (surface sensitive)



E-Tek electrodes



Ionpower CCM

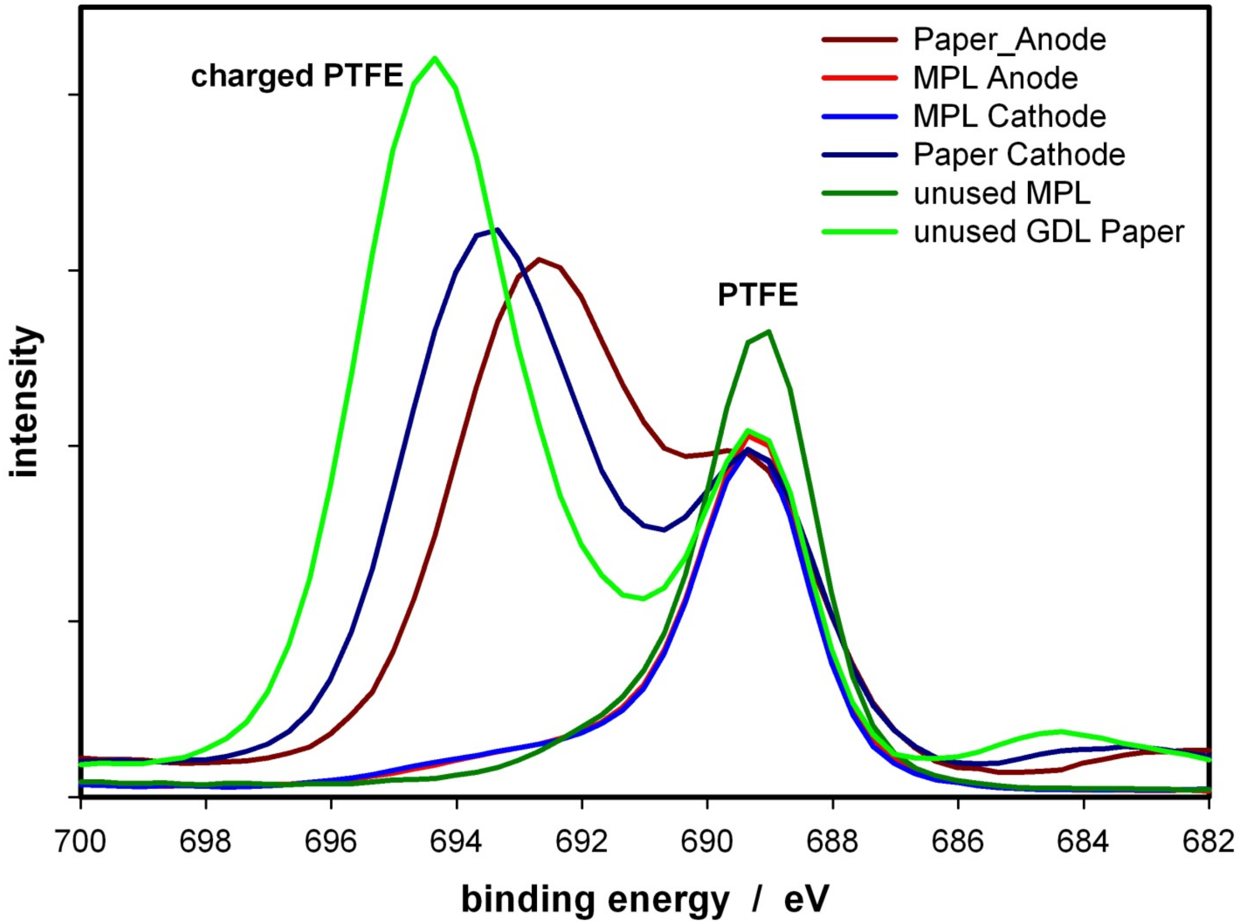
- **Partial decomposition of PTFE identified by XPS**
- **PTFE decomposition mainly on the anode**

→ Decrease of hydrophobicity

→ Changed water balance

Degradation in PEFC

PTFE decomposition in GDL (fluorine signal)



- PTFE decomposes in GDL

→ Decrease of hydrophobicity

→ Changed water balance

Carbon black content [wt%]	Wetting behavior of non-stressed surface	Wetting behavior of mechanically stressed surface
30	Hydrophobic	Hydrophobic
40	Wetted by liquid water, not by water vapor	Hydrophobic
50	Wetted by liquid water, not by water vapor	Hydrophobic
60	Wetted by liquid water, not by water vapor	Hydrophobic
70	Hydrophilic	Hydrophilic
80	Hydrophilic	Hydrophilic
90	Hydrophilic	Hydrophilic
100	Hydrophilic	Hydrophilic

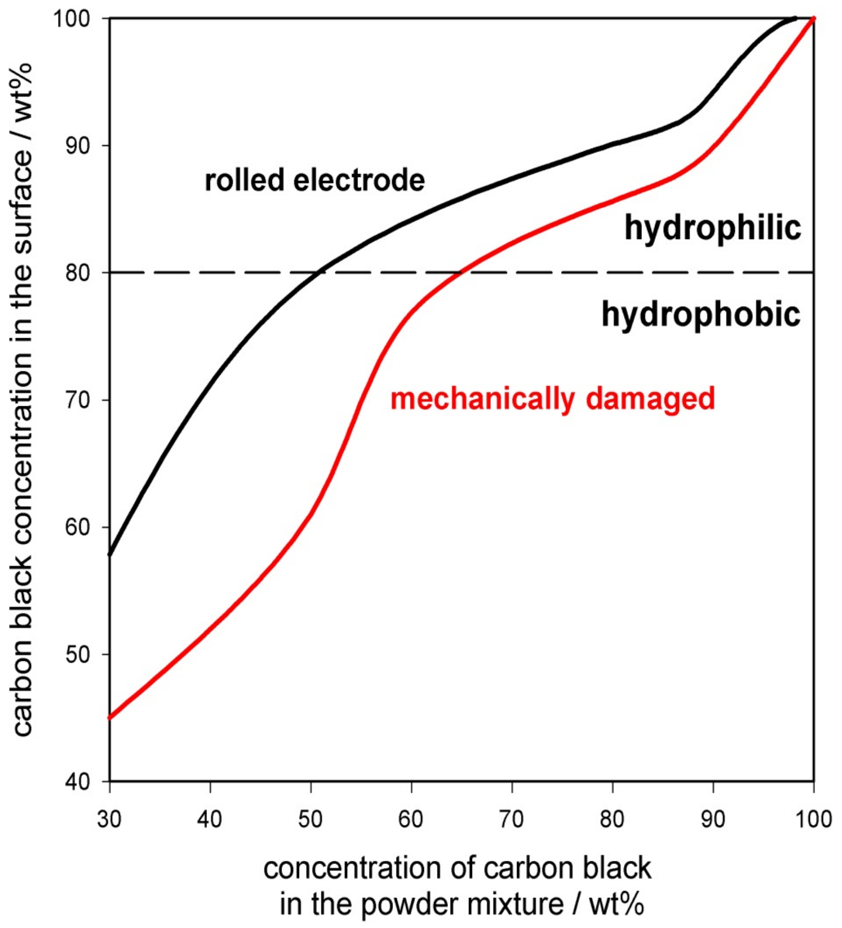
Correlation between PTFE-concentration in the surface determined by XPS and the hydrophilic/hydrophobic character

-carbon concentration at the surface of electrodes prepared from different mixtures of carbon black and PTFE

-➢ hydrophilic surface at carbon black concentrations above 80 wt%

-➢ hydrophobic surface at PTFE concentrations above 20 wt%

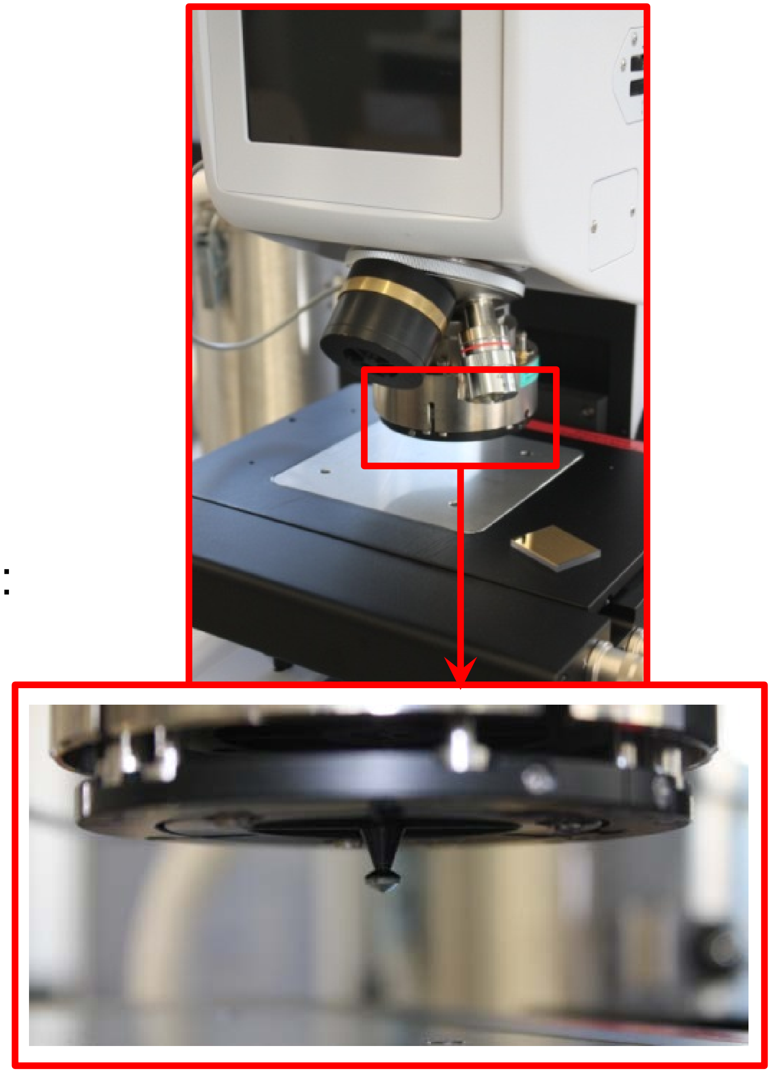
- distribution of PTFE ist important
- preparation process influences the PTFE distribution
- XPS measurements allow to assess the hydrophilic/hydrophobic character



Infrared Spectro*micro*scopy

- Single HgCdTe (MCT) detector:
Lateral resolution ~30 µm
XY stage → large scale mapping

- Imaging focal plane array (FPA) detector:
Lateral resolution ~1 µm
→ small scale mapping



IR microscope with
Ge ATR-Crystal

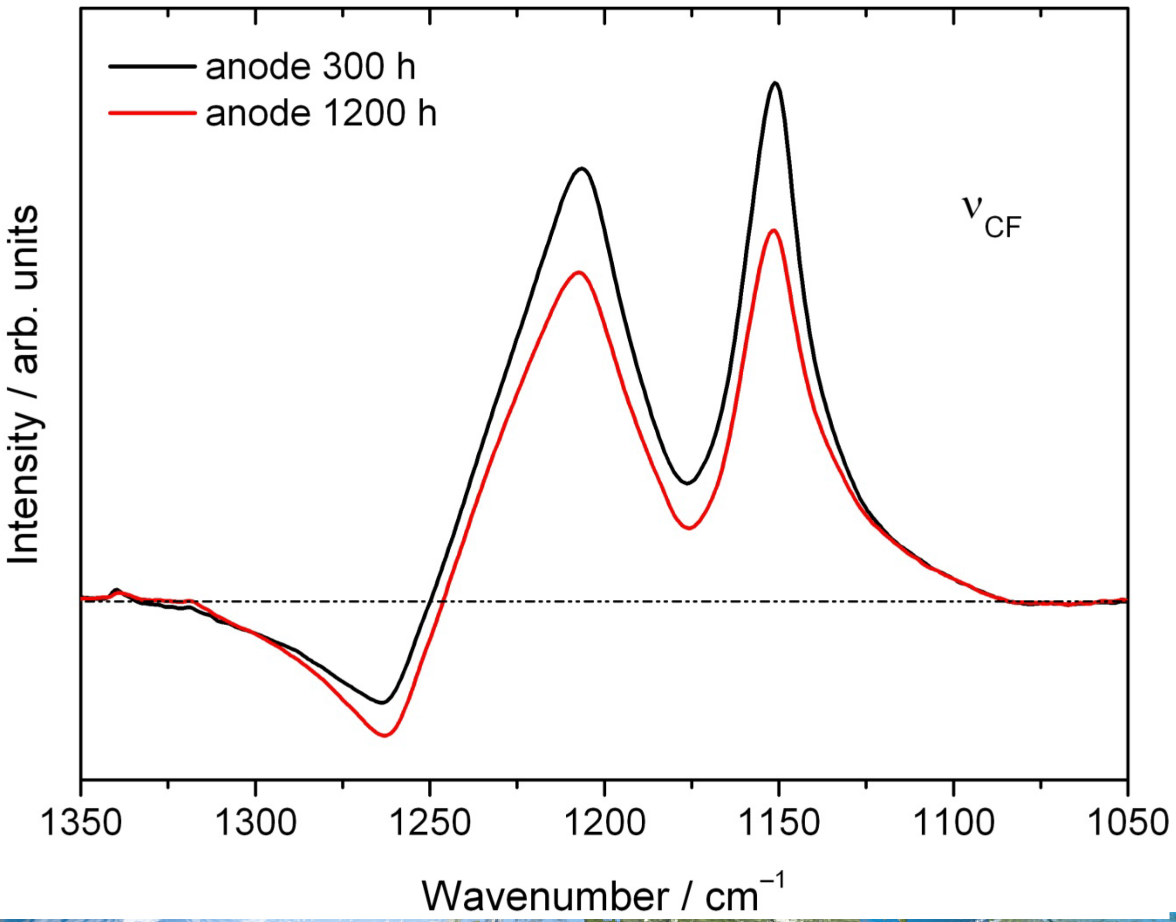
Degradation in PEFC in the reactive layer

FT-IR (ATR) – CF vibrational modes

-Ionpower CCM

-Decreasing intensity of PTFE signals of used anode and cathode

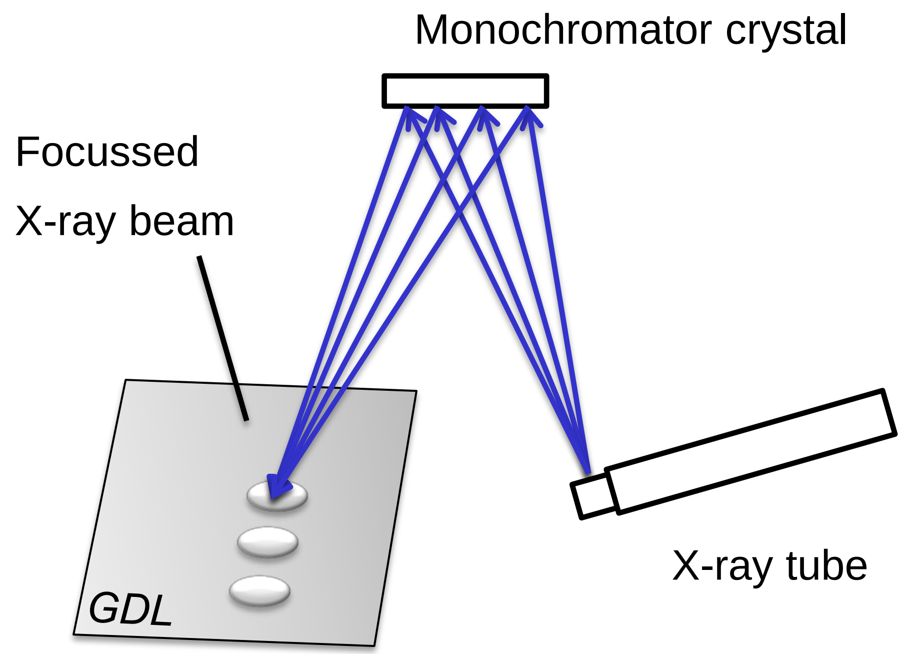
FT-IR (ATR) possess higher penetration depth (ca. 100 nm), XPS is more surface sensitive (penetration depth ca. 10 nm)



X-ray irradiation

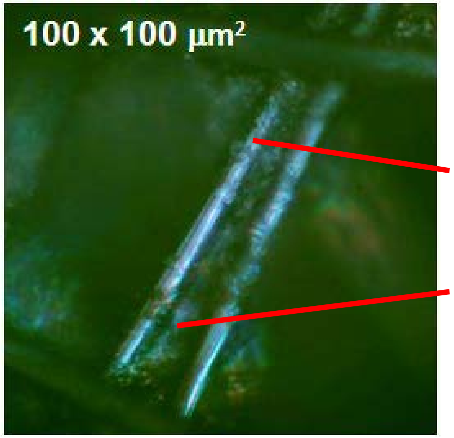
- Spot patterning
- Decomposition of PTFE: breaking of the C-F bond
- Reduced PTFE – C ratio

→ Reduced hydrophobicity
- Backing and microporous layer



(Al Kα, 1486,7 eV, 400 W, spot size ~0.8 mm)

X-ray irradiation

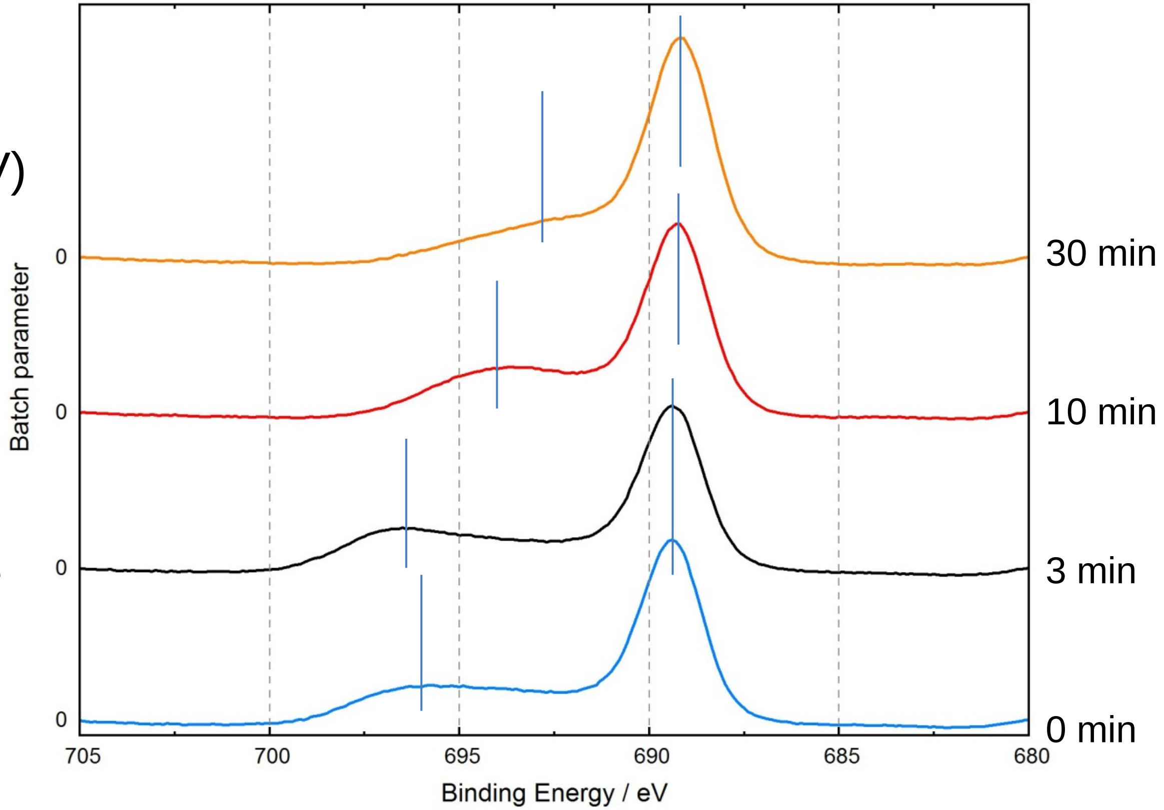


Small spot XPS analysis (GDL backing)

Fluorine 1s signal:
- Main signal (689 eV) slightly shifted

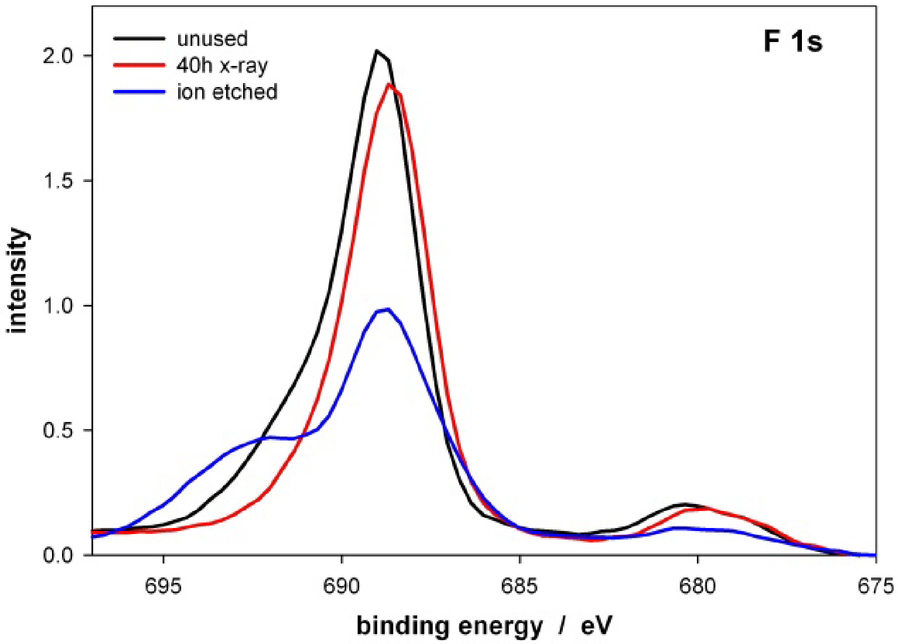
- Bysignal (696 eV): Charging reduced

Modification possible and scalable

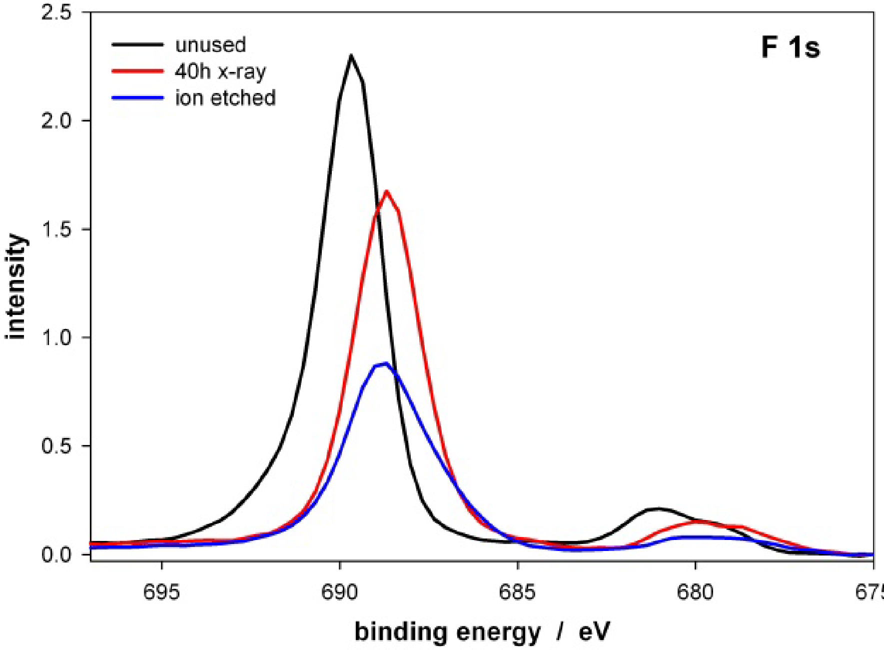


XP spectra F1s after exposure to ionizating radiation

GDL

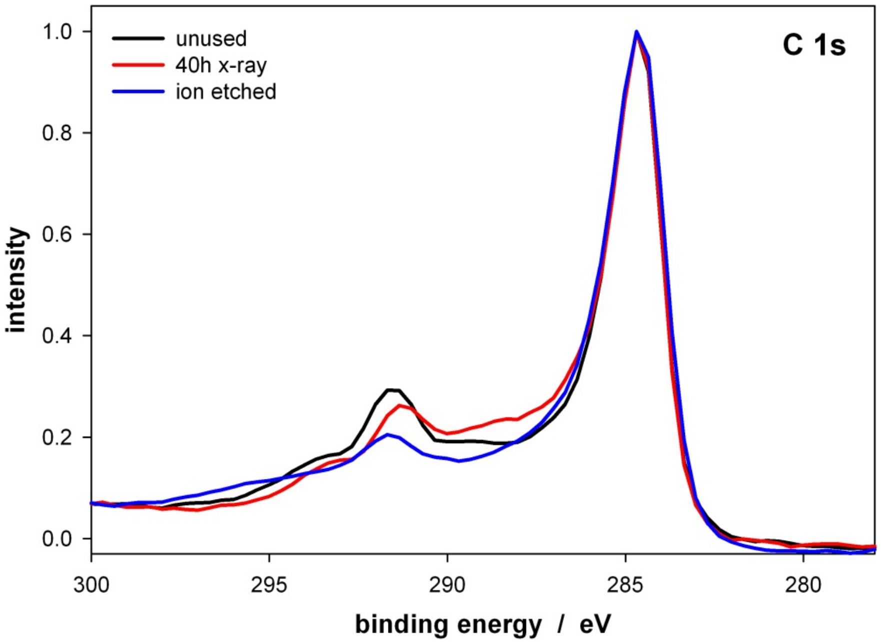


MPL

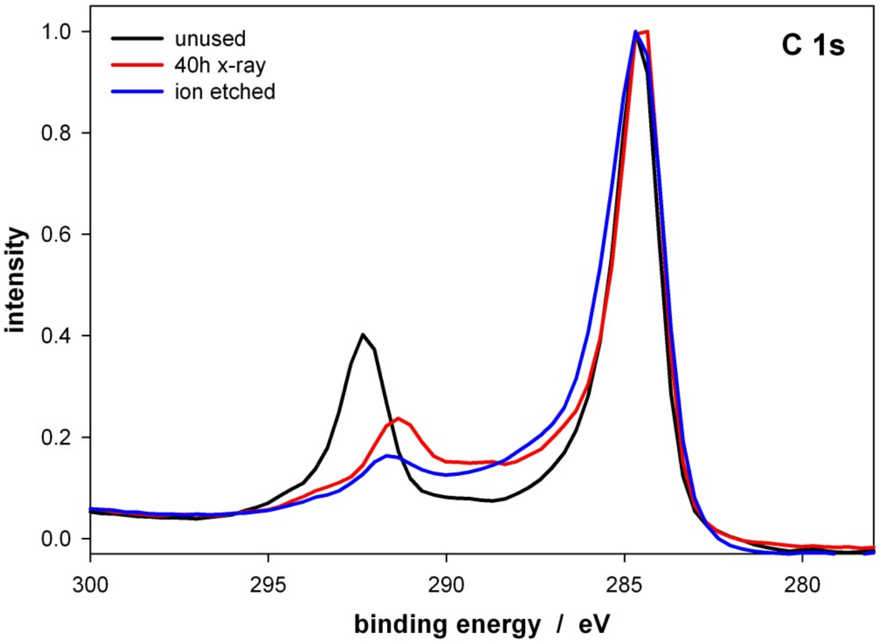


XP spectra C1s after exposure to ionizating radiation

GDL

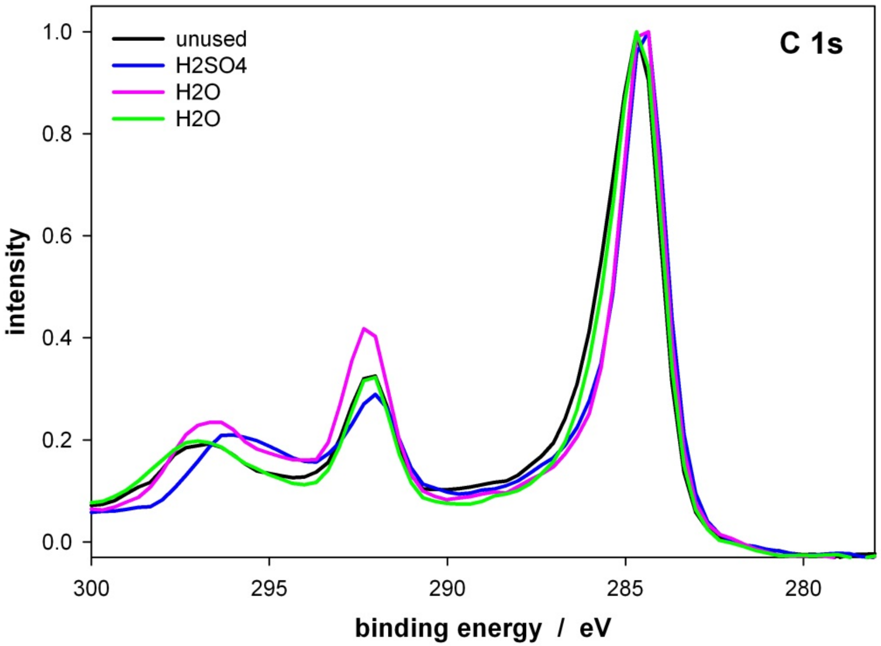


MPL

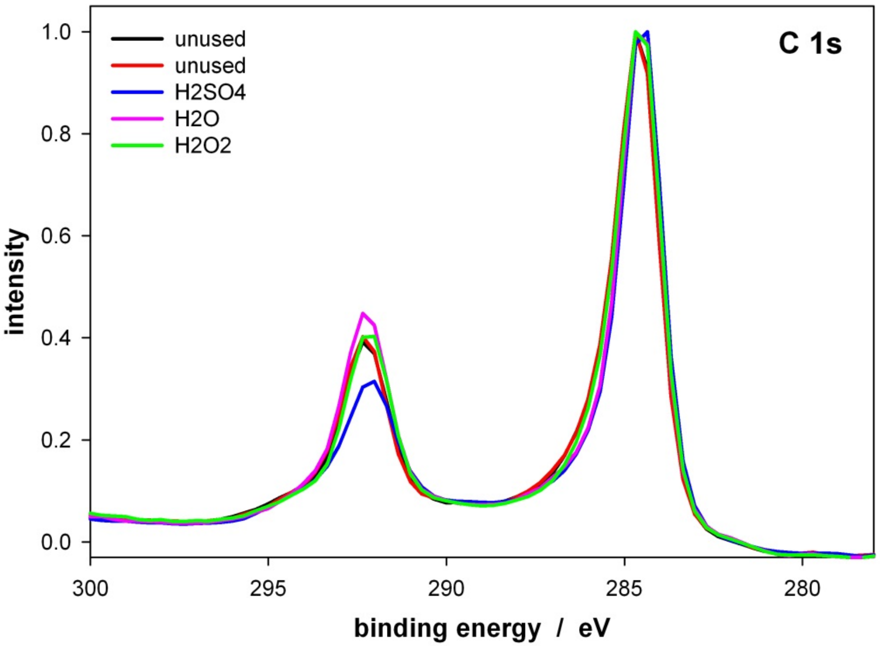


XP spectra C1s after chemical modification

GDL

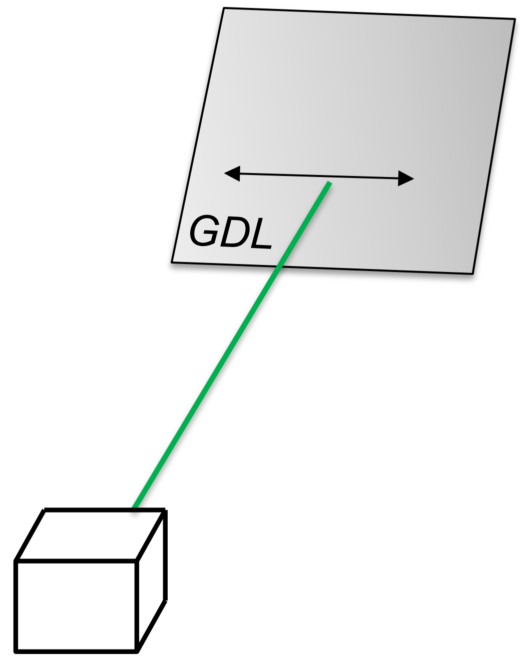


MPL

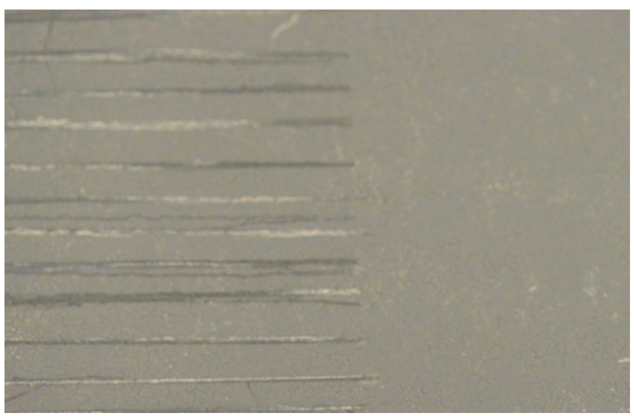


Laser irradiation

- Line patterning
- Thermal load
- Quick burning of MPL material → trenches



(532 nm, 400 mW)

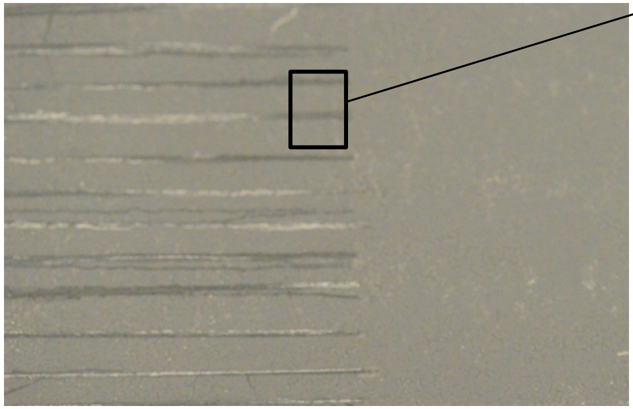


Partially laser irradiated MPL

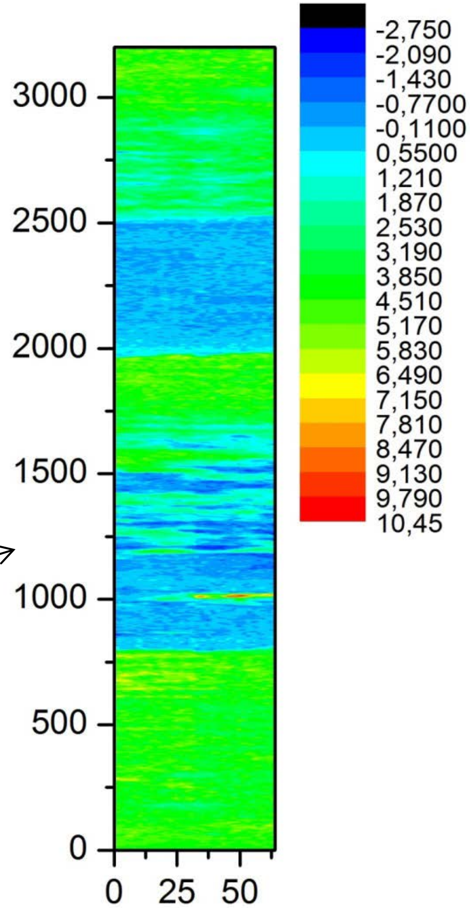
Laser Irradiation

MPL: Imaging IR absorption analysis

Intensity of C-F stretch vibrations missing inside trenches → no PTFE



Partially laser irradiated MPL

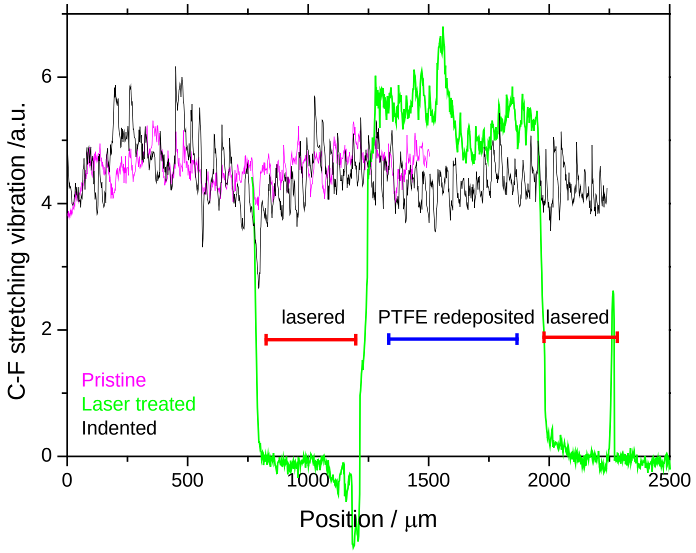


ATR-FTIR mapping of C-F stretch vibration

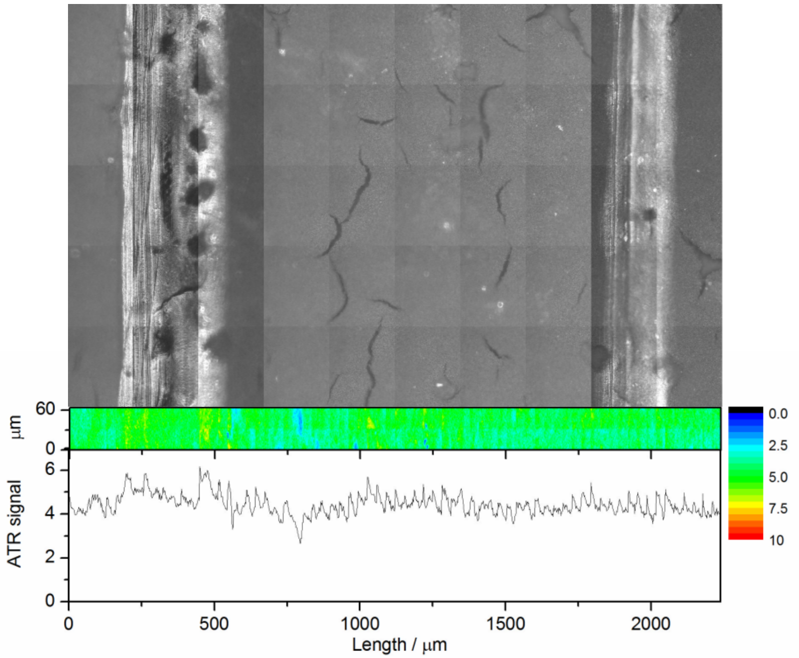
Mechanical indenting

MPL indented with spine of scalpel
→width similar to laser trenches

No chemical influence



Line profiles from ATR-FTIR data (C-F stretch vibration)



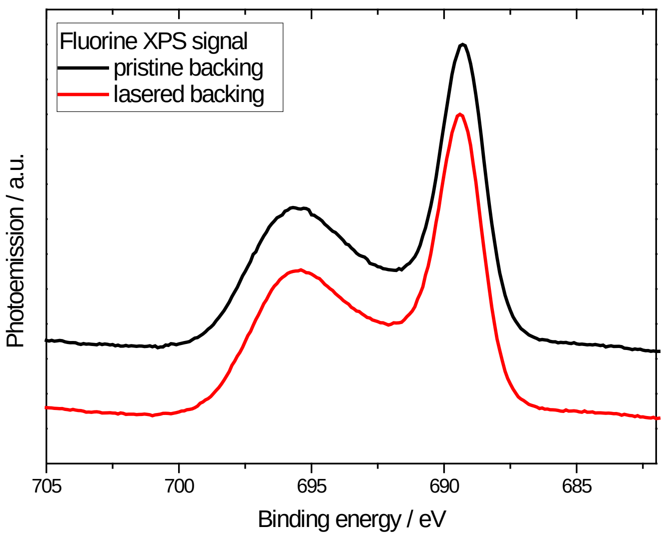
ATR-FTIR mapping of C-F stretch vibration

Laser irradiation

GDL backing

No impact visible by eye

Small spot XPS analysis:
Fluorine 1s signal does not
Reveal PTFE decomposition



Weak impact on GDL backing – heat dissipation
→ GDL unchanged with 532 nm / 400 mW within >10 min spot irradiation

Applicability and Feasibility

Method	X-rays	Laser	Ion beam
Mechanism	Breaking of chemical bonds in PTFE	Thermal decomposition	Atomic scale decomposition
Effectivity	medium	MPL: very high Backing: very low	high
Lab scale time demand	high	low	high
Lab scale effort	high	low	high
Production scale time demand	Reasonable: batch processing with masks	low	high
Production scale effort	Low to reasonable: possibly ambient pressure irradiation	low: easy automisation	high
Feasibility	Reasonable	MPL: OK Backing: difficult	?

Acknowledgements

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