Numerical Simulation of the Electrolyte (H_3PO_4) Loss in HT-PEM Fuel Cells

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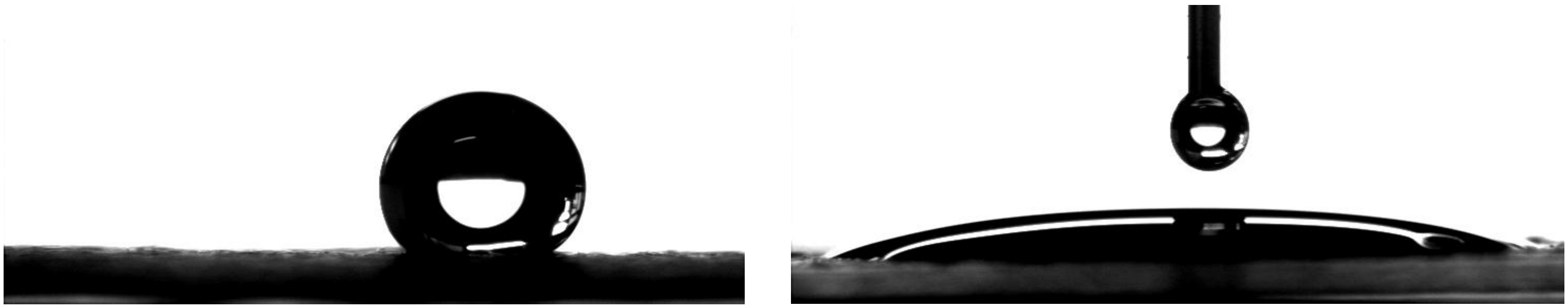
3rd Carisma Conference 2012



Agenda

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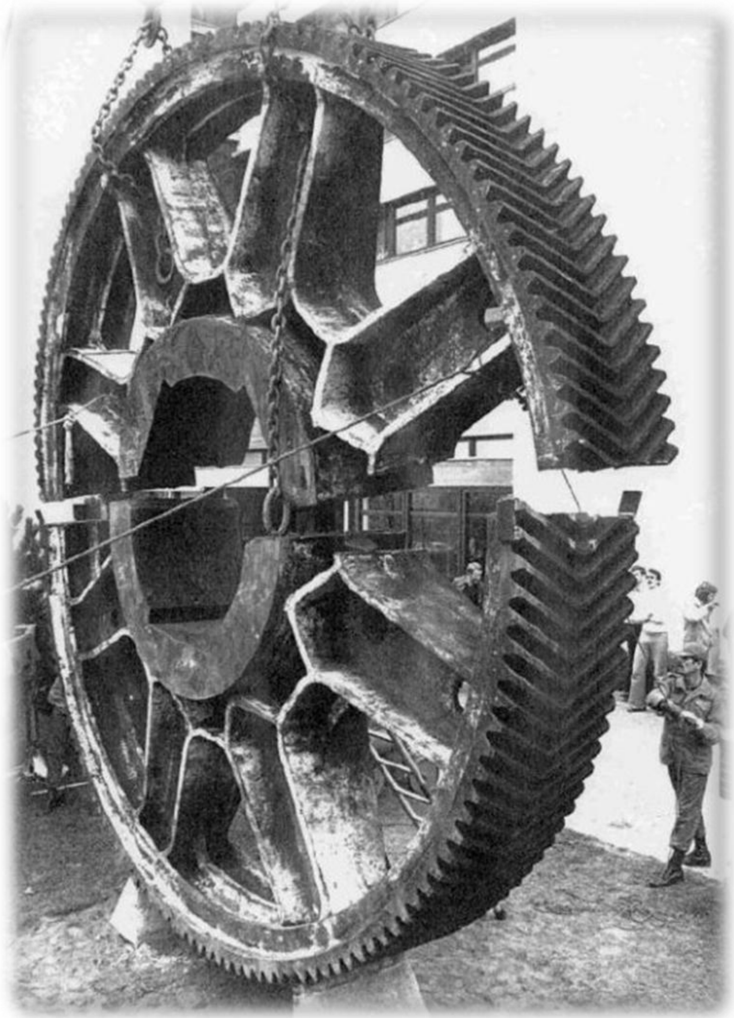

Degradation of HTPEMs

Durability targets

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Motivation:

- DOE Target 2020: Operating lifetime of 60k h with a degradation rate of 0.3%/1000 h (with cycling) for stationary applications
- Reported degradation data:

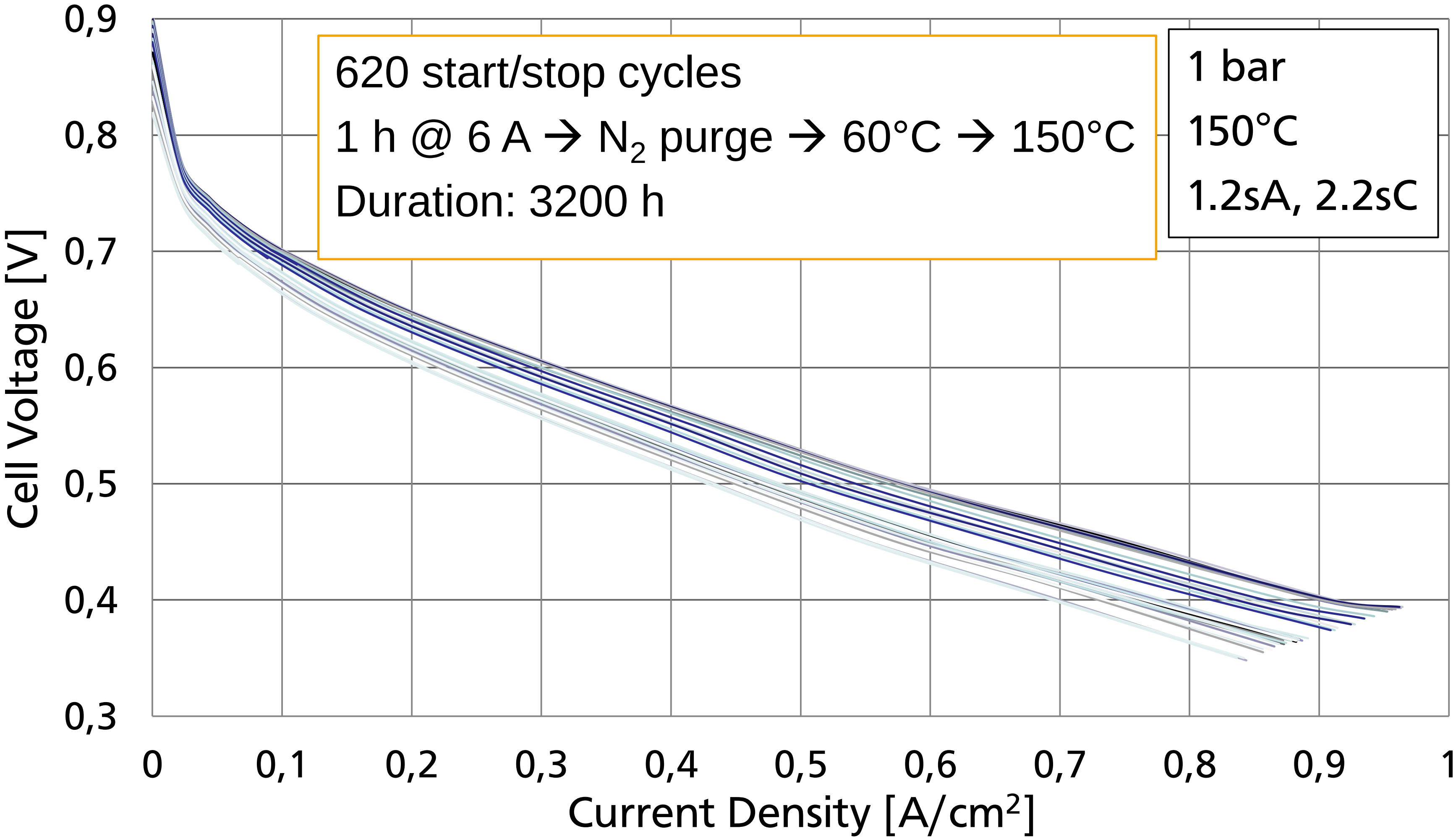
Author	Temperature [°C]	Voltage degradation rate [µV/h]	PA loss rate [µg/cm^2/h]	Duration [h]	Membrane
Bandlamudi	160	32	0,09	1000	P-1000
	170	44	0,18	1000	P-1000
Benicewicz et al.	160	4,9	0,01	1000	para-PBI
	190	60	0,11	1000	para-PBI
Modestov et al.	160	25	-	780	P-1000

Conclusion:

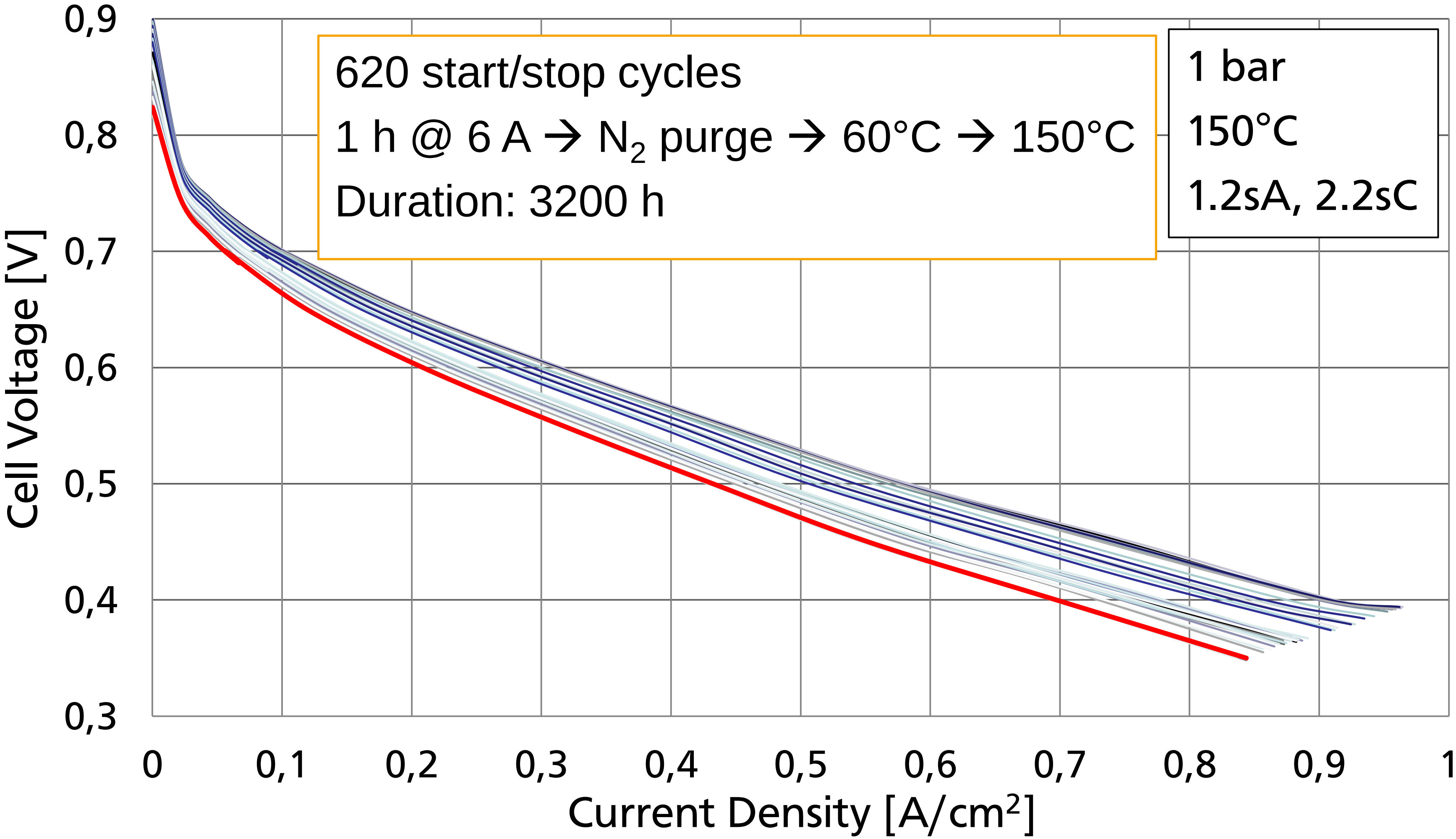
- Mechanism of acid loss is not fully understood yet
- Acid loss becomes significant for 60k h of operation

Long Term Test

Start/stop cycling and constant load



Long Term Test
Start/stop cycling and constant load



Long Term Test
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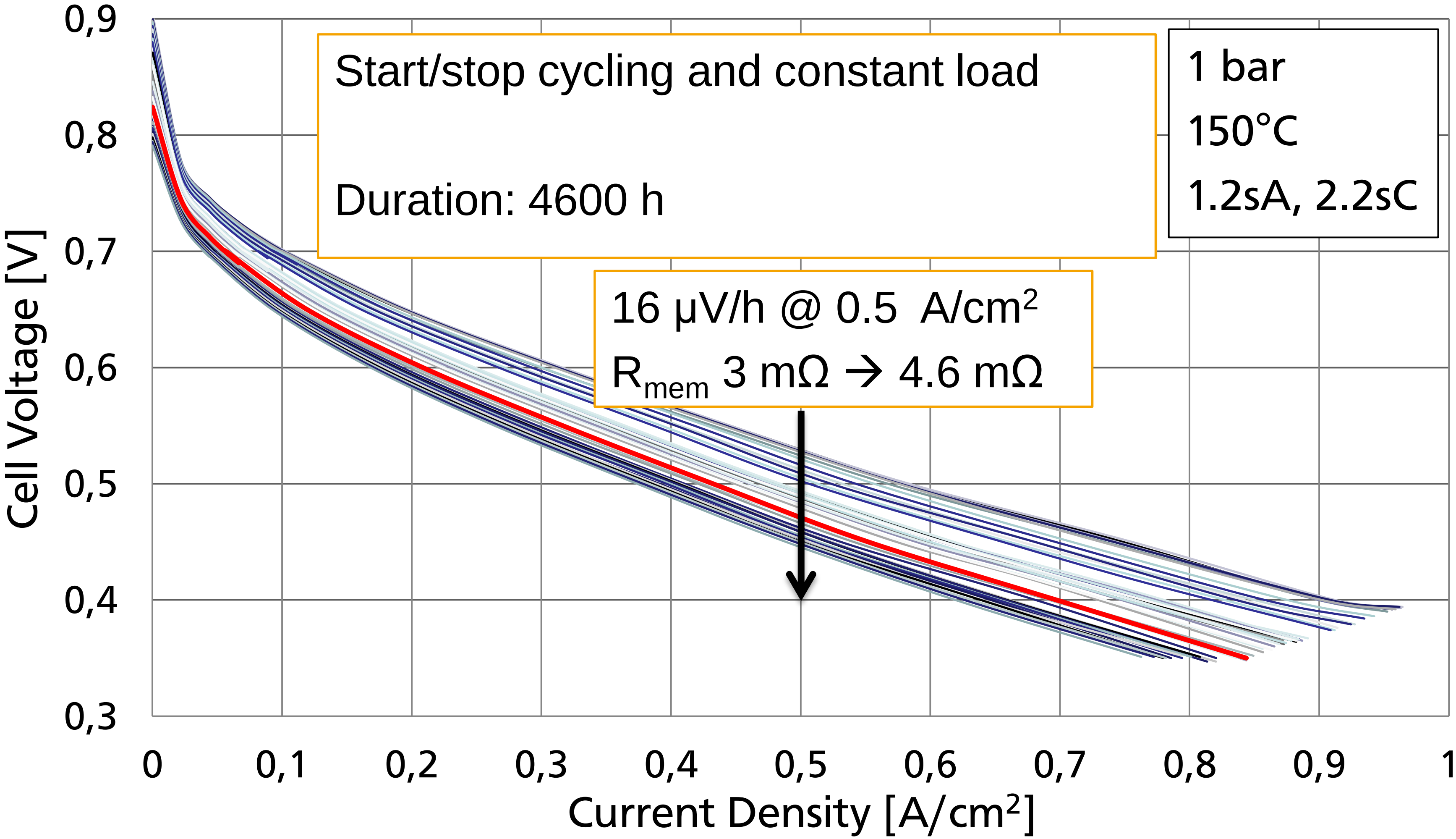
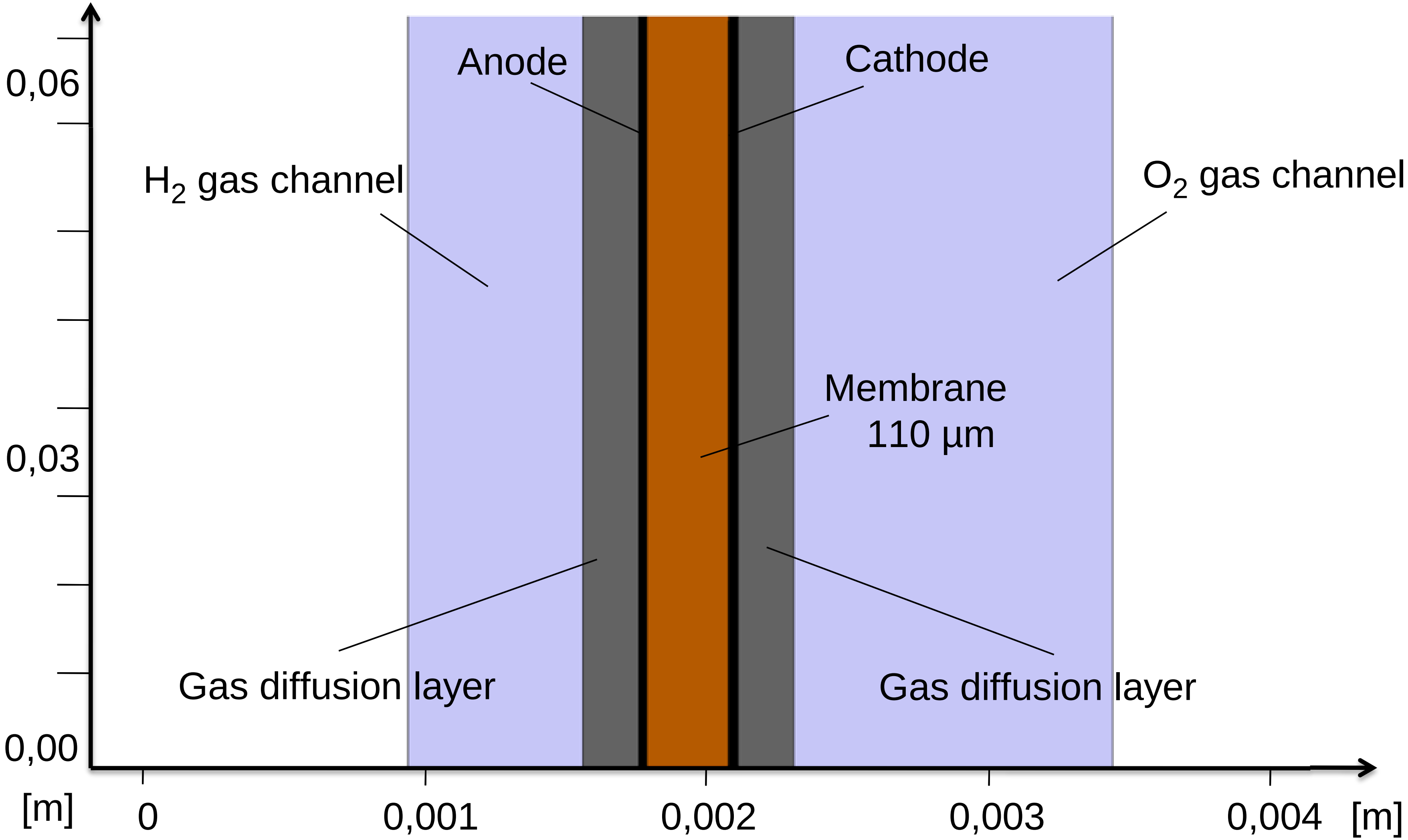


Numerical Model
Geometry



Numerical Model
Assumptions

General:

- Anisothermal
- Steady state
- ORR dominates activation overpotentials
- No gas permeation through the membrane → No mixed potential
- Operation on hydrogen and air

Materials:

- Macro homogeneous and isotropic
- Pore size distribution in the catalytic layer has two maxima
- Effect of porosity on transport parameters is described by the Bruggemann correlation

PA:

- No polycondensation of phosphoric acid
- Diffusion coefficient of PA depends on temperature and concentration
- Vapor pressure of the species PA is neglected
- Acid expansion and contraction is completely reversible during one simulation run
- Capillarity does not effect evaporation

Membrane:

- Contains “free acid” and can be considered as porous medium
- No thickness change over lifetime
- Ionic conductivity depends on acid concentration, temperature and morphology (ε,τ)
- Water gradient through the membrane >> than along the channel

Numerical Model
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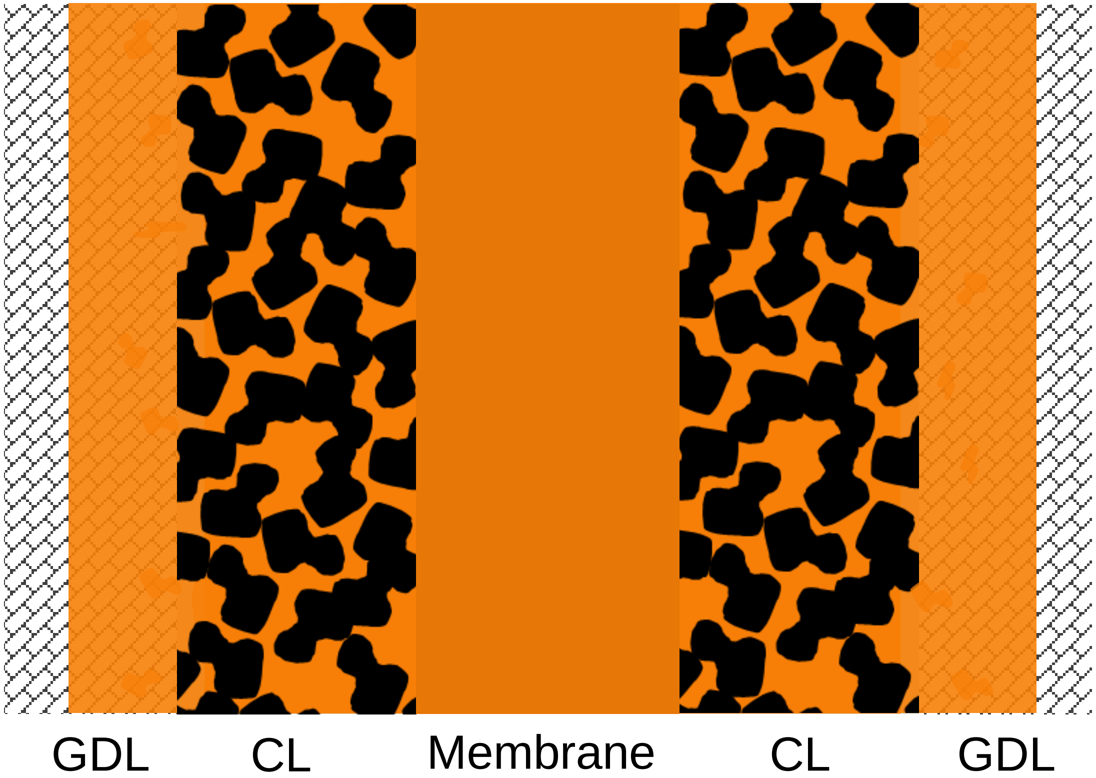
Numerical Model
Implemented Physics

• Navier-Stokes equations	Pressure and velocity field
• Maxwell-Stefan diffusion	Substance distribution in liquid and gas (H_2O, H_3PO_4), (H_2, O_2, N_2, H_2O)
• Butler-Volmer kinetics	Current density distribution
• Poisson´s equations	Electric and ionic potential distribution
• Energy balance	Temperature field
• Hertz-Knudsen kinetics	Evaporation and condensation terms

Numerical Model

Mobility of phosphoric acid in the MEA



Status:

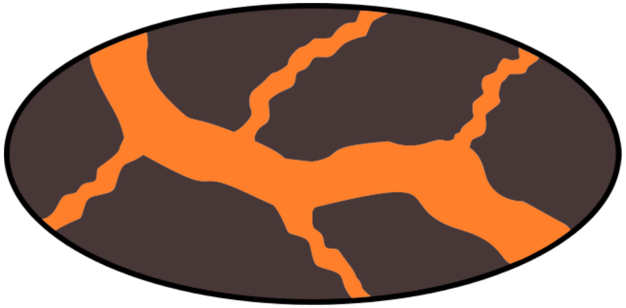
(1) Assembly
(2) Compressed MEA
(3) Break-In operation
(4) Standard operation
(5) High current density or humidification
(6) Standard operation

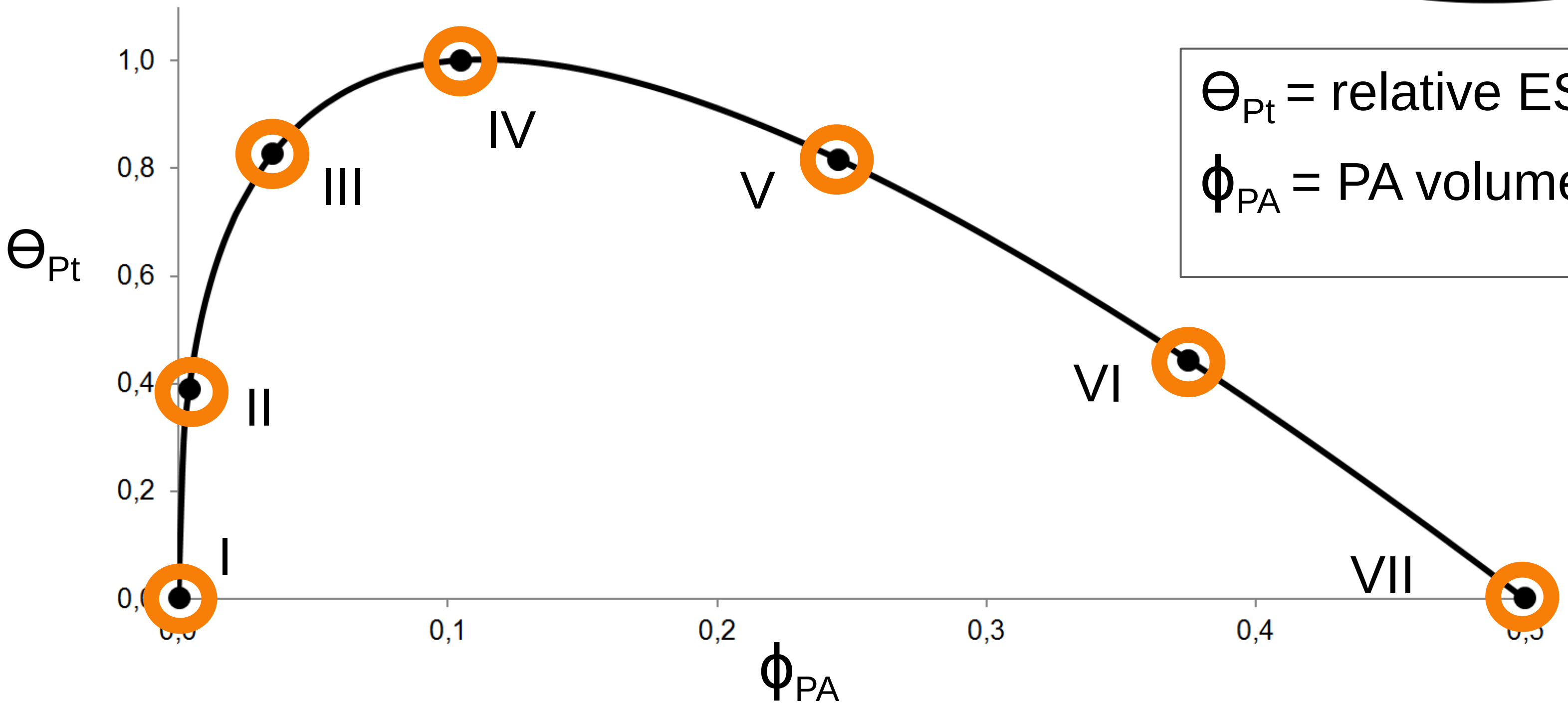
Numerical Model

Ionic contacting

$$\Phi_{PA} + \Phi_{Gas} + \Phi_{Solid} = 1$$

Pore system:



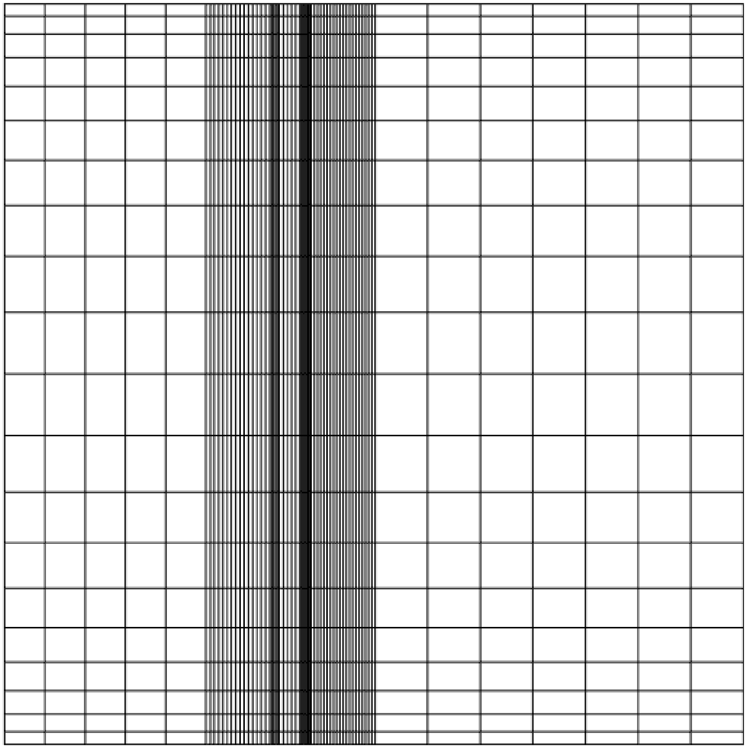


ΘPt = relative ESA

ϕPA = PA volume fraction

Numerical Model
Meshing and Solving

- Model:
  - COMSOL Multiphysics® 4.3
  - Number of dependent variables: 14
  - Number of degrees of freedom: 14802
  - Solver: MUMPS parametric/stationary
  - Solution time: 57s

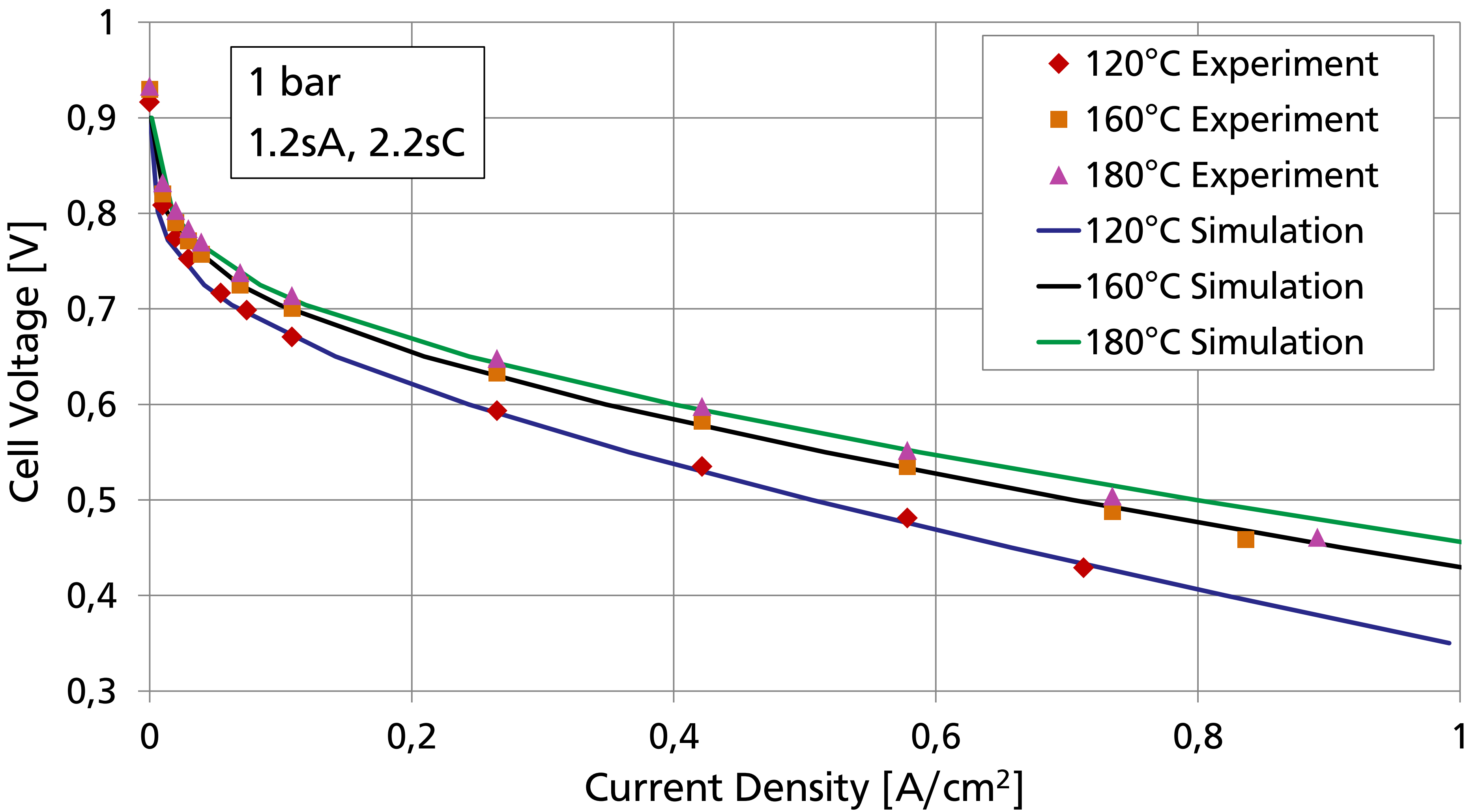


- Mesh:
  - Number of elements: 1280
  - Average element quality: 0.05

- Computer:
  - CPU: Intel® Core™ i7-3930K
  - RAM: 32GB

Model Validation

Temperature and pressure sweep



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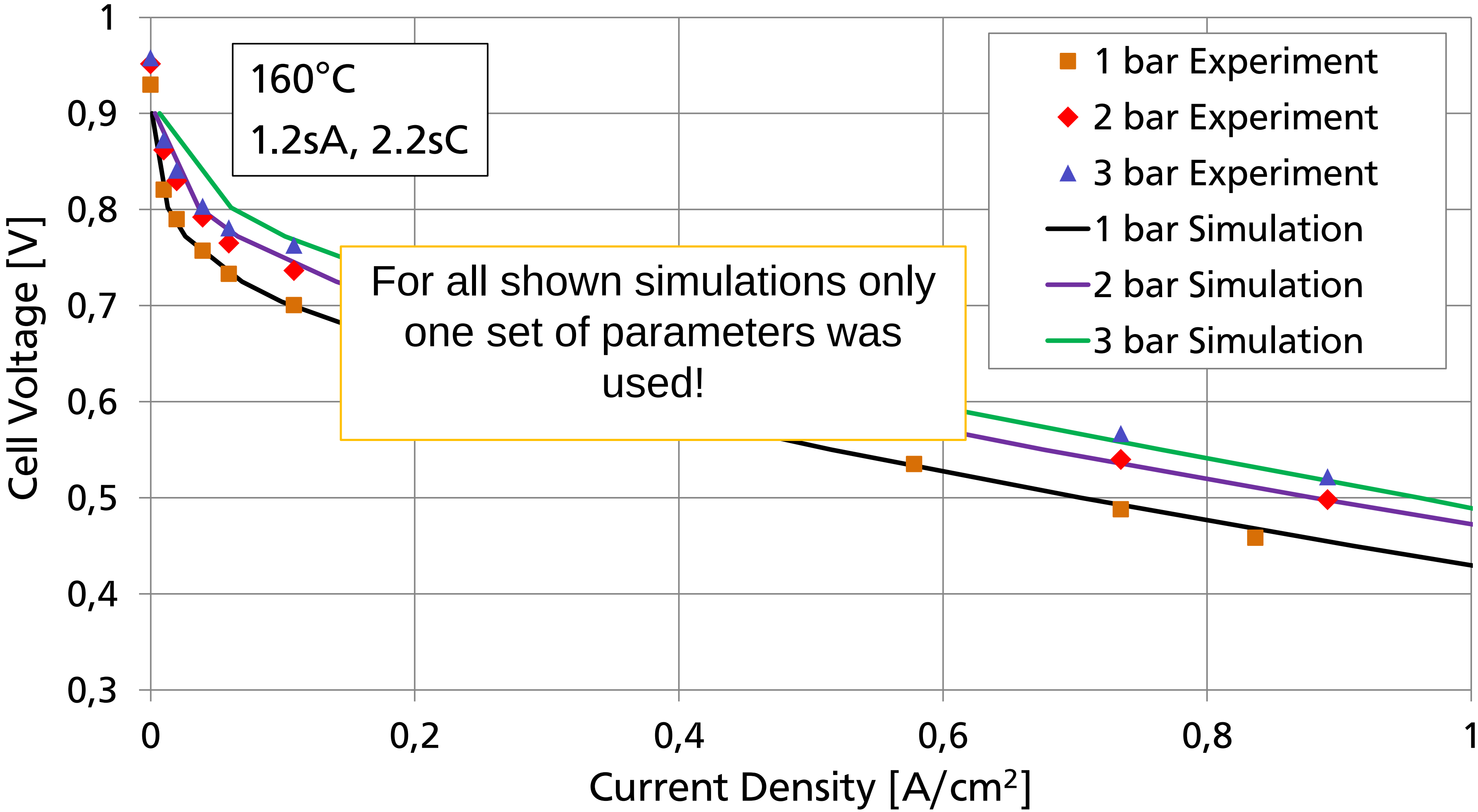
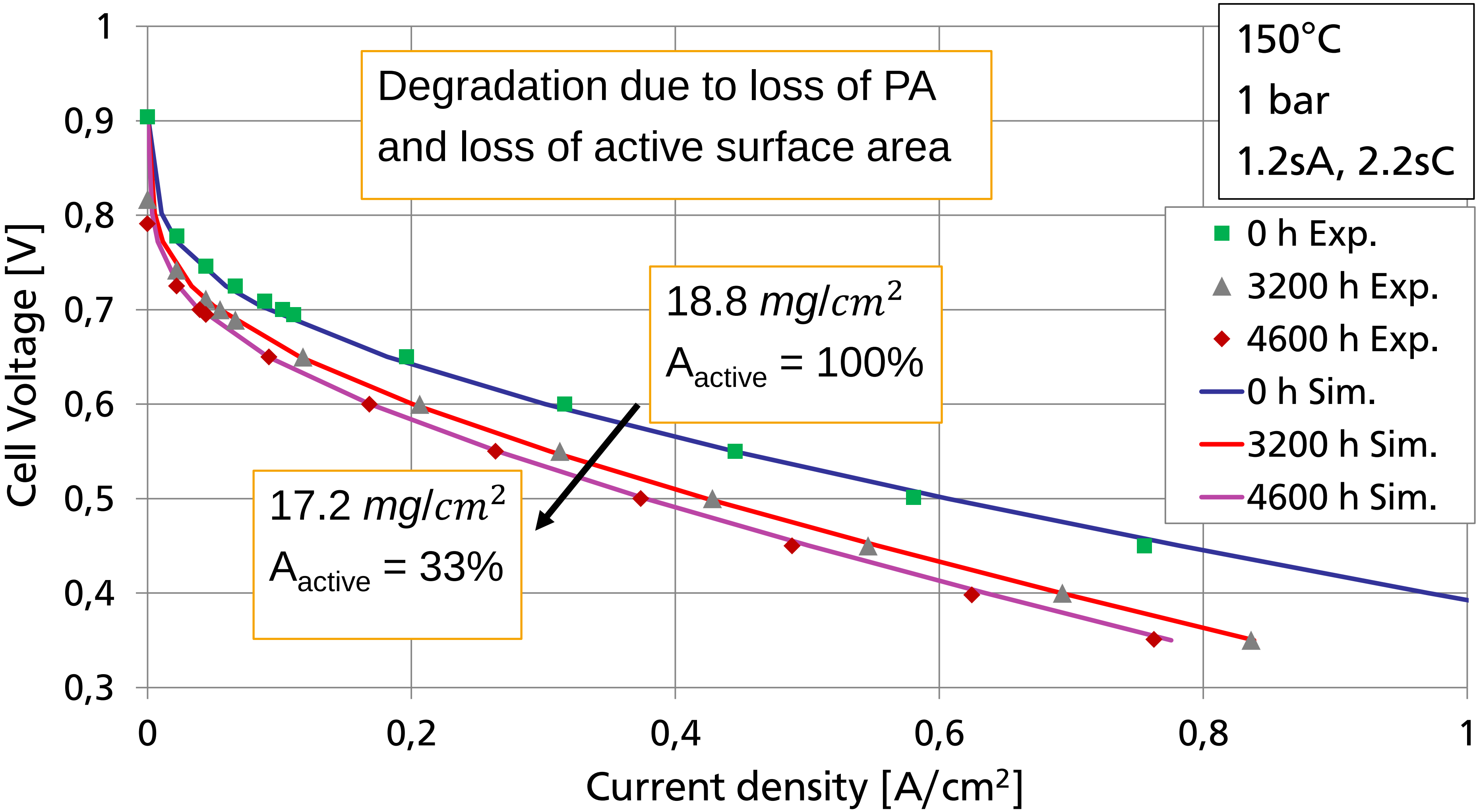


Simulation Results I

Long Term Measurement ~ 4600 h



Simulation Results II

Water stress test ~ 90 h

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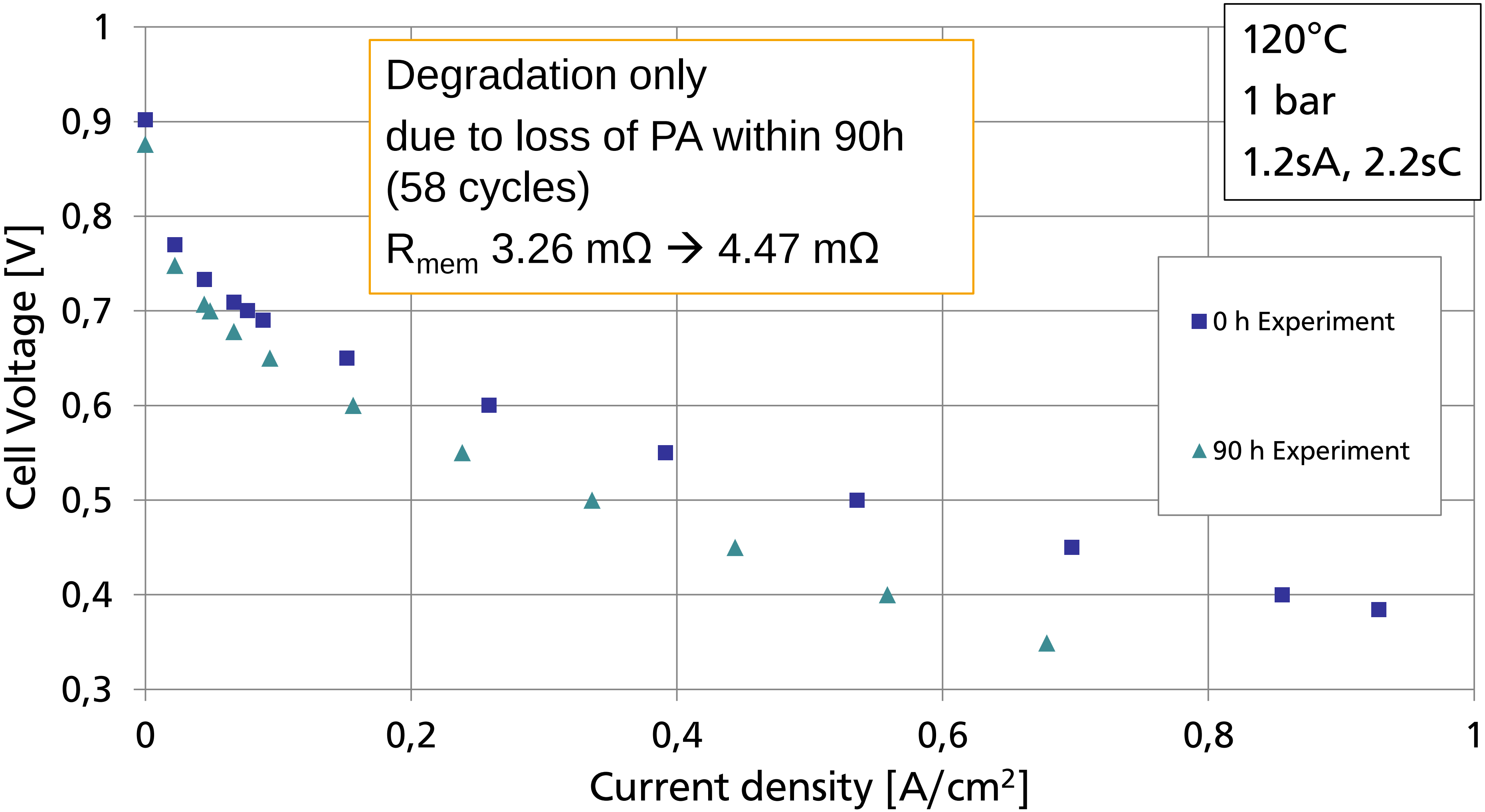

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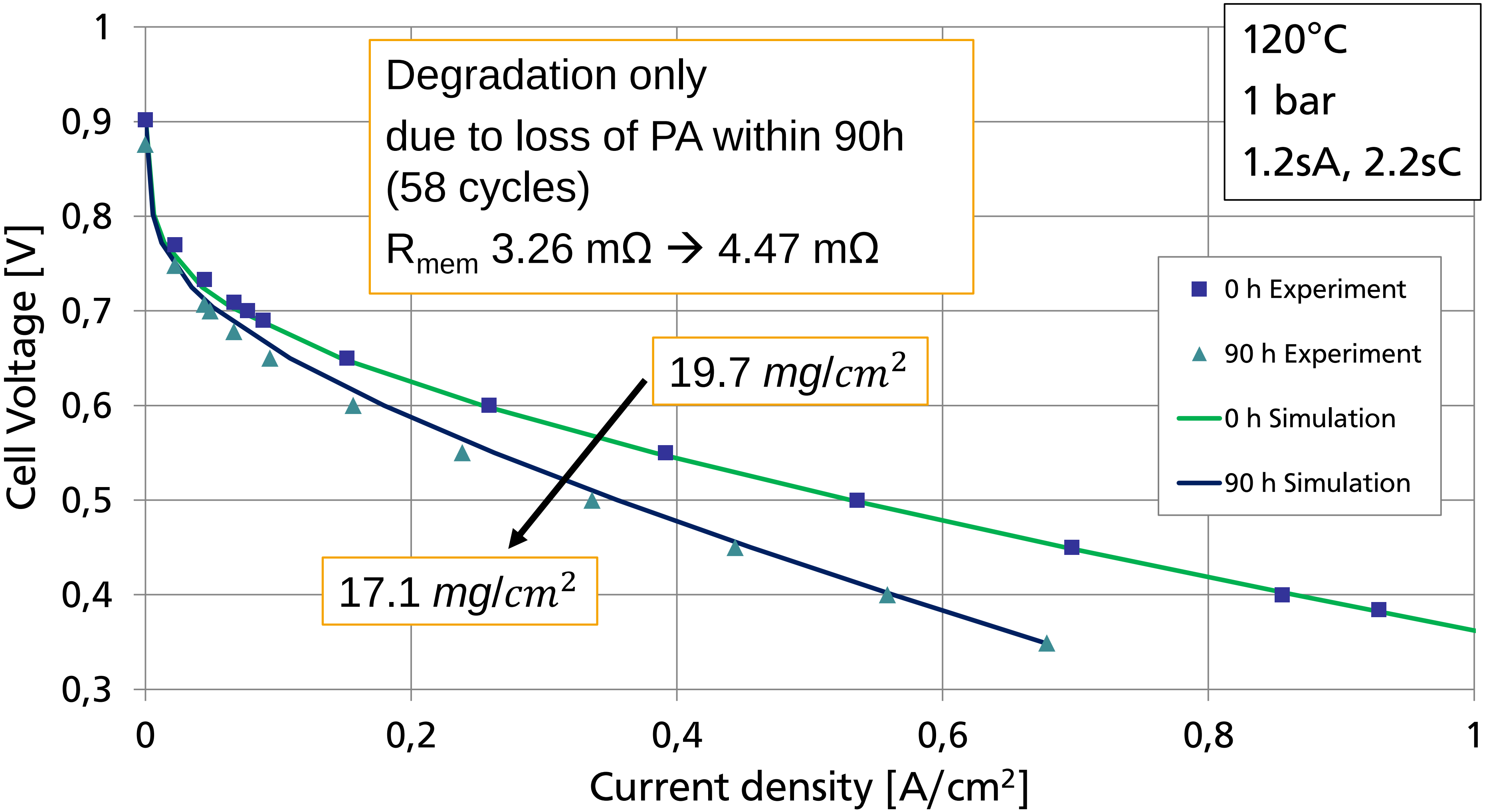

Summary and Conclusion

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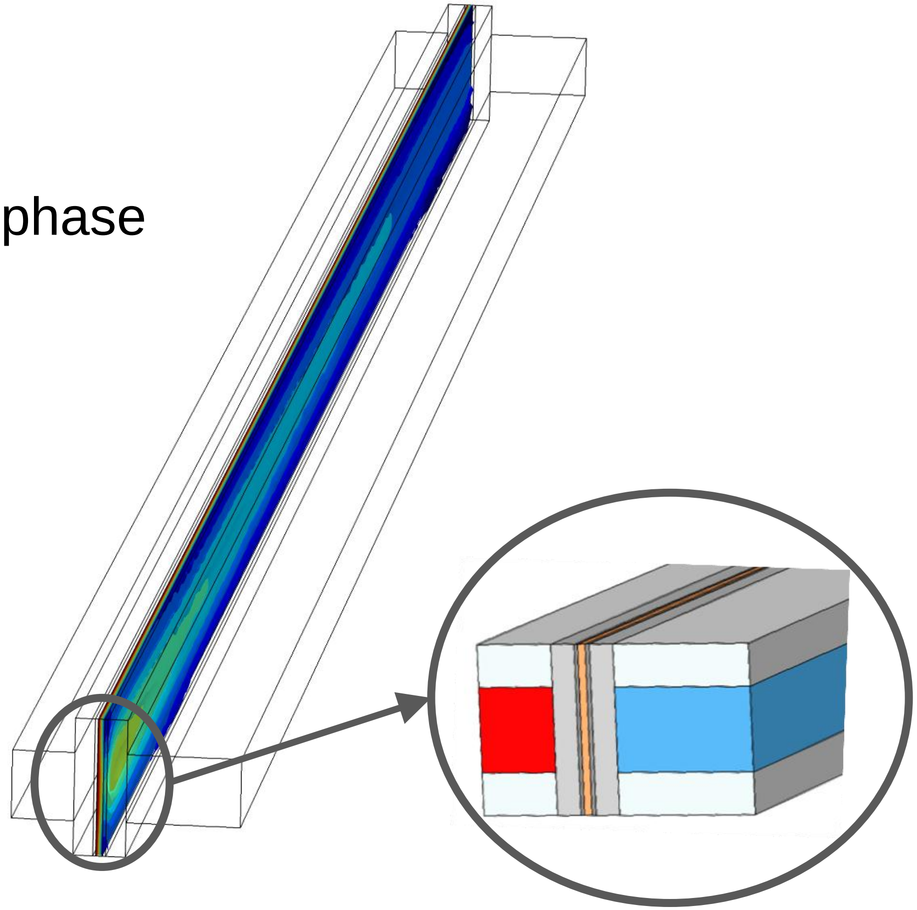
- Implementation of the VLE of water and PA leads to a water crossover, which allows the calculation of the concentration field of PA
- Volume fraction and concentration of PA influences mass transport properties, ionic conductivity and the electrochemical active surface area
- PA leaching caused by expansion can be identified to be the main loss mechanism, leading to a redistribution of PA from the MEA to the GDL and further out
- Start/stop cycling is much more harmful than constant operation (0.45 $\mu g/cm^2/h$, 0.07 $\mu g/cm^2/h$)
- Acid loss is caused by high values of relative humidity

Outlook

- 3D-Model
- Capillarity effects in porous media
- More sophisticated model for the two-phase boundary
- Solubility of reactants in PA
- Thickness change of the membrane
- PA intrusion into the GDL
- Strategies that prevent PA loss



Thank you for your kind attention!

Questions?