FURTHER-FC

Clean Hydrogen Partnership

Co-funded by the European Union

Further **U**nderstanding **R**elated to **T**ransport limitations at **H**igh current density towards future **E**lect**R**odes for **F**uel **C**ells

Electrochemical Characterization

(**Jens Mitzel**, CEA, **DLR**, PSI, ICL)

Outline

Electrochemical characterization methods in FURTHER-FC for:

- Performance benchmarking
- Investigation of transport properties
- Evaluation of degradation behavior

Outline

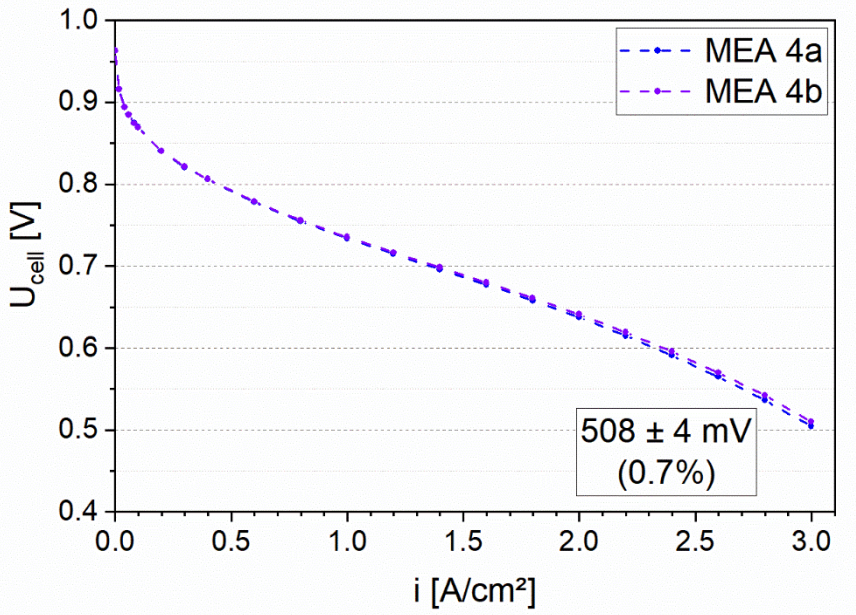
Electrochemical characterization methods in FURTHER-FC for:

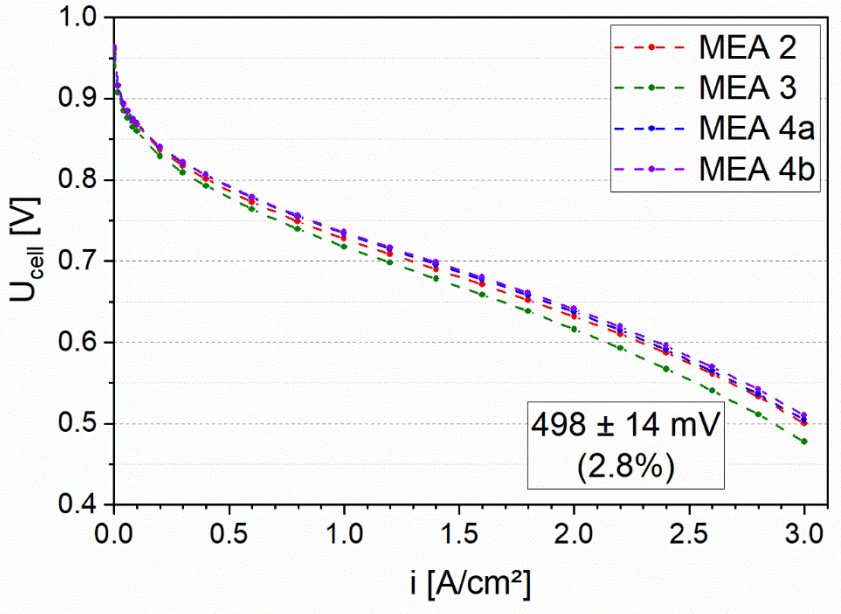
- **Performance benchmarking**
- Investigation of transport properties
- Evaluation of degradation behavior

Reproducibility and Comparability

- Reliability of test results is key for understanding transport phenomena
- Requires high reproducibility in each lab regarding:
  - Characterization setup
  - Applied test procedures

  -> proven



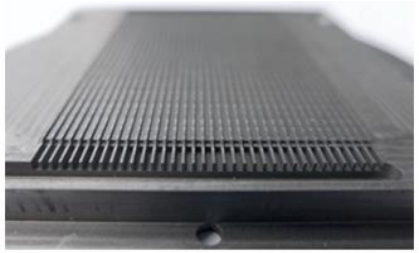


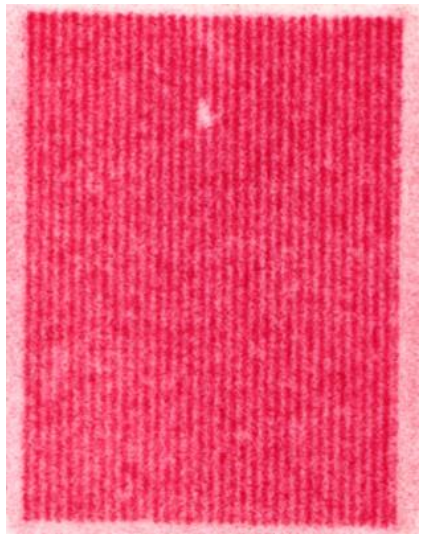
- Requires high reproducibility of CCM manufacturing:
  - **using the same manufacturing batch**
  - Between different batches
- CCMs from the same batch used for in-depth analysis in different facilities

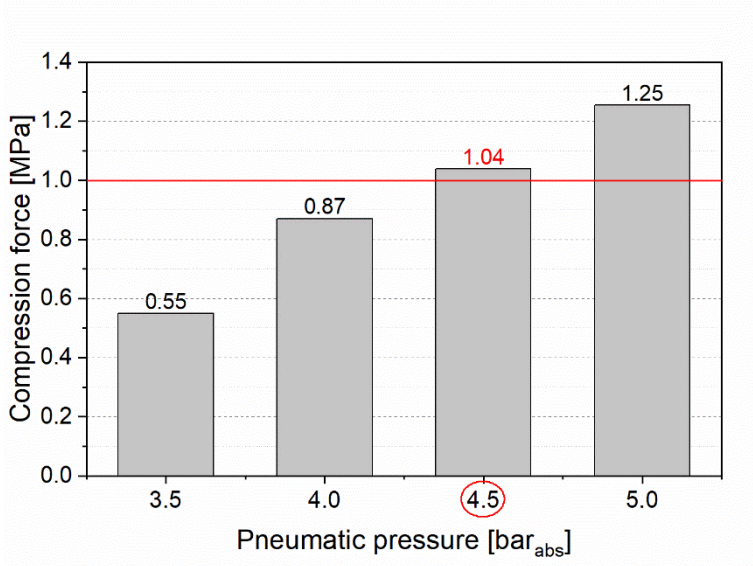
Reproducibility and **Comparability**

technical cell

differential cell





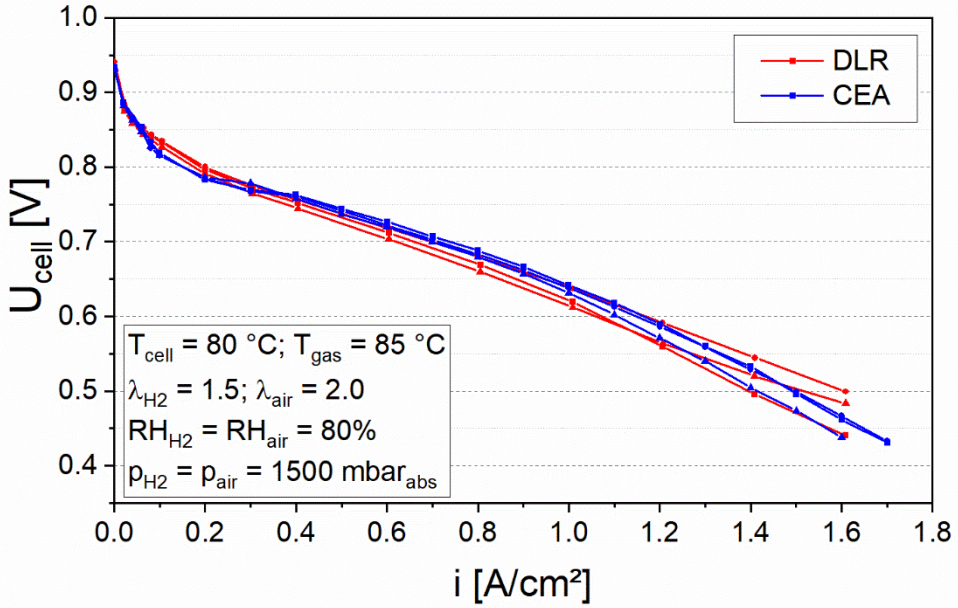


- High importance to achieve comparability of test results between different facilities
- Important parameters to achieve comparability:
  - Harmonized flow field design
  - Same MEA **compression force**
  - Identification of differences in setup (channel length, sensor position, cell cooling,…)

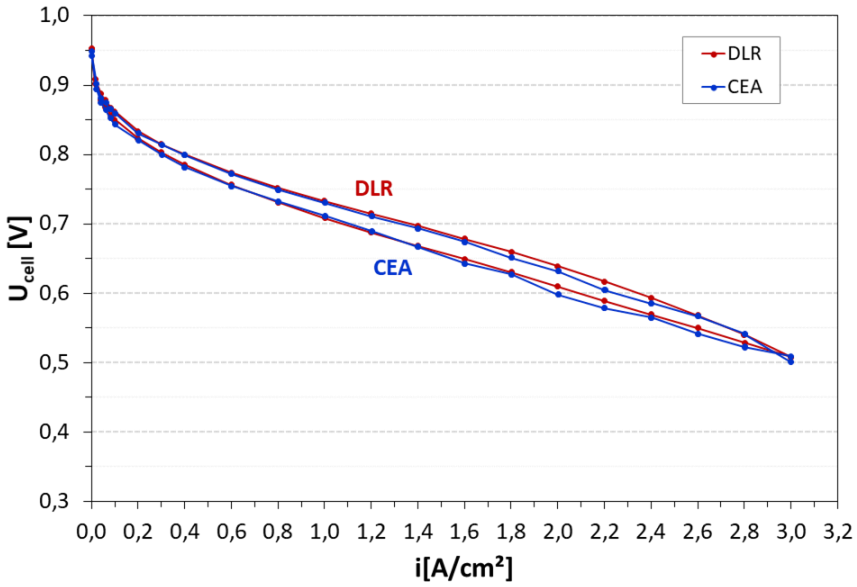
Reproducibility and **Comparability**

- Optimization and harmonization of test equipment and test protocols required
- High comparability between the partners can be assured in FURTHER-FC using:
  - technical cells: performance and durability validation
  - differential cells: characterization of transport properties

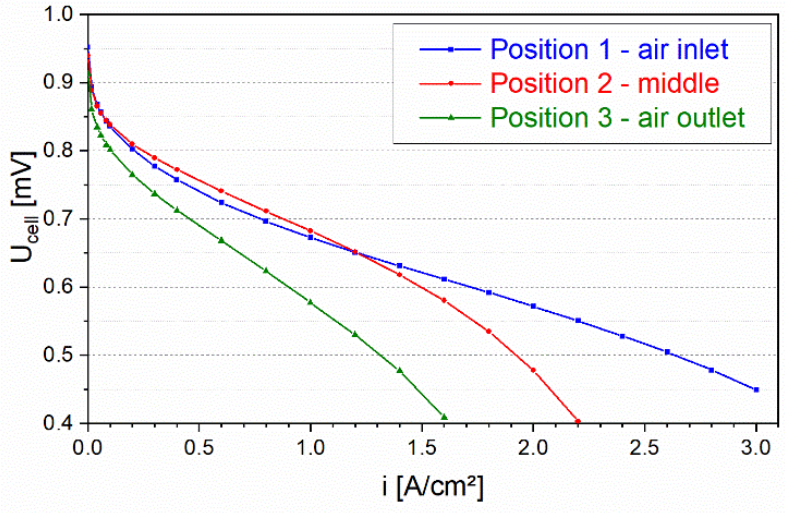
technical cell

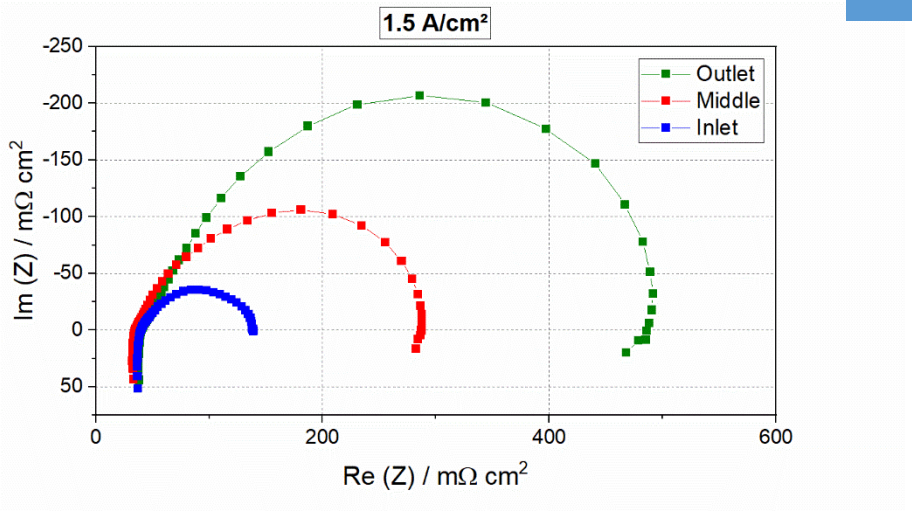


differential cell



Performance validation
Impact of stack position

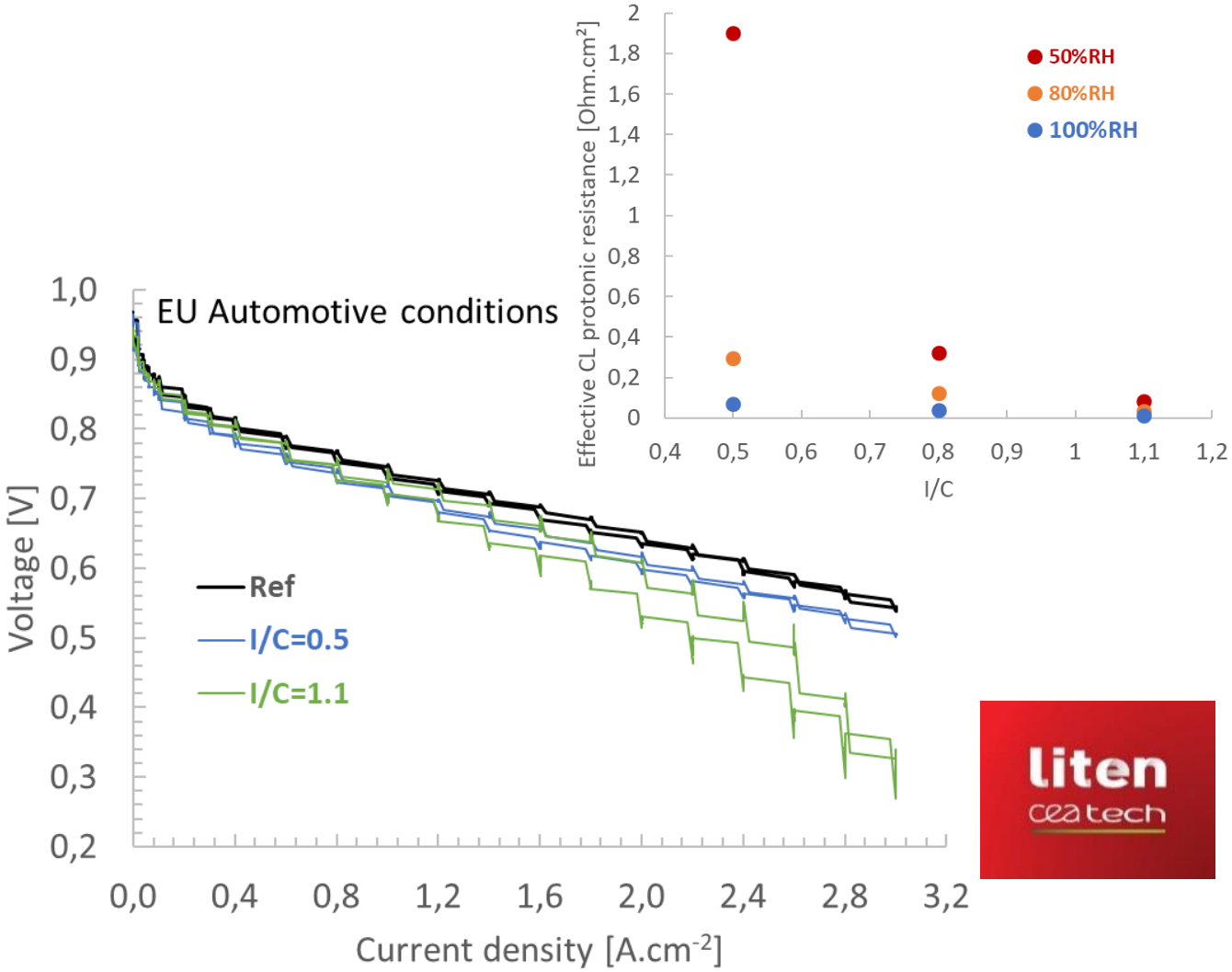




- Impact of transport properties depends on operating conditions
- Operating conditions in automotive stacks vary significantly along the flow field
- Differential cell conditions can mimic conditions in different positions
- Significant impact by:
  - **Oxygen concentration**
  - Cell temperature
  - Relative humidity

	Step1: Air inlet	Step 2: Middle	Step3: Air outlet
Cell temperature [°C]	68	77	80
H_2/O_2 content in dry gas at anode/cathode [%]	100/20.8	100/13.6	100/7.7
Total Pressure anode / cathode [bar_{abs}]	2.25/2.3	2.3/2.1	2.5/1.9
RH anode / cathode [%]	100/53	100/100	50/100
Gas inlet temperature anode/cathode [°C]	75/75	84/84	87/87
Min. H_2 / O_2 stoichiometry for 4 cm long channel [-]	8/8	8/5.25	8/3
Min. gas flow according to current density [A/cm²]	3	3	3

Performance validation
Impact of ionomer content



- Reference CCM (I/C=0.8) shows highest performance
- Lower ionomer content (I/C=0.5) decreases performance and activity
- Higher ionomer content (I/C=1.1):
  - decreases performance and activity
  - increase transport resistance at high current density
- Effective proton transport resistance decreases
  - with increasing I/C ratio
  - with increasing relative humidity

Outline

Electrochemical characterization methods in FURTHER-FC for:

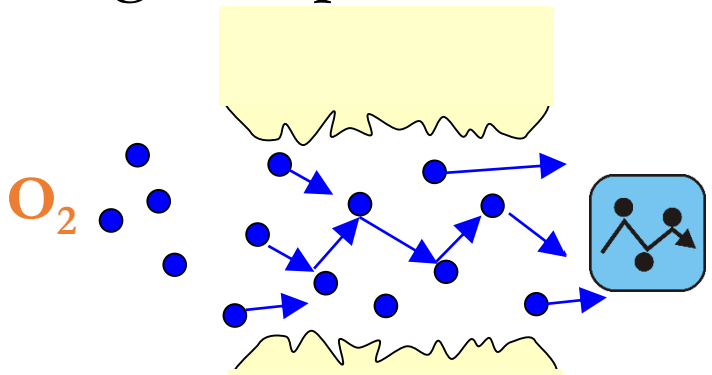
- Performance benchmarking
- **Investigation of transport properties**
- Evaluation of degradation behavior

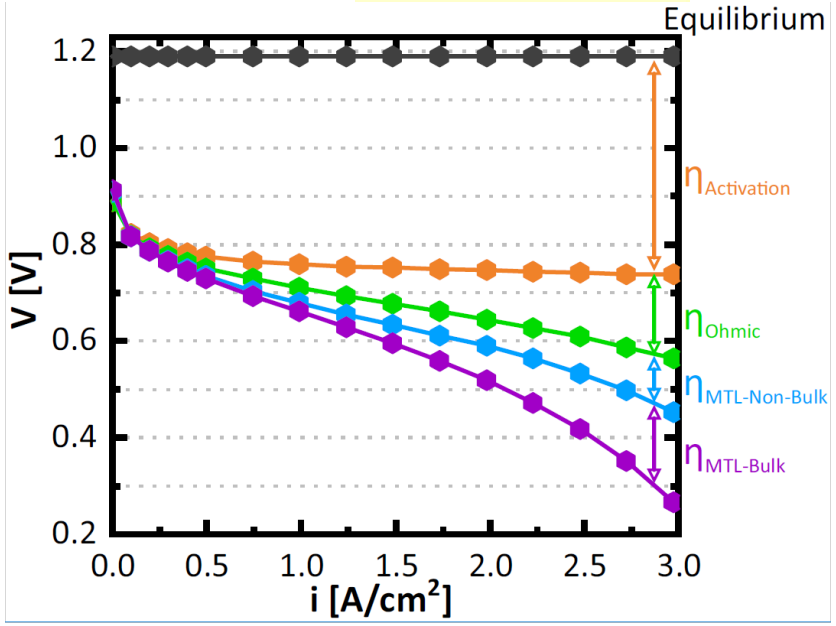
Pulse Gas Analysis (PGA) Method

~~Convection~~

~~By bulk diffusion~~

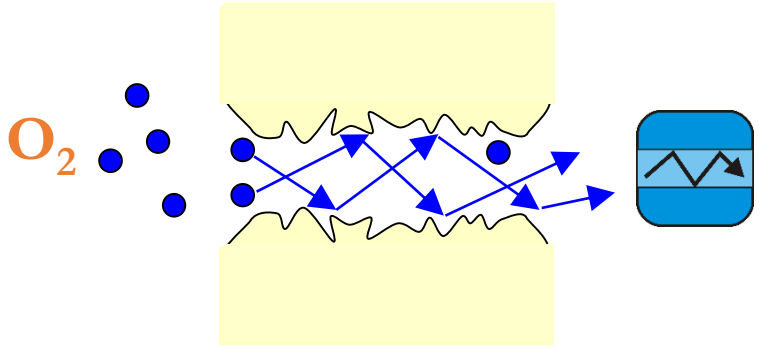
- large size pore



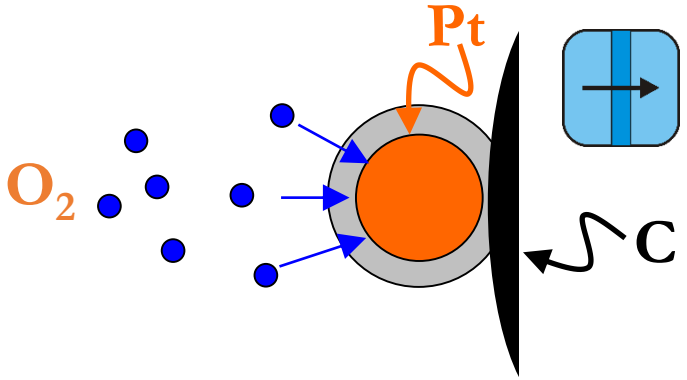


By non-bulk diffusion

- small size pore (Knudsen)



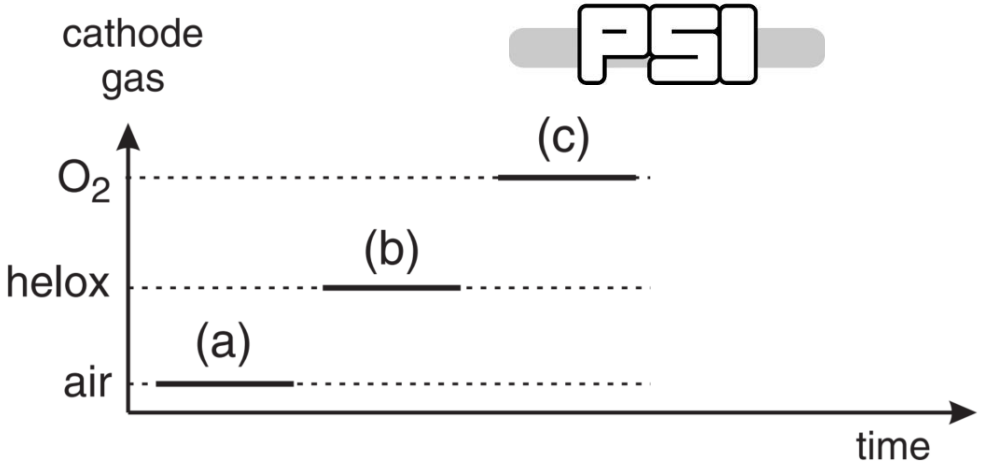
- thin film (ionomer or water)

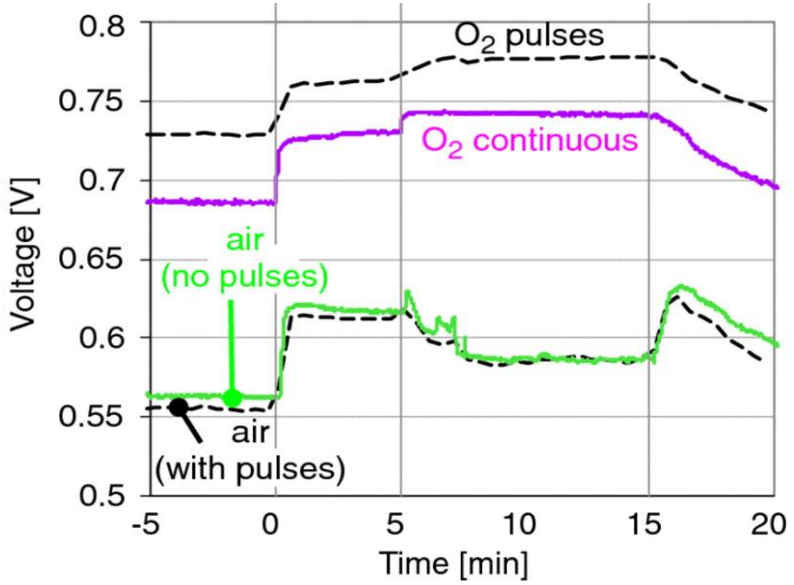


P. Boillat et al., *J. Electrochem. Soc.* **159**, F210 (2012)

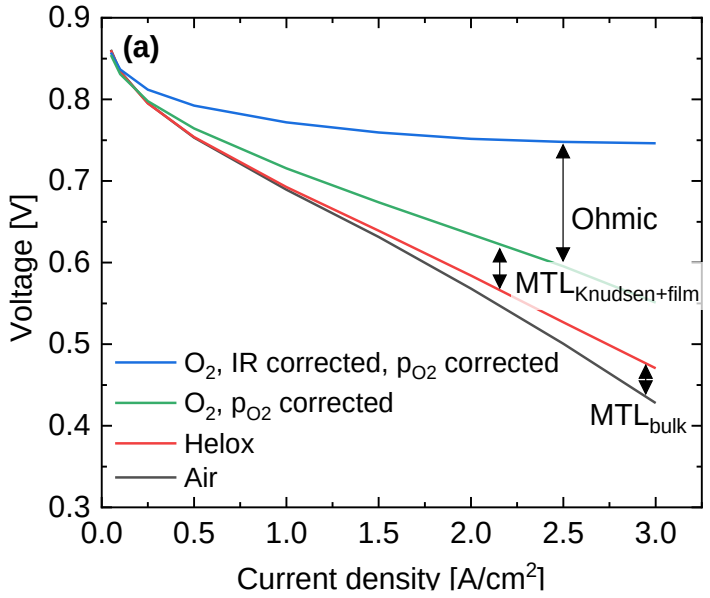
Pulse Gas Analysis (PGA) Method

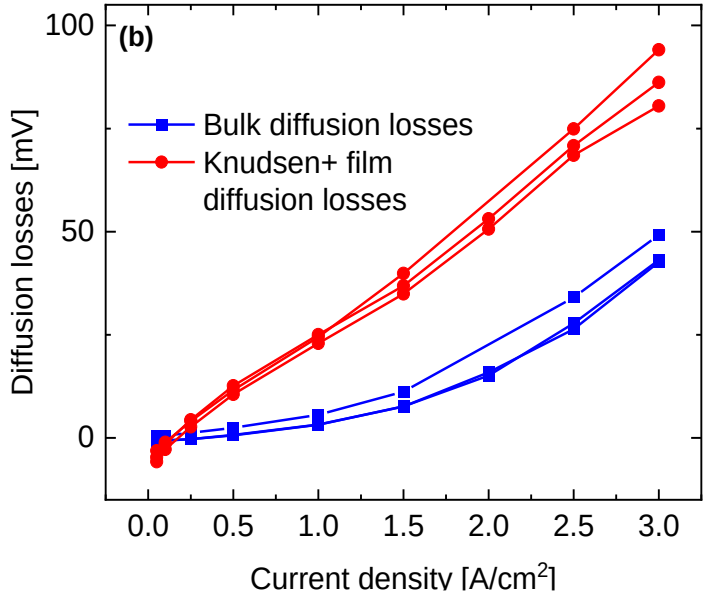
- Helox/oxygen voltage gain measurement for evaluation of mass transport losses
- Classical measurements suffer from artifacts due to:
  - Different physical properties of air, helox and oxygen
  - Different water management
  - Different oxidation states of the catalyst and electrode potential
- PGA only applies helox /oxygen for short periods and operates mainly on air
  - Enables more reliable break down of transport losses

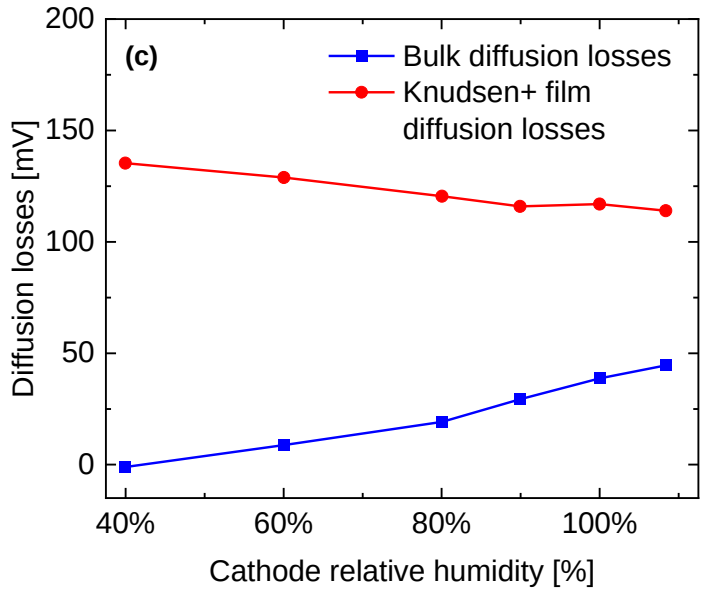




Pulse Gas Analysis (PGA)
Impact of current density





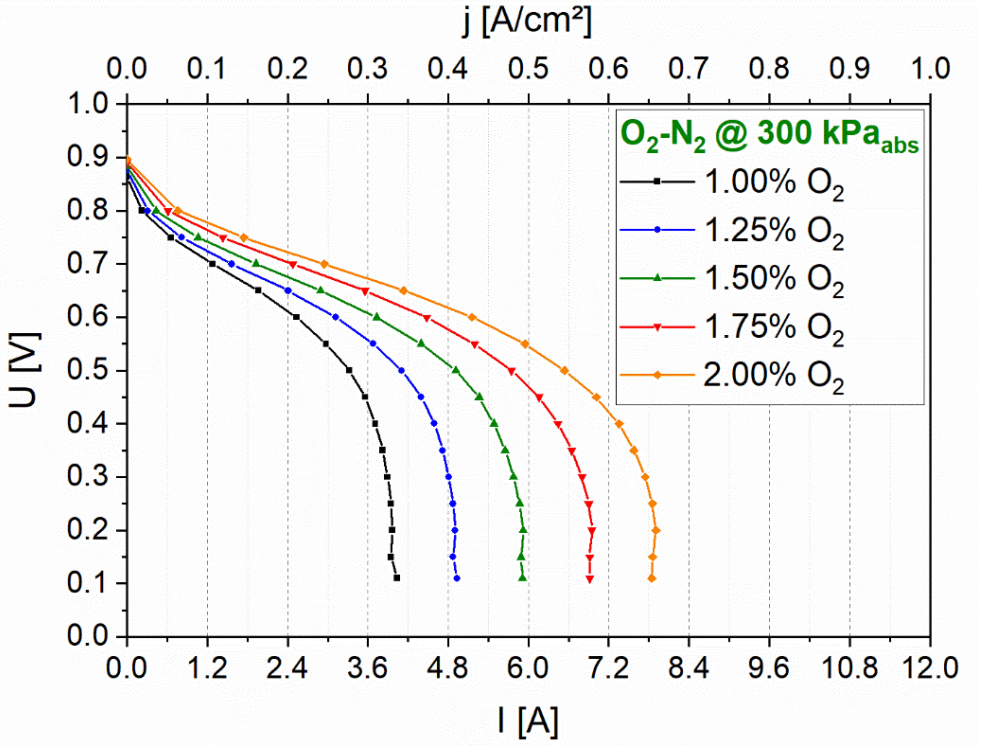


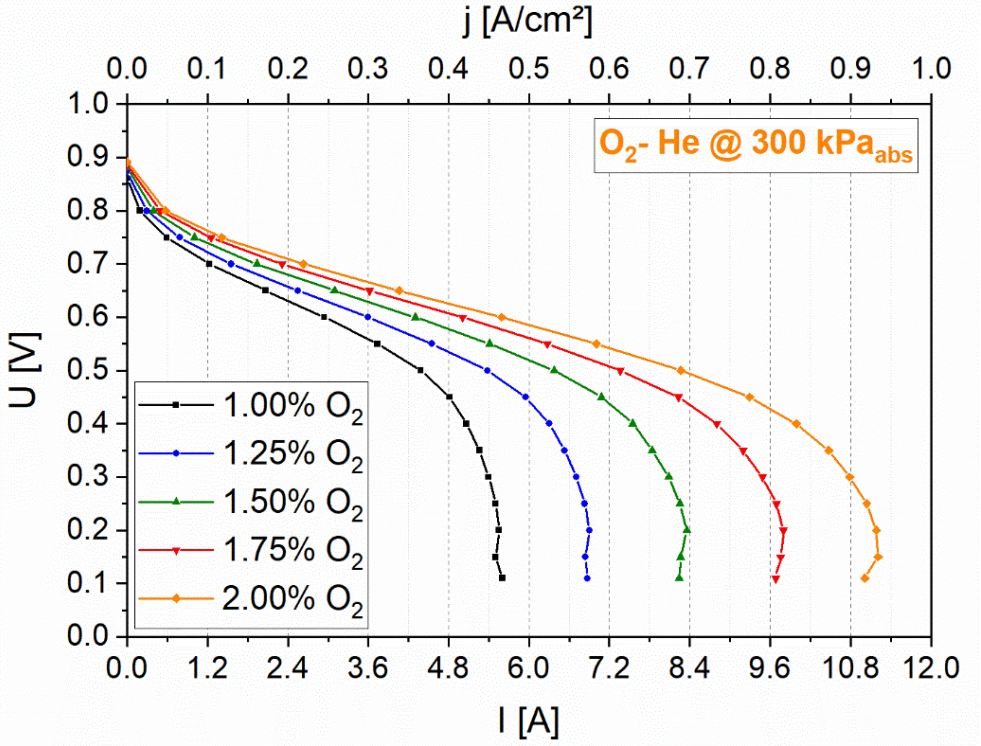
Bulk diffusion losses only observed at high cathode humidity

« Knudsen+film » diffusion losses dominate, in particular at low humidity

Limiting Current Analysis (LCA)
Method

- Potentiostatic limiting current analysis at low oxygen concentration
- Variation of oxygen concentration, total pressure and carrier gas (oxygen diffusion resistance)

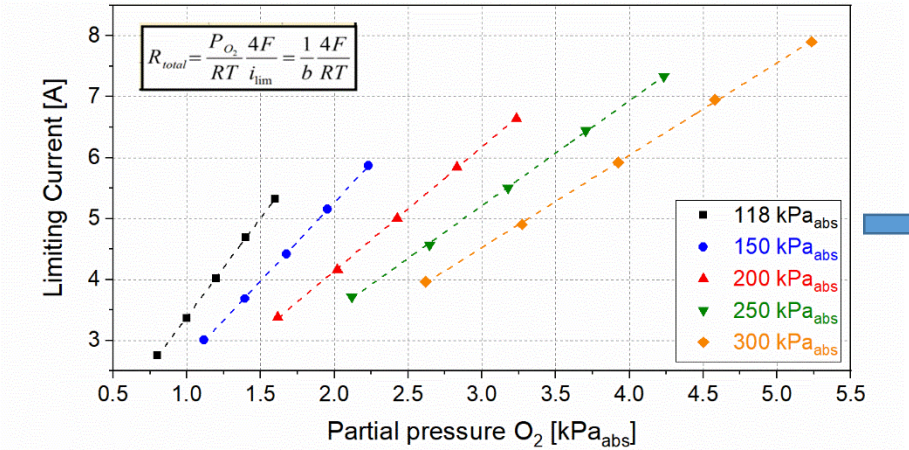


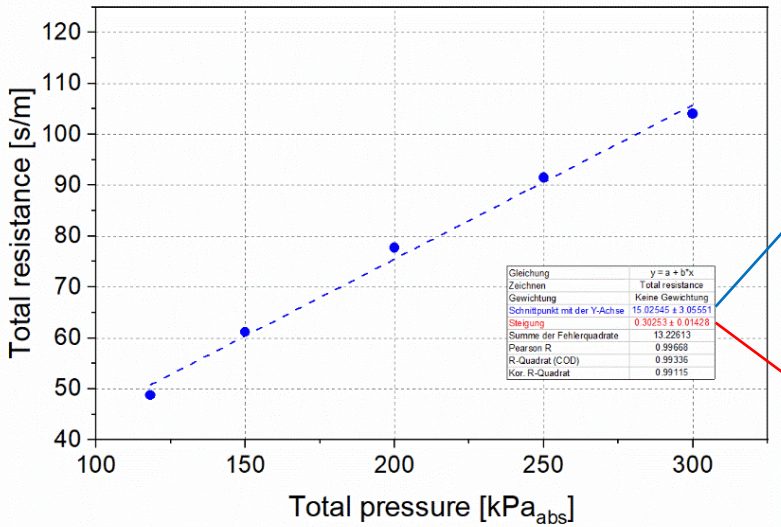


Limiting Current Analysis (LCA)
Method

$$R_{\text{total}} = R_{dif,P} + R_{dif,0} + R_{\text{other}}$$

$R_{dif,P}$: pressure dependent resistance (molecular diffusion), $R_{dif,0}$: pressure independent (mostly Knudsen diffusion), R_{other}: transport resistance through other transport processes





$R_{dif,0}$: Mostly Knudson diffusion:

- **y-axis intercept**
- **p-independant**
- **In CL / MPL**

$R_{dif,P}$: Molecular diffusion:

- p-dependant
- Slope
- Mainly GDL backing (+ CL / MPL)

- Enables separation of different oxygen transport mechanisms
- Can improve understanding of oxygen transport effects in different MEA components (GDL, MPL, CL)

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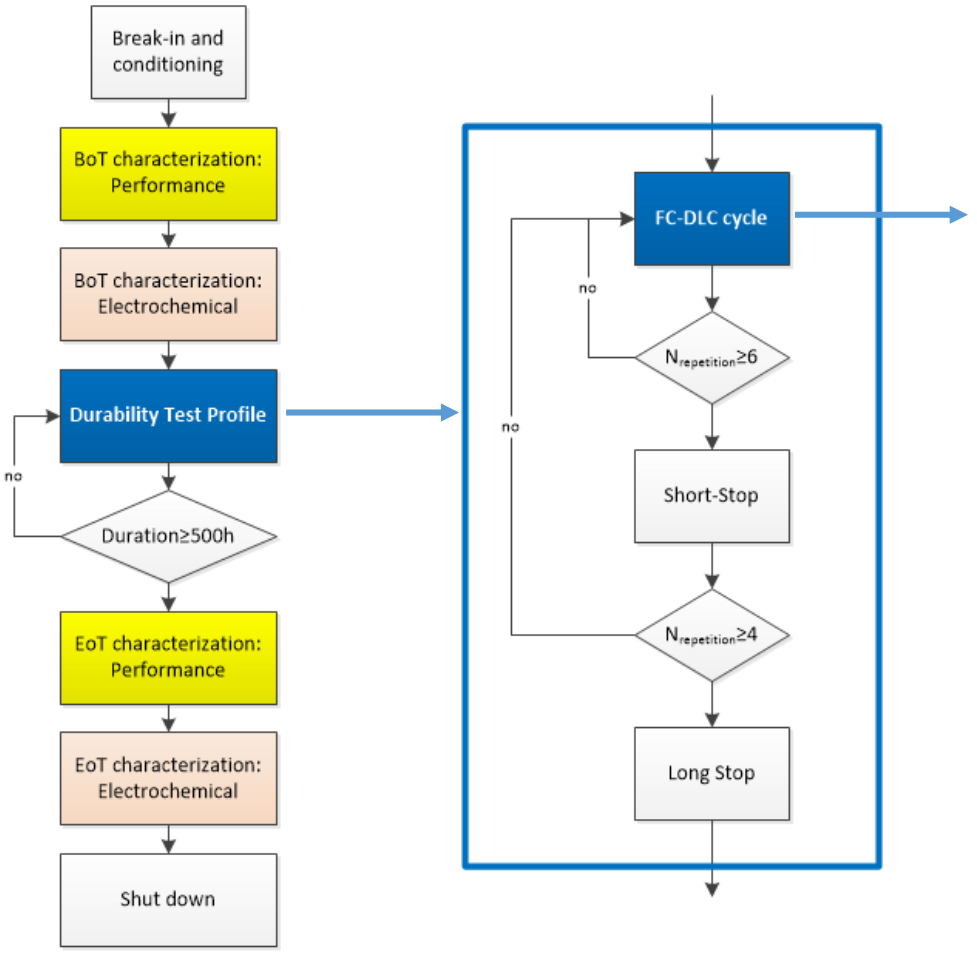
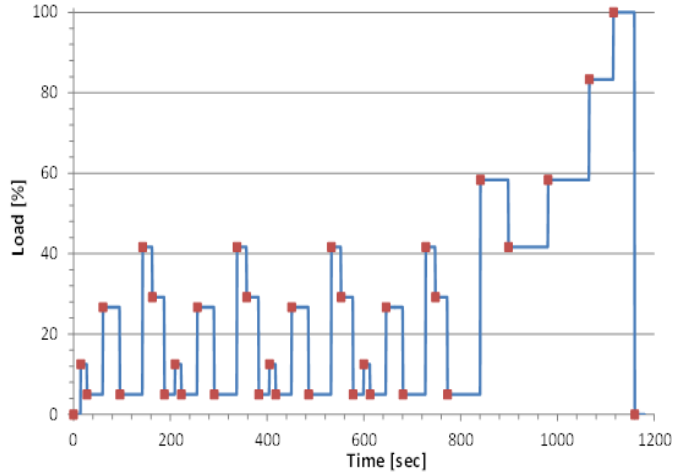
- **Evaluation of degradation behavior**

MEA Durability
Test profile and conditions

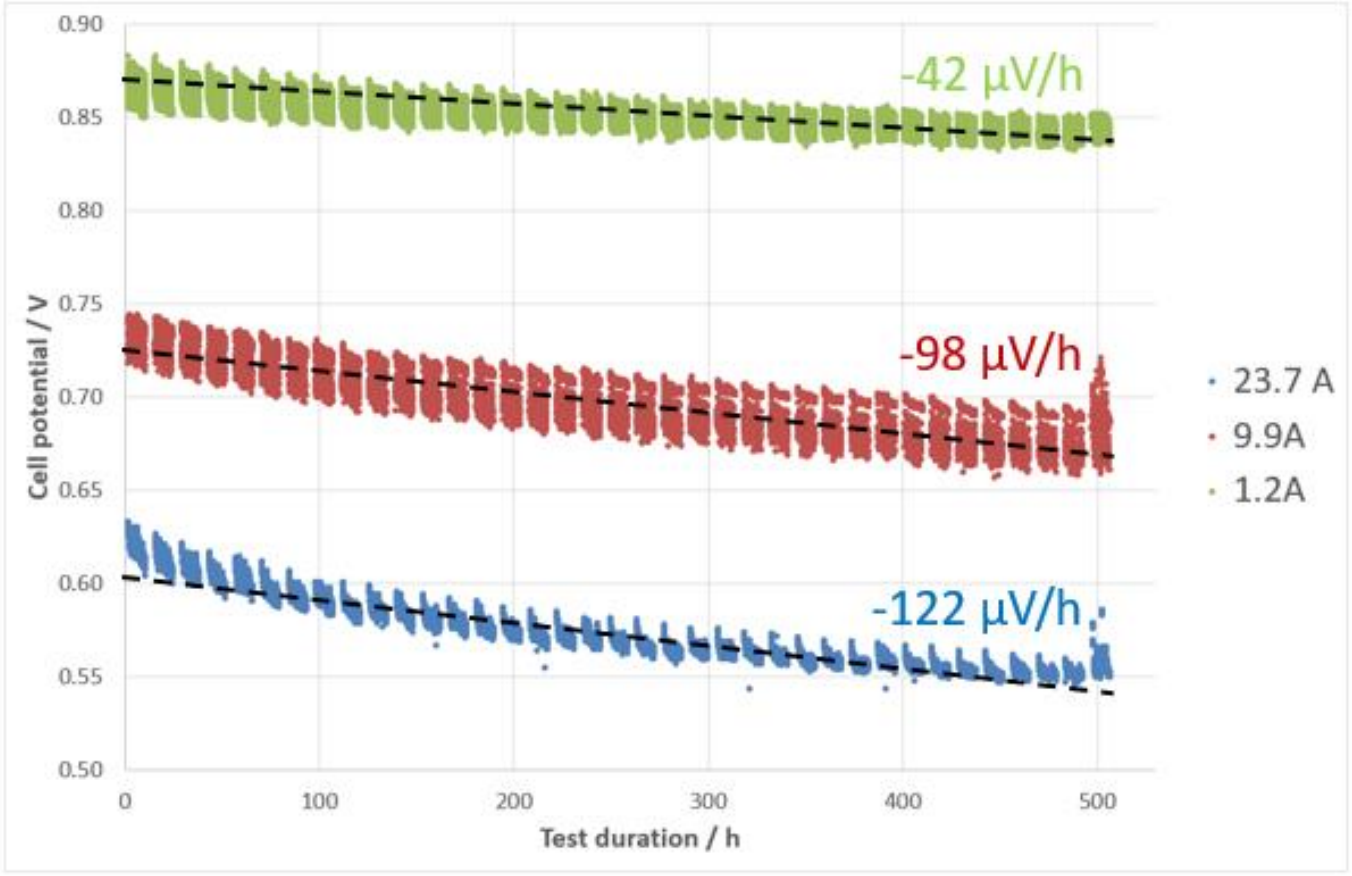


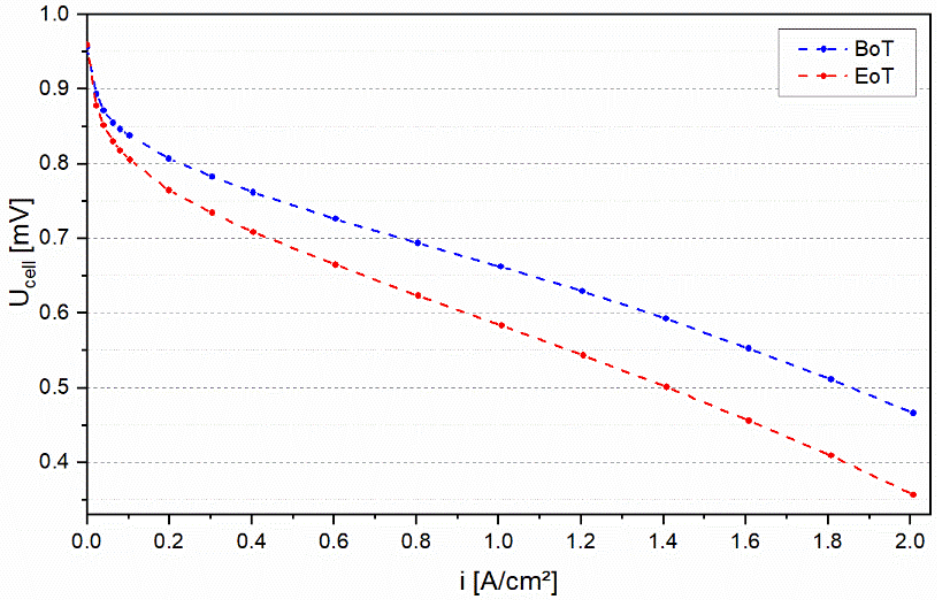


	Automotive test conditions
Cell temperature [°C]	80
Gas composition	H_2/Air
Pressure anode / cathode [bar_{abs}]	2.5/2.3
Gas inlet temperature anode/cathode [°C]	85/85
RH anode / cathode [%]	50/30
Stoichiometry anode / cathode [-]	1.3/1.5
Min. gas flow according to current density [A/cm²]	0.4

- Durability test using EU-harmonized test protocol and automotive conditions
- **Focus on changes of transport properties over time**

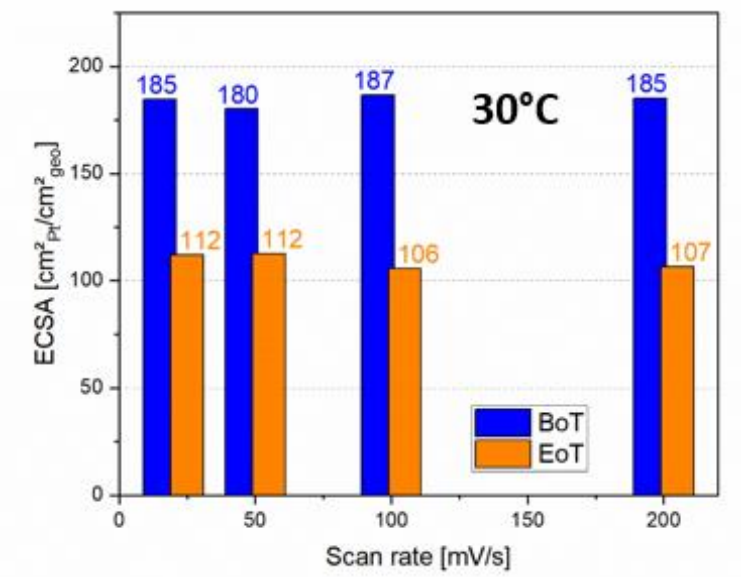
MEA Durability
Durability of reference MEA

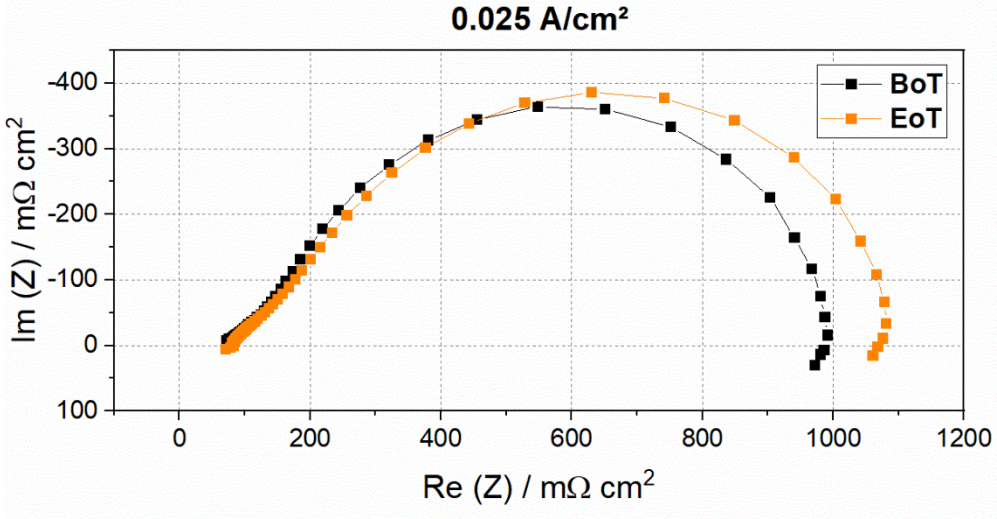


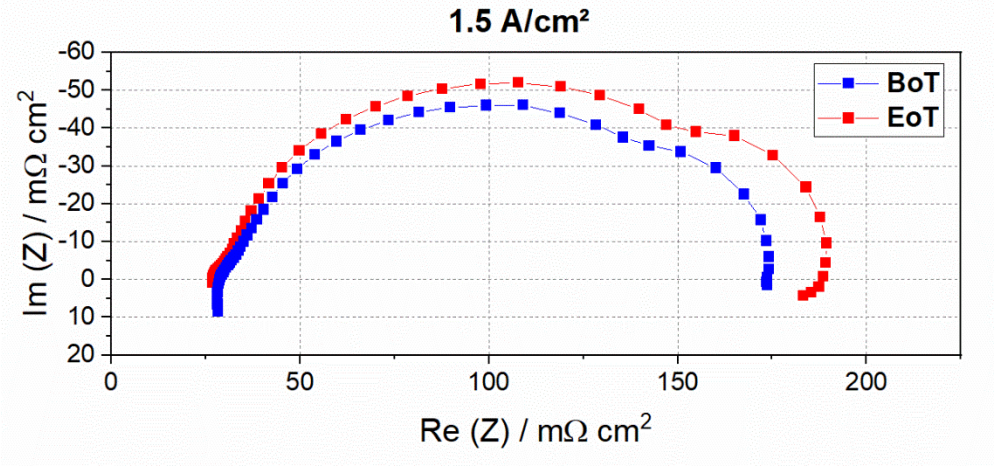


- Significant performance decay during durability test
- Most severe impact at high current density
- Polarization curve suggest impact by catalyst activity

MEA Durability
Durability of reference MEA







Obvious reasons for performance loss over time

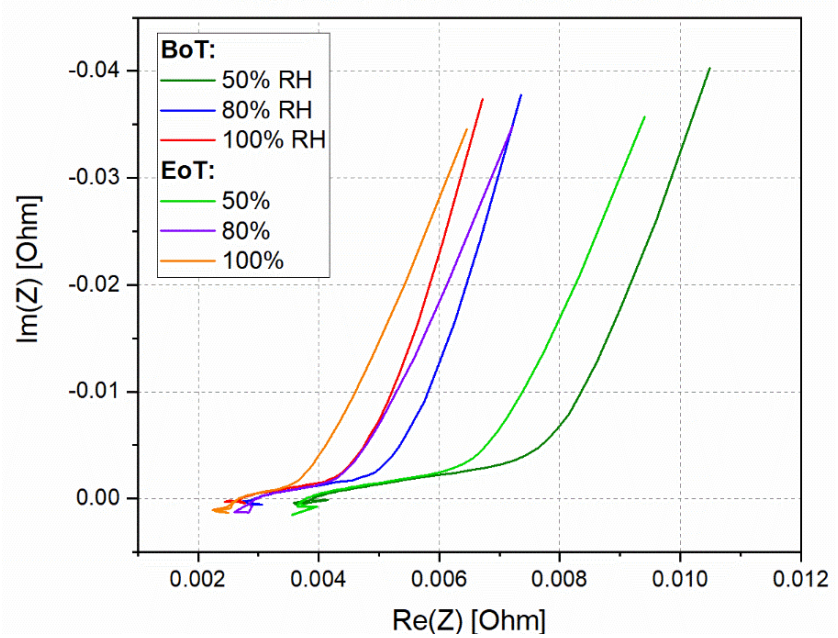
- Significant decrease of ECSA and reduced access to catalytic active sides
- Increased polarization resistance
- **Increase of transport resistance**

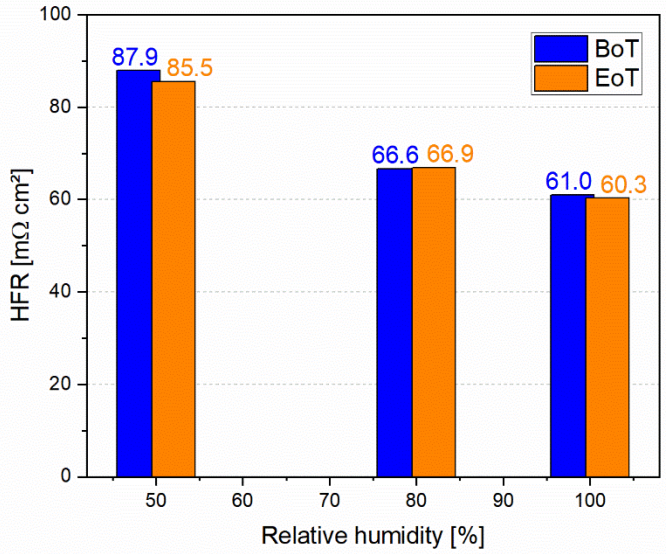
  -> Under investigation

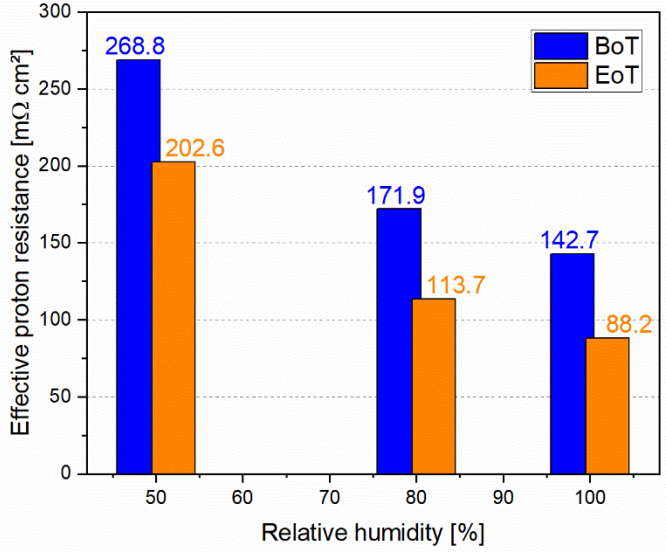
MEA Durability
Durability of reference MEA

Interesting to note:

- HFR seems to be not affected by durability test
  - Only minor impact of membrane degradation
- Effective proton resistance decreased over time
  - Decreased hydrophobicity and higher water content in catalyst layer?



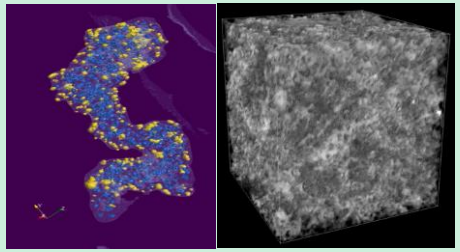




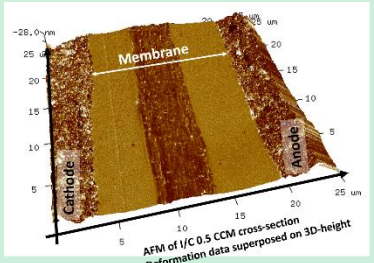
Thank you for your attention.
Your questions are welcome!

Co-funded by the European Union

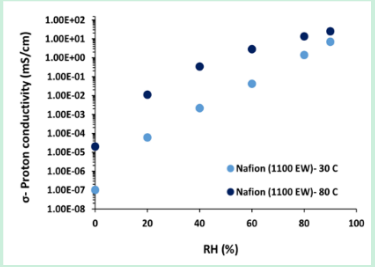
Multiscale characterization



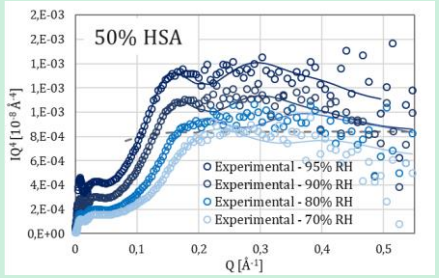
3D TEM and FIB/SEM



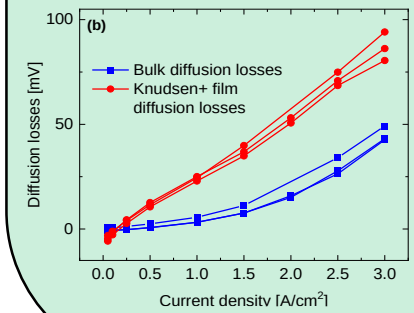
AFM



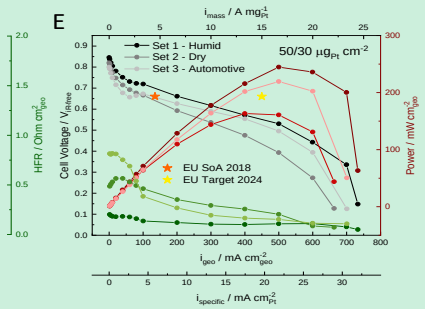
Ionomer transport properties



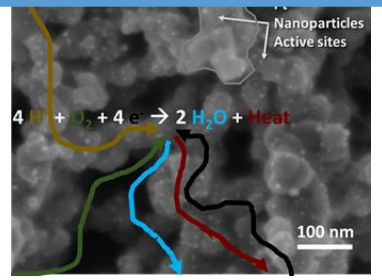
Small Angle Scattering

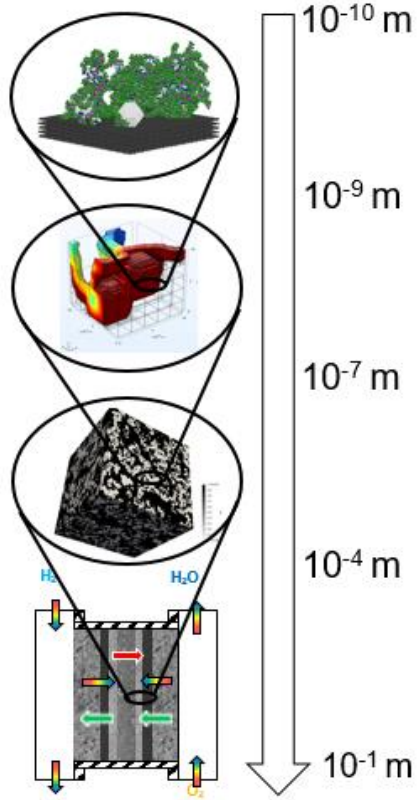


Mass transport losses



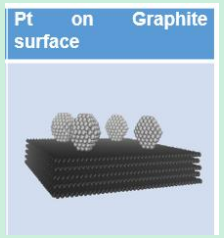
Ultra-thin electrode

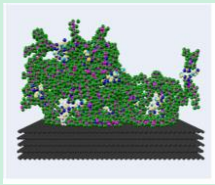


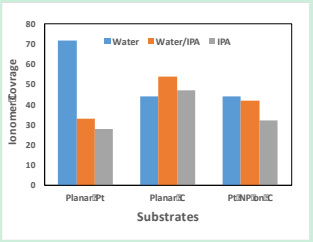


Multiscale modeling

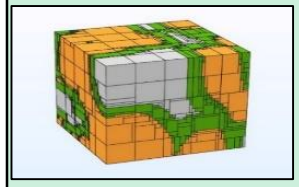
Ionomer film scale



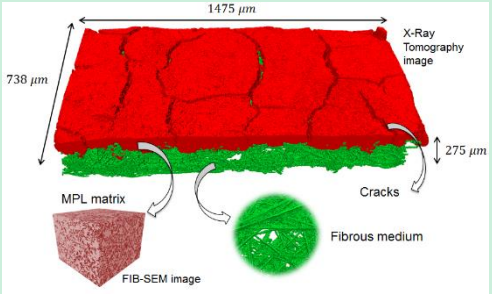




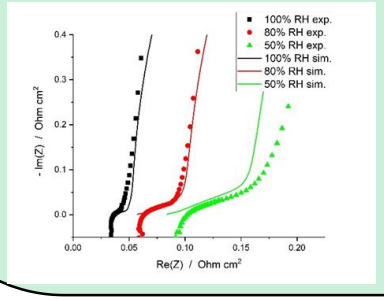
Sub μm scale

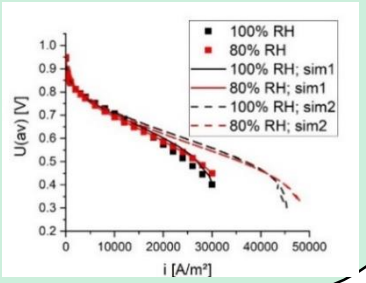


CCL scale



Cell scale





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