REPLACING PTFE IN HTPEM CATALYST LAYERS

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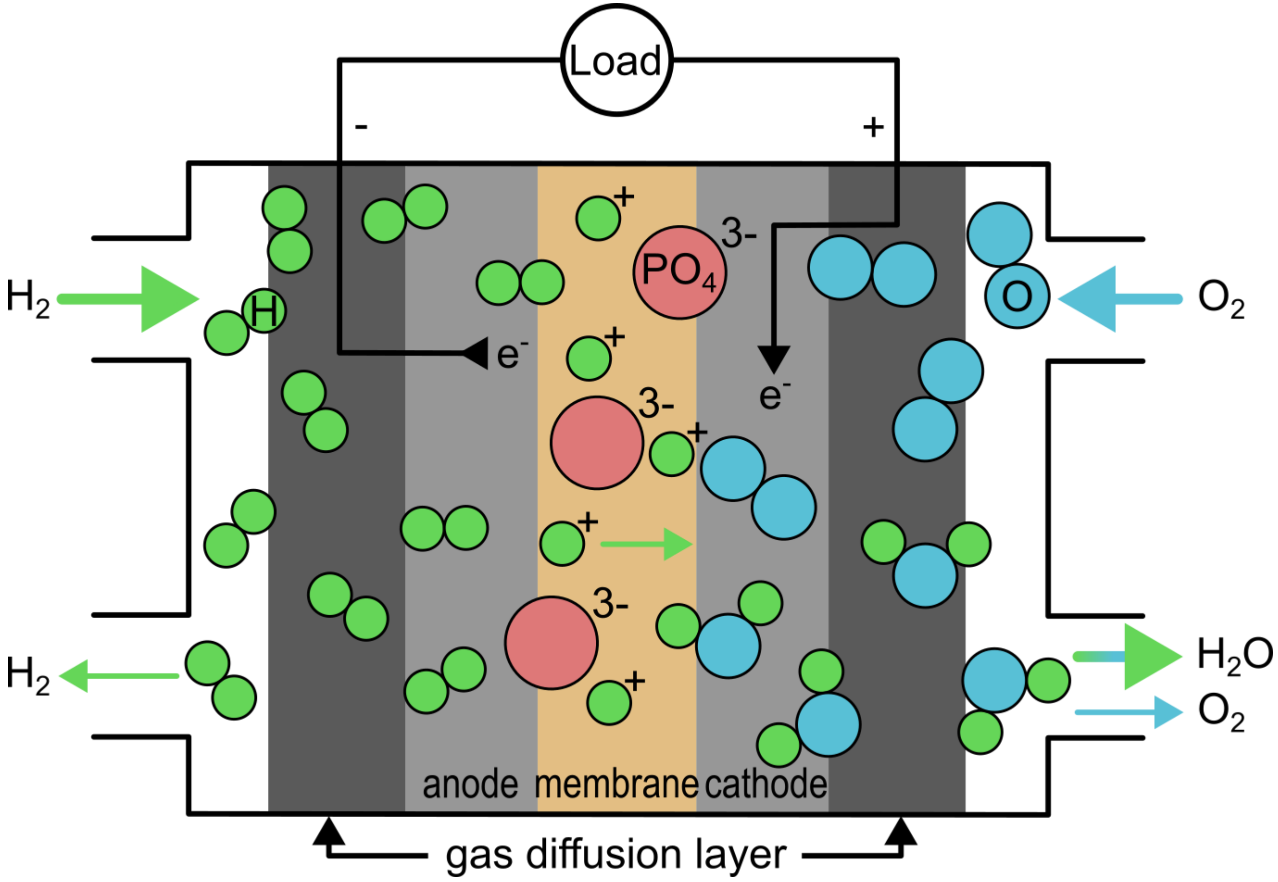
DLR

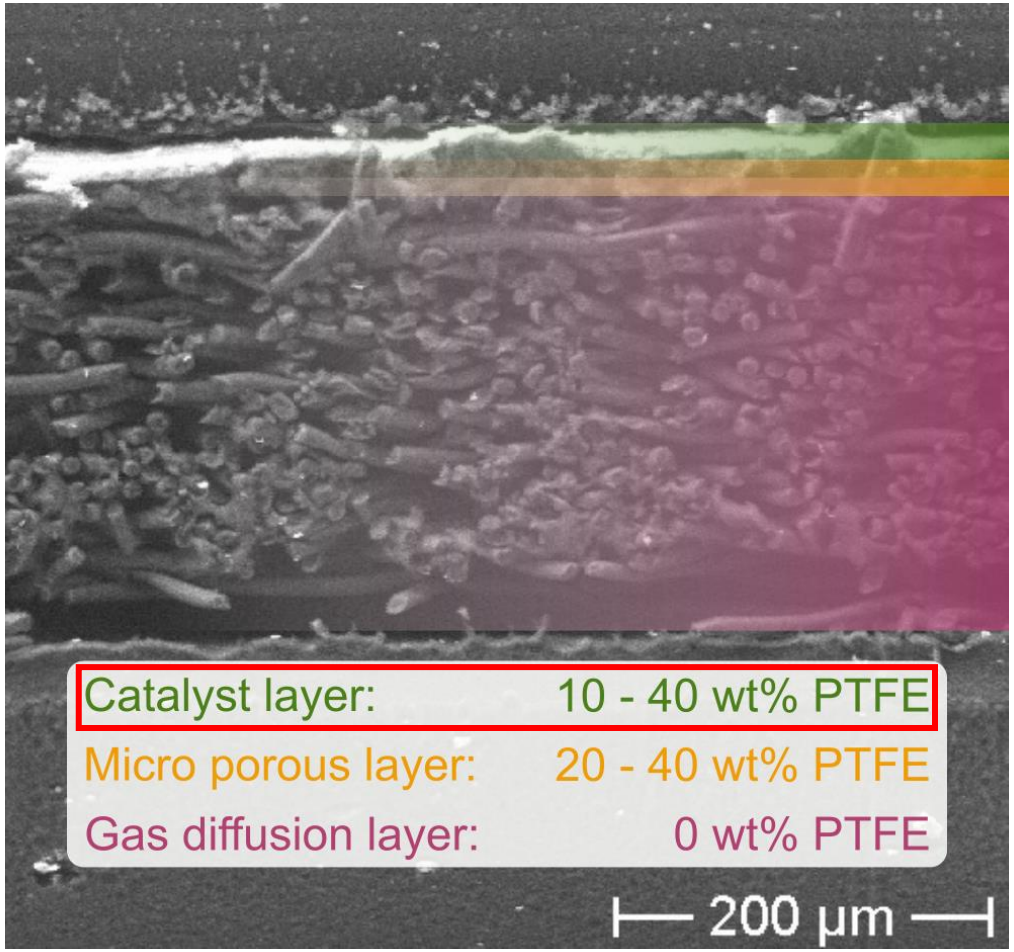
Development of per- and polyfluoroalkyl substance (PFAS)-free electrodes and their characterization using combined element quantification methods

High temperature proton exchange membrane fuel cells (HT-PEMFC)

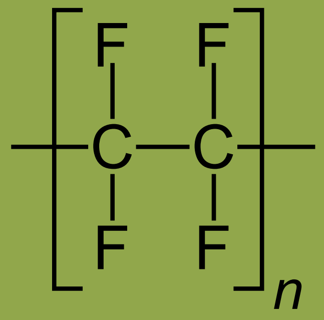
- High temperature → 160 °C
  - Better kinetics for ORR and HOR
  - Easier heat and water management
  - Less sensitive to H_2S and CO impurities in H_2
  - Higher platinum loadings due to phosphate poisoning
- Polybenzimidazole (PBI) membrane
- Phosphoric acid instead of ionomers for proton conduction



PTFE in gas diffusion electrodes (GDE)



SEM cross section of a GDE (Freudenberg H23C8 with Pt/C)



Binder

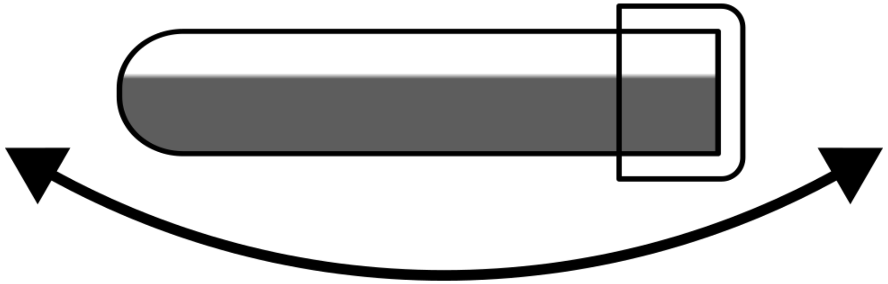
Hydrophobic polymer

PFAS!

Problematic!

Preparation of catalyst suspension and coating

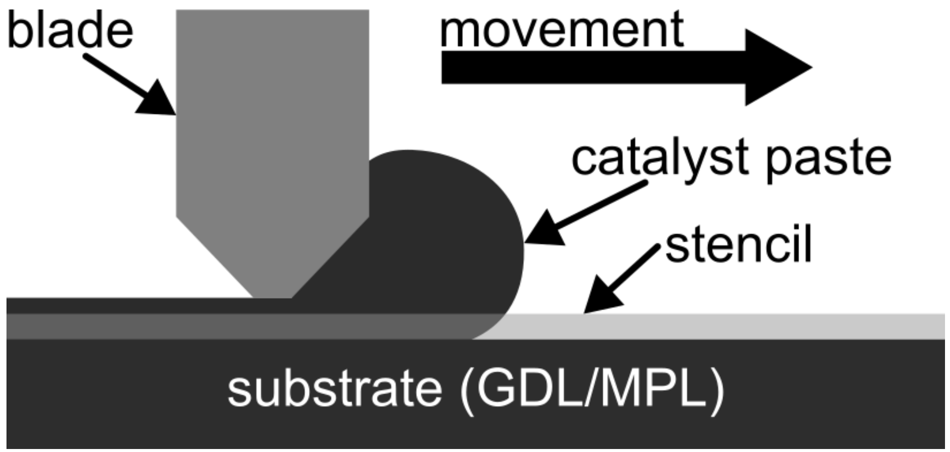
- **PtNi** (3:1) catalyst on Vulcan XC-72
  - From FuelCellStore
- **H_2O** (0.6 ratio to catalyst weight)
- **IPA** (7-10 times of catalyst weight)
- Different **polymer** loadings: 5, 10, 20, 40 wt%
  - **PTFE, PEEK**, other polymers
- Freudenberg H23C2 GDL
  - 40 wt% PTFE in MPL



30 Hz, 10 min

Mixing with ball mill

- In 5 mL polypropylene tubes from Eppendorf



Coating via doctor blade

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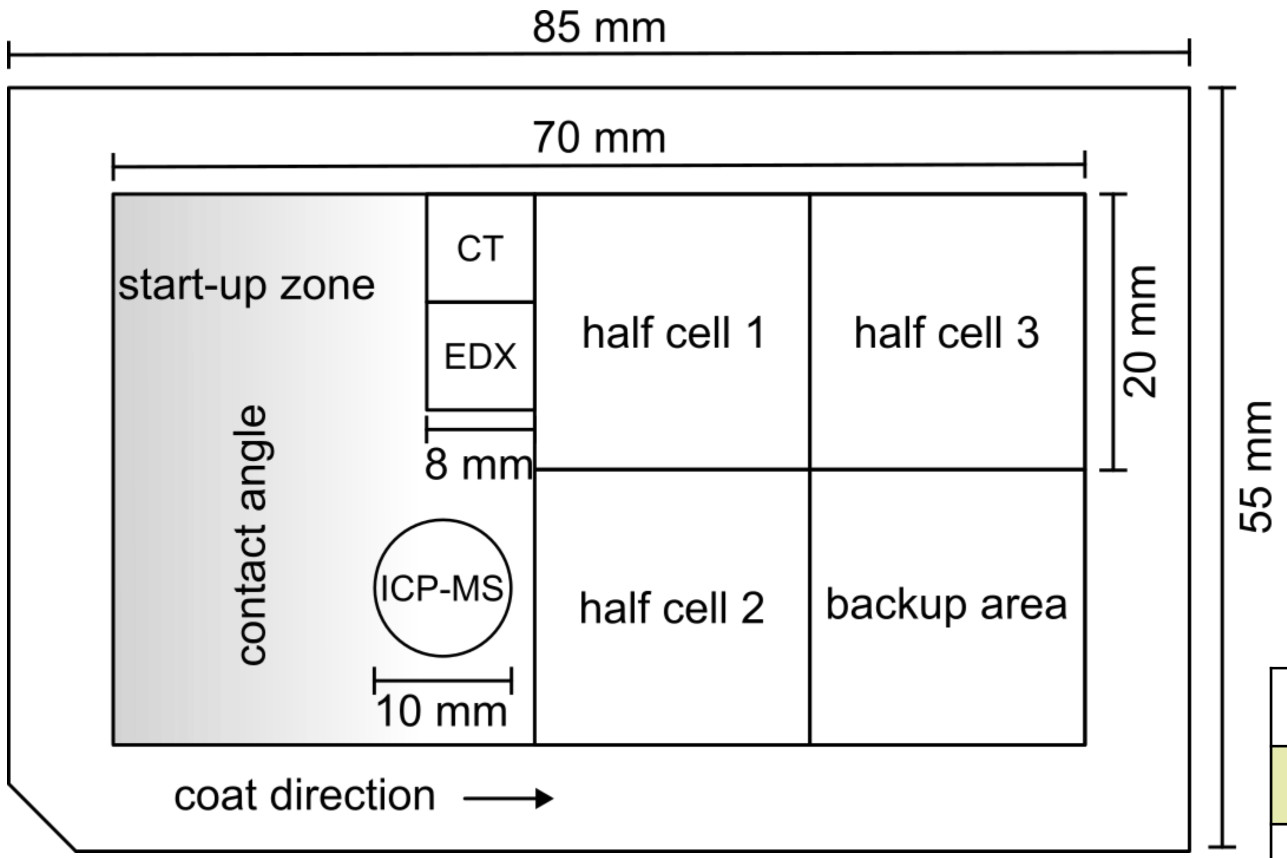
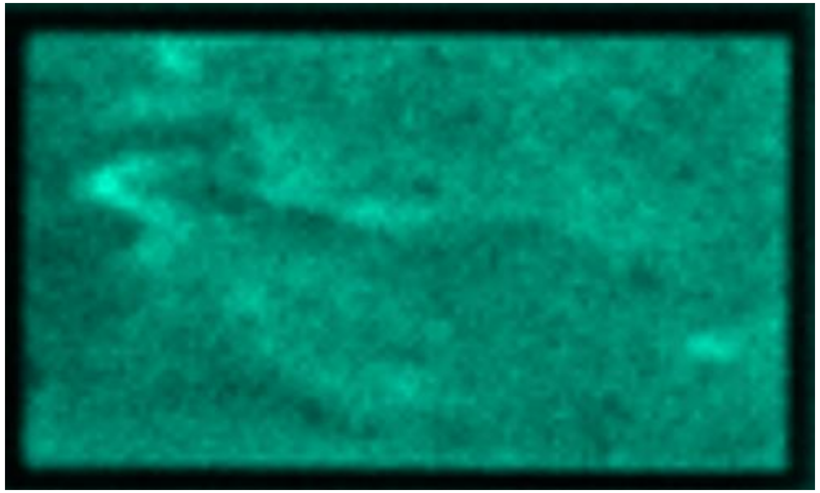
Characterisation of GDE



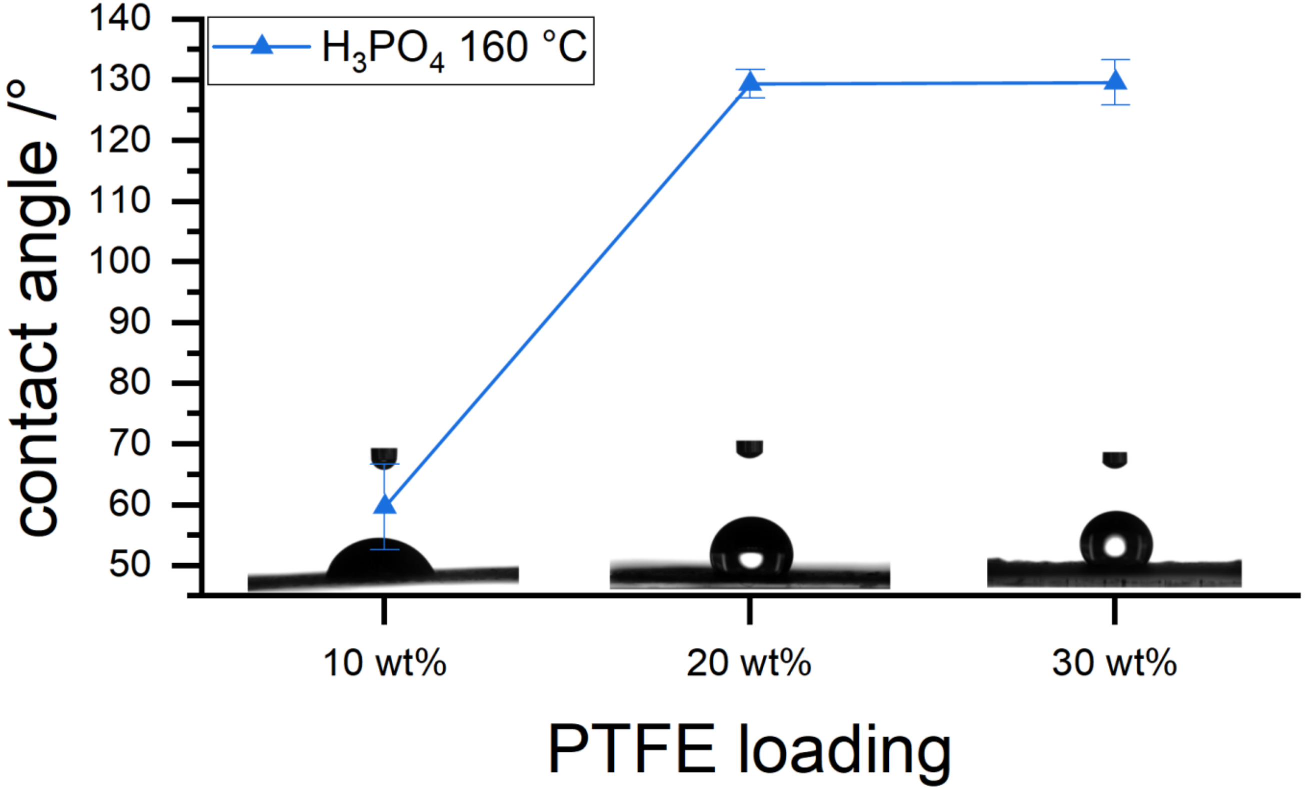


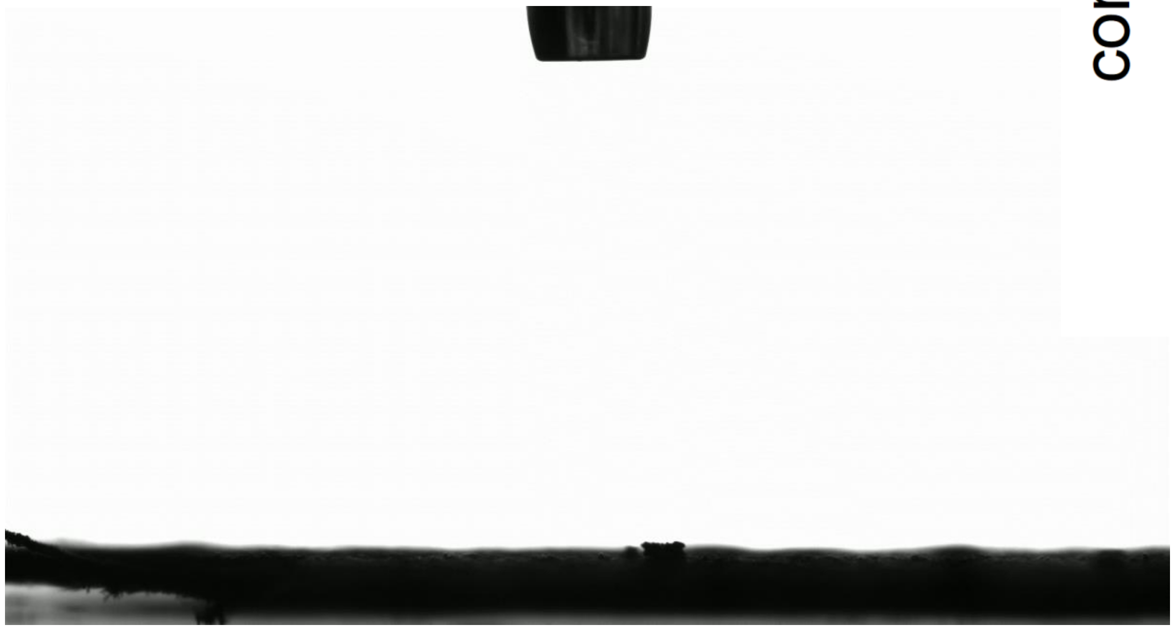
µ-XRF mapping of platinum

Output	**Method**
Electrochemical performance	Half cell
Platinum loading	ICP-MS
Structural analysis	CT
Polymer loading	EDS
Hydrophobicity	Contact angle

Contact angle measurements

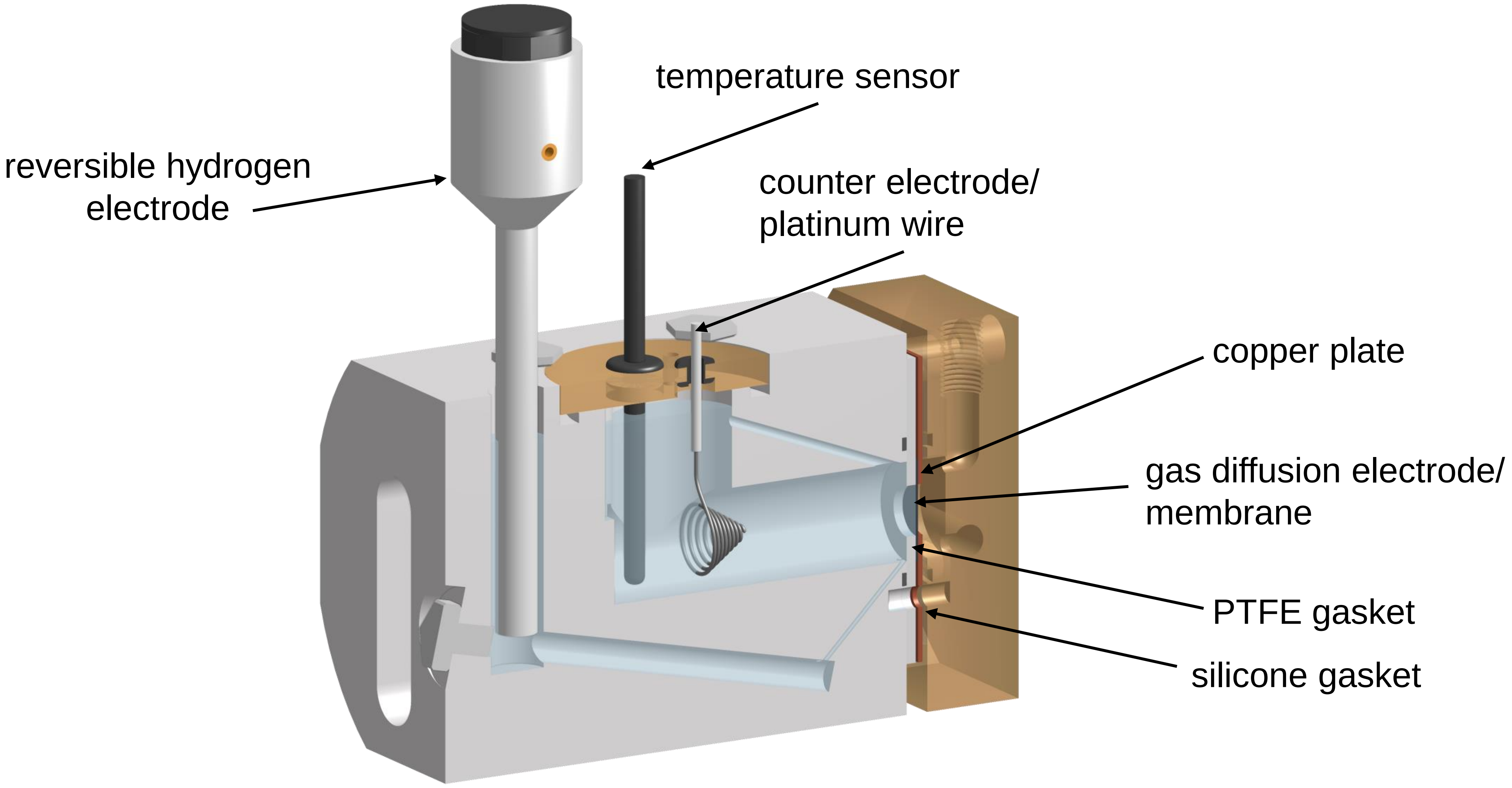
- Investigation of hydrophobicity
  - Higher contact angle means higher hydrophobicity
- Reference point for other polymers





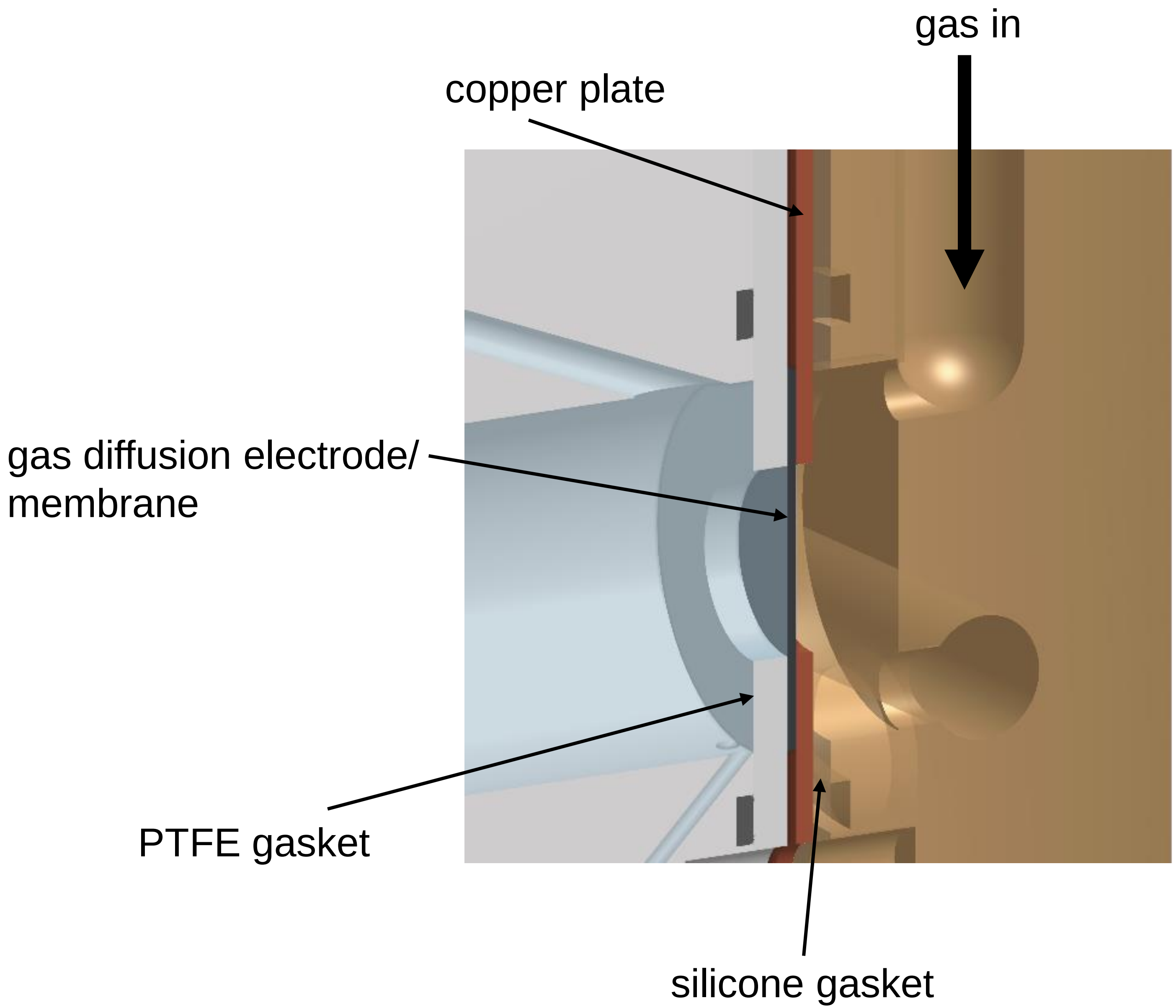
Contact angle measurement with 30 wt% PEEK loading

Half cell measurements



Gaskatel Flexcell® half cell

Half cell measurements



Open circuit potential

Impedance spectroscopy

Cyclovoltammetry
0.04 – 1.05 V, 100 mV/s

Polarisation curve, galvanostatic steps with impedance measurement

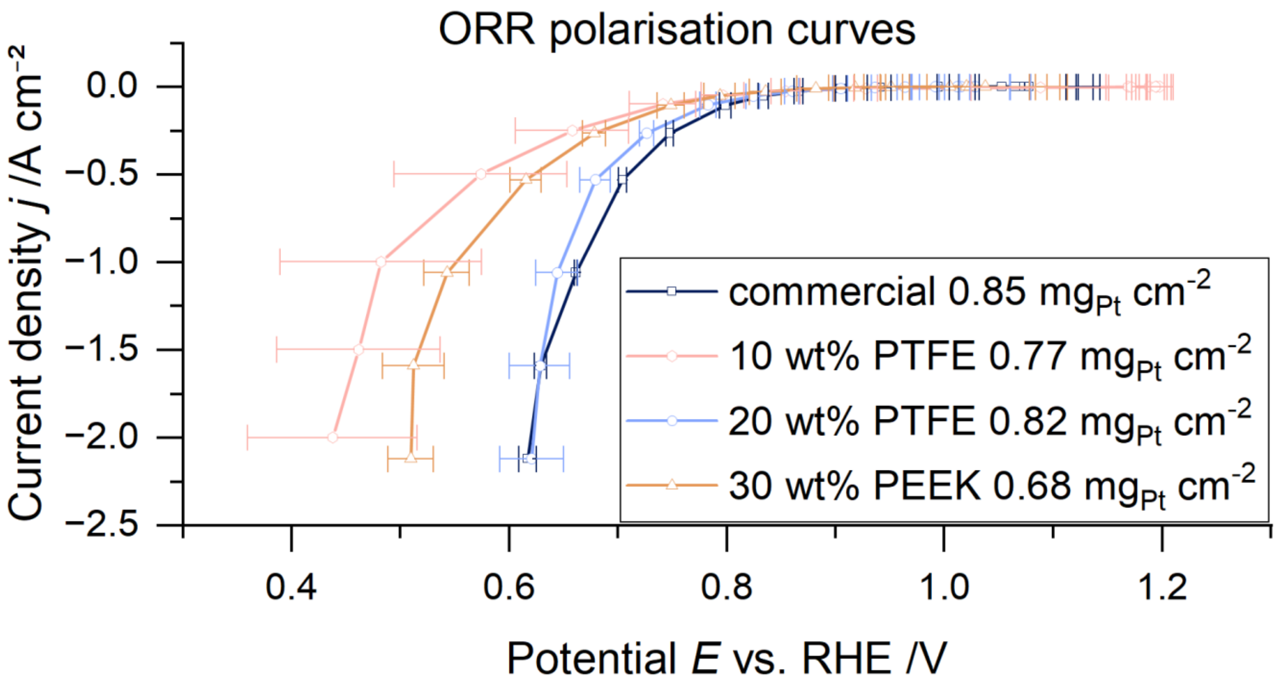
Accelerated stress test (AST)
1000 cycles of 500 mV/s, 0.6 – 1.5 V

Cyclovoltammetry
0.04 – 1.05 V, 100 mV/s

Polarisation curve

Electrochemical half cell measurements

- 20 wt% PTFE electrode leads to similar potentials compared to the commercial electrode
- 30 wt% PEEK electrode is not far off



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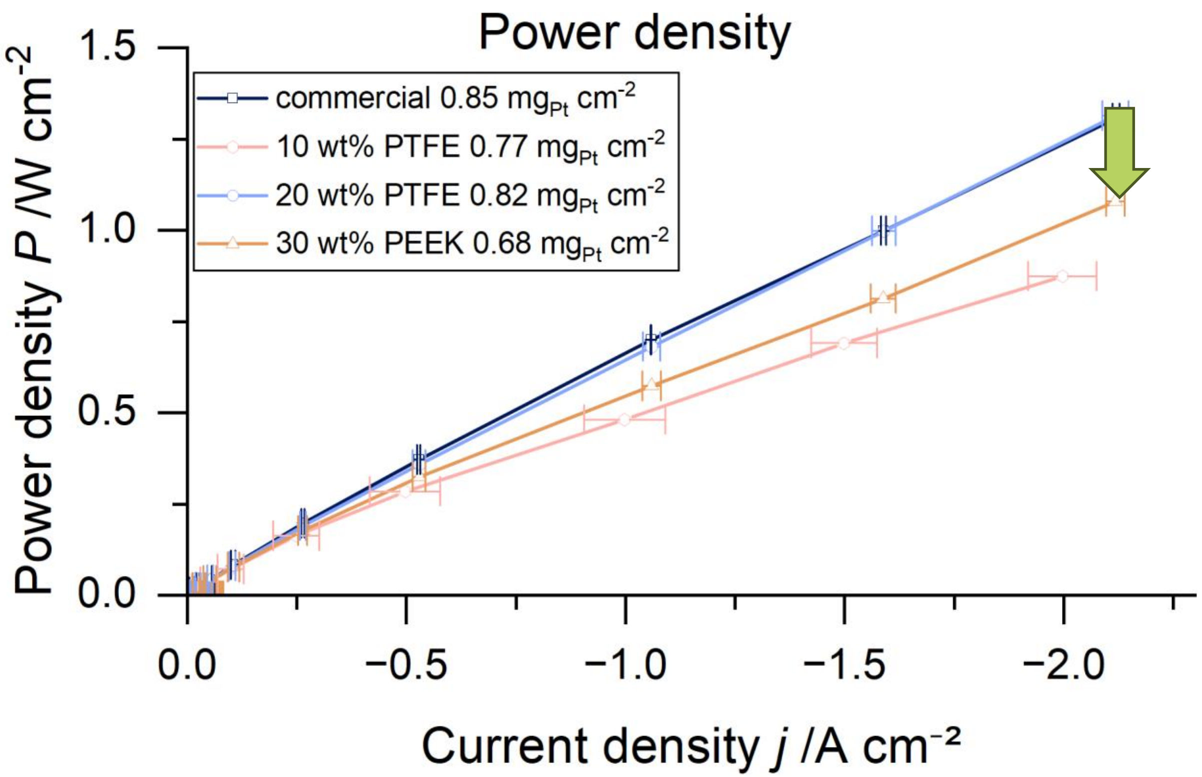
Measured in Gaskatel Flexcell® half cell, 160 °C, conc. H_3PO_4, galvanostatic, 150 mL/min O_2

Electrochemical half cell measurements

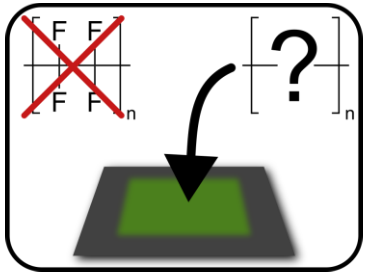
- 20 wt% PTFE electrode leads to similar potentials compared to the commercial electrode
- 30 wt% PEEK electrode is not far off
- With a lower lower PTFE loading of 10 wt% the power density drops below the PEEK values
  - PEEK leads to a positive effect for the performance



Measured in Gaskatel Flexcell® half cell, 160 °C, conc. H_3PO_4, galvanostatic, 150 mL/min O_2

Conclusion and Outlook

- Successfull production of GDEs with PTFE and PEEK
- Electrochemical characterisation:
  - 20 wt% PTFE loading leads to good performance
  - 30 wt% PEEK loading leads to good results



- Other loadings must be tested
  - PTFE and PEEK
- Different polymers will be tested
- Full characterisation of all samples
  - Contact angle, EDS, CT

Thank you for your attention!

Acknowledgements:
- Jana Ewert
- Nils Harder
- Steffen Rehse

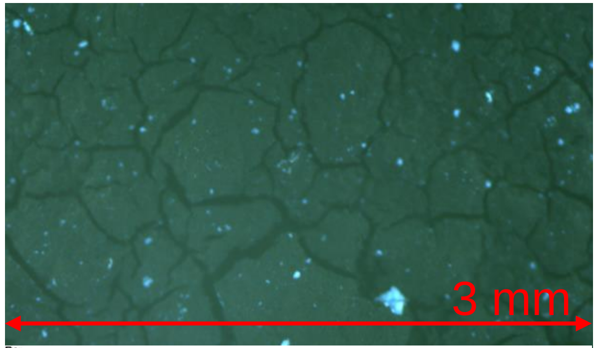
X-ray fluorescence spectroscopy (μ-XRF)

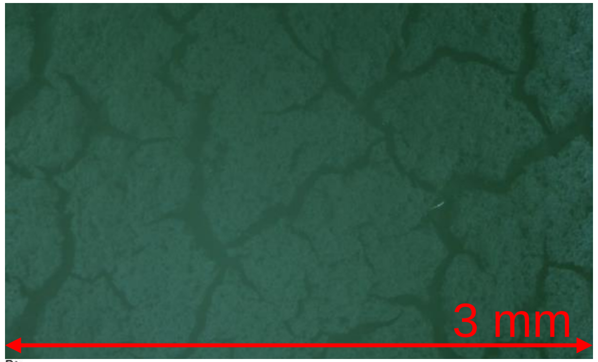
- Elemental analysis of Pt and Ni loading
  - Not applicable for F
- To test for a homogenous catalyst layer

sonication | ball milling

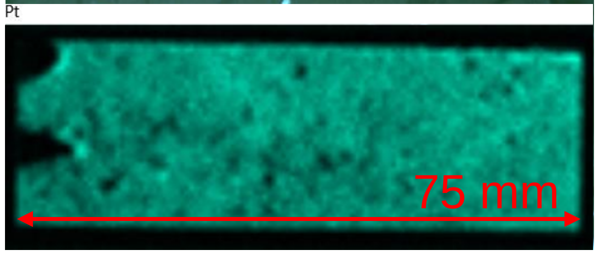
- Example of catalyst layer with 40 wt% PTFE loading:

microscopic image



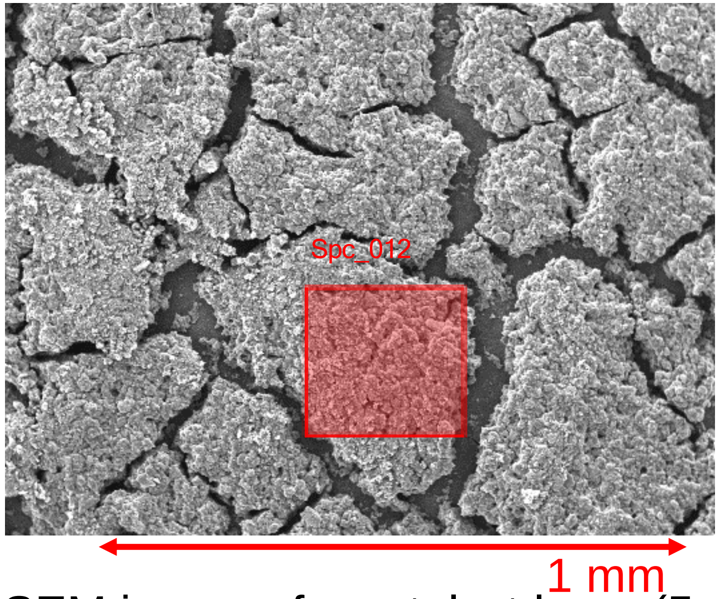


μ-XRF imaging (Pt)

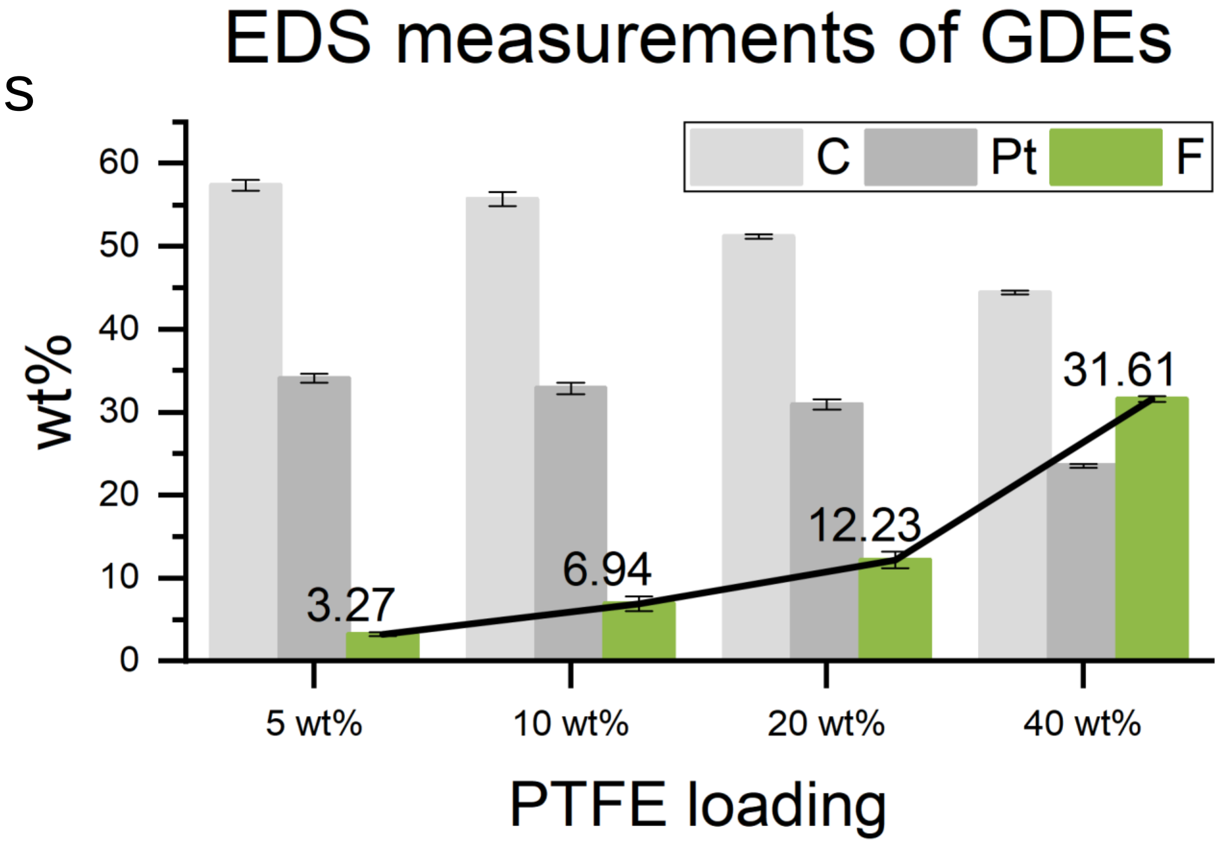


Scanning electron microscope (SEM) with EDS

- Elemental analysis of F content
- To verify the different PTFE loadings
  - 5 – 7 small areas are measured

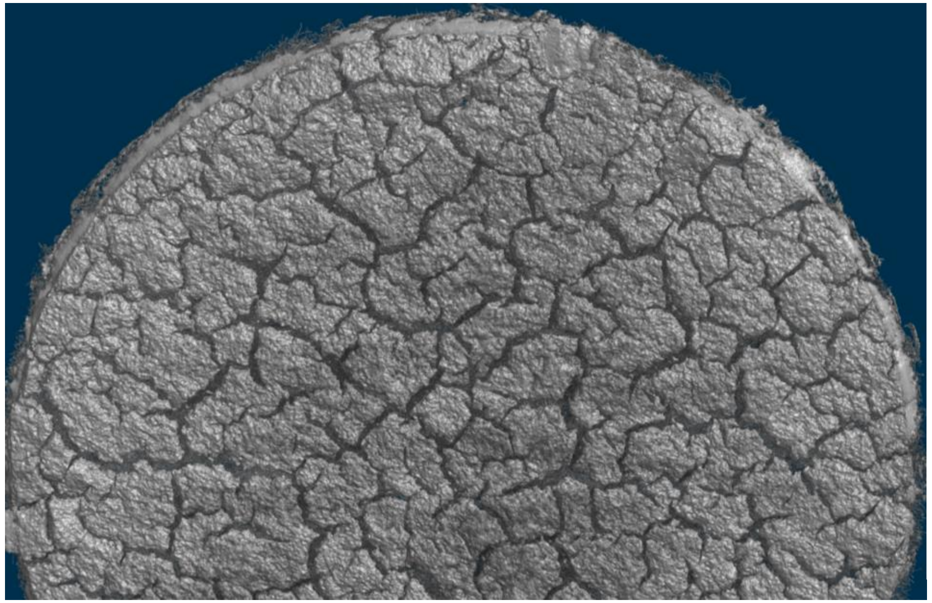


SEM image of a catalyst layer (5 wt% PTFE)
Measured with JSM-IT800, acceleration voltage = 10 kV, measurement time = 5 min

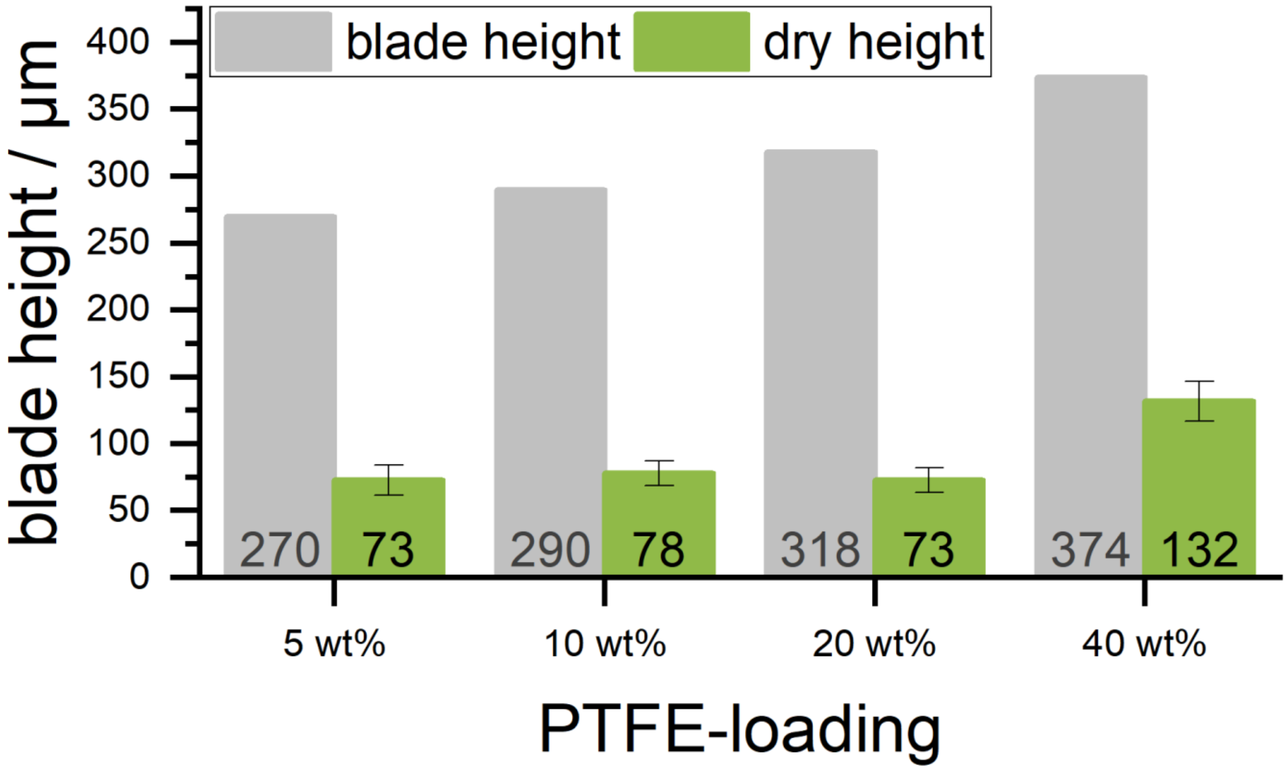


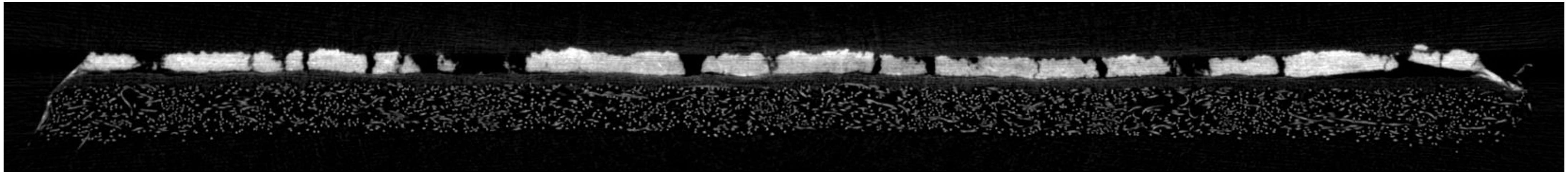
Computed tomography

- Layer height
- Information about structure



CT image of GDE with 10 wt% PTFE (top view)

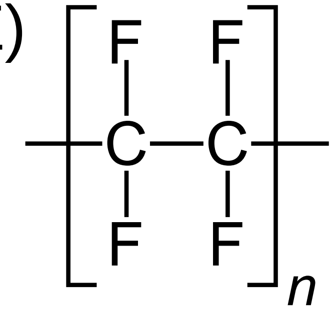




CT image of GDE with 10 wt% PTFE (side view)

Per- and polyfluoroalkyl substances (PFAS)

- Substances with multiple fluorine atoms attached to their alkyl chains
- Popular example: polytetrafluoroethylene (PTFE)



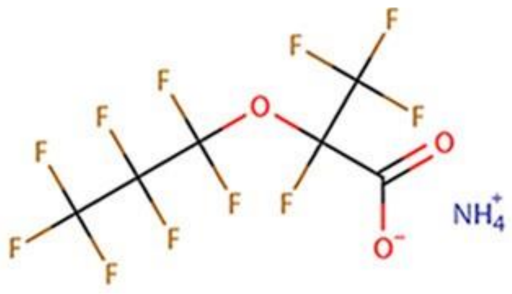
- The European Chemical Agency (ECHA) proposed to ban over 12 000 PFAS[2]

➢ <u>Eventually replacements for PFAS in fuel cells are needed</u>

[1] R. Lohmann et al., *Environmental science & technology* **2020**, *54*, 12820.
[2] F. Spyrakis, T. A. Dragani, *Toxics* **2023**, *11*.

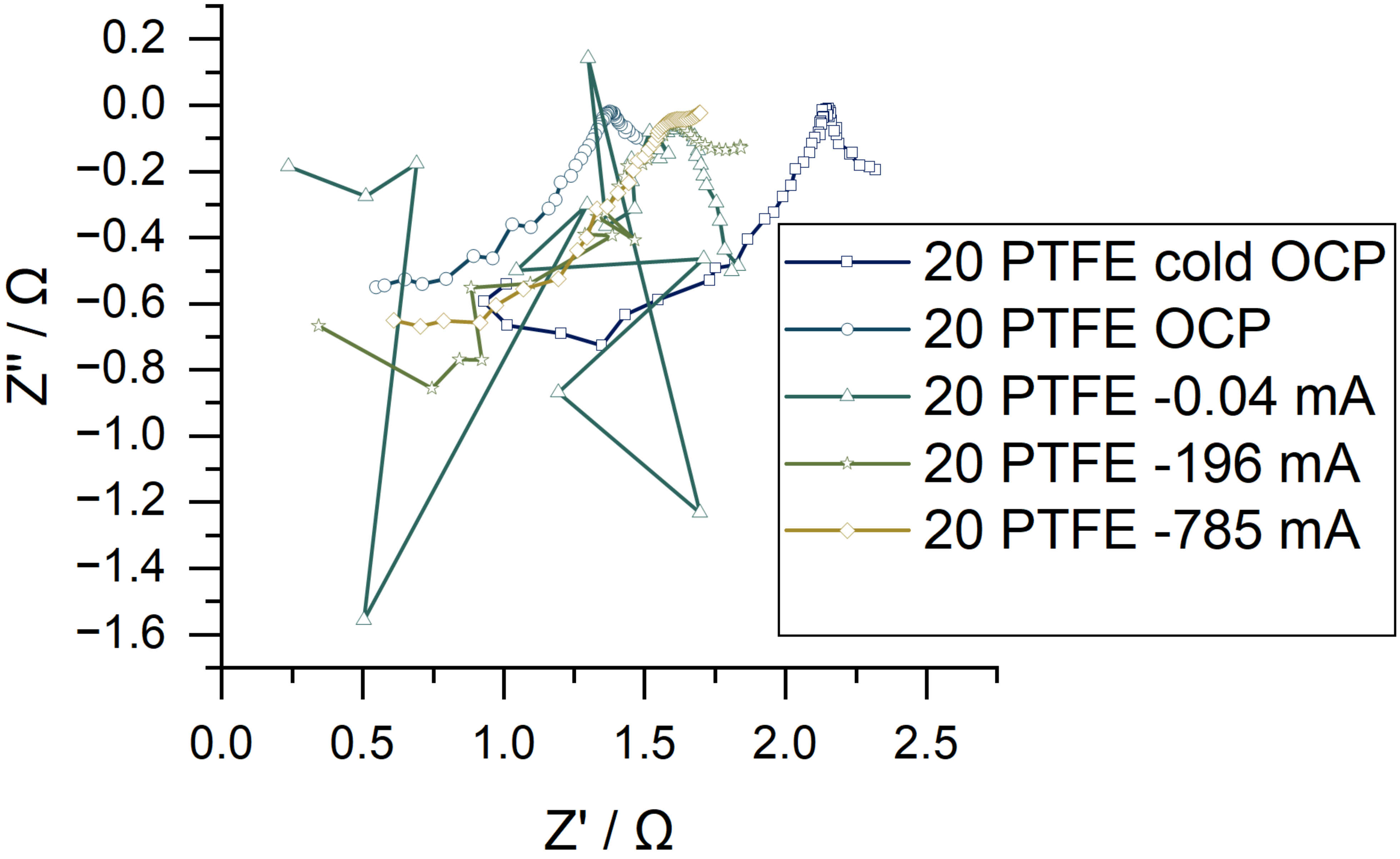
More on PFAS problems

- Highly resistant to breakdown
  - ➢ Accumulation in water, soil, plants, animals
  - ➢ Humans accumulate PFAS through consumption of those things[3]
- Health related costs to society are estimated at 52 – 84 billion € annually[4]
  - Only high cholesterol, decreased immune system and cancer included
- Remidiation of polluted soil and water is expensive
- Example PTFE:
  - Gen X is a substitute emulsifier for other fluoropolymers
  - Already on the E.U.'s Candidate List of Substances of Very High Concern (SVHC)[1]
  - ➢ Production is a problem, not just the use (Gen X is already in the environment)



[1] R. Lohmann et al., *Environmental science & technology* **2020**, *54*, 12820.
[3] R. Ghisi, T. Vamerali, S. Manzetti, *Environmental research* **2019**, *169*, 326.
[4] G. Goldenman, et al., *The cost of inaction*, Nordic Council of Ministers, Copenhagen, **2019**.

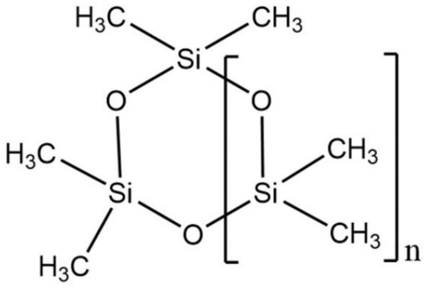
Impedanzbeispiele



Polysiloxanes

Environmental impact:

- Volatile organic siloxanes can be released during production
  - Cyclic methylsiloxanes could be cancerogenic and mutagenic[5]
  - Synthesis is possible without cyclic byproducts[6]



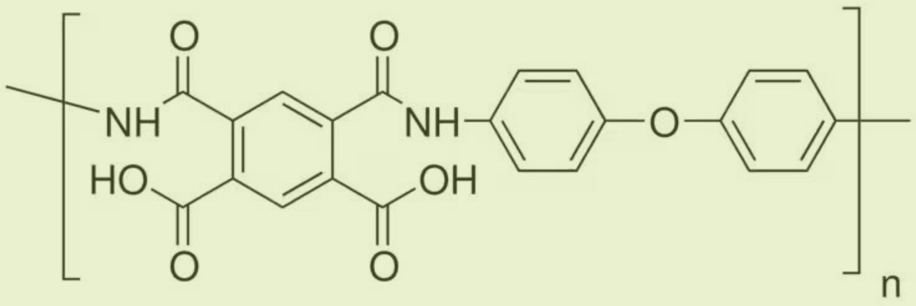
Cyclic Methylsiloxanes

Properties:

- High temperature resistance T ~ 200 °C
- Hydrophobic but penetrable by steam
- Great oxidation resistance
- Si detectable by LIBS

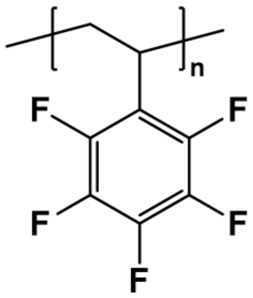
[5] X. Xiang, N. Liu, L. Xu, Y. Cai, *Ecotoxicology and environmental safety* **2021**, *224*, 112631.
[6] L. Shi, et al., *Science (New York, N.Y.)* **2023**, *381*, 1011.

Potential alternatives for PTFE

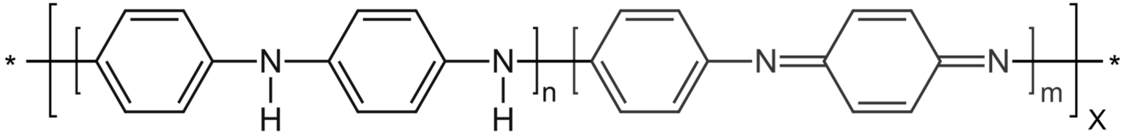


Poly(pyromellitic dianhydride-*co*-4,4′-oxydianiline) (amic acid)

Polysiloxanes, methylated and phenylated



Polypentafluorostyrene



Polyanyline

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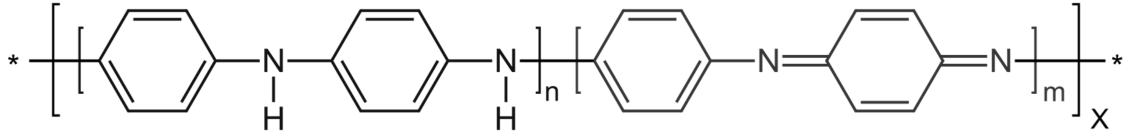
Polyaniline



- Already used as coating for MPLs in some papers[7]
  - hydrophobic
  - Low temperature PEMFCs
- Used in HT-PEMFC as nanowire MPL[8]
- Unclear environmental impact

[7] F. Tritscher, A. Mularczyk, A. Forner-Cuenca, V. Hacker, M. Bodner, *Mater. Adv.* **2023**, *4*, 2573.
[8] X. Fu, et al., *International Journal of Hydrogen Energy* **2021**, *46*, 8802.