MAIN DEGRADATION MECHANISMS IN PEMFC AND HOW TO ANALYZE THEM

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DLR

Content

- Introduction to fuel cell research at DLR
- Durability requirements
- Durability testing
- Reversible degradation voltage losses
- Irreversible degradation mechanisms
  - Electrode degradation
  - Membrane degradation
  - GDL degradation
  - Local degradation analyses and contaminants
- Summary

DLR – Deutsches Zentrum für Luft- und Raumfahrt eV.

- 10.000 employees, 55 institutes, 30 sites, headquarters Cologne
- Topics: Aerospace, Energy, Transport, Security , Digitalisation
- Site in Stuttgart with focus on energy research
- Institute of Engineering Thermodynamics with sites in Stuttgart, Oldenburg, Ulm, Hamburg, Köln
  Director André Thess

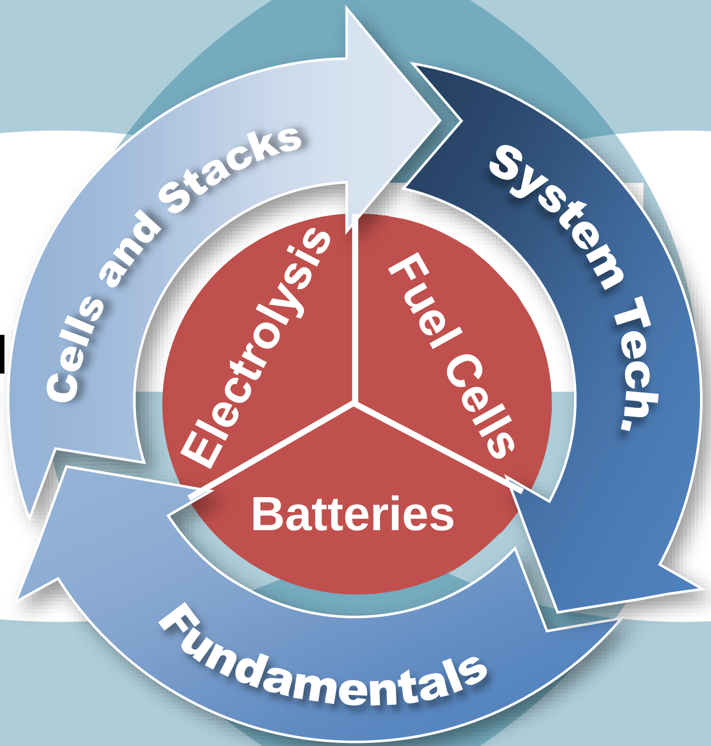
Energy storage and energy conversion based on renewable energies

Institute of Engineering Thermodynamics

Electrochemical Energy Technology @ DLR

MODELLING

- Multiscale
- Nano-, Micro- and Mesostructure
- Prediction and Design
- Digital Twin



EXPERIMENT

- Operando Diagnostics
- Quality Control Diagnostics
- Validation
- Performance
- Breakthrough Innovations

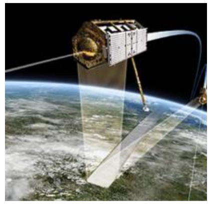
Applications

Energy

Transport

Aeronautics

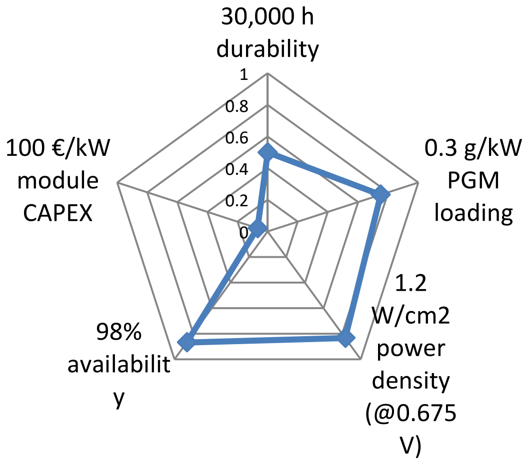
Space



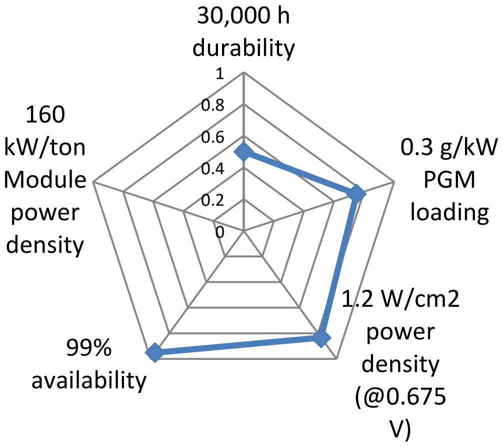
Three Departments: ECE, CEC, ESI

Current achievements and KPIs for PEMFC applications

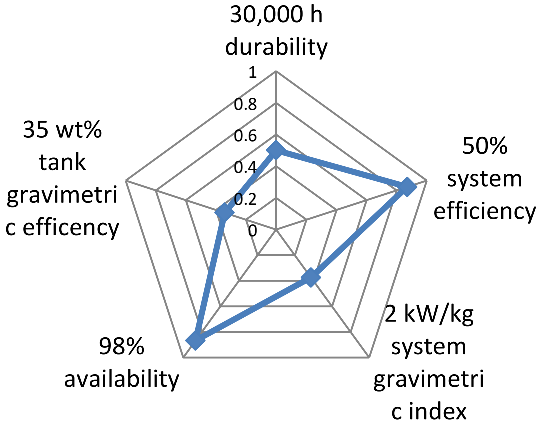
SoA vs HDV Targets 2030



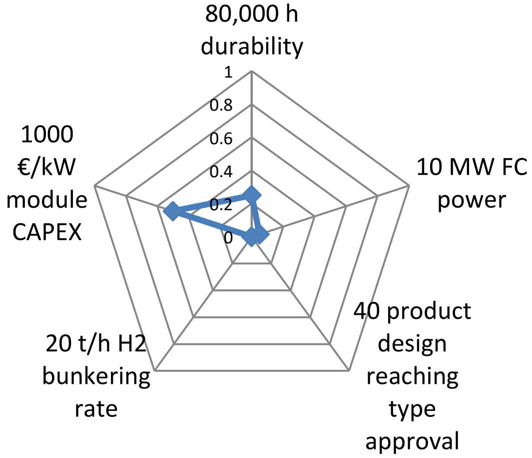
SoA vs Train Targets 2030



SoA vs Aviation Targets 2030

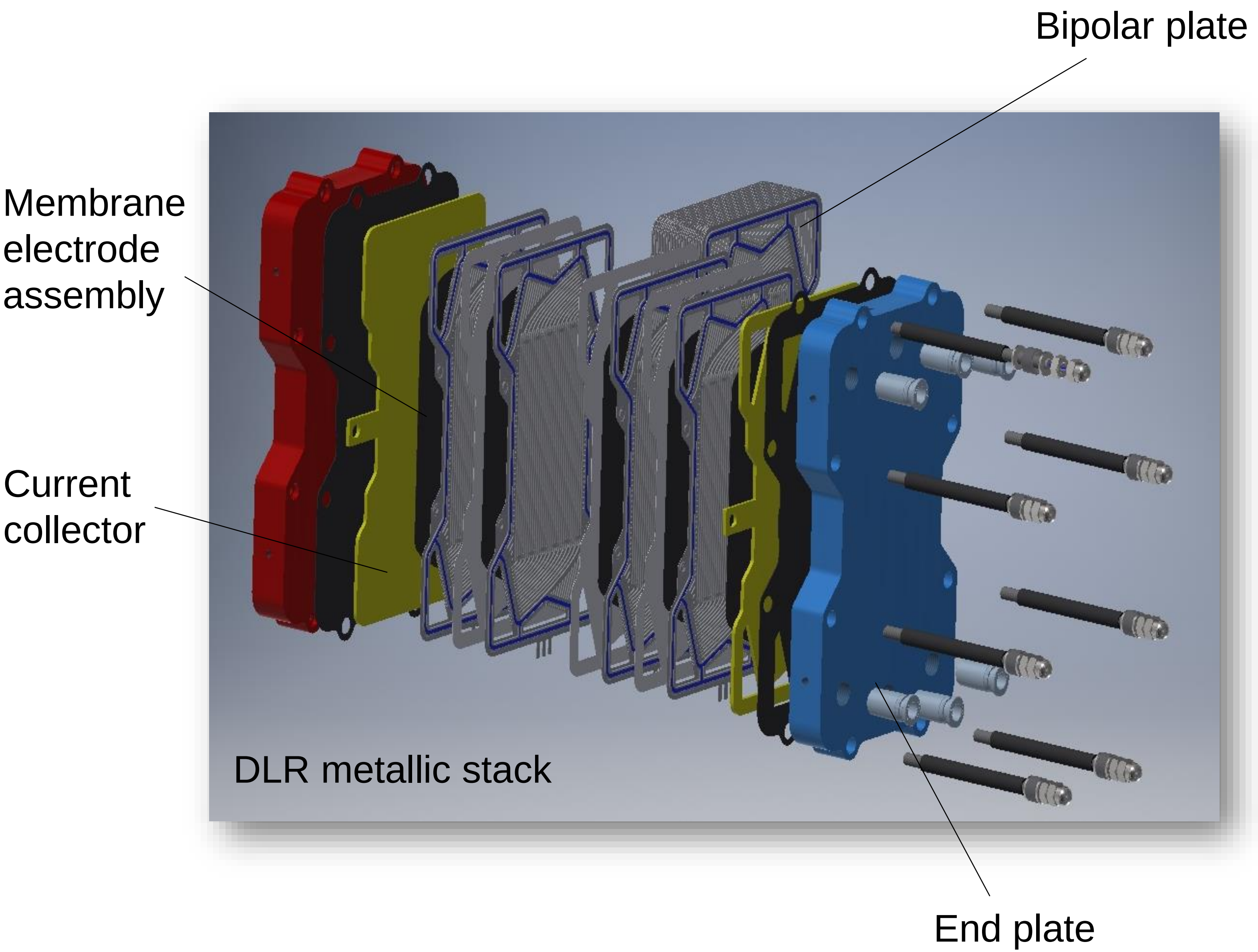


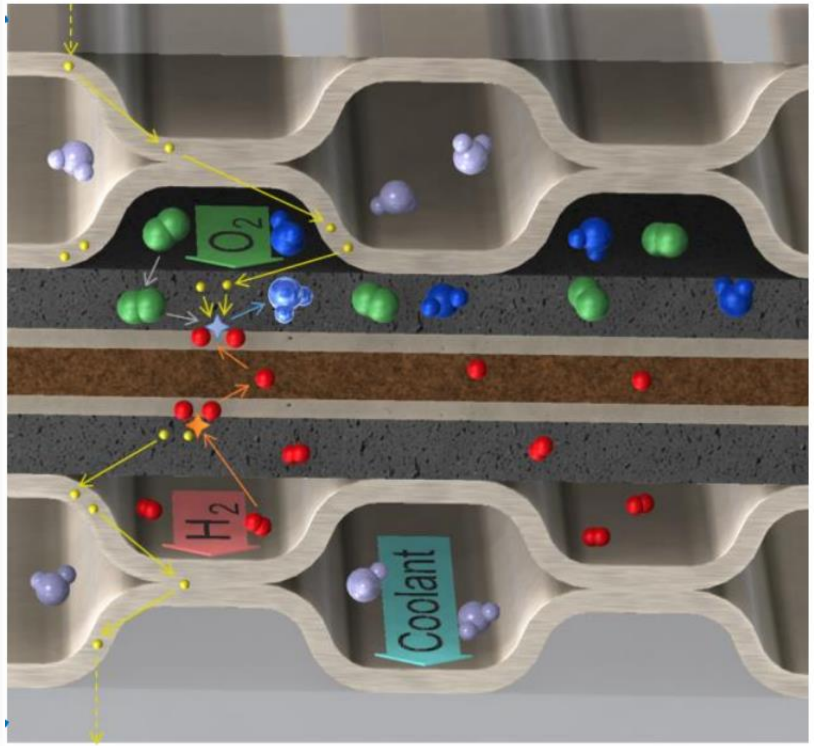
SoA vs Maritime Targets 2030



KPIs according to SRIA 2021-2027 of the Clean Hydrogen JU

PEMFC Stack



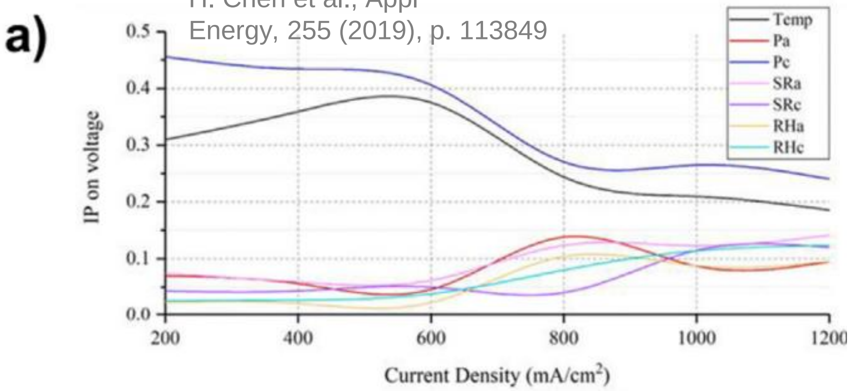


https://www.dolphin-fc.eu/fileadmin/user_upload/1_1_DOLPHIN_Workshop1_Objectives.pdf

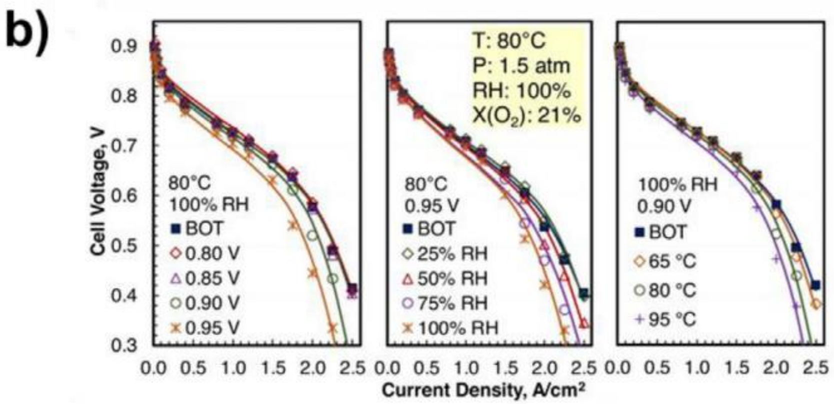
Challenges in reliable determination of degradation rates

Effects of operating parameters on cell voltage

H. Chen et al., Appl Energy, 255 (2019), p. 113849

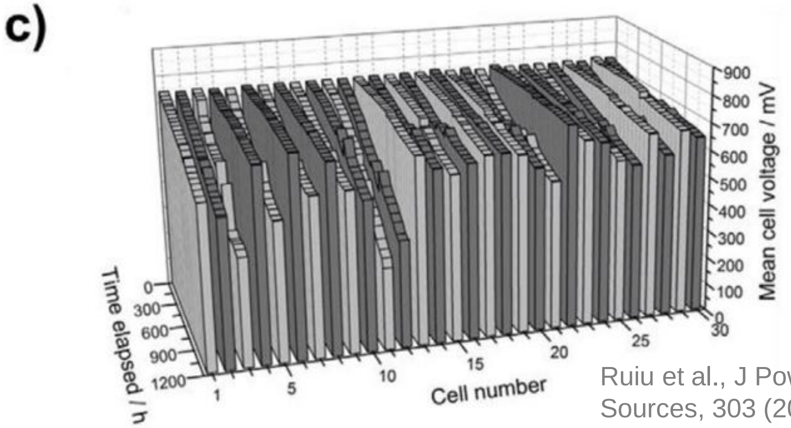


Effect of upper potential limit, relative humidity, and cell temperature on degradation (30k cycles)



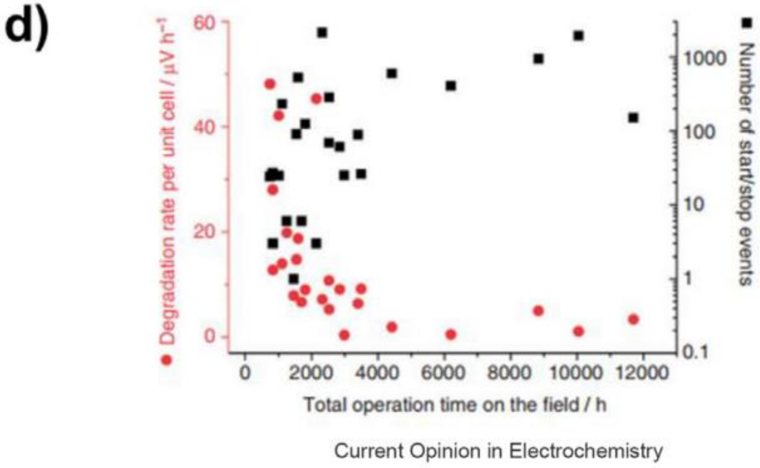
R.K. Ahluwalia et al., J Electrochem Soc, 164 (2017), pp. F306-F320

Distribution of voltage decay during a long-term test



Ruiu et al., J Power Sources, 303 (2016), pp. 257-266

Variation of the degradation rate per unit cell versus time

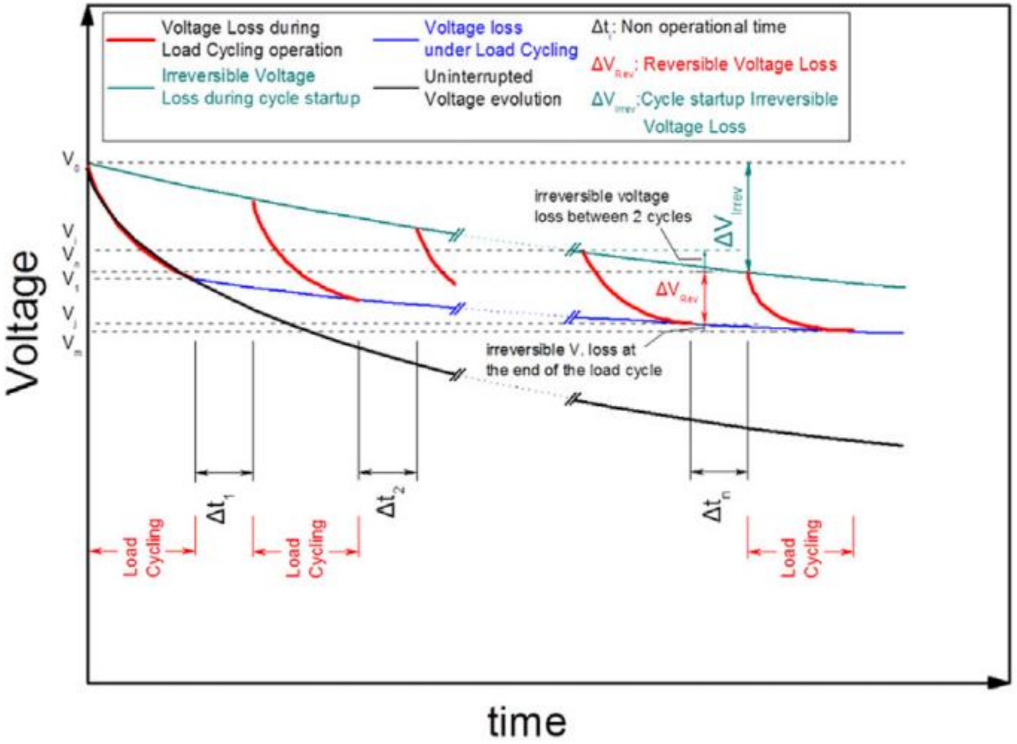


L. Dubau et al., Interdisciplinary Reviews-Energy and Environment, 3 (2014), pp. 540-560

Q. Zhang et al., Current Opinion in Electrochemistry, 31, 2022, 100863

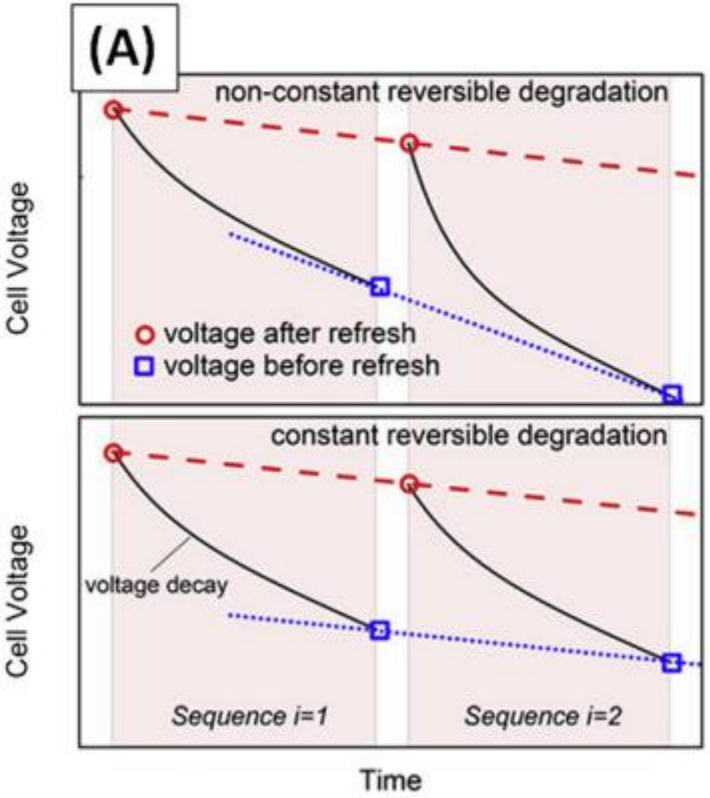
Challenges in reliable determination of degradation rates

Definition of reversible and irreversible voltage losses

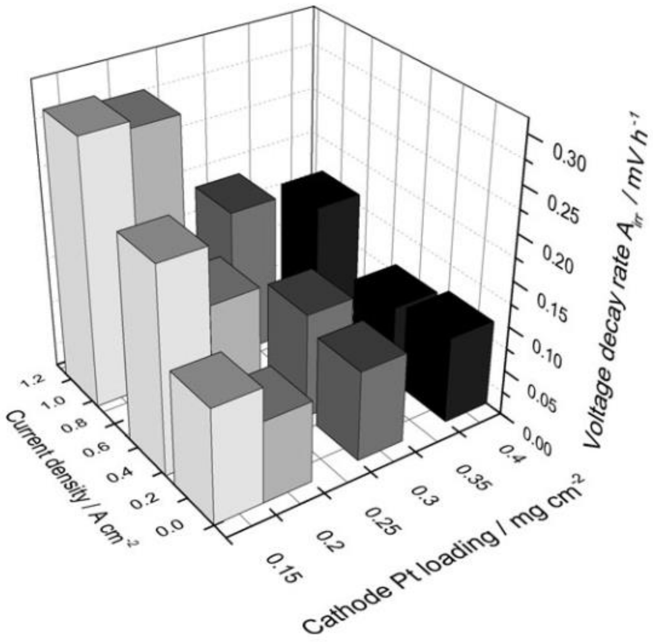


G. Tsotridis, et al. JRC Science for Policy report (2015), p. 27632

Reversible and irreversible losses depend on material properties and operation conditions



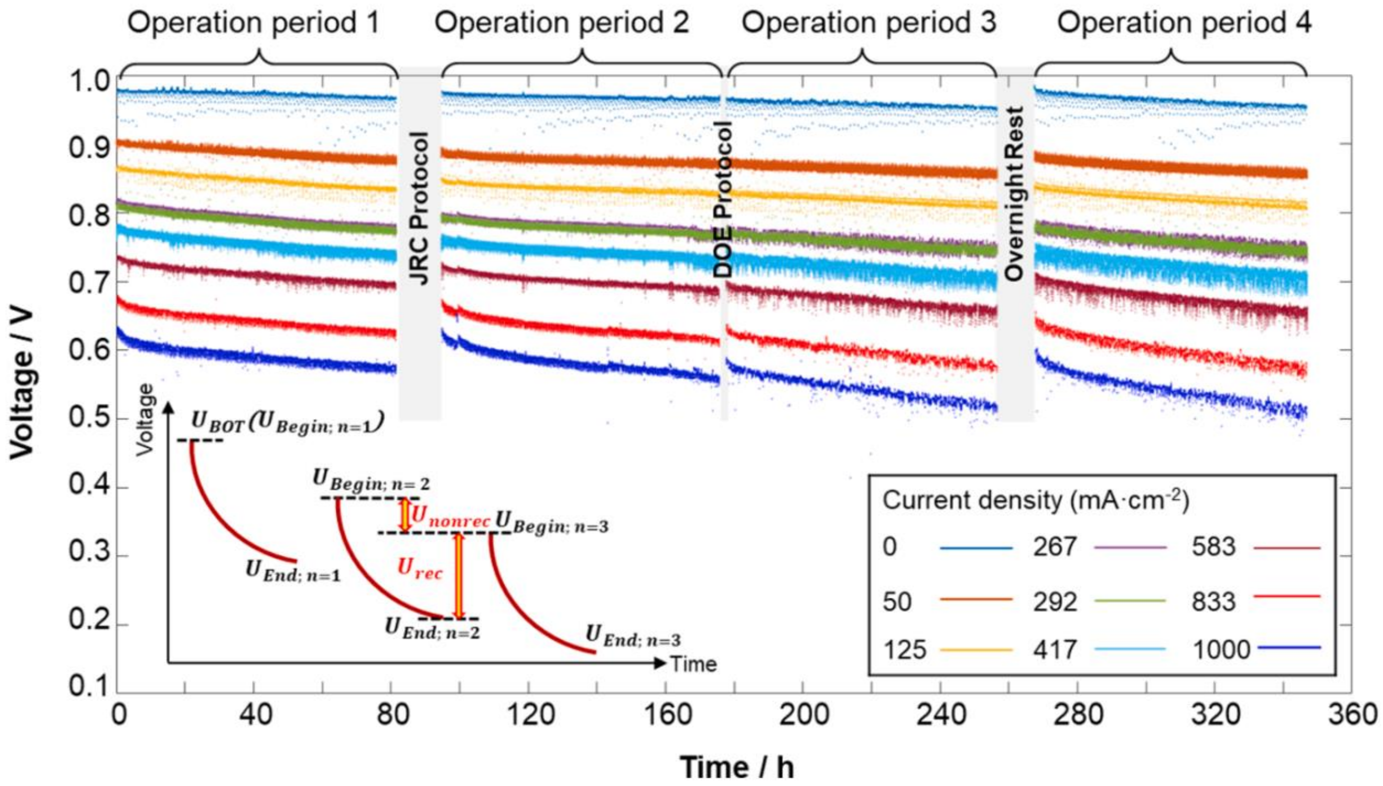
P. Gazdzicki et al., J Power Sources 327 (2016) 86

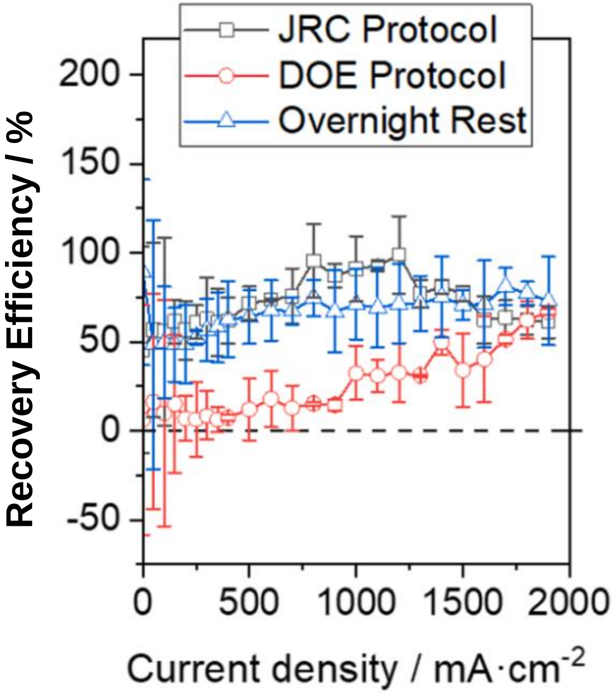


P. Gazdzicki et al., Fuel Cells, 18 (2018) 270

Challenges in reliable determination of degradation rates

Different recovery procedures used to discriminate irreversible/reversible degradation

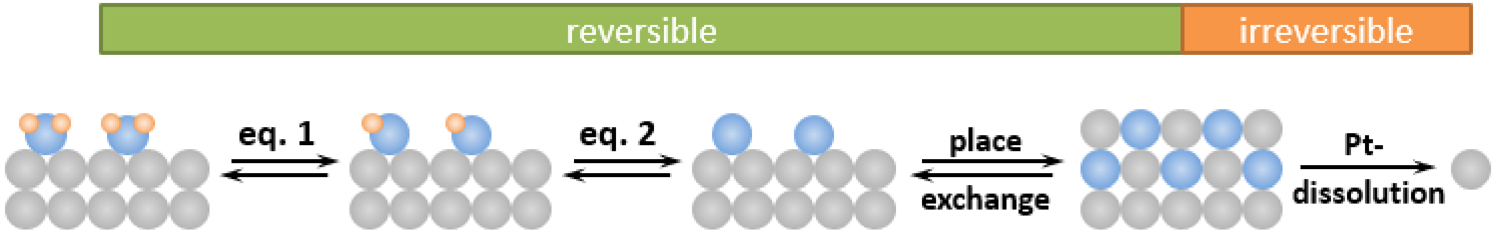




Q. Zhang et al., Appl. Energy, 302 (2021) 117490

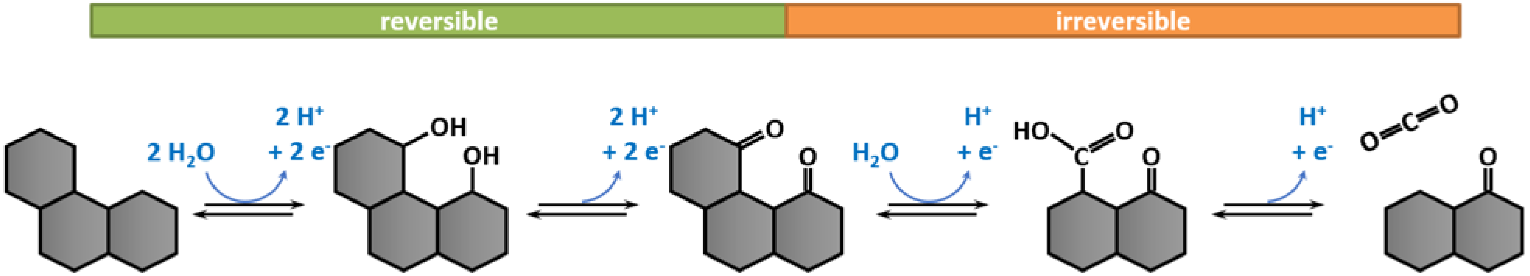
Reversible voltage loss mechanisms

Catalyst surface degradation



- Pt surface oxidation at high cathode potential:
  - >0.7 V: Pt-OH, reversible and fast oxidation/reduction
  - >0.8 V: Pt-O, reversible, but slow oxidation/reduction
  - >1.05 V: Pt-O place exchange and growth of oxidic layer
- Passivation of catalytic active surface

Catalyst support degradation



- Surface oxidation of carbon support at high cathode potential (>> 1.0 V)
- Increase of hydrophilicity of catalyst layer
- Increasing water management issues
- Only partially reversible

J. Mitzel, Q. Zhang, P. Gazdzicki, K.A. Friedrich; Review on mechanisms and recovery procedures for reversible performance losses in polymer electrolyte membrane fuel cells, Journal of Power Sources 488 (2021) 229375

Reversible degradation mechanisms

Contamination of catalyst surface

- Contaminant sources: air, hydrogen and stack components
- Most critical: sulfur contaminants
  - Difficult to recover performance losses in system
- Recoverable: NO_x and CO_x contaminants

Ionomer/membrane degradation

- Loss of ionic conductivity due to dehydration
- Decreased proton conductivity due to cation contamination of sulfonic acid groups (M^{z+}, NH_4^+)
- Reversible ionomer structure changes
  - Ionomer adsorption on Pt surface
  - Changes in secondary ionomer structure depending on water content

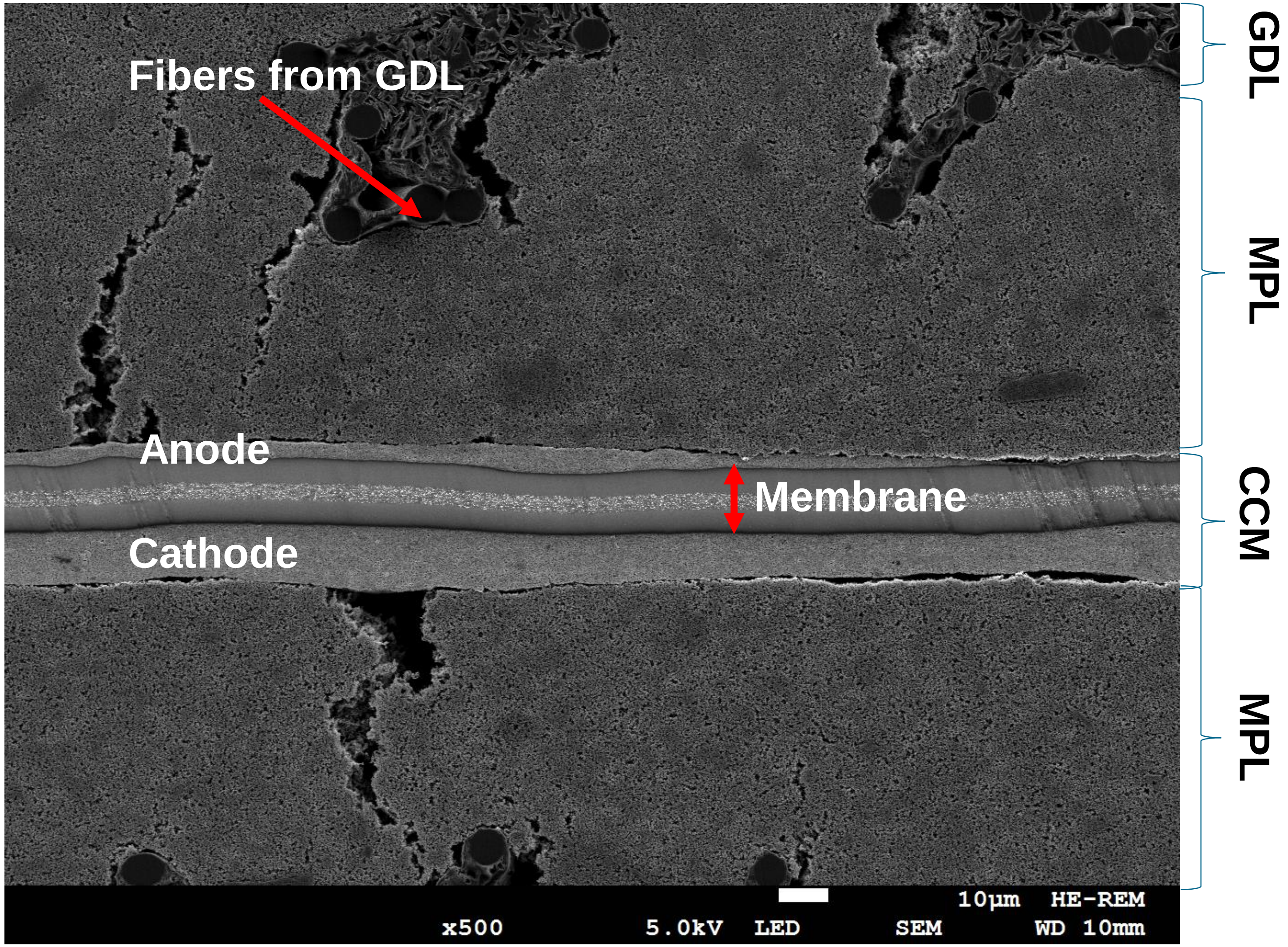
Contaminants causing reversible performance losses in PEMFCs.

Impurity Source	Classification	Contaminant	Mechanism	Impact
Air	Nitrogen contaminants	NO_x: NO, NO_2	Catalyst poisoning	Kinetic
		NH_3	Membrane poisoning	Ohmic, kinetic
	Sulfur contaminants	SO_x: SO_2, SO_3 H_2S COS	Catalyst poisoning	Kinetic
Hydrogen	Carbon contaminants	CO_x: CO, CO_2	Catalyst poisoning	Kinetic
	Sulfur contaminants	H_2S	Catalyst poisoning	Kinetic
Bipolar plate	Metal ions	Fe^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Cr^{3+}	Membrane poisoning	Ohmic
Membrane	Degradation products	SO_4^{2-}	Catalyst poisoning	Kinetic
	Metal ions	Na^+, Ca^{2+}	Membrane poisoning	Ohmic

J. Mitzel, Q. Zhang, P. Gazdzicki, K.A. Friedrich; Review on mechanisms and recovery procedures for reversible performance losses in polymer electrolyte membrane fuel cells, Journal of Power Sources 488 (2021) 229375

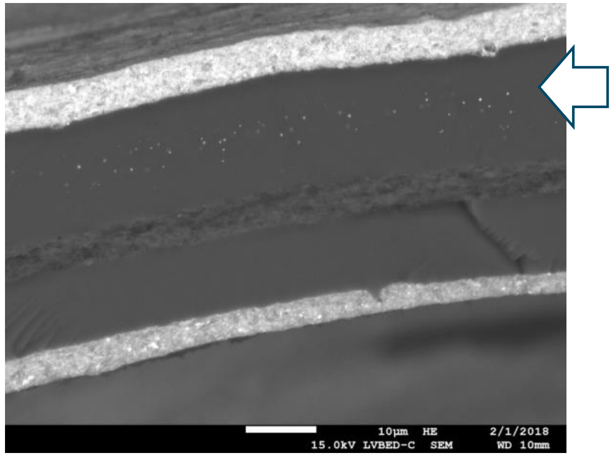
Common analyses of MEAs

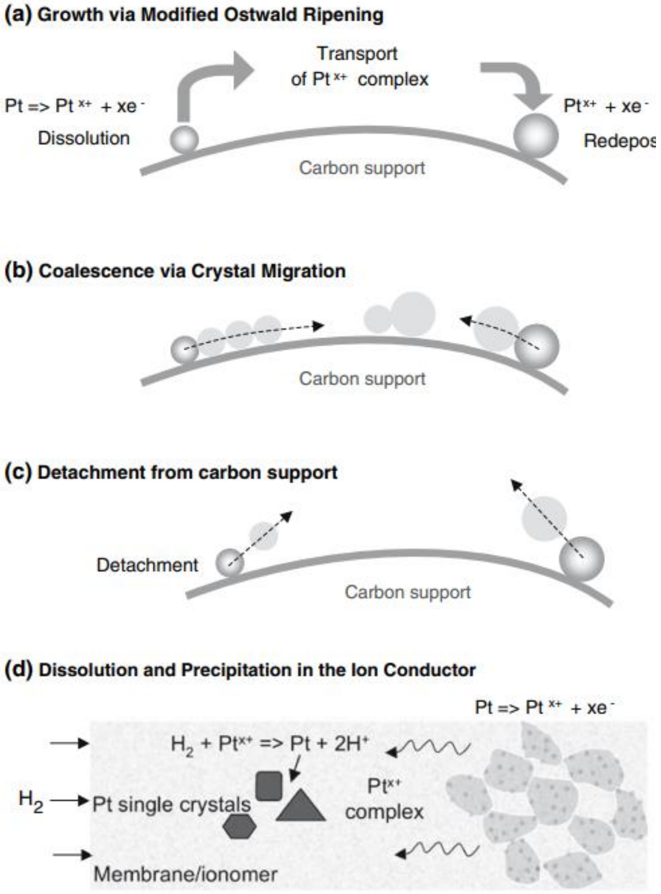
- Operando and in-situ investigations (EIS, CV, LSV or FER …)
- Dimensional investigations of cross sections (SEM or AFM)
- Compositional investigations (EDX, XPS, XRD …)
- 3D-structure investigations (CT, FIB-SEM)



Electrode degradation: Catalyst

- Four mechanisms lead to Pt degradation (besides poisoning)
  - Ostwald Ripening: Growth of larger particles
  - Coalescence via Crystal Migration
  - Detachment from support
  - Dissolution and Precipitation in Ionomer





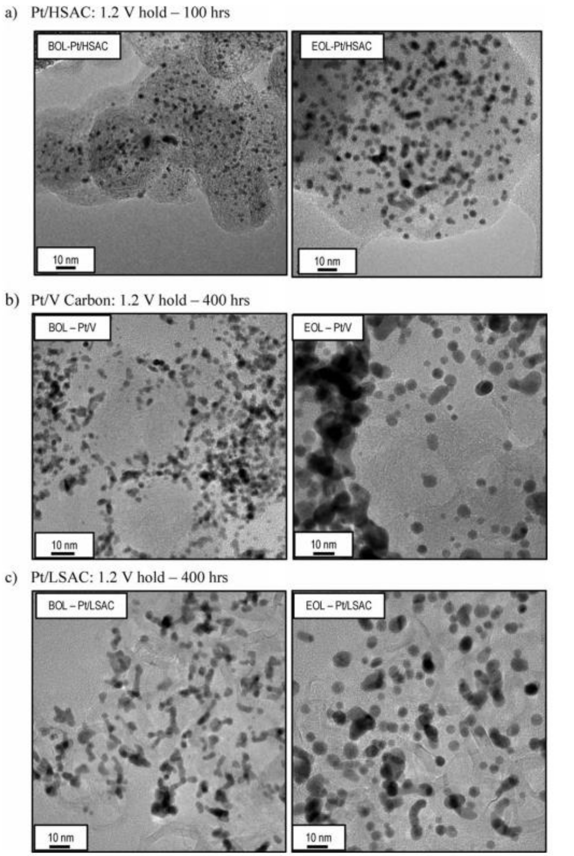


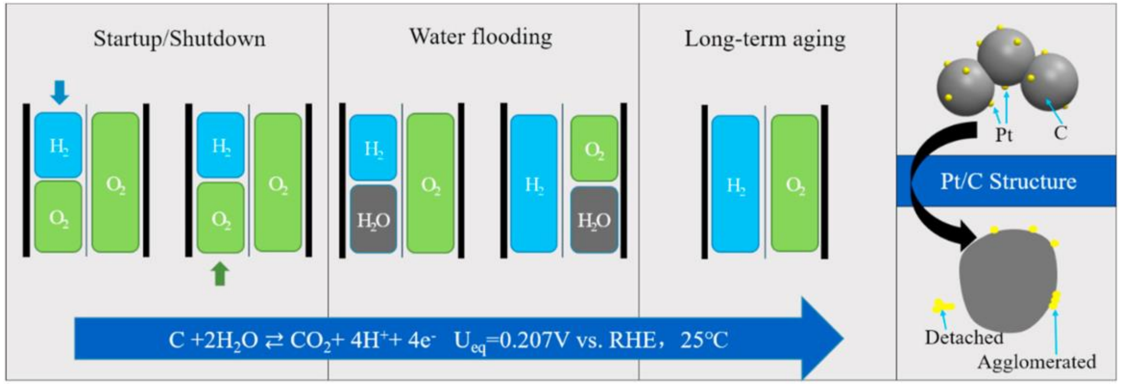
Figure 12. Pt particle agglomeration due to carbon corrosion in a) Pt/HSAC, b) Pt/V, and c) Pt/LSAC.

Top Catal (2007) 46:285–305

➔ More details during presentation by Tobias Morawietz

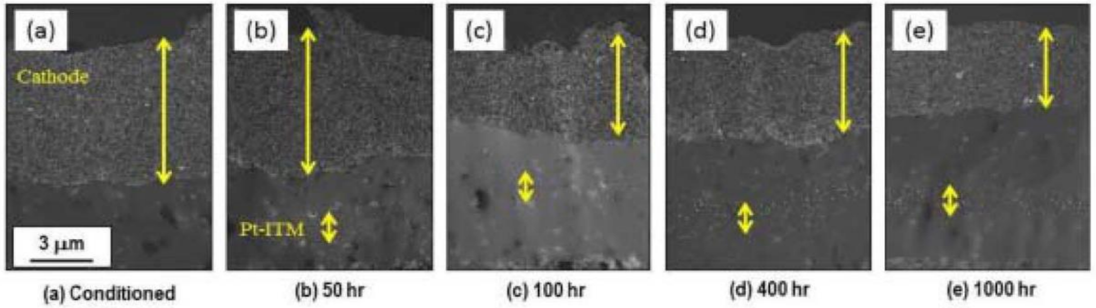
Electrode degradation: Carbon Corrosion

- Carbon corrosion is defined as the reaction of carbon with water as oxidant
  - Mainly at cathode due to high potential
  - At anode due to reversed voltage
- Results of Carbon corrosion:
  - CO_2 / CO formation -
  - Detachment of Pt-particles
  - Loose of electronic/ionic networks
  - Thinning of electrode
  - Reduced porosity

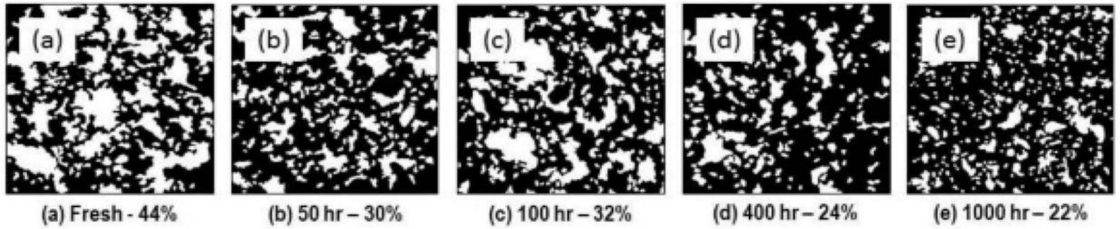


https://doi.org/10.1016/j.jpowsour.2020.229434

I. TEM



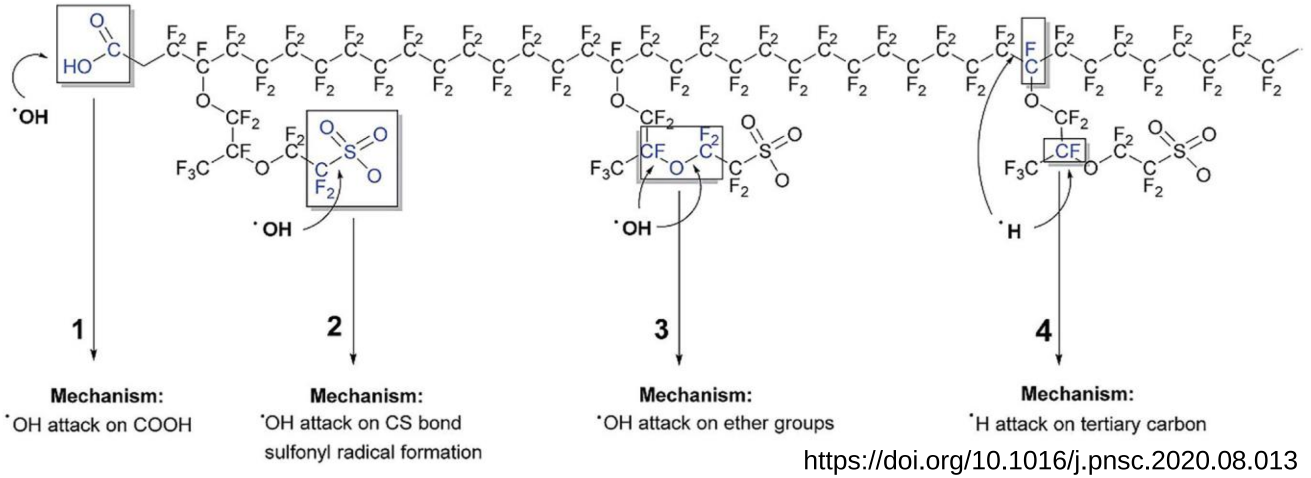
II. TEM



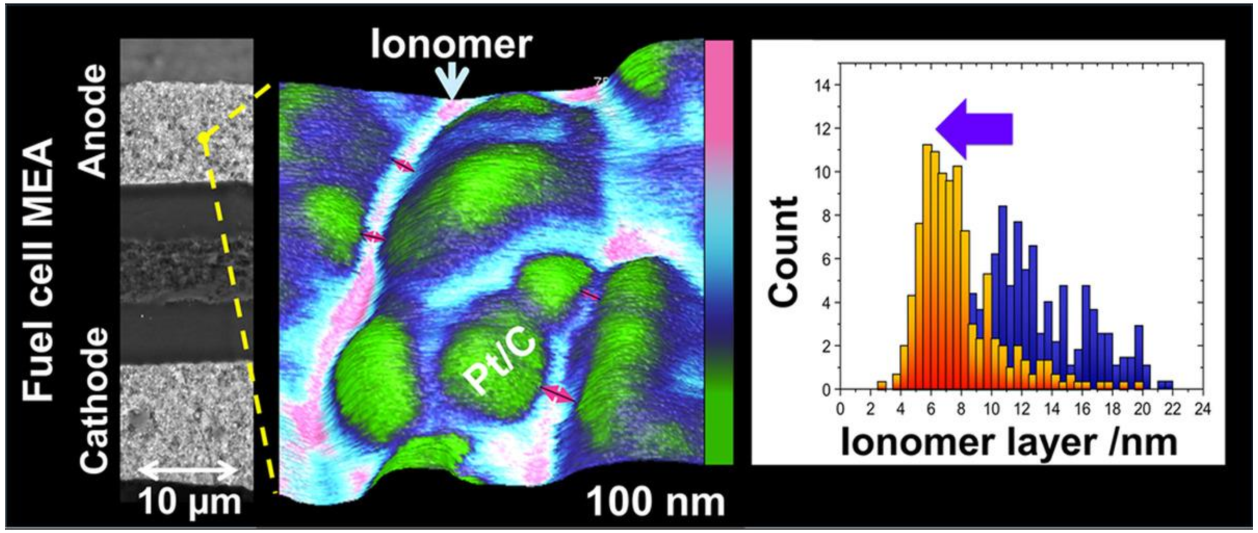
Journal of The Electrochemical Society, **165** (6) F3148-F3160 (2018)

Electrode degradation: Ionomer degradation

- Degradation of the Ionomer not only in membrane, but also in electrodes
- Radicals (H2O2, HO*, HOO*) are formed during fuel cell operation
- Attack possible at:
  - Terminal Carboxy
  - C-S bond
  - Ether groups
  - Tertiary carbons
- Side chain unzipping
- Reduction of thickness of ionomer layers measured



https://doi.org/10.1016/j.pnsc.2020.08.013

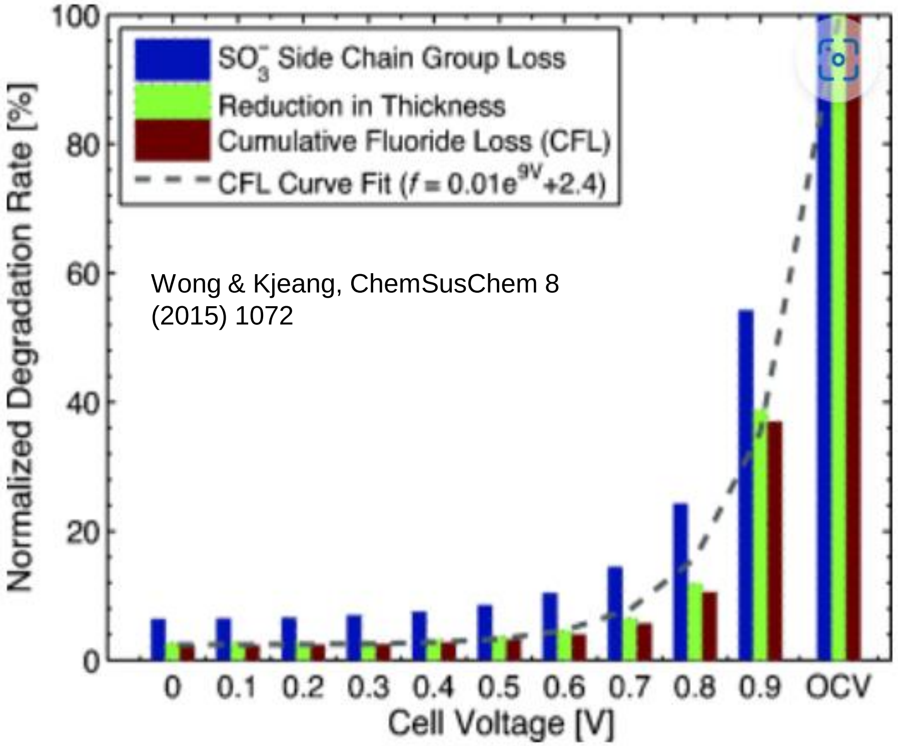


T. Morawietz et al., ACS Appl. Mater. Interfaces 2016, 8, 40, 27044–27054

➔ More details during presentation by Tobias Morawietz

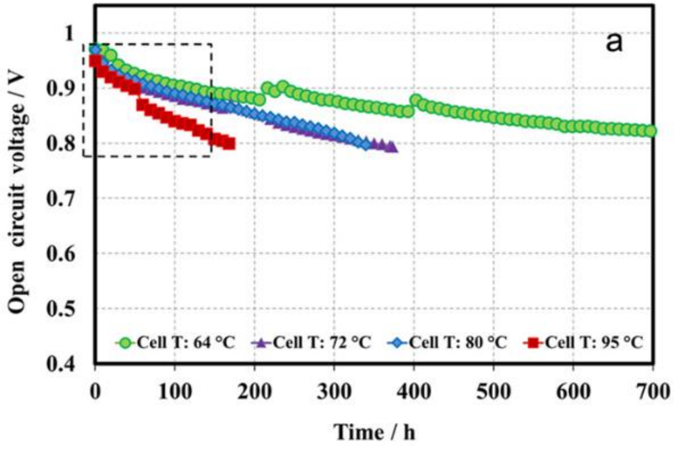
Membrane chemical degradation (e.g OCV AST)

… due to contamination of trace metals, impurities, hydroxyl radical attack (same mechanisms as for ionomer in the electrode)….

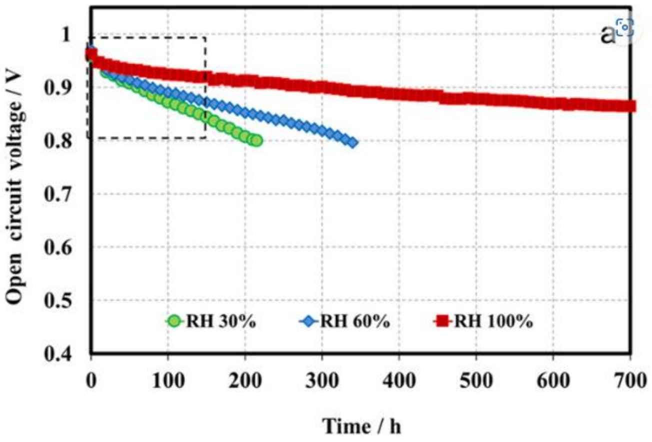


Wong & Kjeang, ChemSusChem 8 (2015) 1072

N. Zhao, Fuel Cells 20, 2020, 176



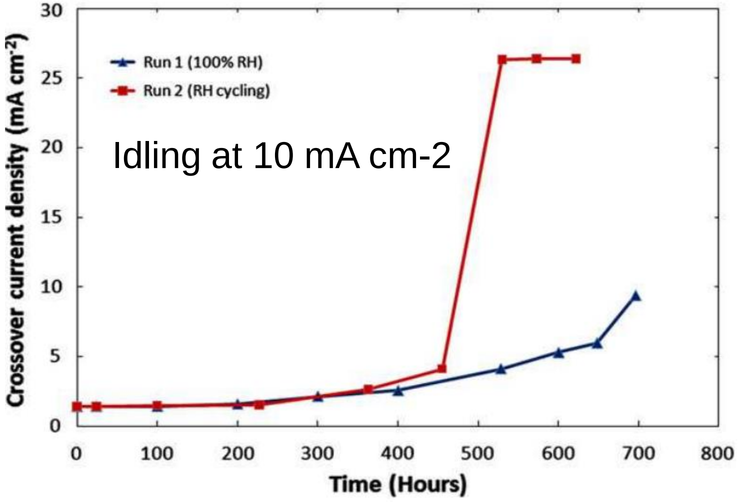
N. Zhao, Fuel Cells 20, 2020, 176

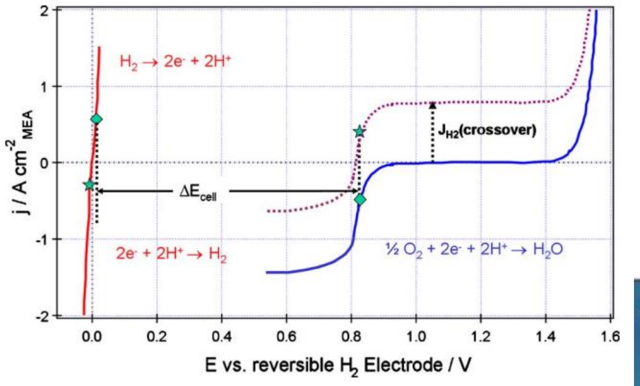


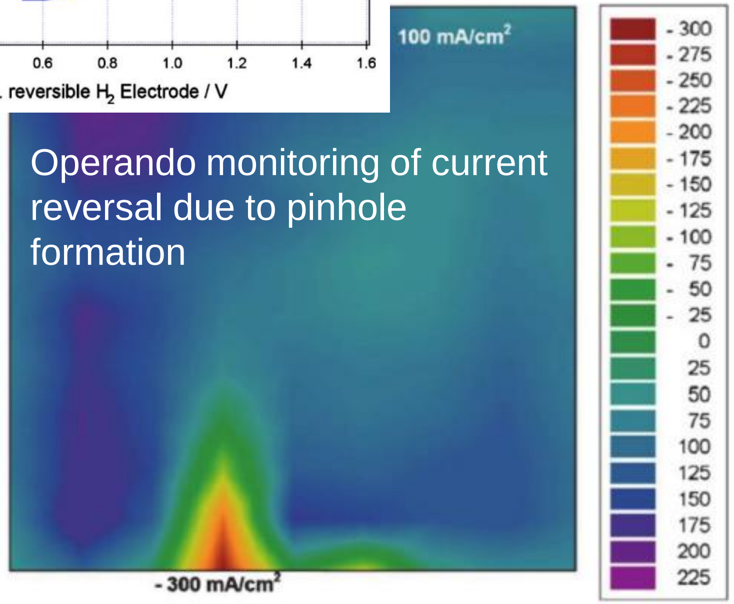
Membrane mechanical degradation

… due to T, RH or freeze/thaw cycling

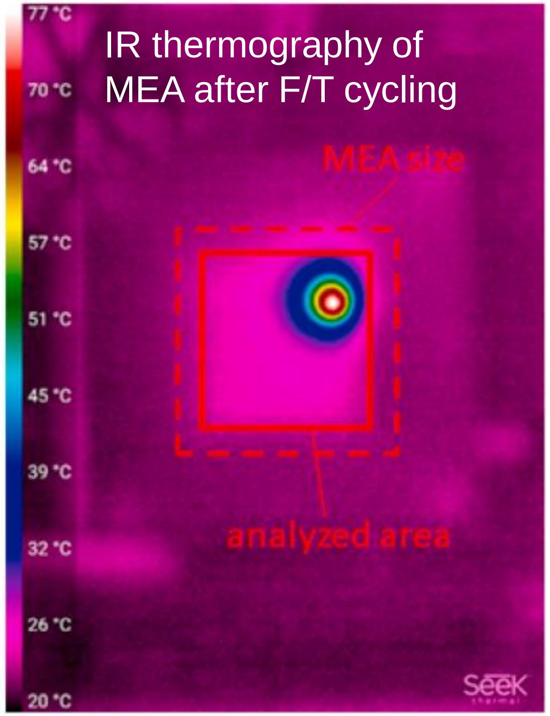
K. Panha, Appl. Energy 93 (2012) 90





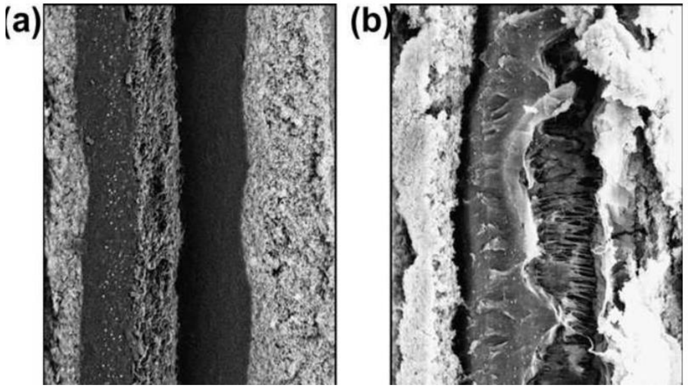


R. Lin et al., JES, 158 (1), B11 (2011)



F. Knorr et al., Appl. Energy 238 (2019) 1–10

K. Panha, Appl. Energy 93 (2012) 90

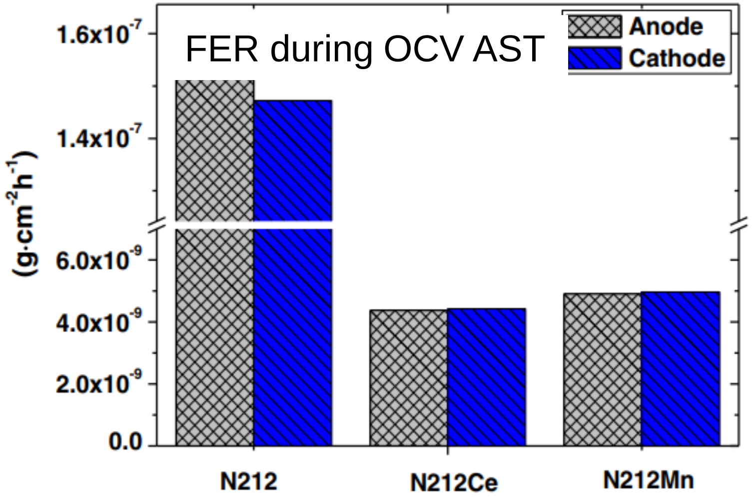


Local delamination of PEM and CL after RH cycling

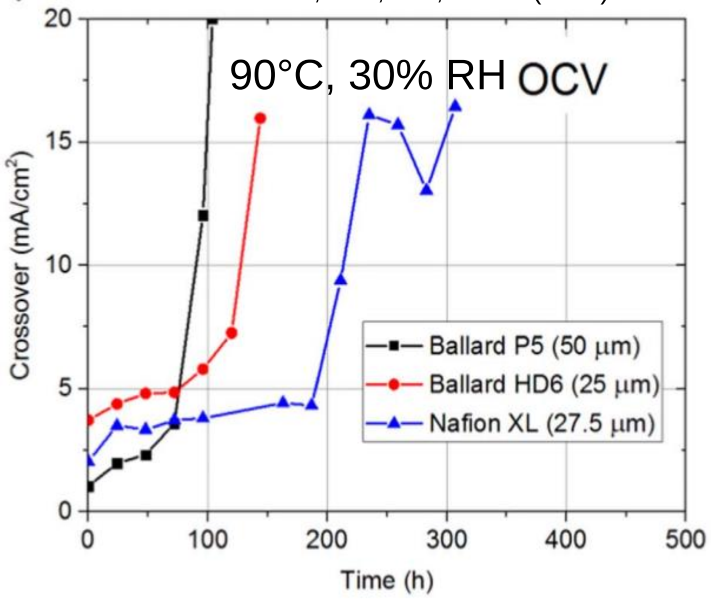
Quantifying membrane degradation

- ➔Hydrogen cross over
- ➔Component thinning
- ➔Release rates of degradation products
- ➔Local analyses

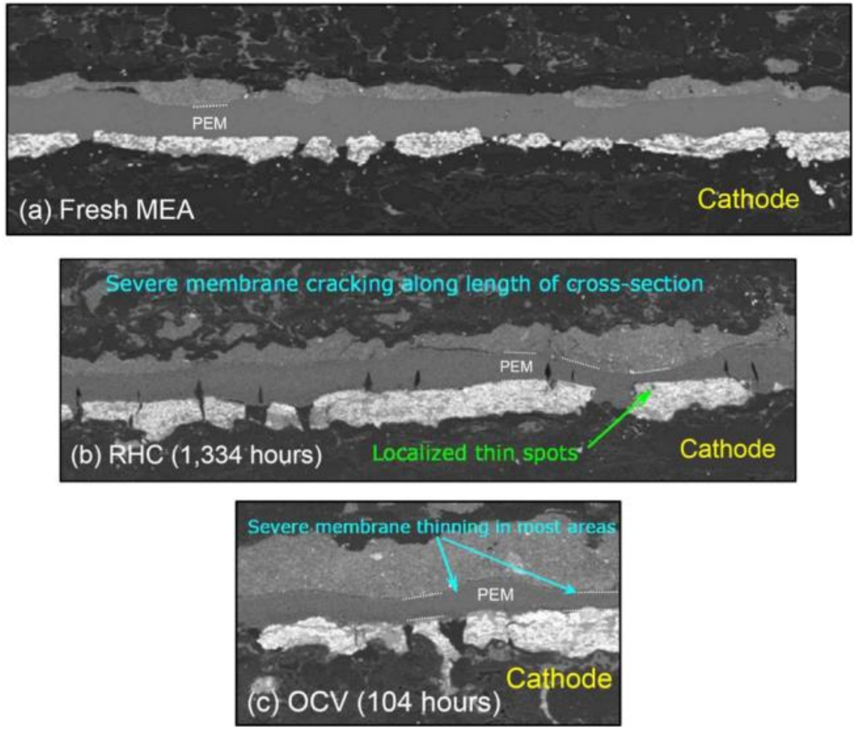
M. Zatoń et al. JES 165 (2018) F3281



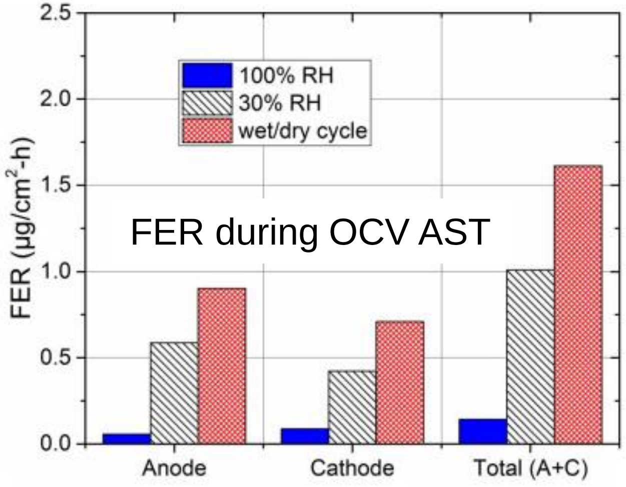
R. Mukundan et al., JES, 165, F3085 (2018)



R. Mukundan et al., JES, 165, F3085 (2018)

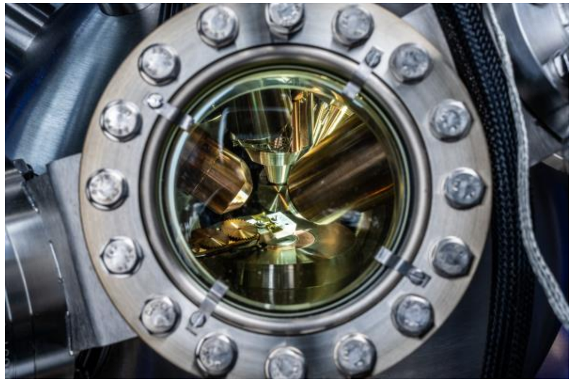


A. M. Baker et al 2016 JES. 163 F1023



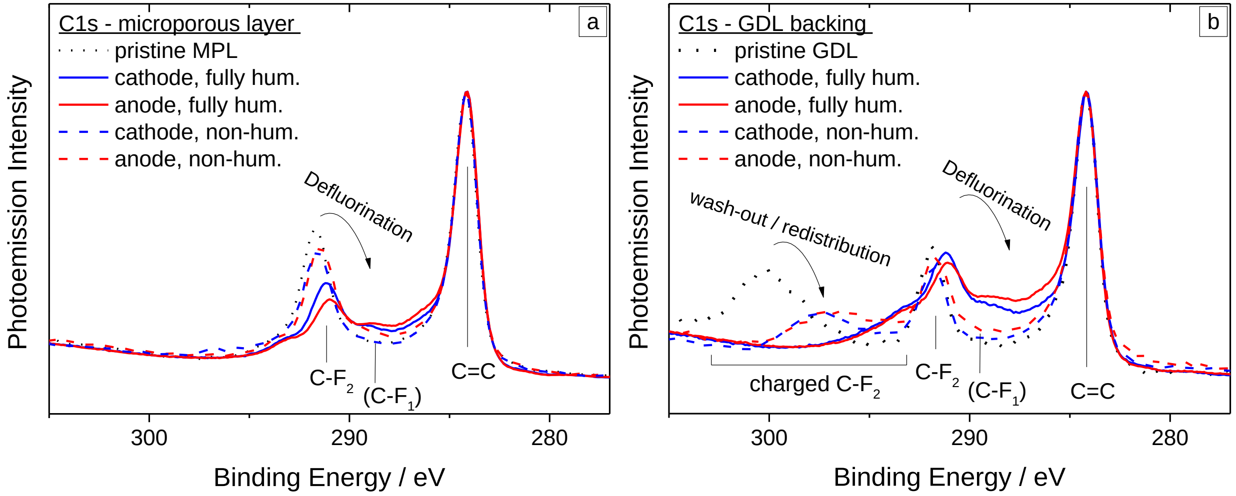
Quantifying GDL degradation

- ➔ Wettability
  - ➢ Impact on water management
- ➔ Possible surface contaminations
- ➔ Local analyses



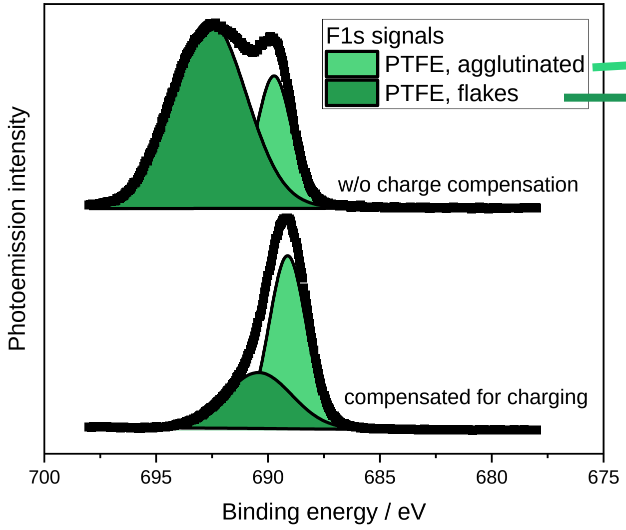
X-Ray photoelectron spectroscopy (XPS)

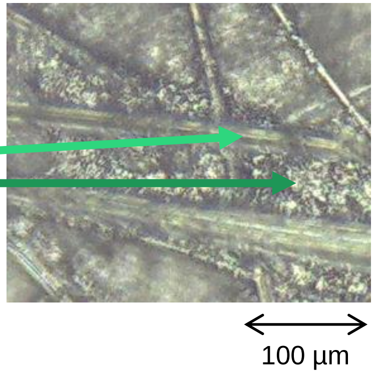
Quantification:
- Fluorinated and non-fluorinated GDL compounds
- Partially defluorinated degradation products



D. G. Sanchez et al., *Journal of Power Sources* 352 (2017) 42.

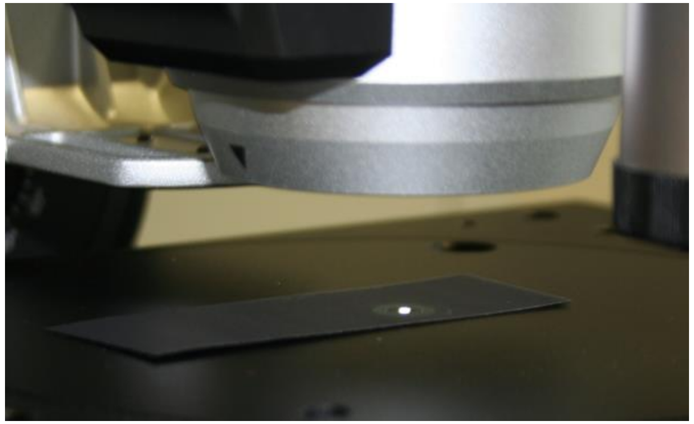
Quantification:
- Well agglutinated PTFE
- Loosely attached PTFE



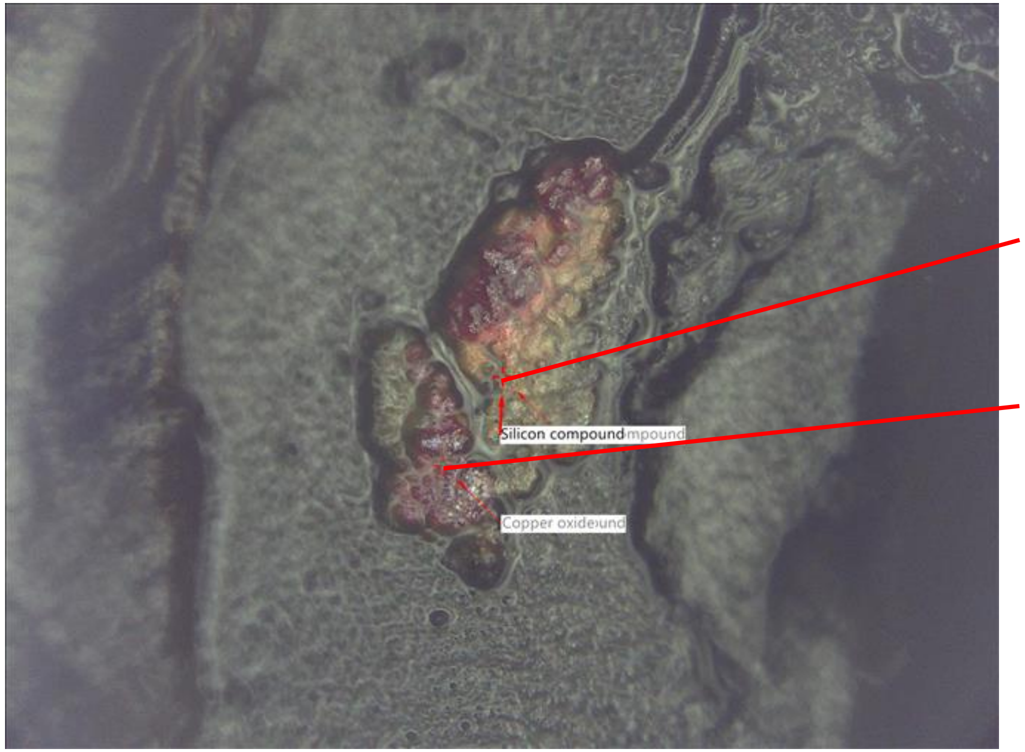


BPP degradation

➔ Elemental analysis
➔ Surface contaminations
➔ Surface corrosion



Laser induced plasma spectroscopy (LIPS)



100 µm

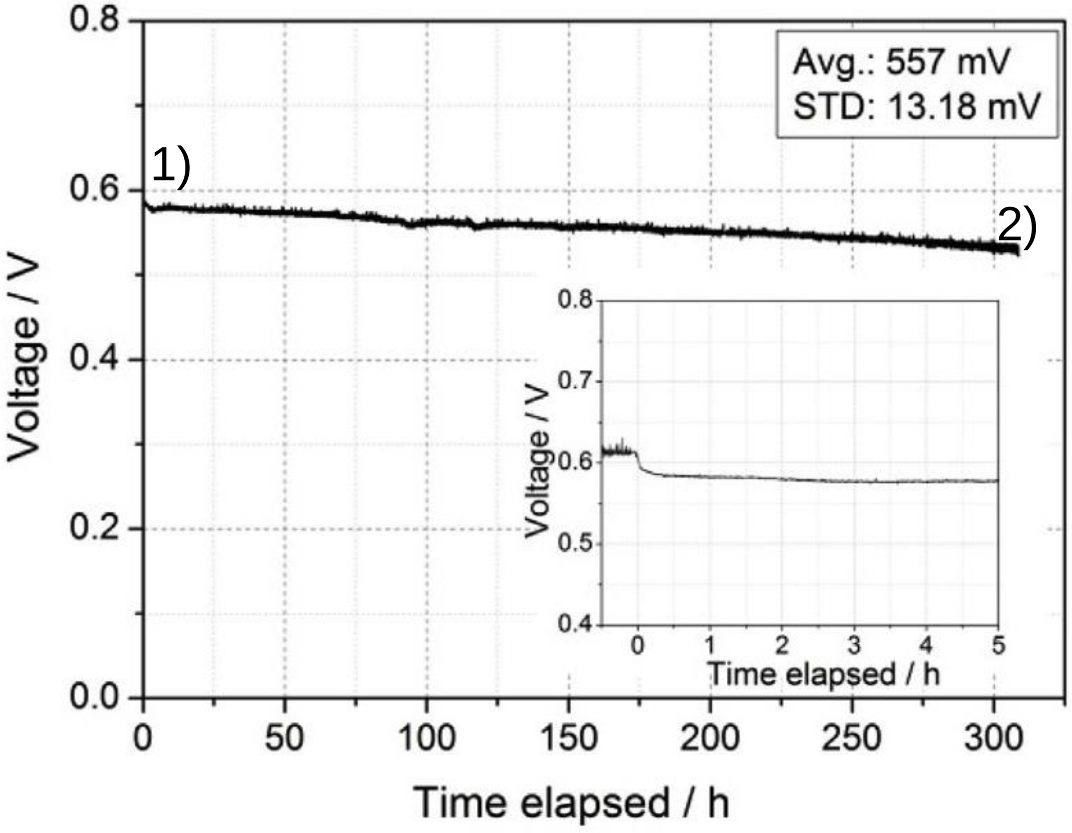
	[mol%]
H - Hydrogen	56,7%
C - Carbon	19,8%
O - Oxygen	14,5%
Si - Silicon	7,9%
Cu - Copper	1,1%

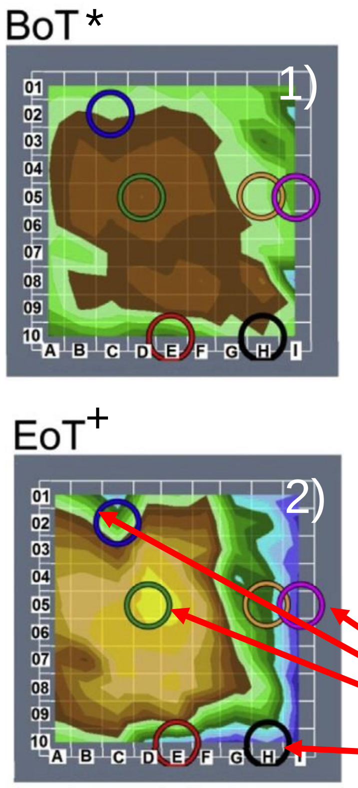
	[mol%]
H - Hydrogen	46,8%
O - Oxygen	27,7%
Cu - Copper	25,5%

Elemental analysis
- Fast: seconds per sample position
- Less effort: ambient conditions
- Local resolution ~10 µm
  → mapping possible
- Information depth: µm range

Local contamination due to Ni and Si

Dry gases, 60°C, 0.7 A cm^2, 1.5 bar, λ_a=1.2, λ_c=2





*BoT: Beginning of the Test
+EoT: End of the Test

Change in current distribution

	A	B	C	D	E	F	G	H	I
1	4	-21	-60	2	11	14	-51	-56	-65
2	26	3	-31	17	11	19	-21	-33	-61
3	34	17	5	42	26	24	-24	-32	-69
4	40	25	24	44	33	1	-47	-36	-76
5	40	27	33	40	43	24	-31	-41	-79
6	38	29	44	38	44	32	-14	-40	-80
7	32	33	49	39	40	34	-1	-32	-79
8	26	24	42	29	39	14	8	-27	-73
9	29	17	32	11	19	-27	-38	-33	-85
10	40	31	32	-27	-39	-70	-83	-69	-89

50 %
0 %
-100 %

Selected for post-mortem analysis

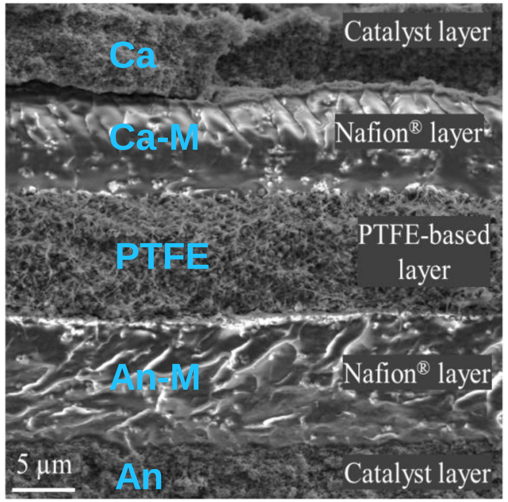
D. G. Sanchez, et al., Journal of Power Sources 352 (2017) 42

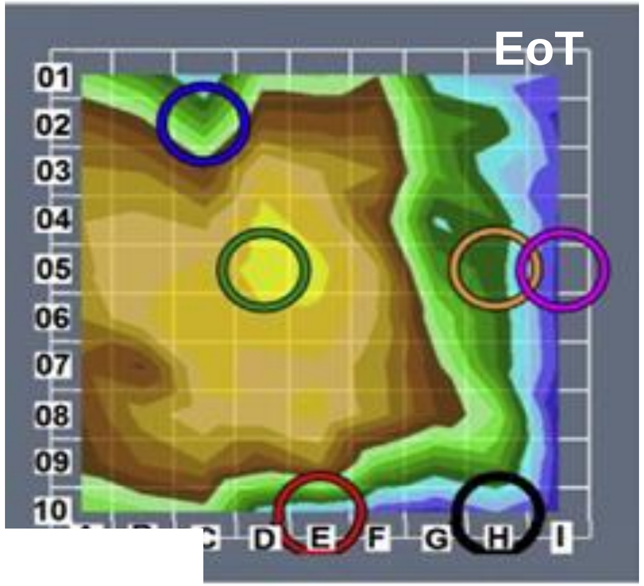
Local contamination due to Ni and Si

EDX Analysis for Ni and Si in selected segments

Segment	Ni/wt%					Si/wt%				
	An-M	PTFE	Ca-M	An	Ca	An-M	PTFE	Ca-M	An	Ca
C2	3.4 ± 2.9	2.6 ± 2.3	3.6 ± 3.2	–	0.5 ± 0.9	2.3 ± 0.7	0.3 ± 0.1	1.5 ± 0.7	1.1 ± 0.5	–
D5	0.1 ± 0.1	<0.1	0.2 ± 0.2	–	–	2.2 ± 0.5	0.3 ± 0.3	1.4 ± 0.6	–	0.3 ± 0.5
H5	–	–	–	–	–	0.6 ± 0.2	0.1 ± 0.1	0.7 ± 0.2	–	0.5 ± 0.2
I5	–	0.2 ± 0.2	<0.1	–	–	3.2 ± 0.6	<0.1	2.3 ± 0.5	1.4 ± 0.8	1.2 ± 0.6
E10	2.9 ± 0.4	1.8 ± 0.9	2.8 ± 0.3	0.5 ± 0.2	0.2 ± 0.2	2.7 ± 0.6	0.2 ± 0.1	2.6 ± 0.0	0.8 ± 0.4	1.9 ± 0.3
H10	–	–	–	–	–	2.4 ± 0.5	0.3 ± 0.3	1.9 ± 0.2	1.2 ± 1.1	2.4 ± 1.3
Pristine MEA	–	–	–	–	–	2.0 ± 0.7	0.1 ± 0.1	1.5 ± 0.6	–	–

SEM* cross-section



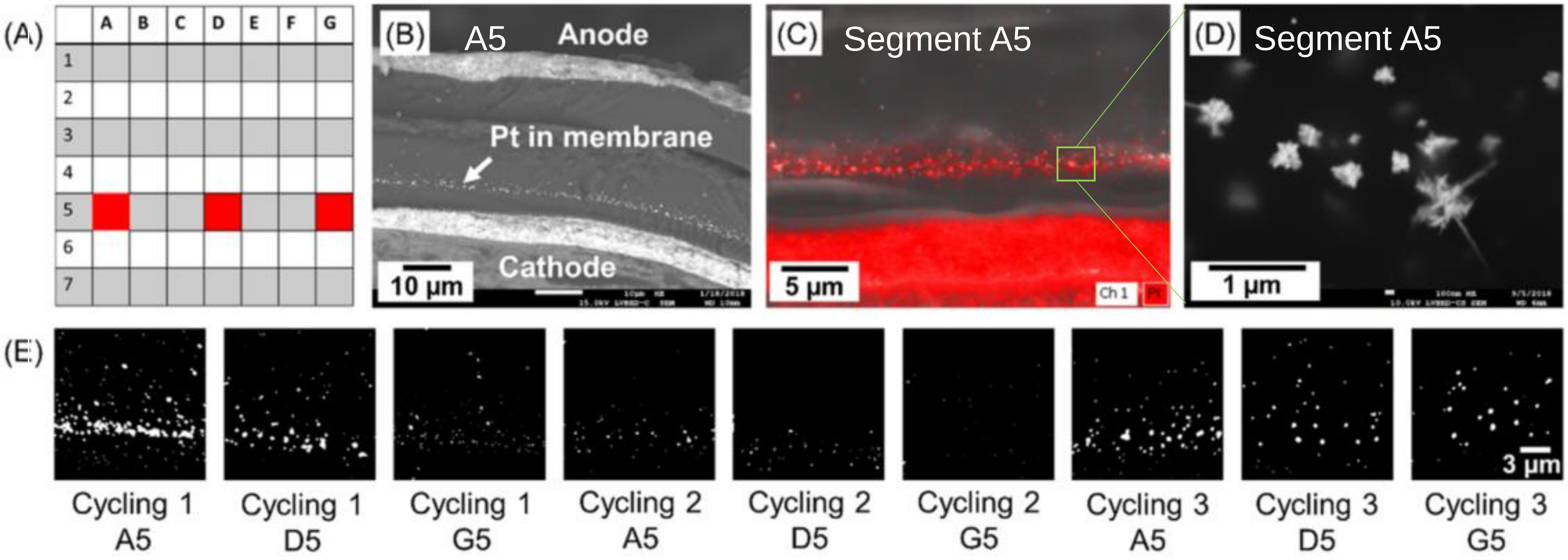


Increased RH facilitates Ni contamination, but impedes Si contamination

* SEM : Scanning Electron Microscope
\+ MEA: Membrane Electrode Assembly

Local impact of load cycling

SEM/EDX Analysis of selected segments



Local Pt band in the membrane

➔ Local analyses is essential to understand degradation (in non-differential cells)

D. Garcia-Sanchez, et al. Applied Energy 259 (2020) 114210

Investigation of durability – definition of FC testing protocols for heavy duty application

J. Sanchez-Monreal (DLR-TT)

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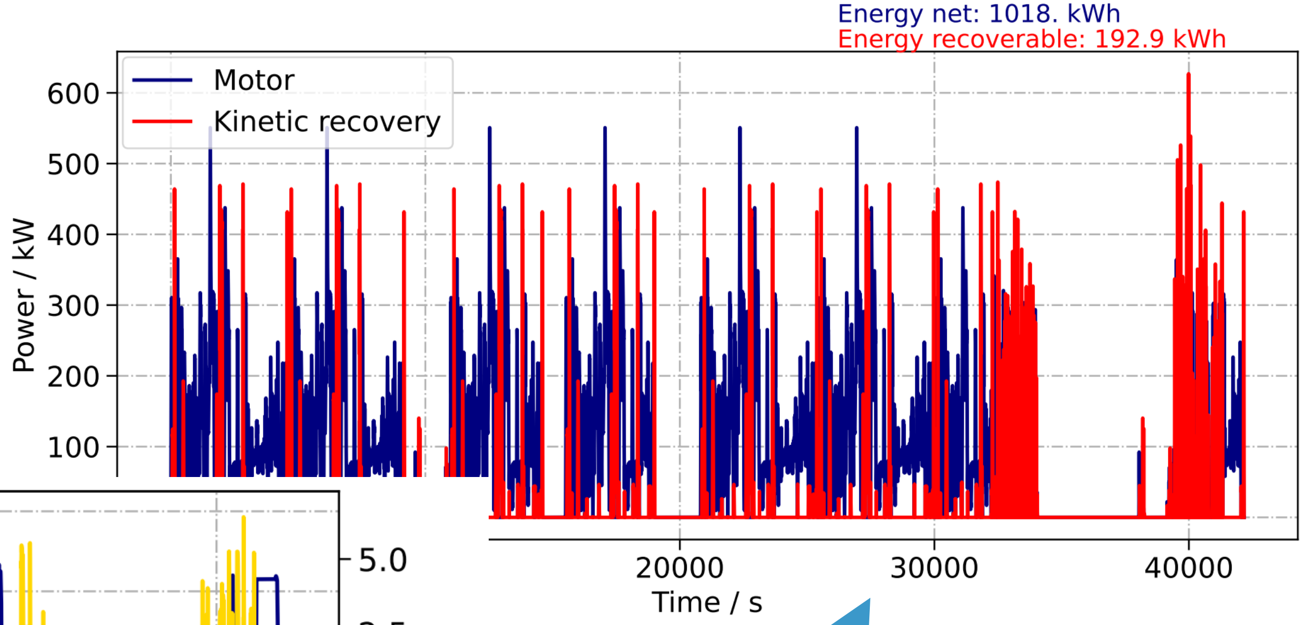
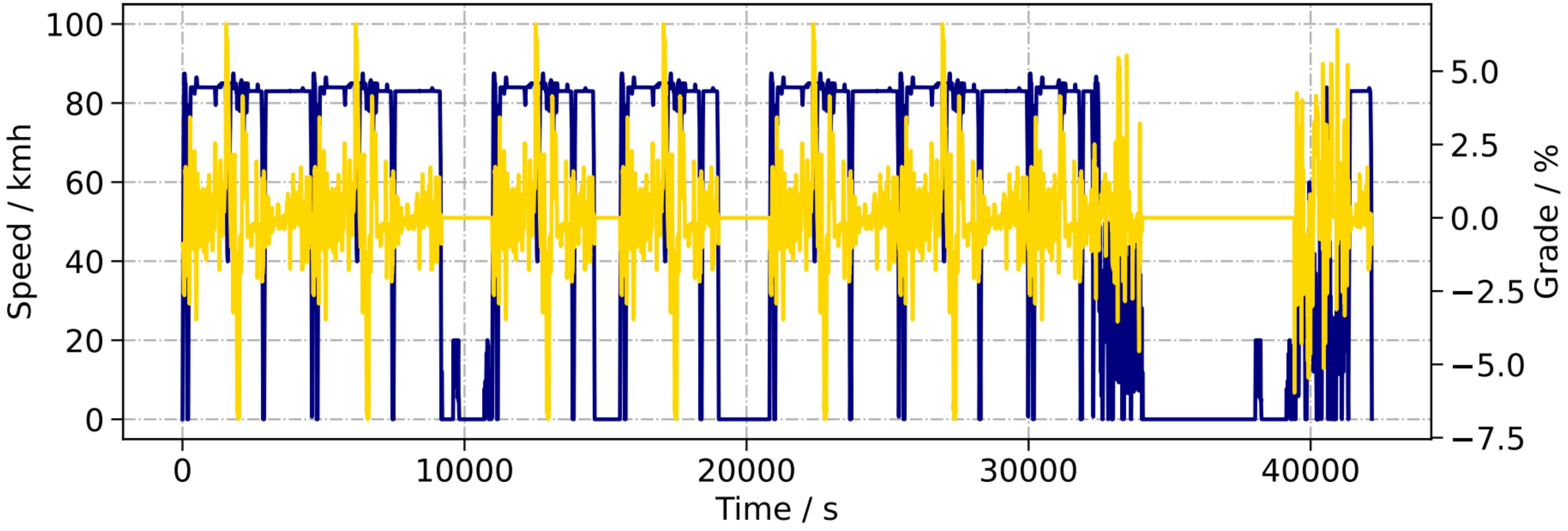
GVW	35029 kg
Vehicle	15729 kg
Load	19300 kg
$A \times C_d$	5.3 m^2
C_r	0.006





Mechanical simulation

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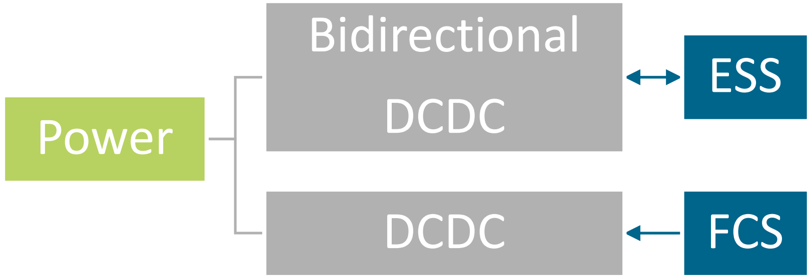
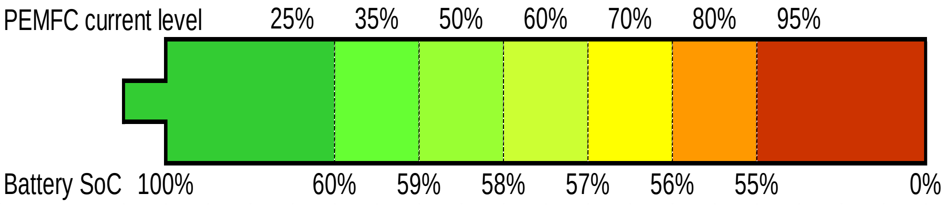
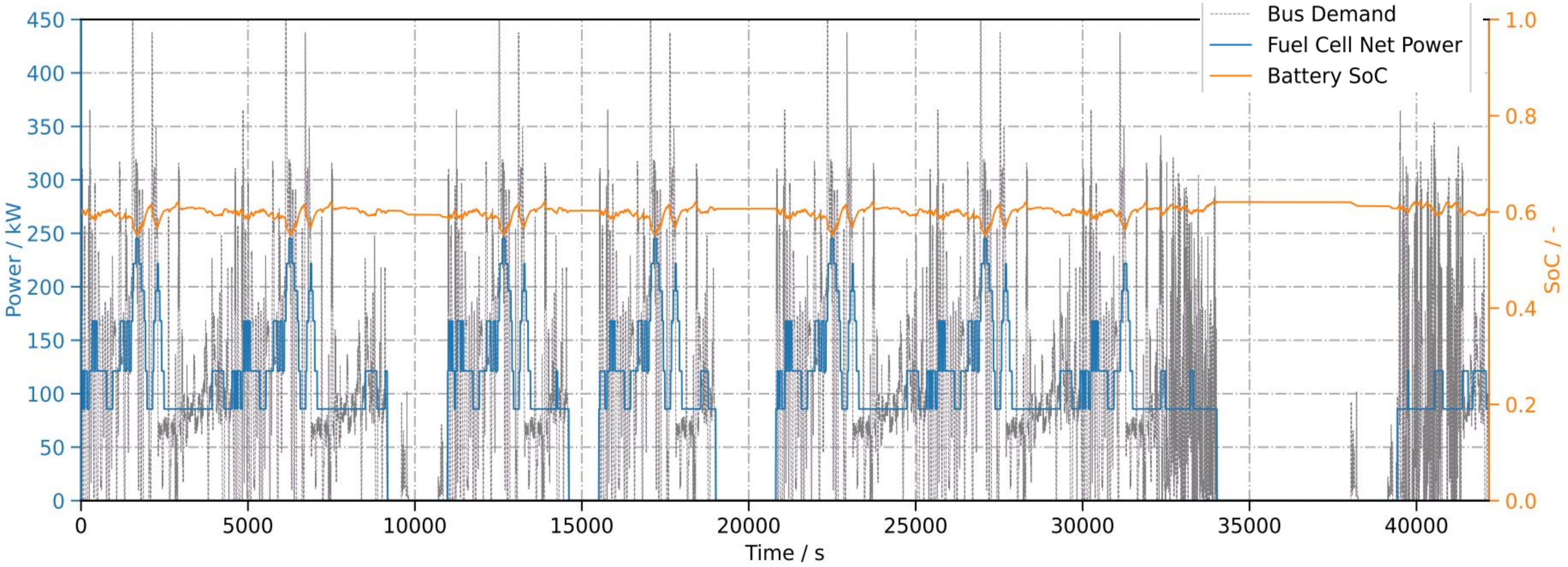
Hybrid Architecture



Hybrid Strategy





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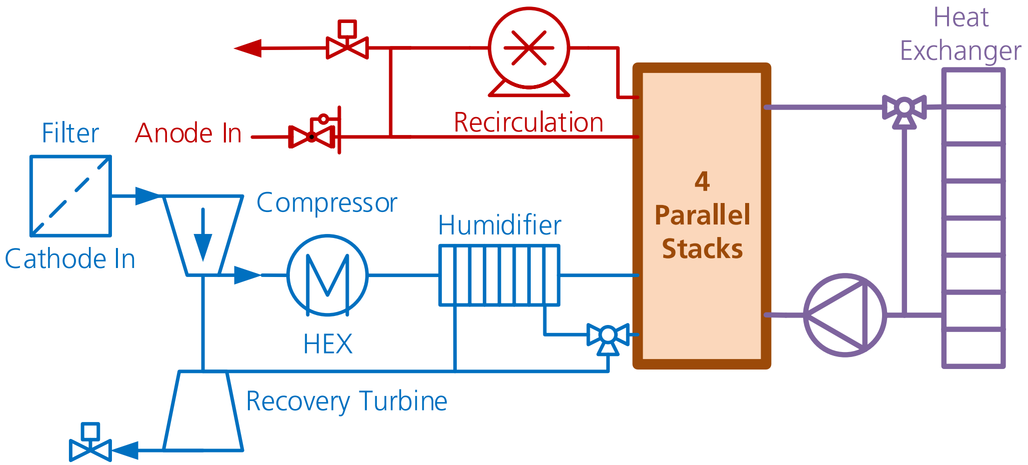
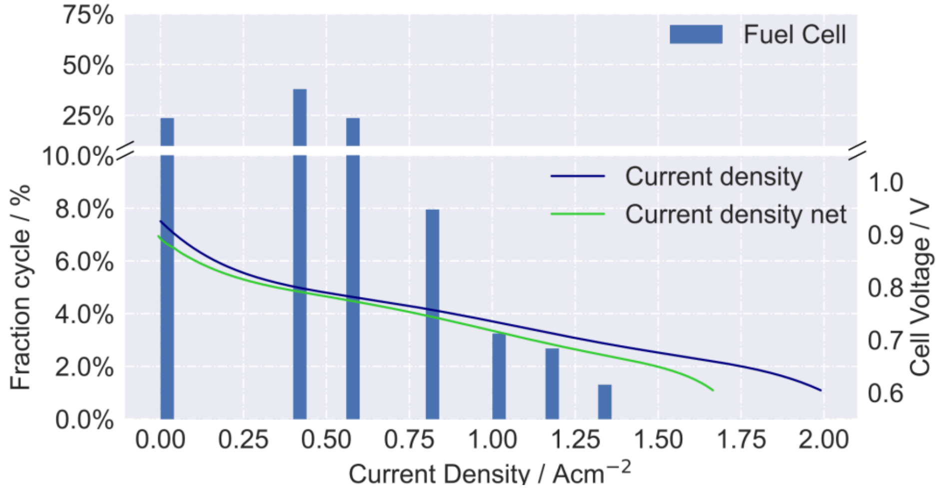
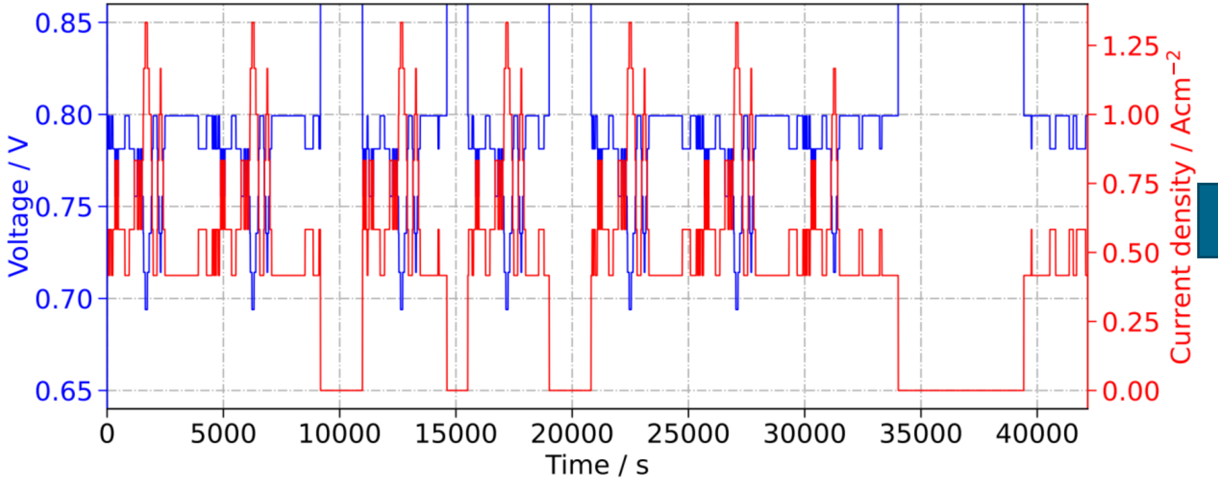




New fuel cell test protocol representative for heavy duty



Next step define accelerated stress test specific for heavy duty

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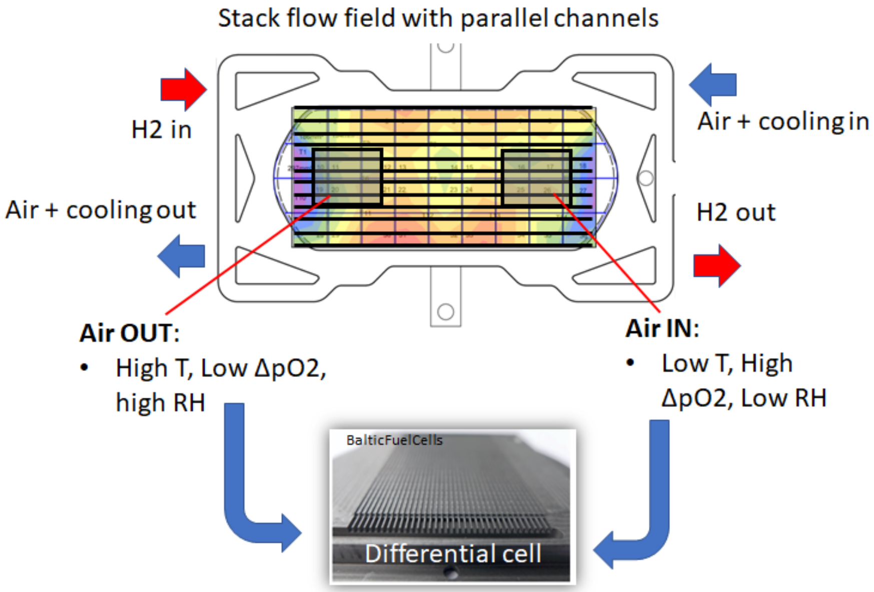
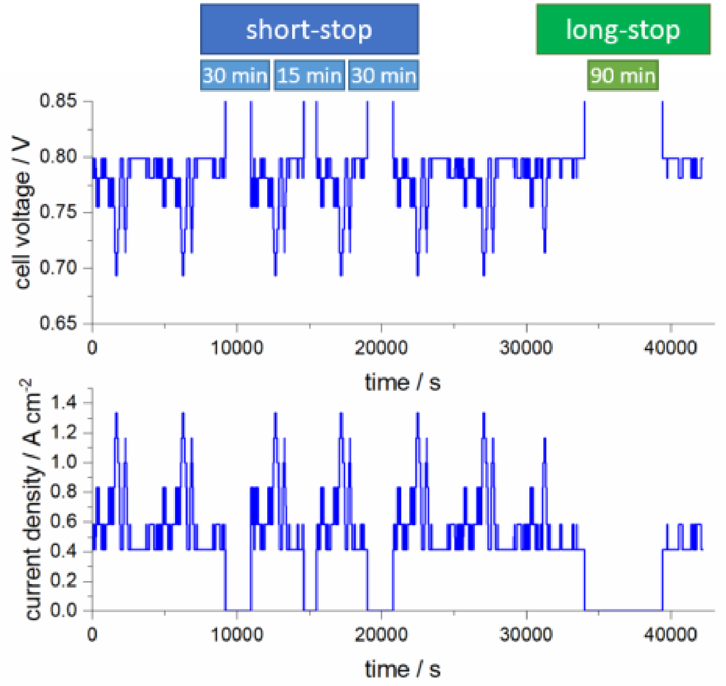
Deliverable 1.3: Public report on definition of FC test protocols

- Leak Test
- Break-in
- Shut-Down and Start-Up
- Polarization Curve
- Cyclic and Linear Sweep Voltammetry
- Electrochemical Impedance Spectroscopy
- Limiting Current Analysis
- HD Load Cycling Durability



Proposed by	**PEMTASTIC HD condtions**	
Source	**At air inlet**	**At air outlet**
Comment		(calc by CEA)
Differential Cell		
Cell temperature [°C]	90	105
Gas composition	H2/air	H2/(N2+9%O2)
Outlet pressure anode / cathode [bar_{abs}]	2.5/2.5	2.6/2.2
Gas inlet temperature anode/cathode [°C]	Cell temperature + 5 °C	
RH anode / cathode [%]	80/50	35/60
H2 and O2 stoichiometry for 4 cm channel length [-]	10/10	
Fixed gas flow according to current density [A/cm²]	3.0	
Stack / technical single cell		
Coolant inlet temperature [°C]	90	
Gas composition	H2/air	
Inlet pressure anode / cathode [bar_{abs}]	2.6/2.5	
Gas inlet temperature anode/cathode [°C]	95	
RH anode / cathode [%]	50/35	
Stoichiometry integral cell / stack [-]	1.2/1.8	
Fixed gas flow according to current density [A/cm²]	0.2	



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Summary

- Not all degradation effects are irreversible
- Main irreversible effects are:
  - Increase of Pt particle size (TEM, SEM) ➔ loss of catalyst (ECSA)
  - Oxidation of carbon support (SEM) ➔ loss of cat and CL layer thickness
  - Ionomer thinning in the CL (AFM)
  - Membrane chemical/mechanical degradation (SEM, cross-over, FER, IR imaging)
  - Contaminations from metallic components, coatings, … (SEM/EDX, XPS, …)
  - GDL degradation, loss of hydrophobicity (XPS, …)
- Often degradation occurs locally ➔ need to monitor local conditions or reduce gradients in operation conditions
- Need for protocols for comparable testing of MEA relevant for HD applications

THANK YOU FOR YOUR ATTENTION

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