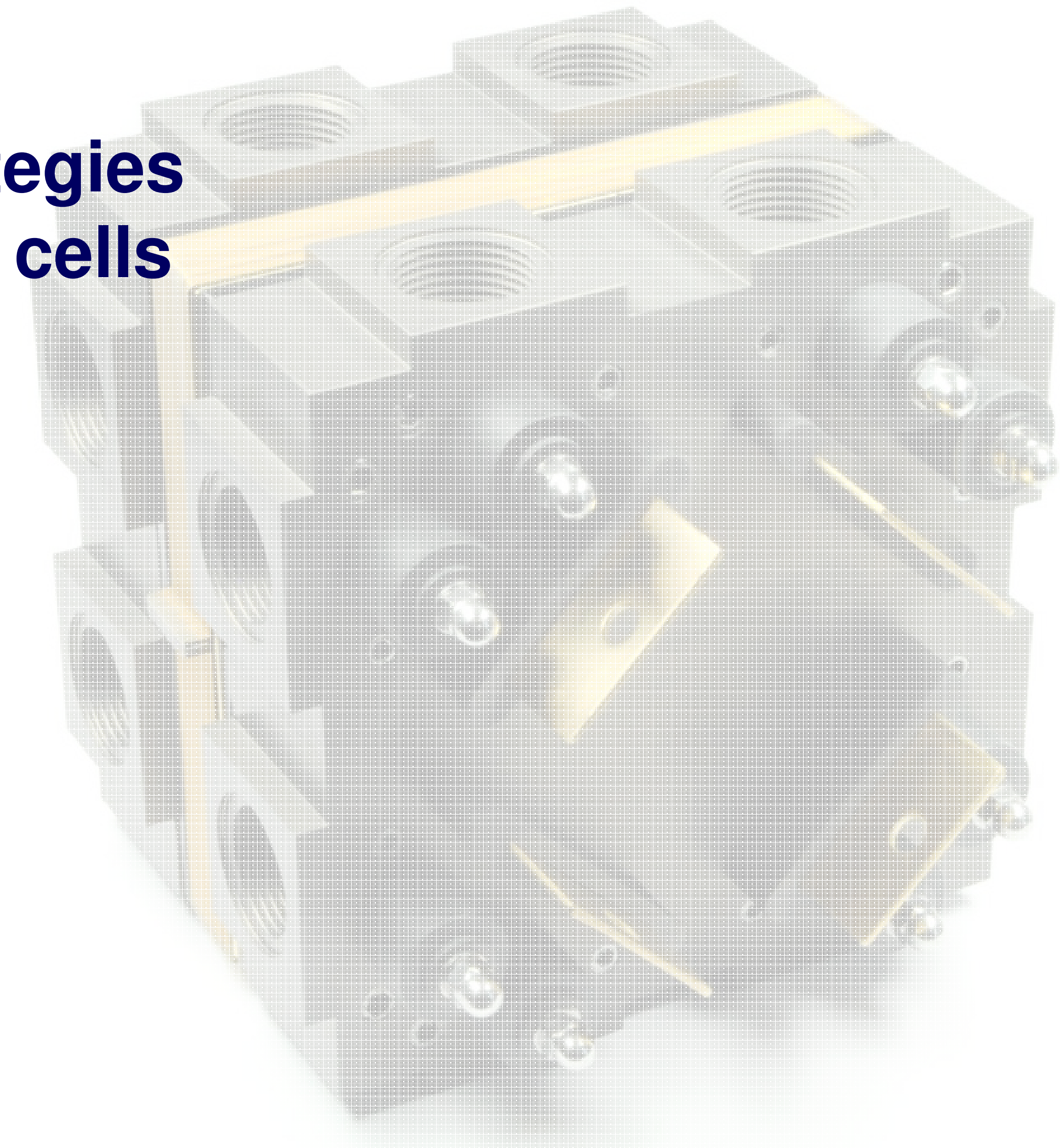
Influence of operation strategies on the life time of PEM fuel cells



Dr.-Ing. Peter Beckhaus,
head of group fuel cells and systems

F-Cell, Stuttgart, 30.09.-02.10.2013

Influence of operation strategies on the life time of PEM fuel cells
content

- Introduction
- Degradation mechanisms
- Mechanical issues of load cycling
- Electrochemical issues of load cycling
- Outline and Summary

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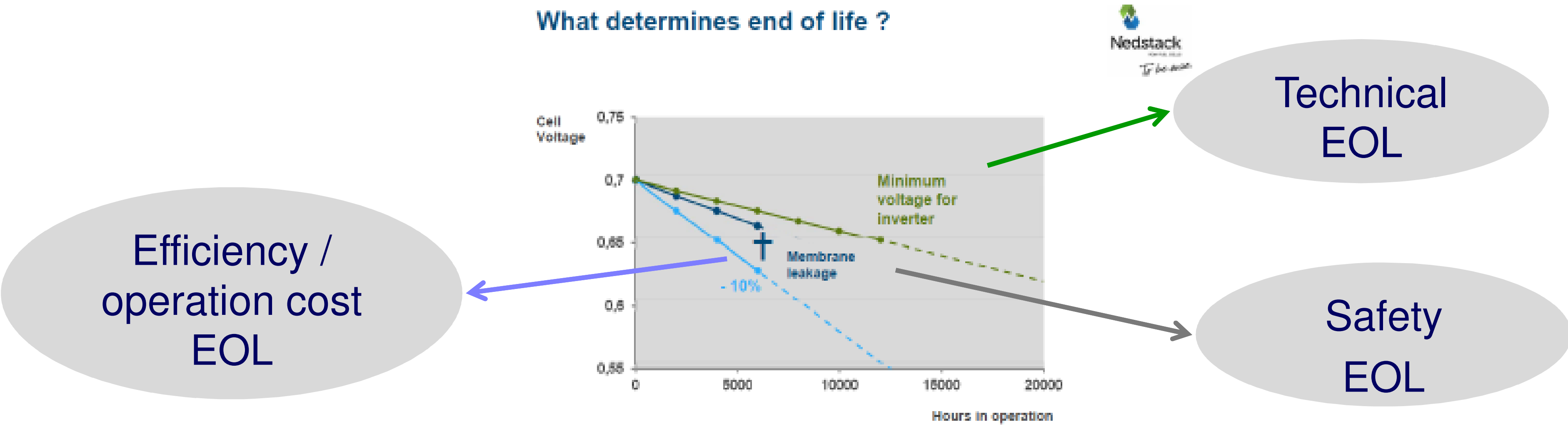
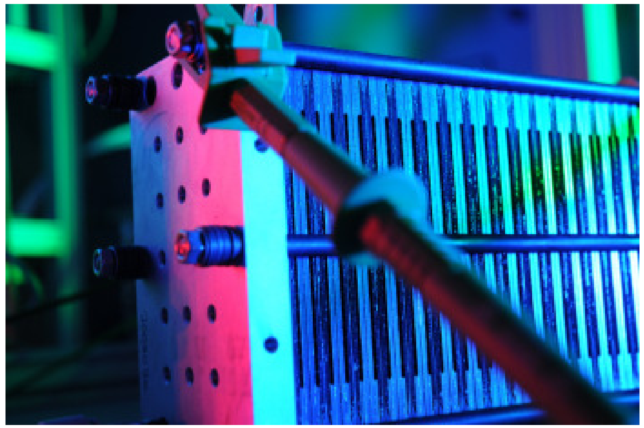
Lifetime of fuel cells
Definition Stack End of Life EOL



- A sufficient life time is basis for commercial (fuel cell) products
- Counting the required operation hours determins the lifetime
  - Small, portable systems 2.000 h
  - cars 4.000 – 5.000 h
  - busses 20.000 h
  - µCHP (house energy) 40.000 – 50.000 h

[Jinfeng Wu et al., JoPS 184 (2008) 104-119] [S.D. Knights et al. JoPS 127 (2004) 127-134]



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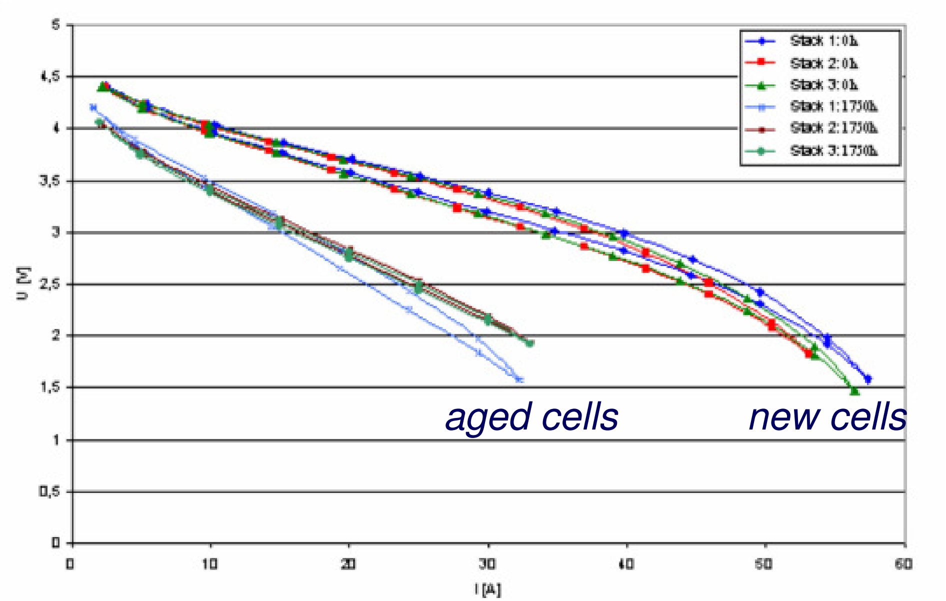
Life Time of fuel cells

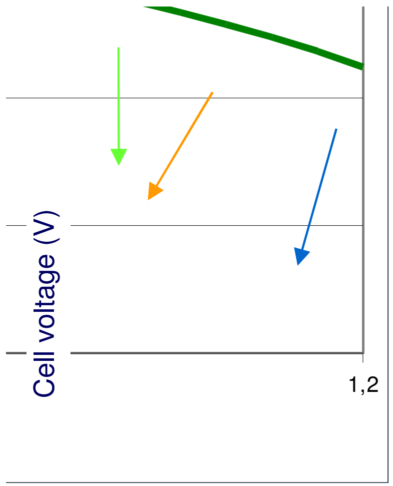
I-V- characteristics changes during life time



I V curve new stacks and aged stacks

An aged stack has

1. A reduced open circuit voltage (OCV)
2. Higher activation losses
3. Higher ohmic losses
4. Mass transport problems



aged cells
new cells

Current density (A/cm²)

IV-curves taken from final report „Stromwelligkeit an Brennstoffzellen"; AiF-IGF ZVEI - Uni Duisburg-Essen / EAN; 15279 N; 01.08.2007; 31.12.2009 / Gößling, Beckhaus, Stark, Krost 2010

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Lifetime of fuel cells
How can I avoid Degradation?

Causes and remedies for degradation are

- **Selection of fuel cell materials**
  - Use suitable materials (Consider chemical composition, cross-influences, operating conditions, life requirements, costs)
  - Prepare sufficient thicknesses and reserves

- **environmental influences**
  - Keep the environment away (thermal insulation, filtering)
  - Adapt to the environment (operating strategies, materials)

- **Operation / operational states**
  - Avoid conditions in which the degradation of the individual components is accelerated
  - Seize actions to compensate degradation effects

→ Make fuel cell stack robust
→ bed the fuel cell stack softly
→ Operate the fuel cell stack prudently

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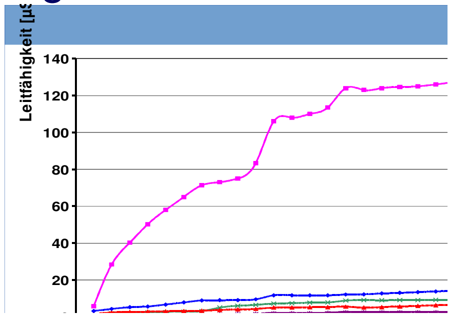
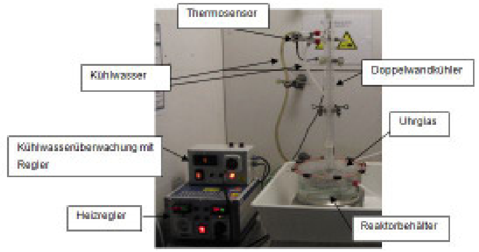
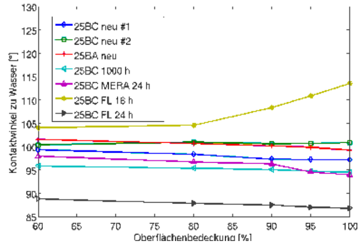
The project life time prognosis
analysing and forecasting PEM stack life time

Ex situ analysis and accelerated aging tests to evaluate the degradation of gasket materials and bipolar plates

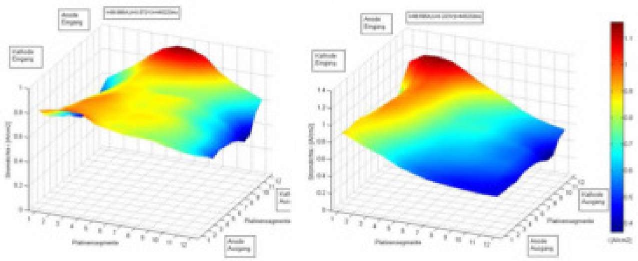


Artificial aging of gas diffusion layers and membranes



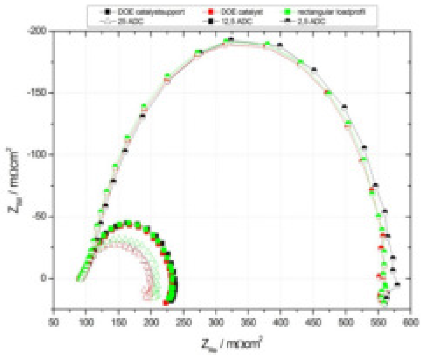


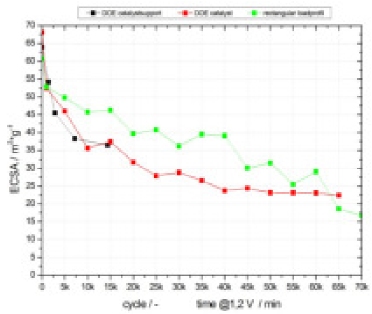
Operational analysis of defined current steps and media supply changes (lower supply of the anode and / or cathode)



Vor den Stromsprüngen (BoL) Nach den Stromsprüngen (EoL)

Selective aging of catalyst, membrane and catalyst support





Energie-Forschungszentrum Niedersachsen

Technische Universität Berlin

Fraunhofer ISE

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Bundesministerium für Wirtschaft und Technologie
aufgrund eines Beschlusses des Deutschen Bundestages

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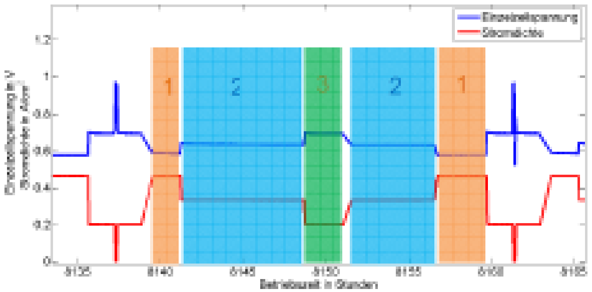
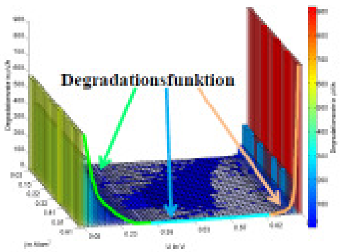
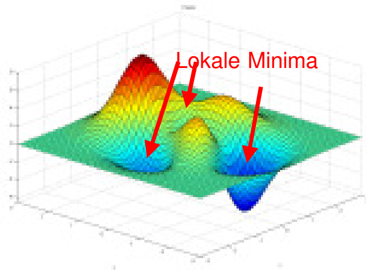
The project life time prognosis
analysing and forecasting PEM stack life time

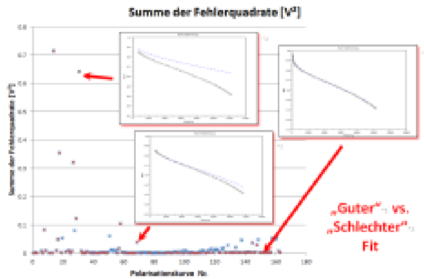
Evaluated operational data and event-based model developed



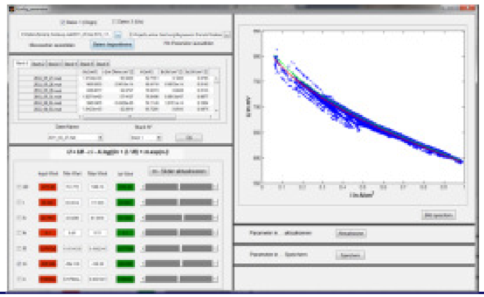


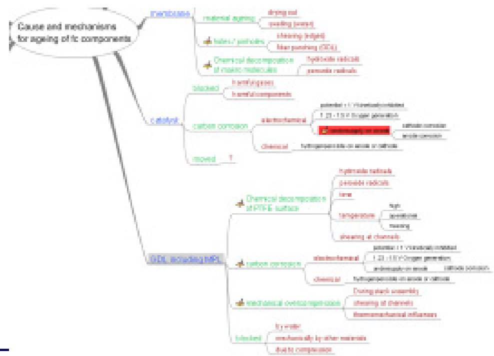
Curve fitting developed to better understand the aging processes





Exploitation of the results by software tools and knowledge databases





Intensive cooperation exchange with industry also within industry workshops

Final Workshop
January 2014

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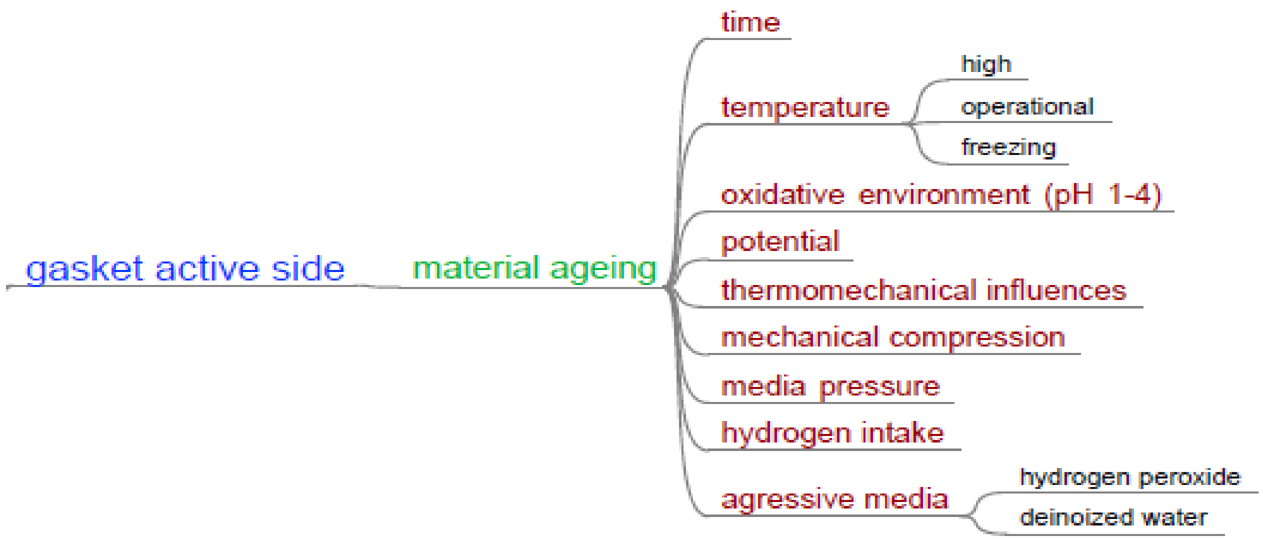
Causes for degradation
Components: single cell elements

- Focussing on single cell elements (MEA, gaskets, bipolar plates)
- Ageing caused by operation is to be analyzed
- Which physico-chemical influcences are affecting which component
- Example gaskets are being harmed by:
  - Oxidative environment
  - Agressive media (hydrogen peroxide, deinoized water, …)
  - Hydrogen intake
  - Time / temperature
  - Thermomechanical influences



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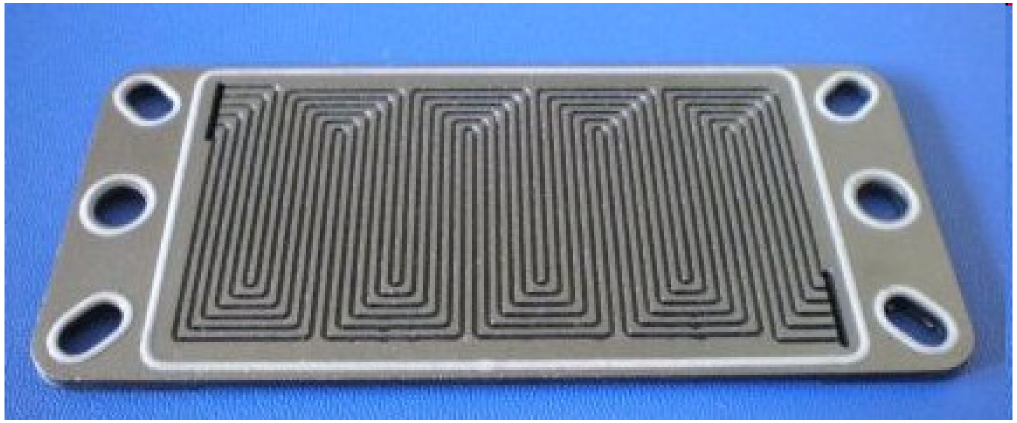
Causes for degradation:
the component gaskets



- loss of force retention
  - compression loss
  - external leaks of coolant
  - gas crossover
  - plate electrical shorting
- migration and accumulation of sealing materials
  - change the hydrophobic character of the electrodes
  - poison the Pt catalysts
- traces from the seal may diffuse into the membrane
  - decrease in membrane conductivity
  - reduction in the mechanical integrity of the membrane.

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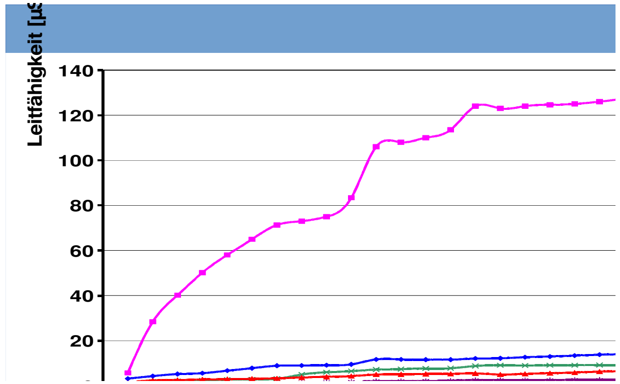
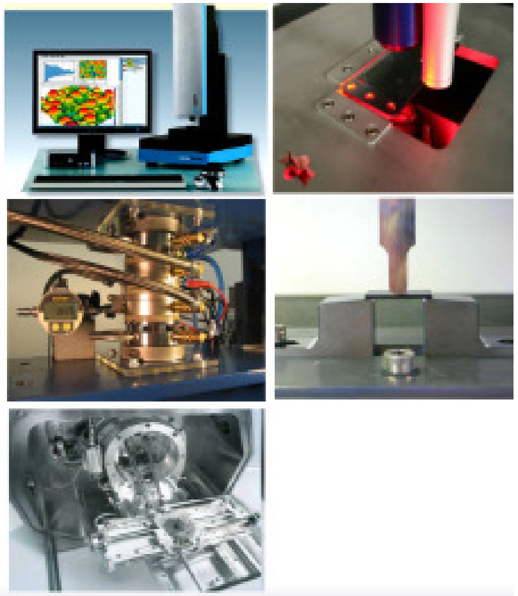
Causes for degradation

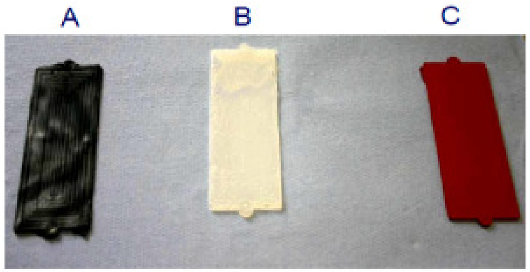
Qualification of gaskets: x-situ and in-situ testing necessary



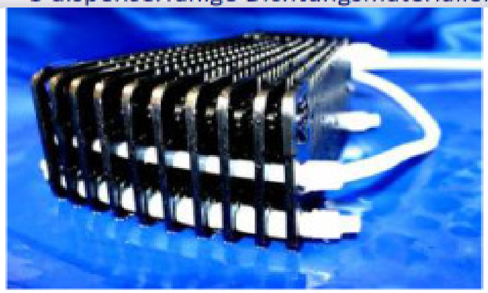
- Ex-situ-testing allows pre-testing of materials
  - Quality control methods established
    (restoring force, permeability, processibility and conductivity)
  - Immersion testing and again quality control methods
- Corellation ex-situ and in-situ is good:
  materials showing abnormalies also show higher degradation of PEM cells

	Dichtungen	BPP
Probengewicht	X	X
Probendicke	X	X
Profilometrie	X	X
Biegemodul	-	X
elektrische Widerstandsmessung	-	X
Elektronenmikroskopie (REM)	X	X
energiedispersive Röntgenanalytik (EDX)	X	X





3 dispenserfähige Dichtungsmaterialien



10 ZBT-Bipolarplatten (SG, bearbeitet)

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Stack mechanics
testing stack elongation

- 5 cell stack for stack elongation tests
  - 20 A (0.4 A/cm2) / 65 C
  - Cathode: dry, Lambda=2
  - Anode: humidity ~ 70%, Lambda=3
  - Air cooled, Temperature-Measurement
    in cooling channels (central and close to edges)
- Fixed bottom, Measurement of elonguation on top
  (Sylvac digital indicator, 1µm resolution)
- Cyclus: Operation / Cooling down until T ~const
  and elongation ~ constant
- Stack data and elongation data logged

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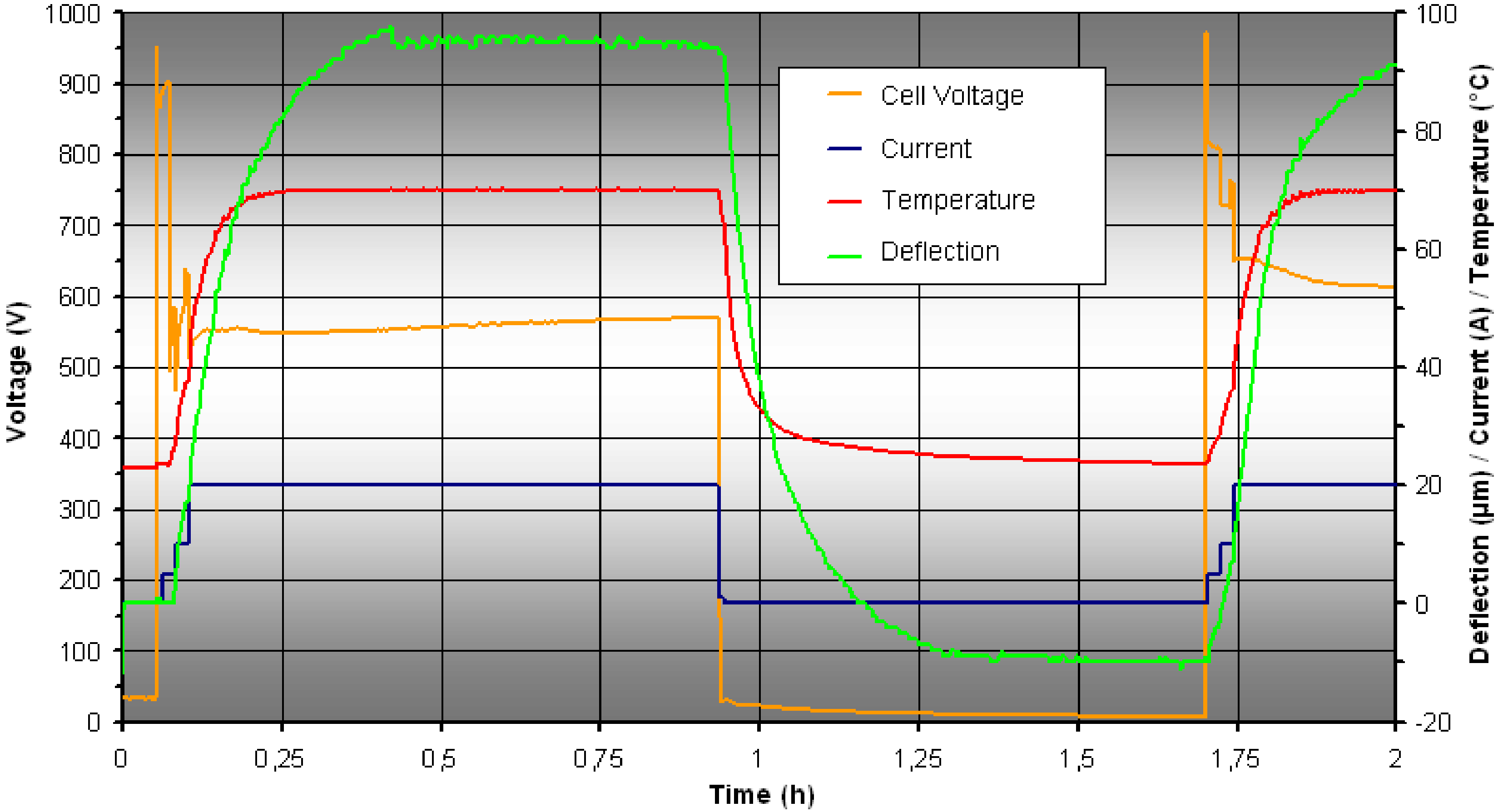
Stack mechanics

testing stack elongation: First start

- Initial stack start (dry)
- Deflection follows central stack temperature delayed (temperature gradients in stack)
- Stack cooles down resulting in negative deflection → ~ 10 µm smaller



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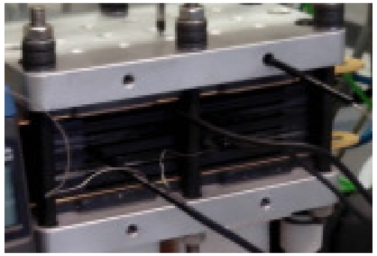
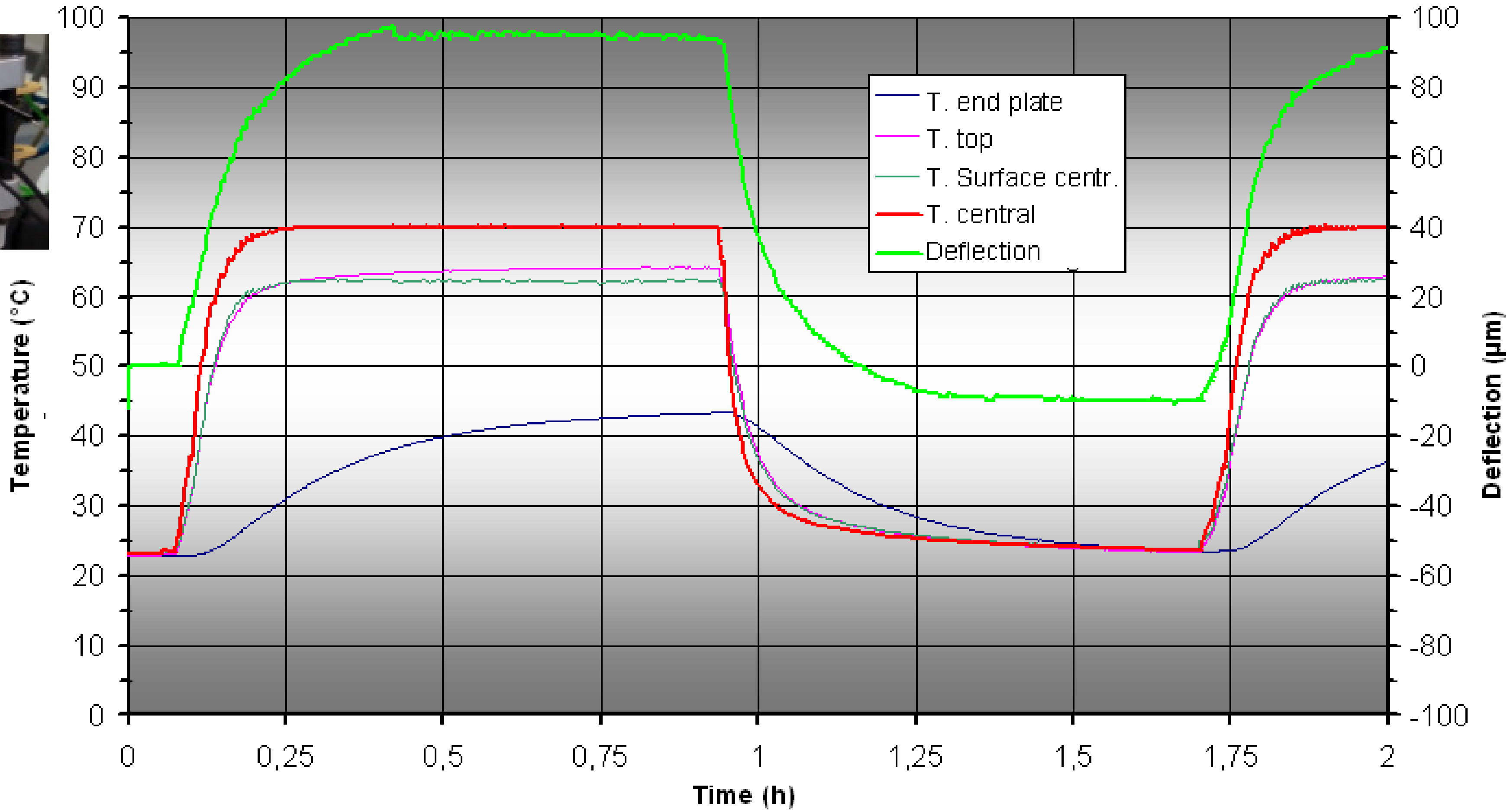
Stack mechanics

testing stack elongation: First start – Temperature dependency

- Deflection is dominated by cell elongation (MEA, Bipolar plates)
- End plate elongation (isolation plate) contributes less





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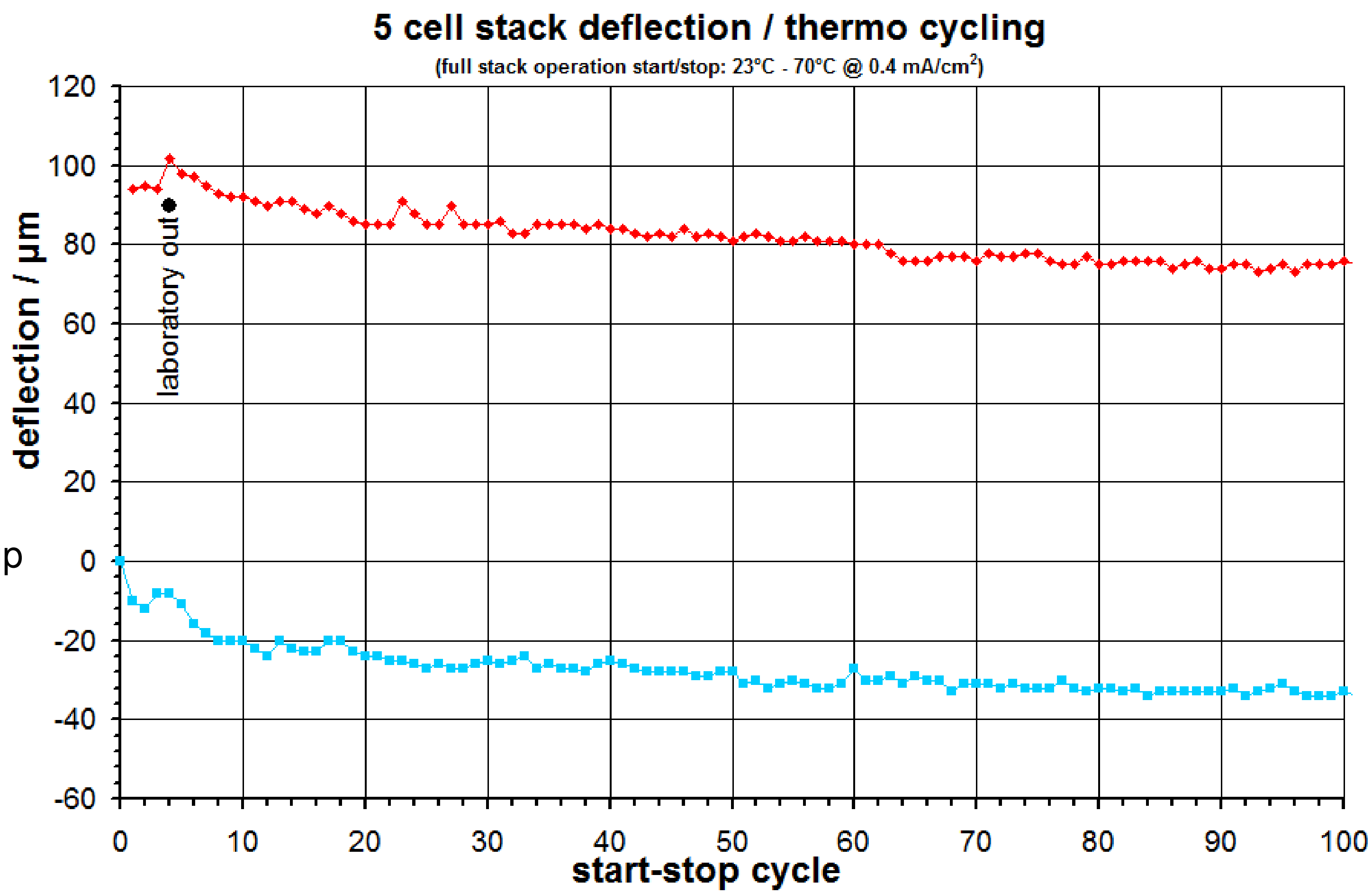
Stack mechanics

testing stack elongation: 100 thermo cycles

- Decrease of approximately 30 µm in 100 cycles
- Differential expansion (cold state - hot state) remains the same
- prolonged stops lead to expansion during next operating

Initial stack setup at RT → 0 µm



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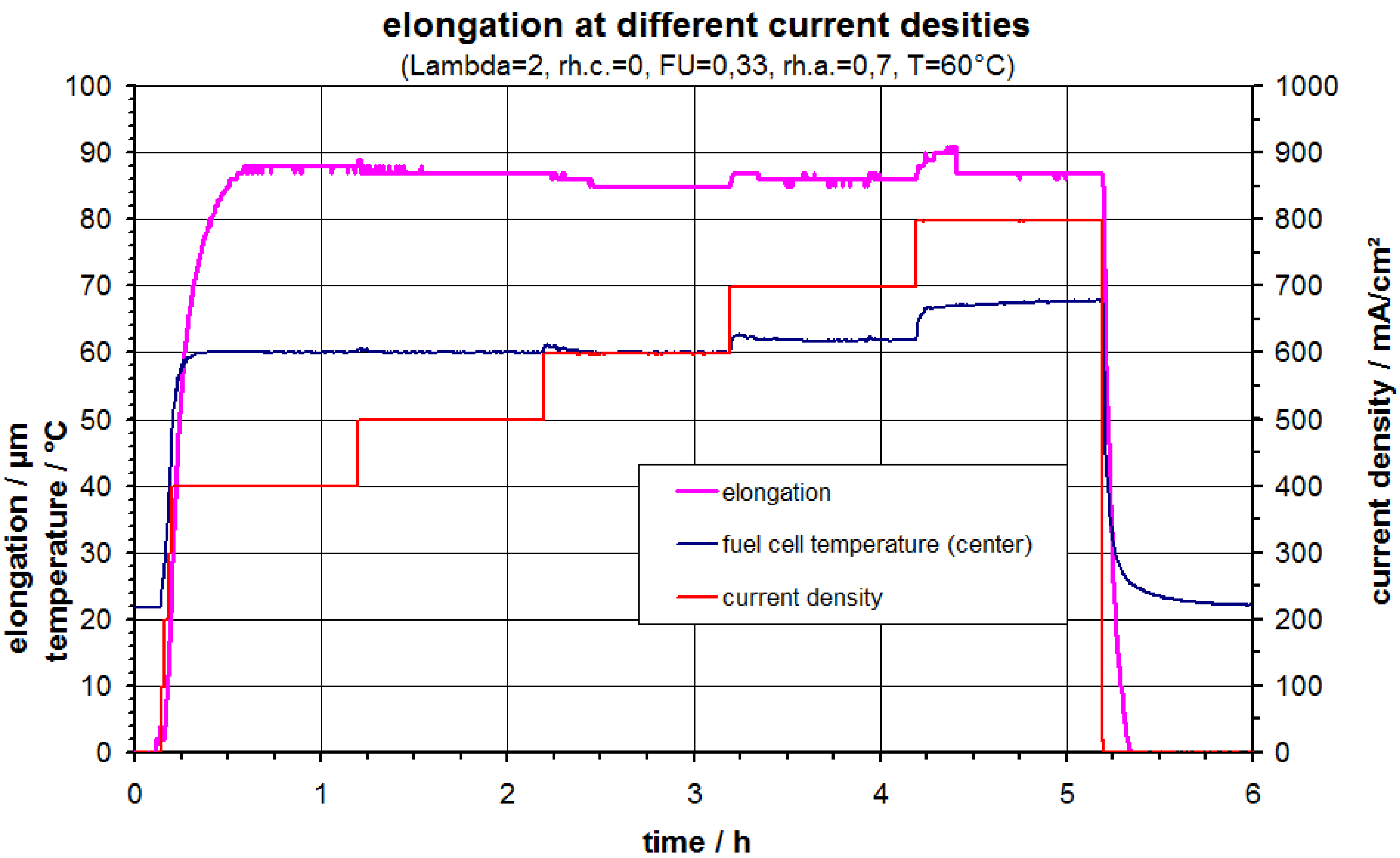
Stack mechanics

testing stack elongation: current density dependency

- stoichiometric operation, controlled temperature
- Stepwise increased current density
- No significant influence of current density on expansion



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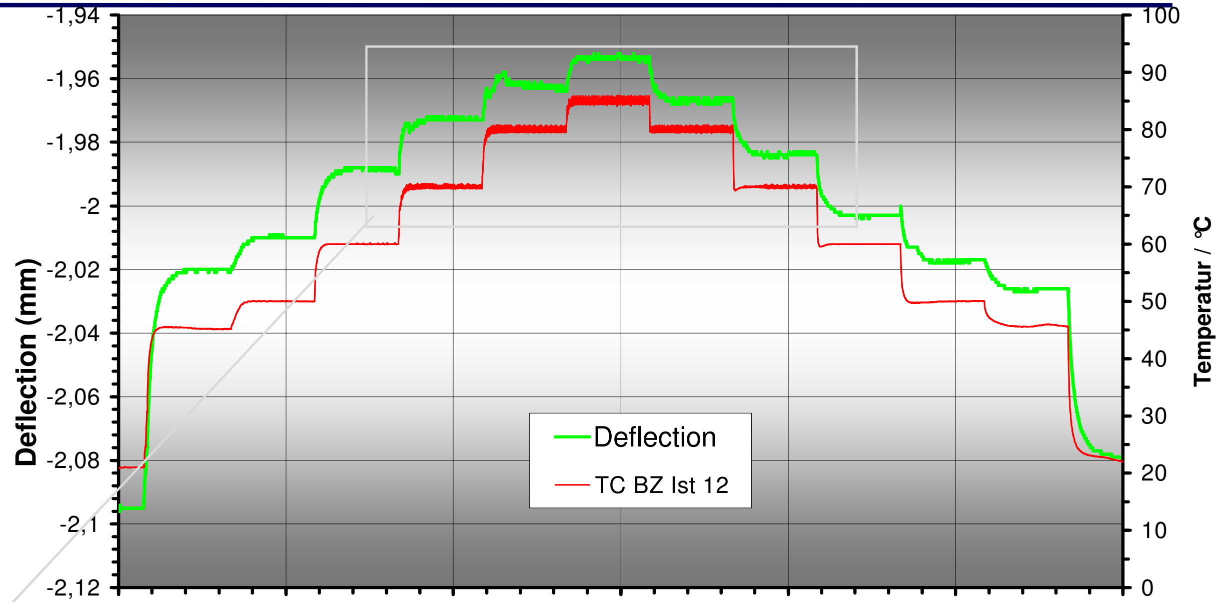
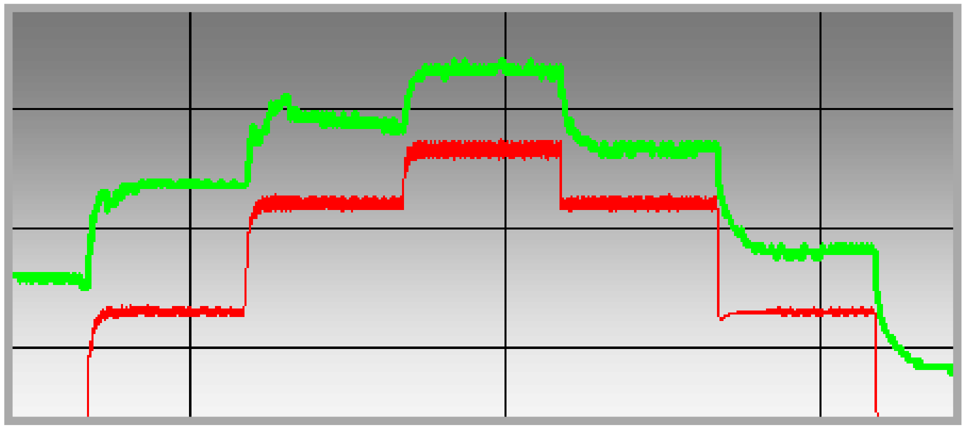
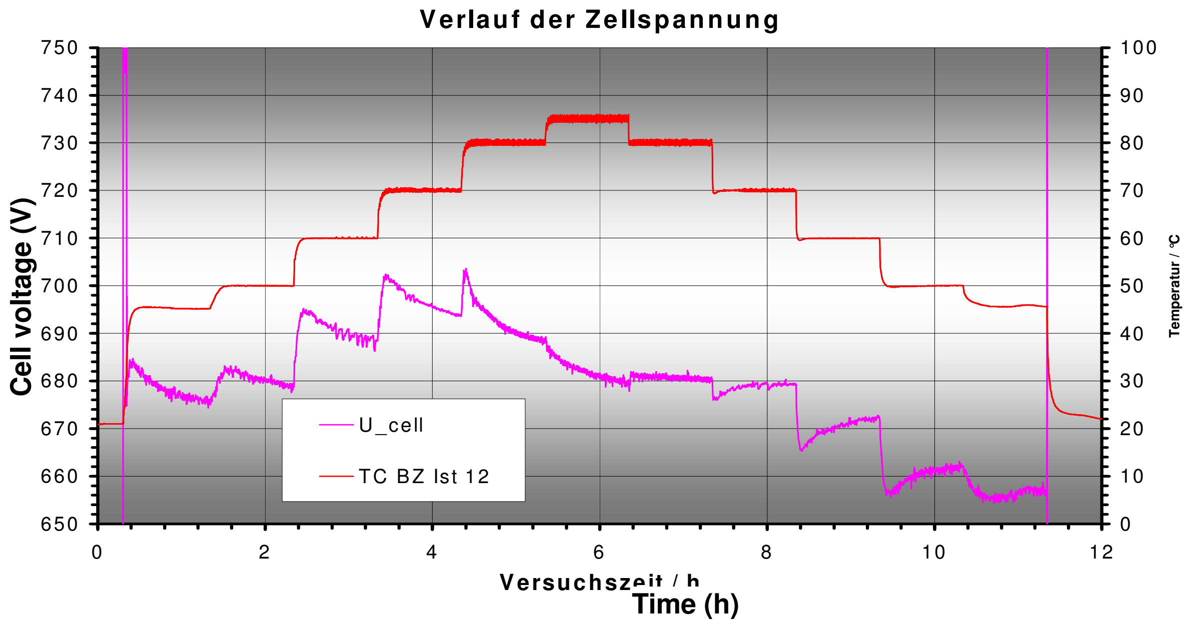
Stack mechanics

testing stack elongation: membrane dependency

- Cell operation at 0.4 A/cm^2
- Thickness decrease at 80 C and during cooling down
- membrane dries out (cell voltage)
- Membrane humidity significant part of elongation







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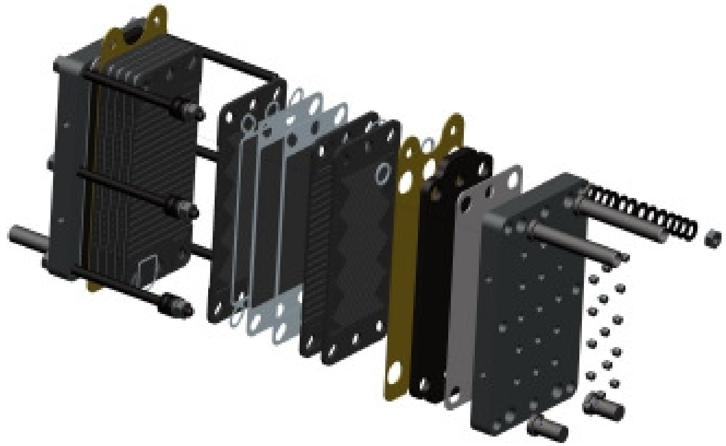
Stack mechanics
intermediate summary

- Stack elongation is dominated by temperature effects
- The cell components contribute most, end plates less
- Humidity of the membrane is also contributing
- This changes the mechanical cell status
- Local forces on GDL and / or gasket change



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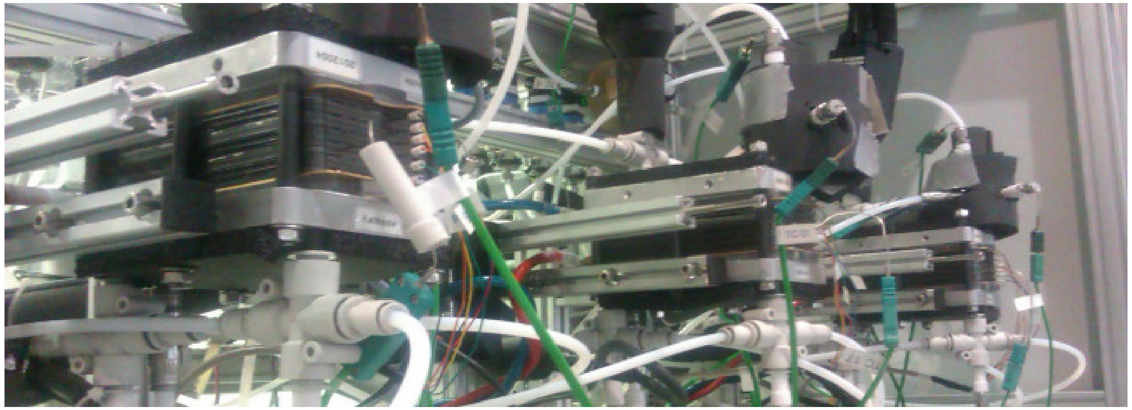
Long term operation of fuel cell stacks
comparing components and operation modes

Comparing test rig with 3 stacks in 3 identical sub-modules

- test with 3 stacks in parallel (ZBT standard setup)
- 5 cell short stacks cross flow (50 cm^2 active)
- Liquid cooling for homogenous stack temperatures
- Constant current or automated cycle operation
- general operating conditions:
  - cathode: stoichiometry 2,0; dry
  - anode: recirculation; heated
  - cross flow
  - Nominal current 0.4 A/cm^2 / 20 A

Test rig already used for
- MEA qualification
- Gasket qualification
- Glue qualification
- Bipolar plate qualification
- Inverter filtering needs (ripple)
- Flow field qualification
- Cooling structure optimization
- Operation mode optimization
- …



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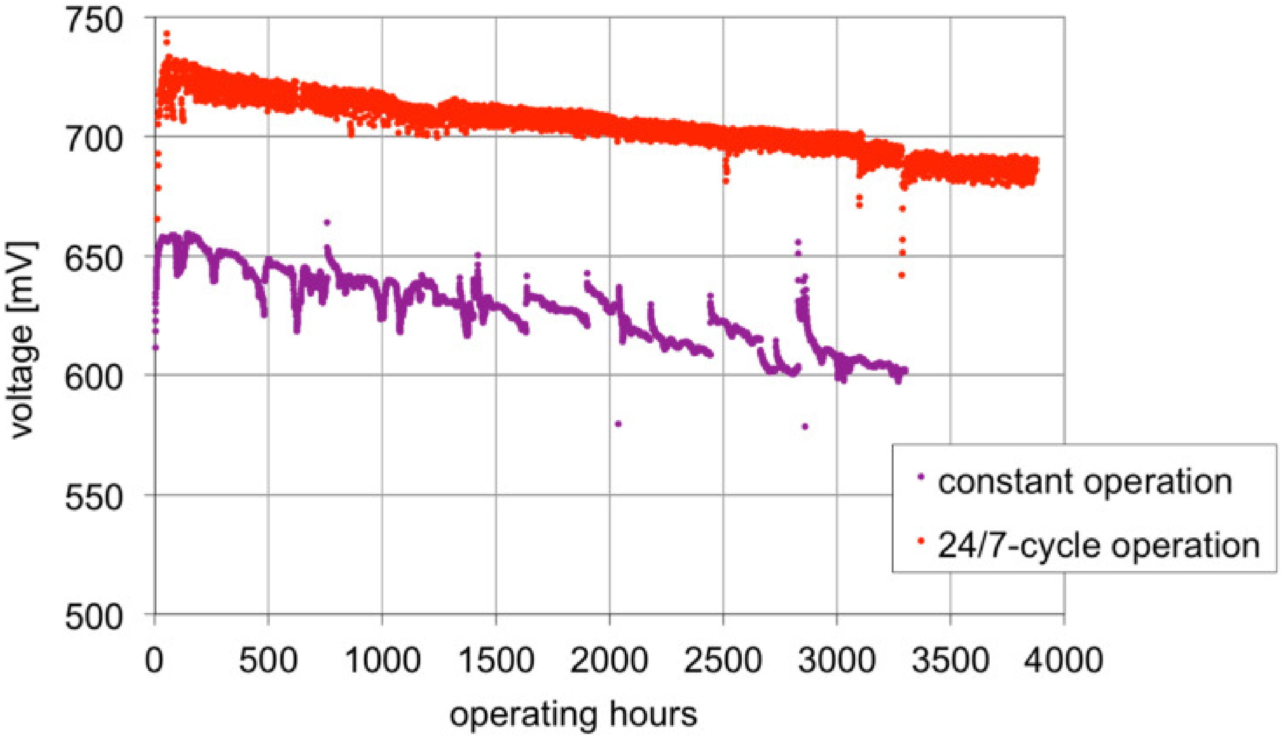
Long term operation of fuel cell stacks
operation modes

- First test have been performed with constant current operation
- A 24/7 cycle was introduced incl. shutdown resulting in:
  - Higher cell voltages (av. 10 % higher at same current density)
  - Reduced environmental influences (NO / NO_2)



comparison of long-term test data at 0.4 A/cm²

→ Analysing the reasons for „negative“ degradation

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Long term operation of fuel cell stacks
24 / 7 cycle

- 1 X measuring cycle 2 h: EIS, IV, EIS
- 18 x load cycle 1 h:
  (0.85 V; 0.4 A/cm^2; 0.45 V)
- 4 x thermal cycle 1 h: 60 C; 20 C; 60 C

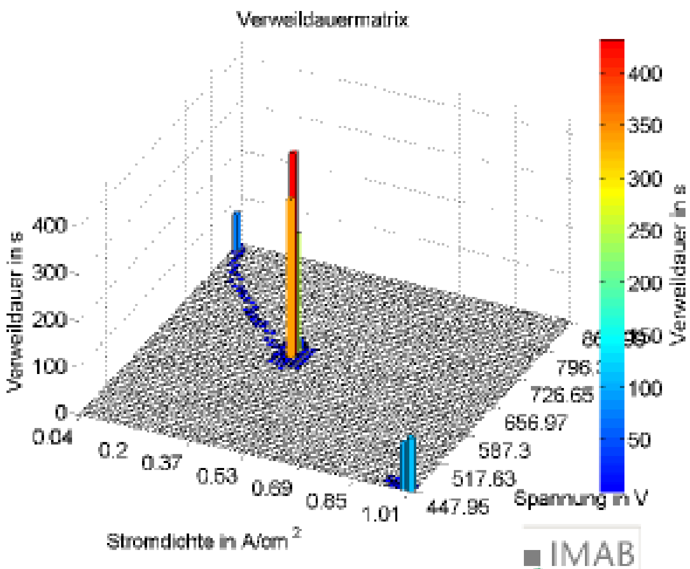
Resulting in following operational states in summ per day (24 hrs / 1440 min)

- 895 mins @ 0.4 A/cm^2 (incl. 2 EIS)
- 270 mins @ > 0.9 A/cm^2 (0,45V)
- 90 mins @ < 0.2 A/cm^2 (0,85 V)
- 160 mins @ 0.0 A/cm^2 (0 V)
  (Cooled down)
- 25 mins @ I-V-Cycling

minute / start	measuring cycle	overall time
0	0.4 A/cm^2	120 min
20	EIS, 0.4 A/cm^2	
45	polarization curve, 0.4 A/cm^2	
95	EIS, 0.4 A/cm^2	

minute / start	load cycle	overall time
0	0.4 A/cm^2	60 min
10	V_{min} I_{max}	
25	0.4 A/cm^2	
45	0.85 V cell voltage	
50	0.4 A/cm^2	

minute / start	thermal cycle	overall time
0	0.4 A/cm^2, cooling	60 min
T_{soll} - 10 °C	shutdown, cooling	
45	start, 0.4 A/cm^2	



IMAB

starting hour	24/7 cycle	overall time
0:00	measuring cycle	24 hours
1:00		
2:00	load cycle	
3:00	load cycle	
4:00	load cycle	
5:00	load cycle	
6:00	thermal cycle	
7:00	load cycle	
8:00	load cycle	
9:00	load cycle	
10:00	load cycle	
11:00	thermal cycle	
12:00	load cycle	
13:00	load cycle	
14:00	load cycle	
15:00	load cycle	
16:00	thermal cycle	
17:00	load cycle	
18:00	load cycle	
19:00	load cycle	
20:00	load cycle	
21:00	thermal cycle	
22:00	load cycle	
23:00	load cycle	

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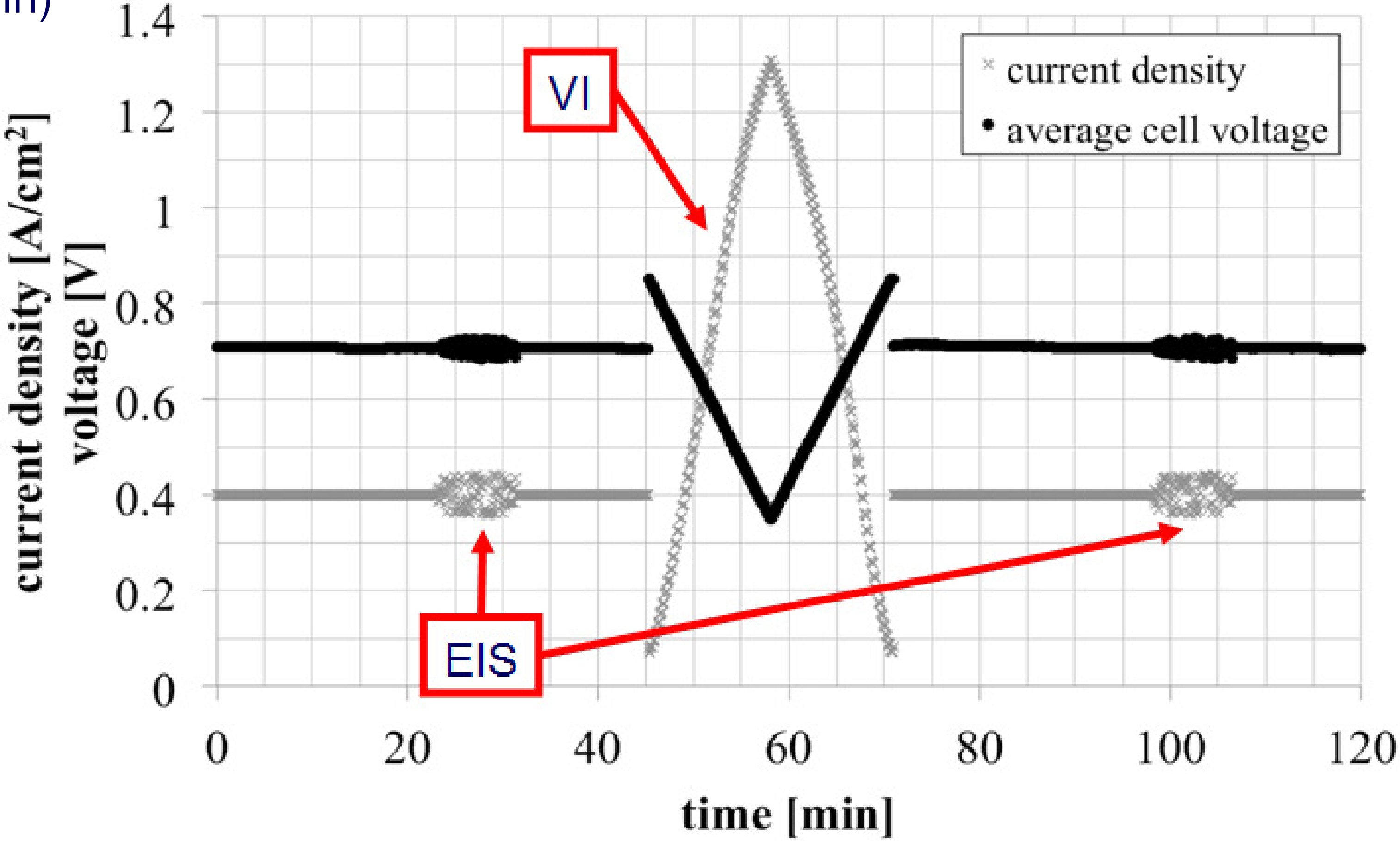
Long term operation of fuel cell stacks
measuring cycle

- electrochemical impedance spectroscopy (EIS) before and after the polarization curve (VI-curve) (0.4 mA/cm²; 0.04 mA/cm²; 100 Hz → 20 kHz → 0.1 Hz)
- VI-curve (0.95 V → 0.35 V → 0.95 V per cell; 50 mV steps; ∑ 30 min)

minute / start	measuring cycle	overall time
0	0.4 A/cm²	120 min
20	EIS, 0.4 A/cm²	
45	polarization curve, 0.4 A/cm²	
95	EIS, 0.4 A/cm²	



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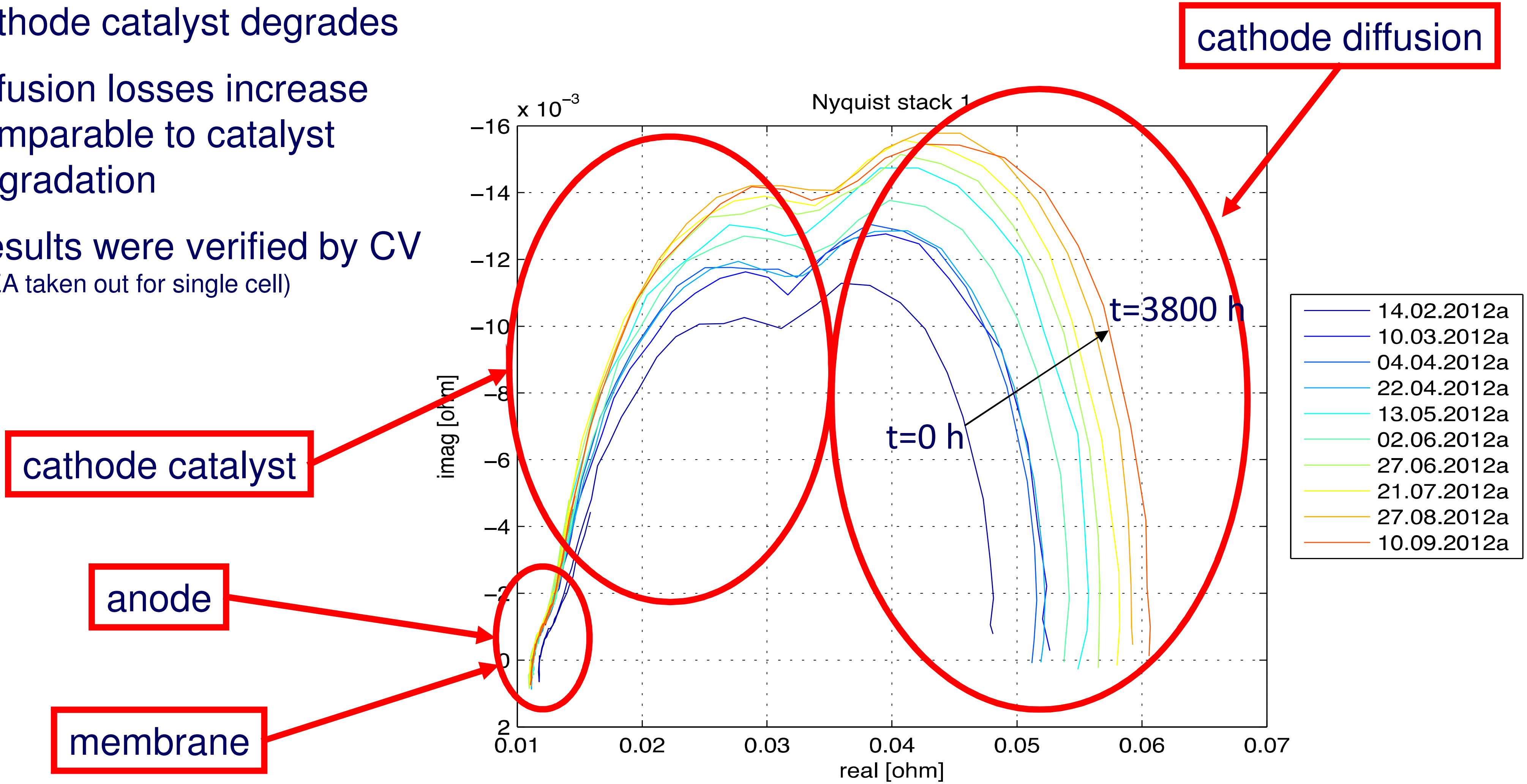
Long term operation of fuel cell stacks
Online EIS analysis

- membrane is stable ("activation process" at the beginning)
- anode is stable
- cathode catalyst degrades
- diffusion losses increase comparable to catalyst degradation

☑ Results were verified by CV
(MEA taken out for single cell)



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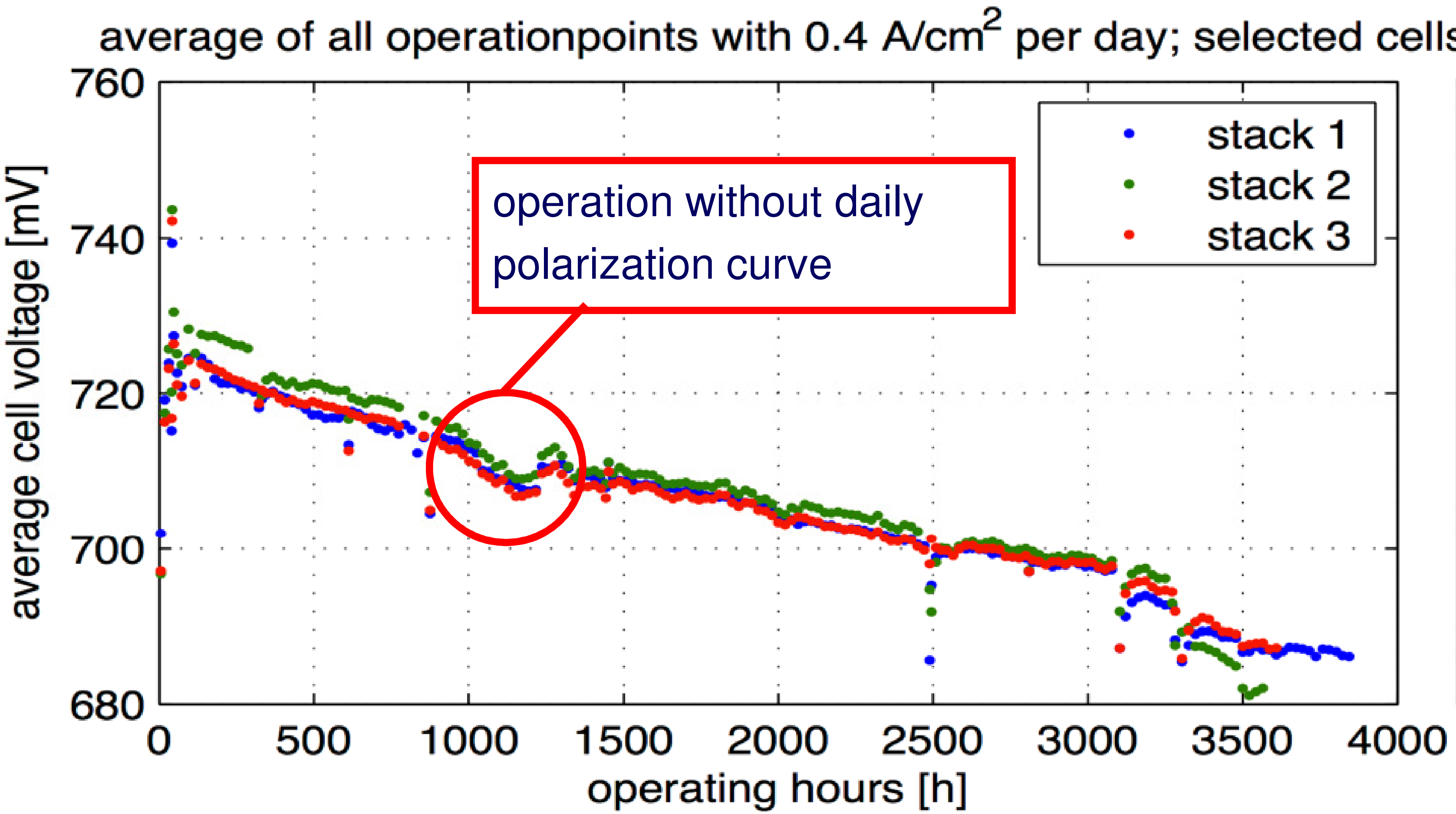
Long term operation of fuel cell stacks
reversible degradation phenomena



starting hour	~~4/7 cycle~~	overall time
0:00	~~mea[illegible] cycle~~	24 hours
1:00		
2:00	load cycle	
3:00	load cycle	
4:00	load cycle	
5:00	load cycle	
6:00	thermal cycle	
7:00	load cycle	
8:00	load cycle	
9:00	load cycle	
10:00	load cycle	
11:00	thermal cycle	
12:00	load cycle	
13:00	load cycle	
14:00	load cycle	
15:00	load cycle	
16:00	thermal cycle	
17:00	load cycle	
18:00	load cycle	
19:00	load cycle	
20:00	load cycle	
21:00	thermal cycle	
22:00	load cycle	
23:00	load cycle	

→ quantification of the influence of different operation conditions on the reversible degradation

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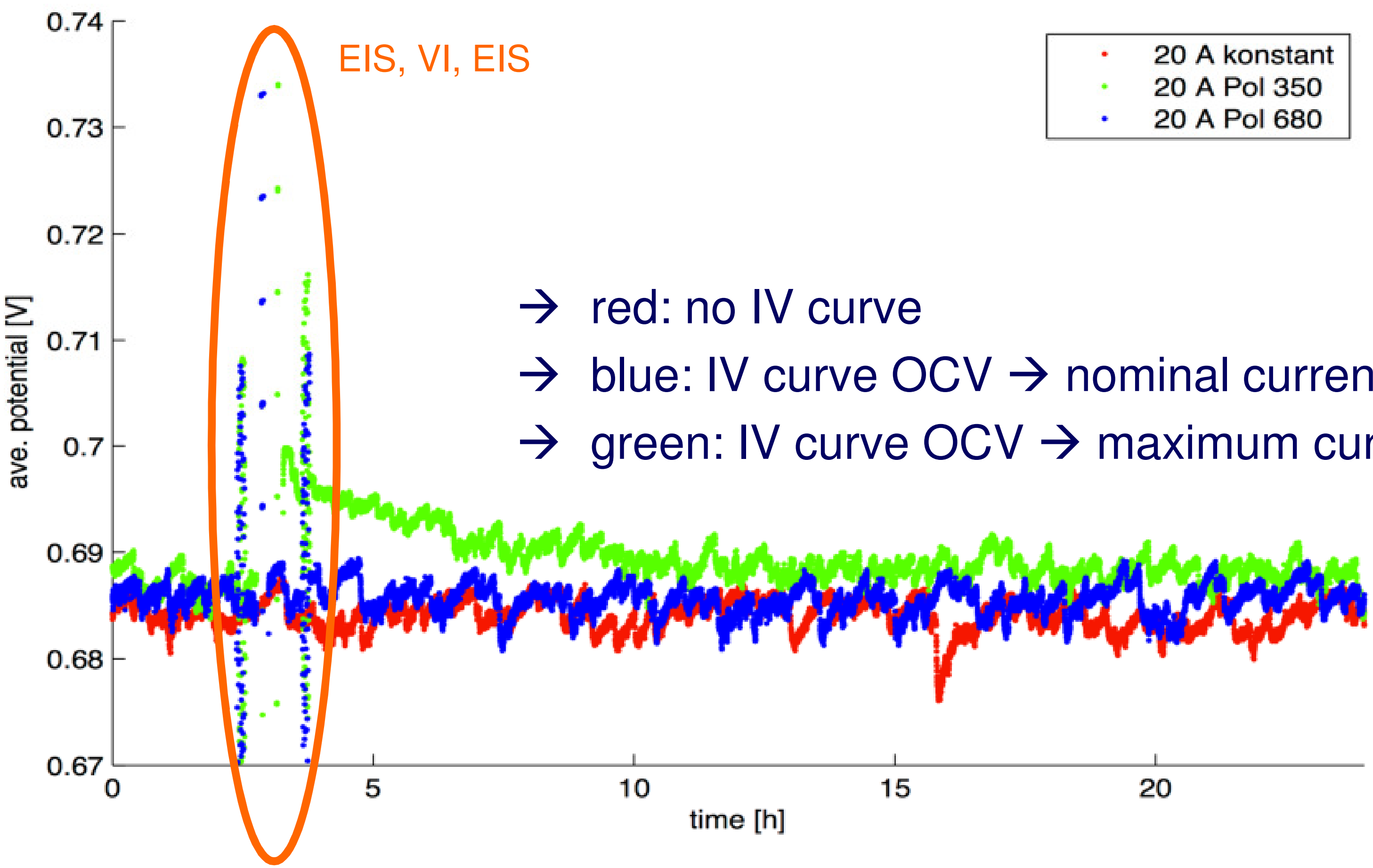
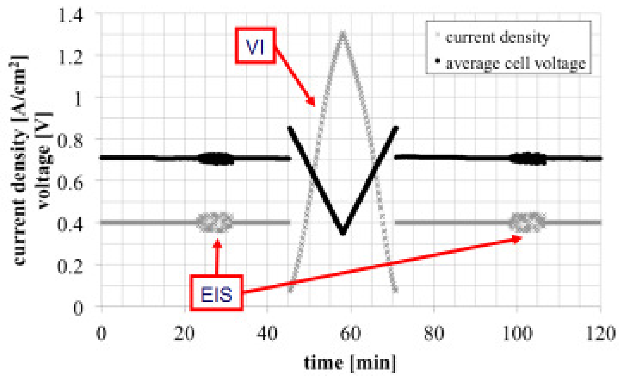
Long term operation of fuel cell stacks
influence of polarization curve on cell voltage





→ red: no IV curve

→ blue: IV curve OCV → nominal current

→ green: IV curve OCV → maximum current

→ A polarization curve with high maximum current refreshes the cell voltage after long constant operation

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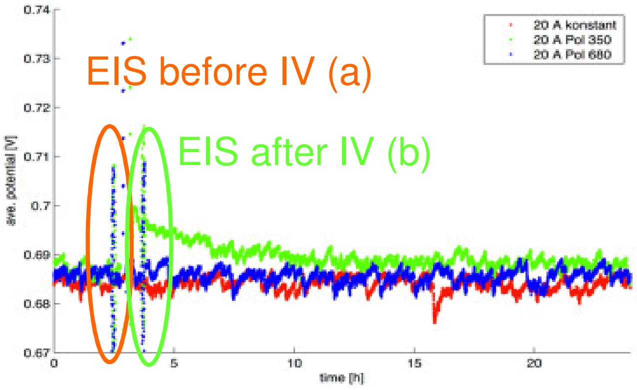
Long term operation of fuel cell stacks

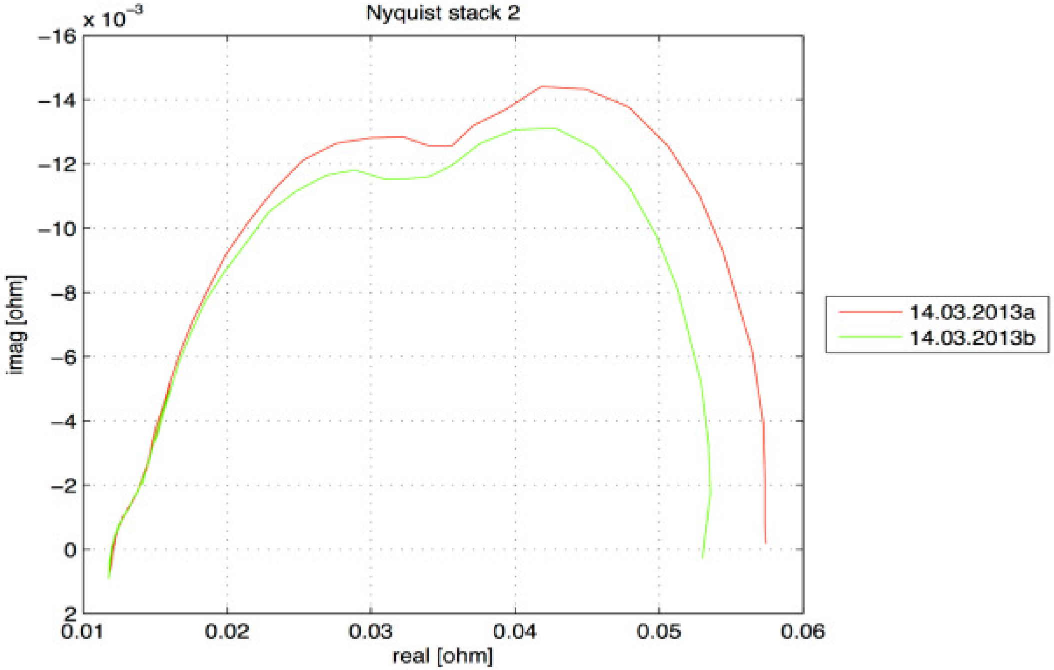
influence of polarization curve on cell voltage → EIS analysis

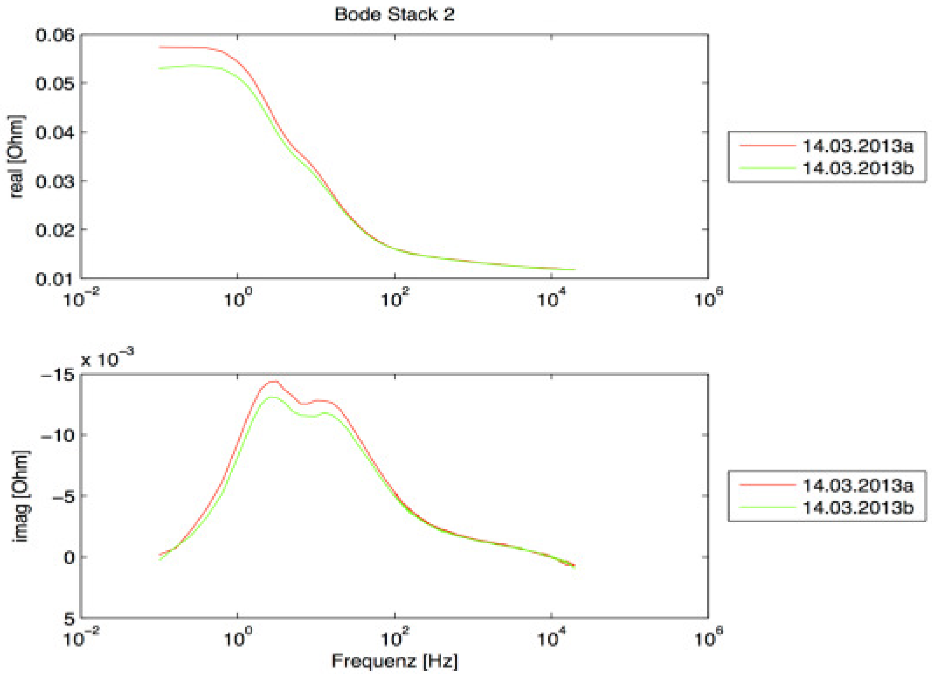


→ The high frequency resistance (HFR) changes insignificantly

→ The low-frequency resistance (LFR) decreases

[mΩ/cm²]	HFR	LFR
14.03.2013a	120.6	574
14.03.2013b	119.8	533





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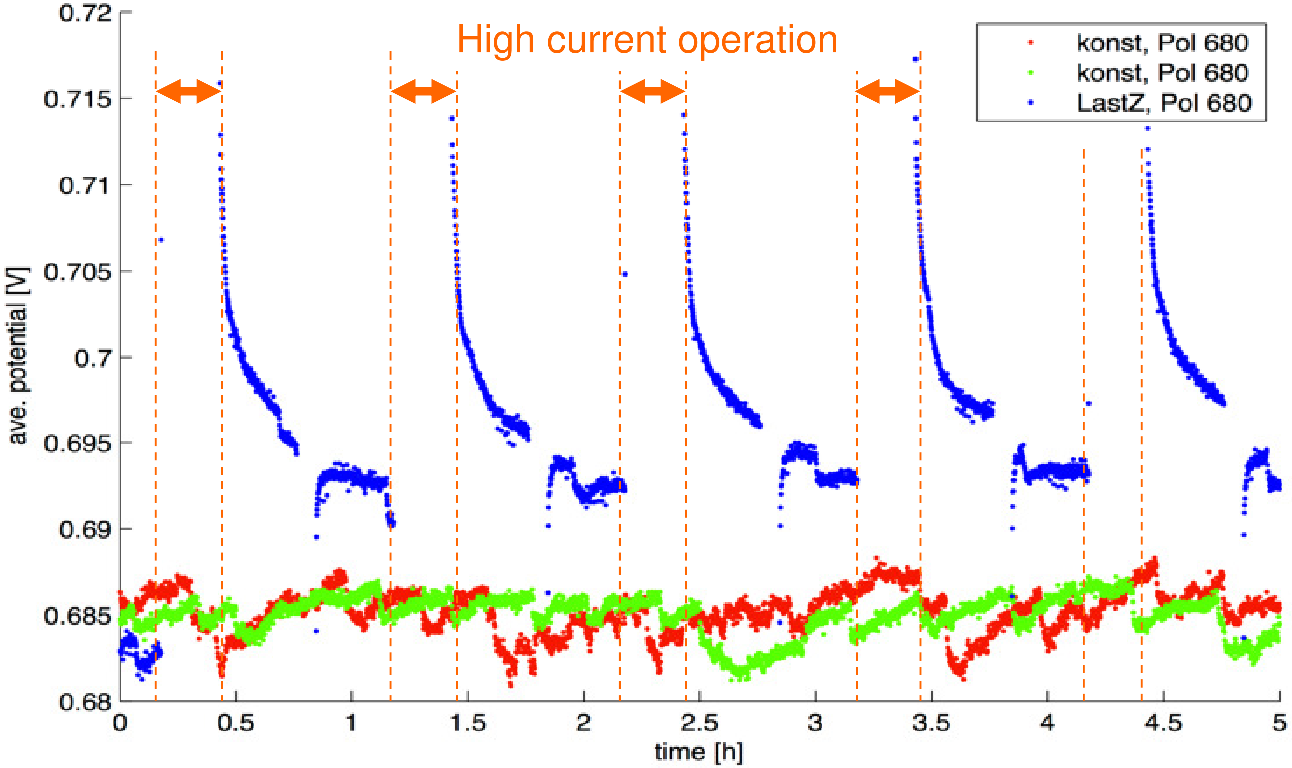
Long term operation of fuel cell stacks

influence of load changes on cell voltage



- → Operation of stack on 0.4 A/cm² for 48 hrs
- → Switching of stack to ~1 A/cm² for 15 mins / back to 0.4 A/cm²
- → Higher efficiency at low current operation restored

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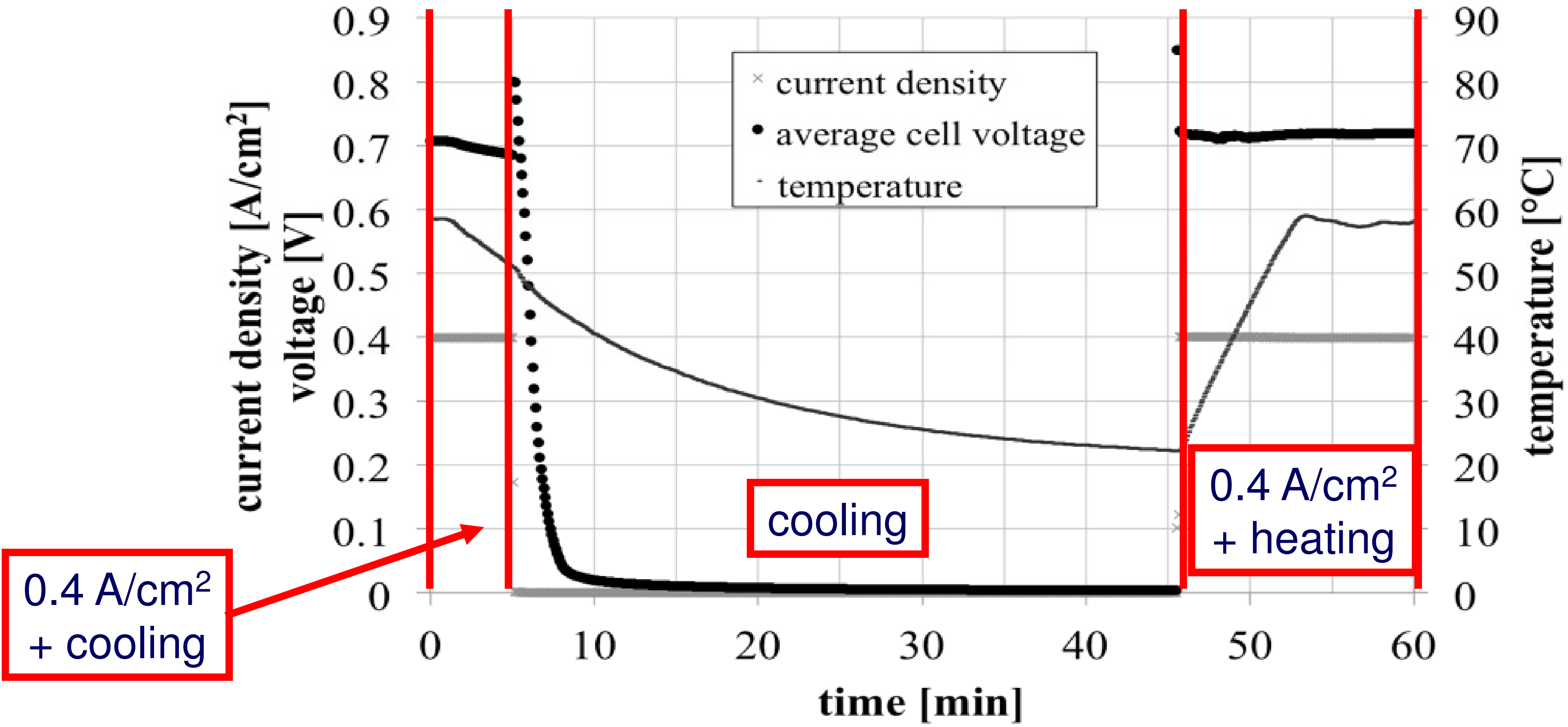
Long term operation of fuel cell stacks

thermo cycle



- → operation at 0.4 A/cm² while cooling down from 60 C to 50 C
- → shutdown with max. 0.85 V voltage control
- → cooling down to approximately 20 C
- → restart and heating

minute / start	thermal cycle	overall time
0	0.4 A/cm², cooling	60 min
T_{soll} - 10 °C	shutdown, cooling	
45	start, 0.4 A/cm²	

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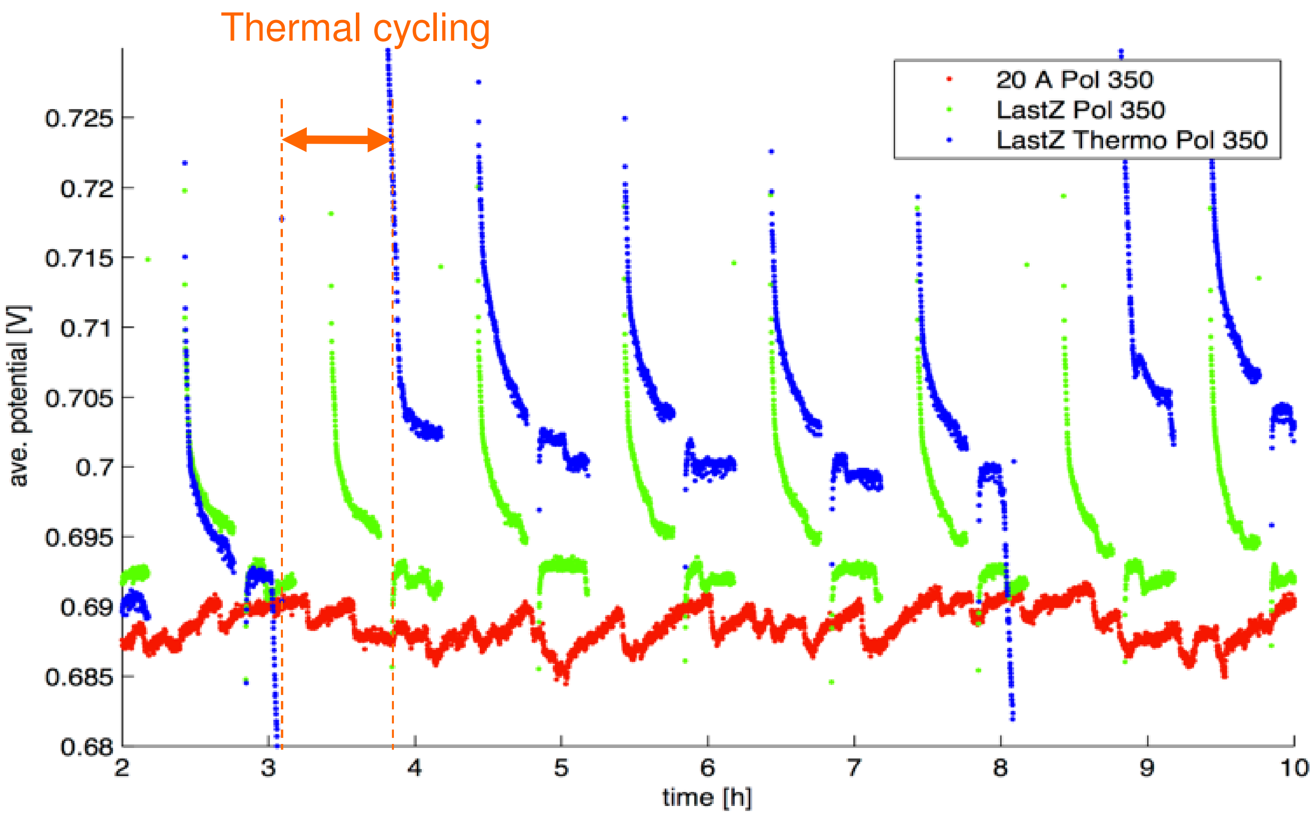
Long term operation of fuel cell stacks

influence of temperature changes on cell voltage



minute / start	thermal cycle	overall time
0	0.4 A/cm², cooling	60 min
T_{soll} - 10 °C	shutdown, cooling	
45	start, 0.4 A/cm²	

→ Shutdown and thermo cycling leads to higher stack voltage afterwards

→ The influence is even higher as caused by high loads

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Influence of operation strategies on the life time of PEM fuel cells

summary and outlook

- Degradation mechanisms → mostly caused by operation
- Mechanical issues of load cycling
  - Membrane humidity has influence on the thermo-mechanics
  - Local forces within the cell are possibly disturbed
- Electrochemical issues of load cycling
  - PEM cells show a strong "memory" for the operating conditions of the last hours (especially if operated without humidification)
  - Electrochemistry does not like boredom
  - High currents and low temperatures optimize the local water management @ dry op.
- Further investigations on force deflection issues and ex-situ analysis of the single cells ongoing
- Final Workshop „life time prognosis“ January 2014 in Ulm

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Contact:

Dr.-Ing. Peter Beckhaus
p.beckhaus@zbt-duisburg.de
+49 (0)203/7598-3020
www.zbt-duisburg.de