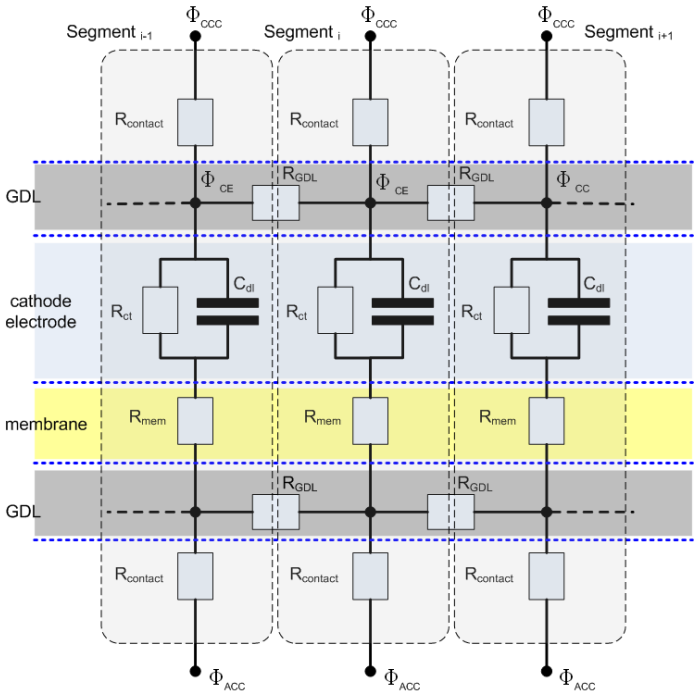
LOCAL EIS STUDIES IN PEMFC-DISTINGUISHING BETWEEN THROUGH-PLANE AND IN-PLANE OXYGEN EFFECTS



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Fraunhofer-Institut für Solare Energiesysteme ISE

Hydrogen + Fuel Cells 2013

Vancouver, June 16-19, 2013

www.h2-ise.de

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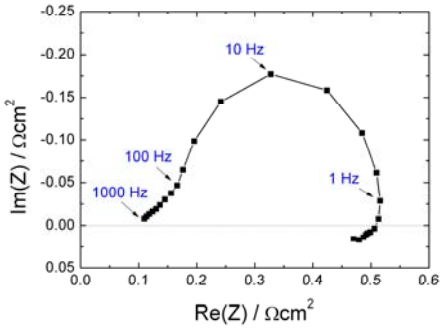
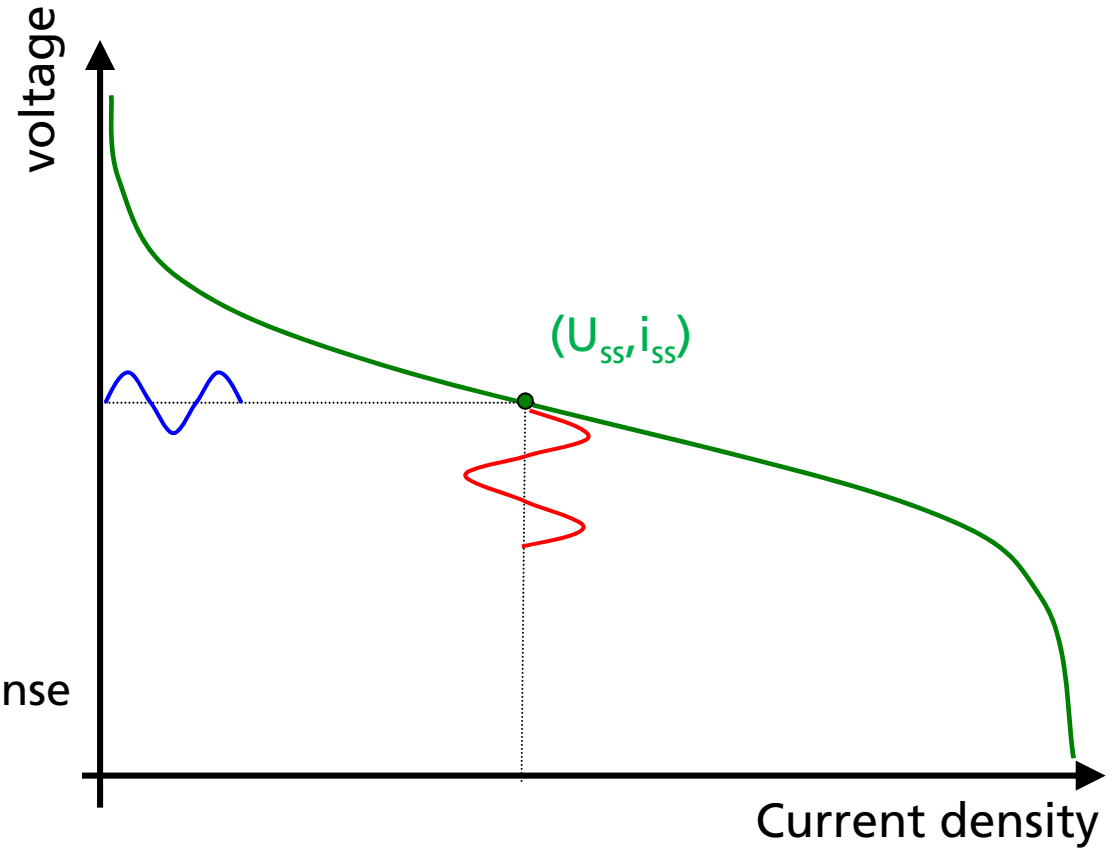
AGENDA

- Introduction into spatially resolved electrochemical impedance spectroscopy (EIS)
  - Multi-Channel Characterization System (MCCS)
  - Segmented test cell
- Experimental findings of local current density distribution and EIS on 49cm^2 test cell
- Brief description of a simple 2+1D model
- Simulation results of steady-state distributions and EIS
- Conclusion and outlook

Introduction into spatially resolved EIS



- Steady-state point (U_{ss},i_{ss})
- Superimposed by small perturbation $U(t)=U_{ss}+U_{AC}\sin(2\pi f t)$
- Frequency dependent response $i(t)=i_{ss}+i_{AC}\sin(2\pi f t+\varphi)$



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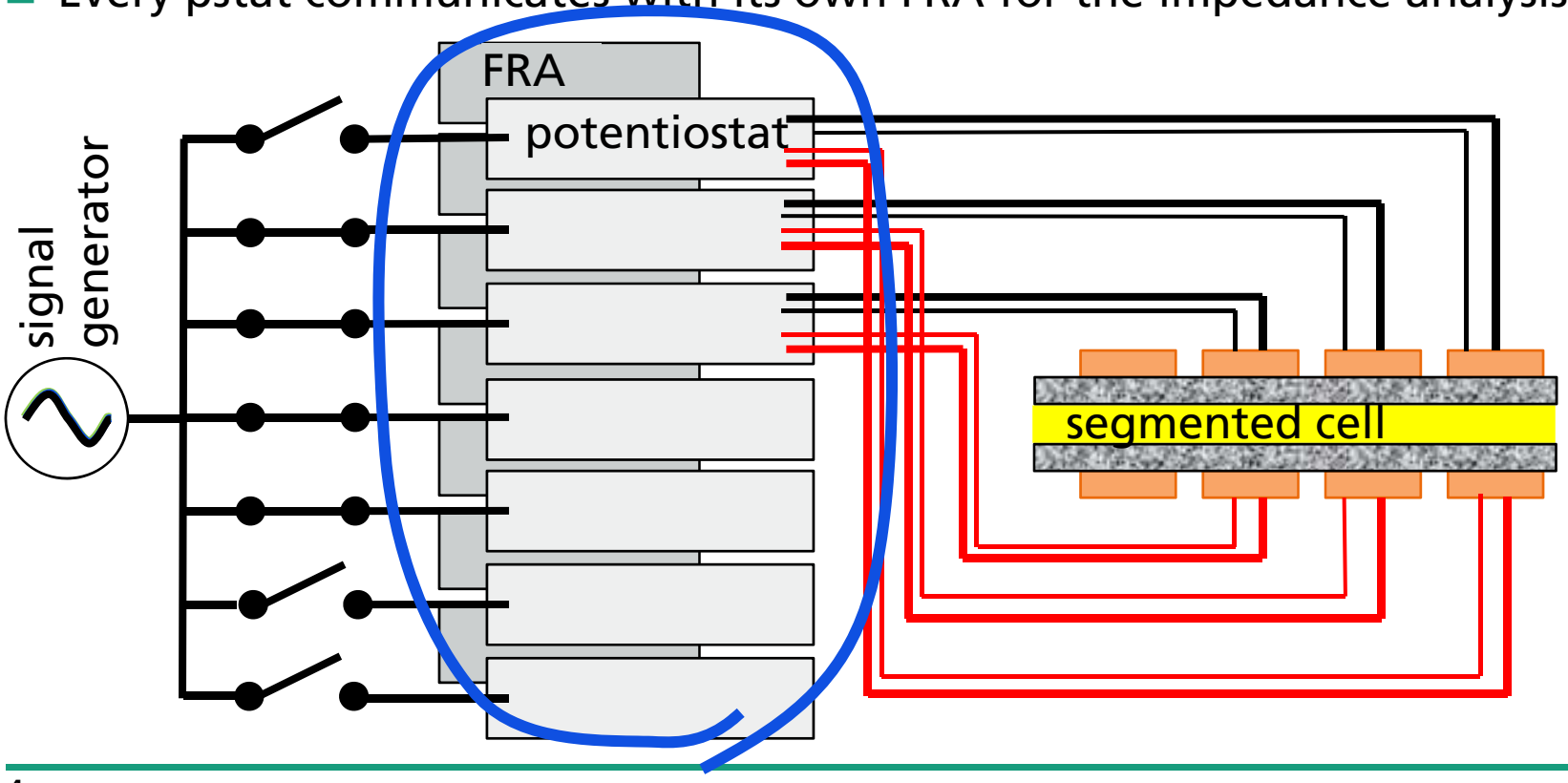
Schematic set-up of the MCCS with the segmented fuel cell

- Every segment is loaded by its own potentiostat (synchronized)
- Every pstat communicates with its own FRA for the impedance analysis



50-channel-characterization system for spatially resolved analysis of electrochemical energy converters

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Schematic set-up of the MCCS with the segmented fuel cell

- Every segment is loaded by its own potentiostat (synchronized)
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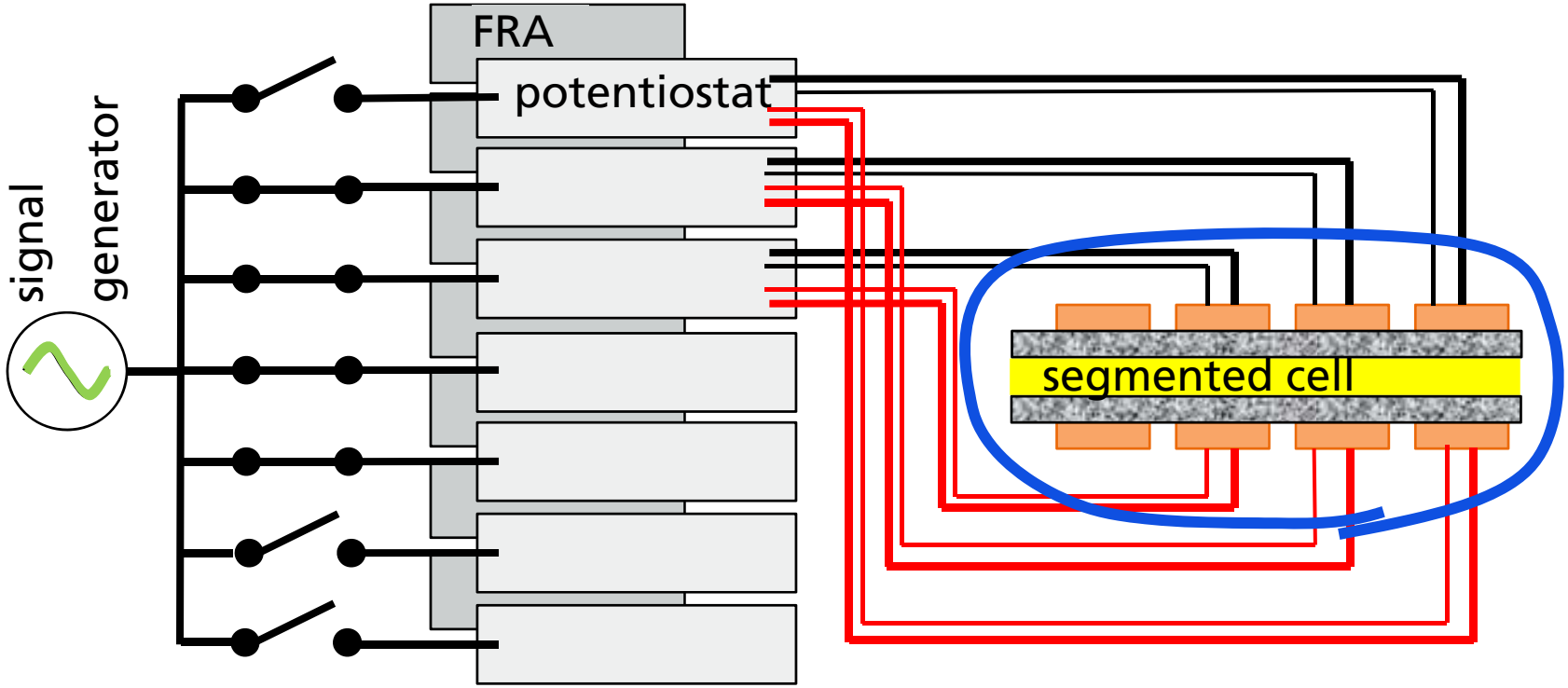
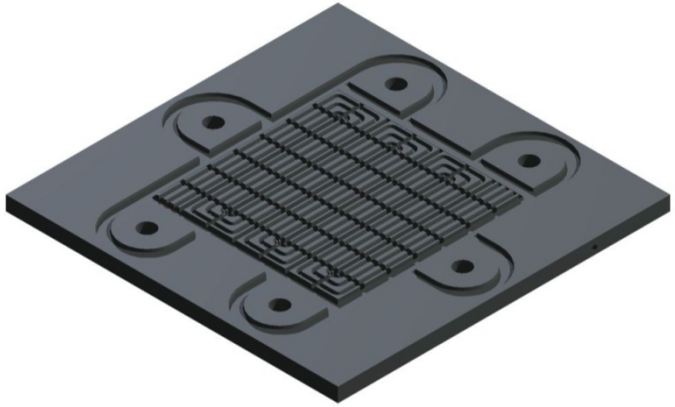
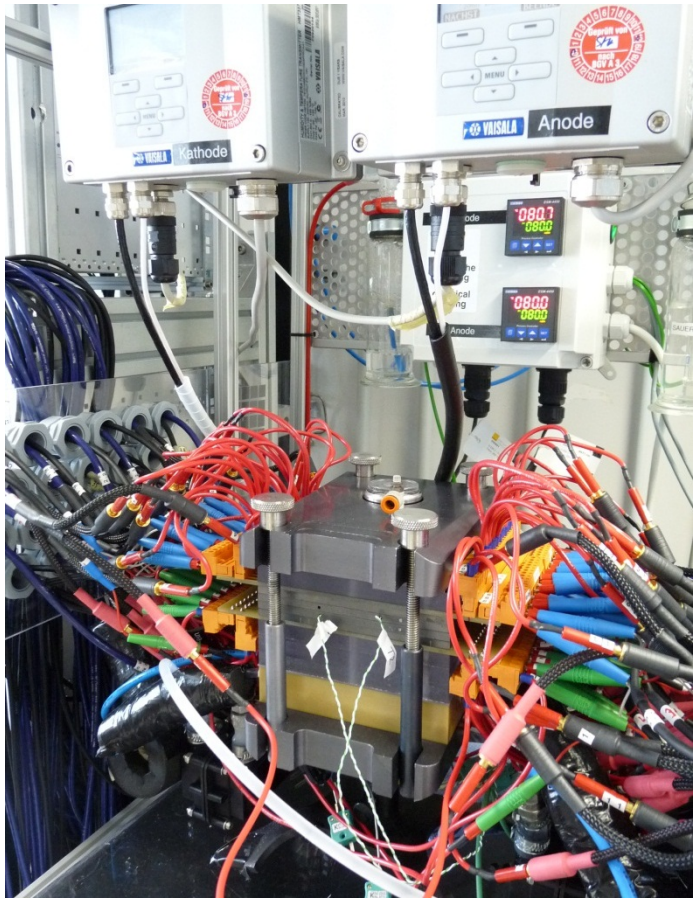


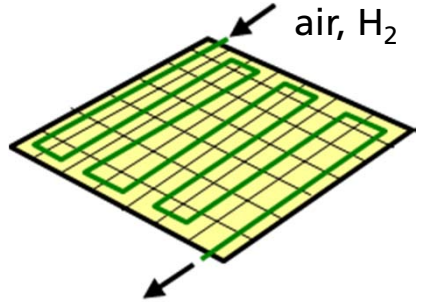
Real set-up of the MCCS with the segmented fuel cell

- Active area: 7x7 cm^2
- Segmented flow field plates
- 49 segments á 1cm^2 (anode & cathode)
- 3-fold serpentine-flow field
- Water cooling on the backside



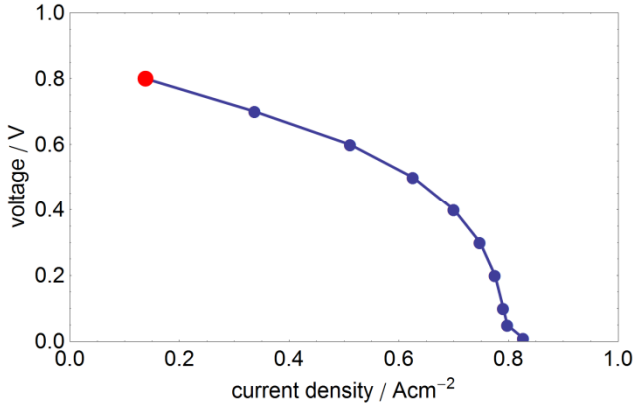


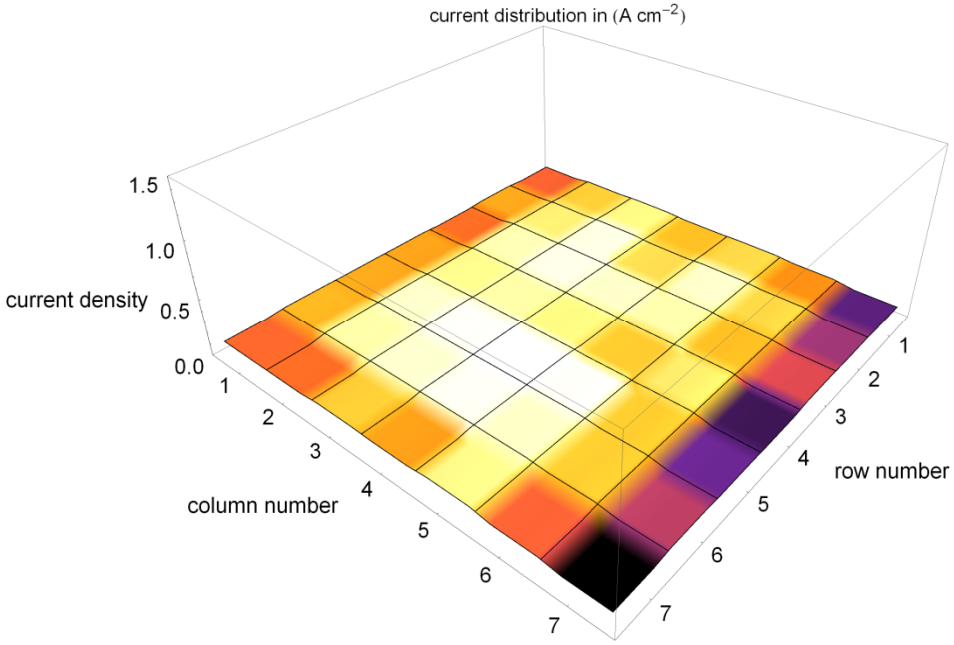
Measured current density distribution at low cathode stoichiometry



Operating conditions

- Anode: H_2 with λ_{H2}>>1
- Cathode: air with λ_{O2}<2 @ U<0.4V
- Co-flow mode
- Atmospheric pressure





Fraunhofer ISE

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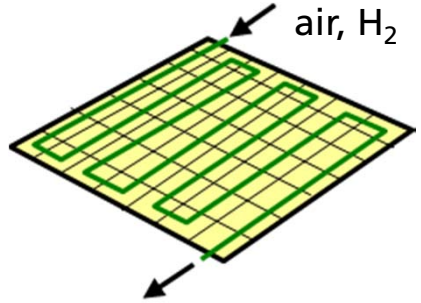

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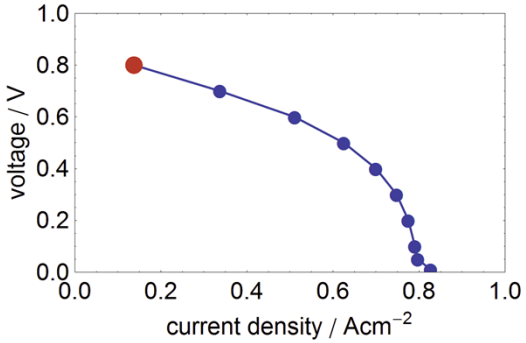

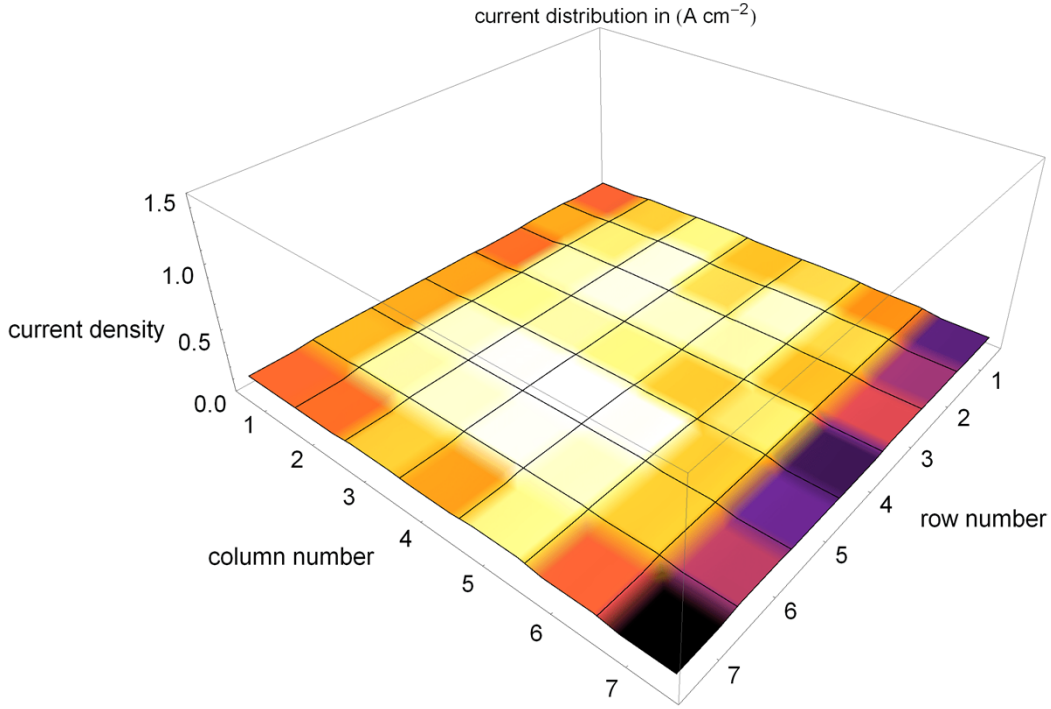

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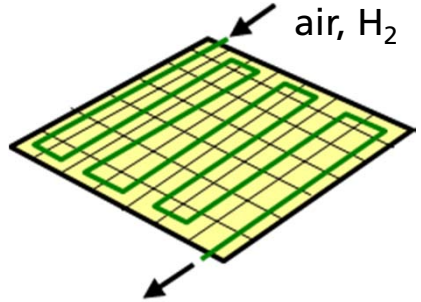
Measured current density distribution at low cathode stoichiometry



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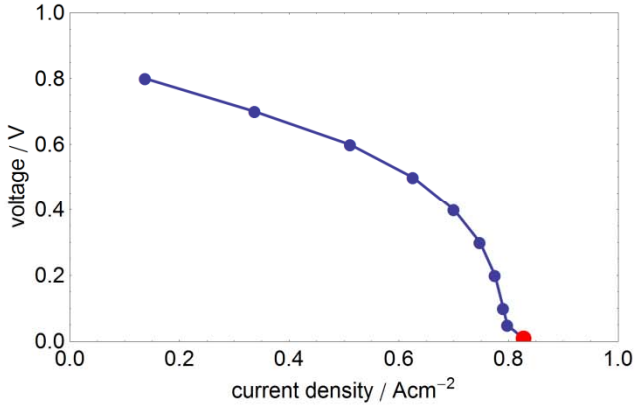

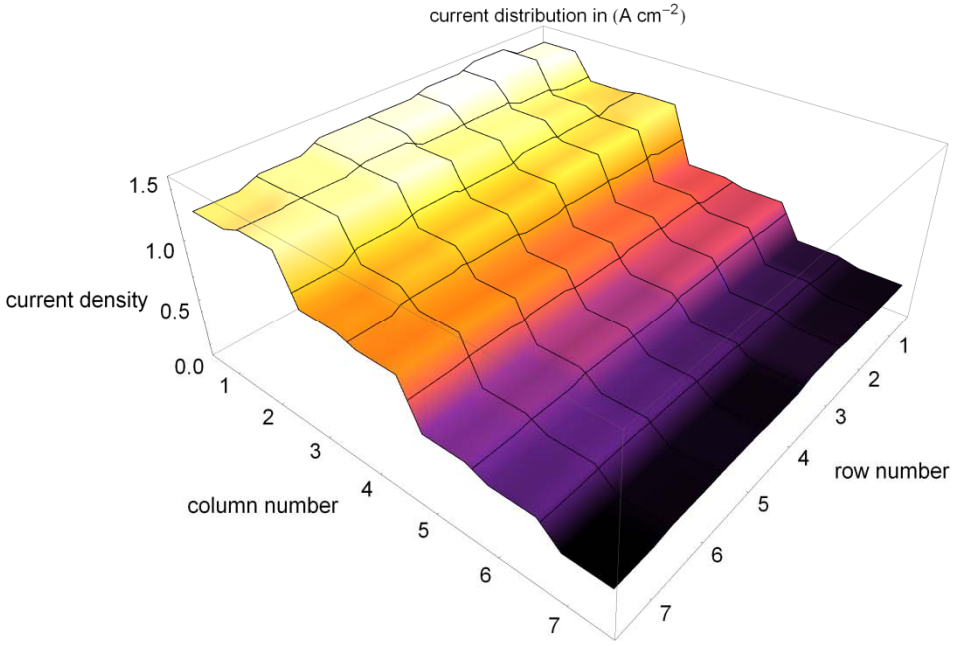

Fraunhofer ISE

Local analysis of the electrochemical impedance spectra

Operating conditions

- Anode: H_2 with λ_{H2}>>1
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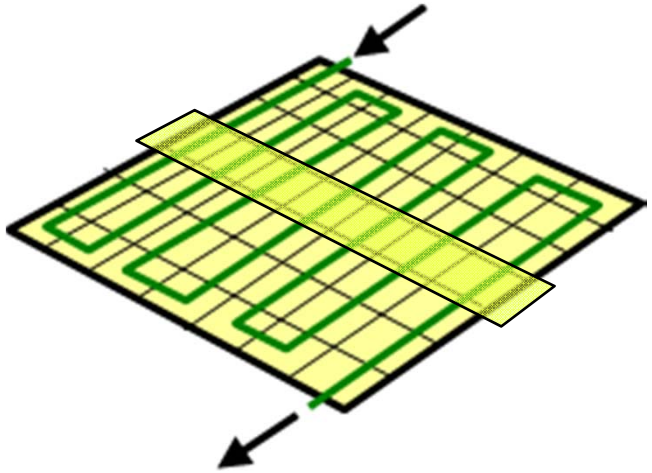

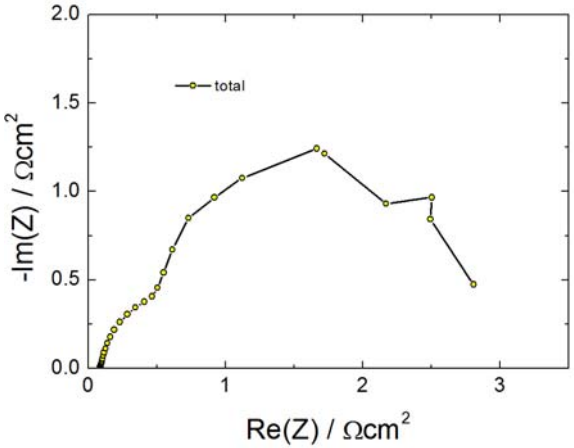

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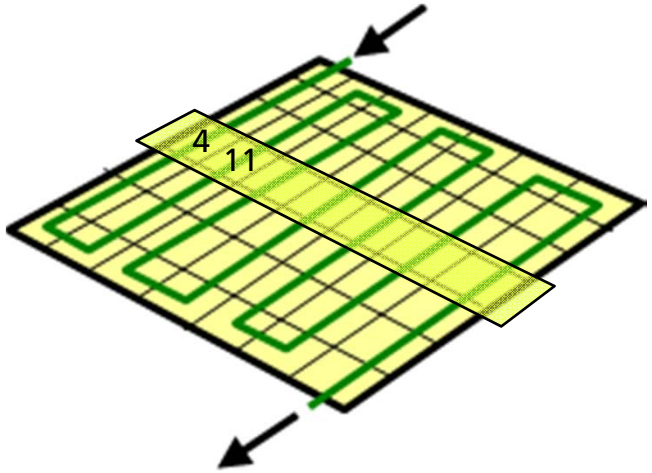

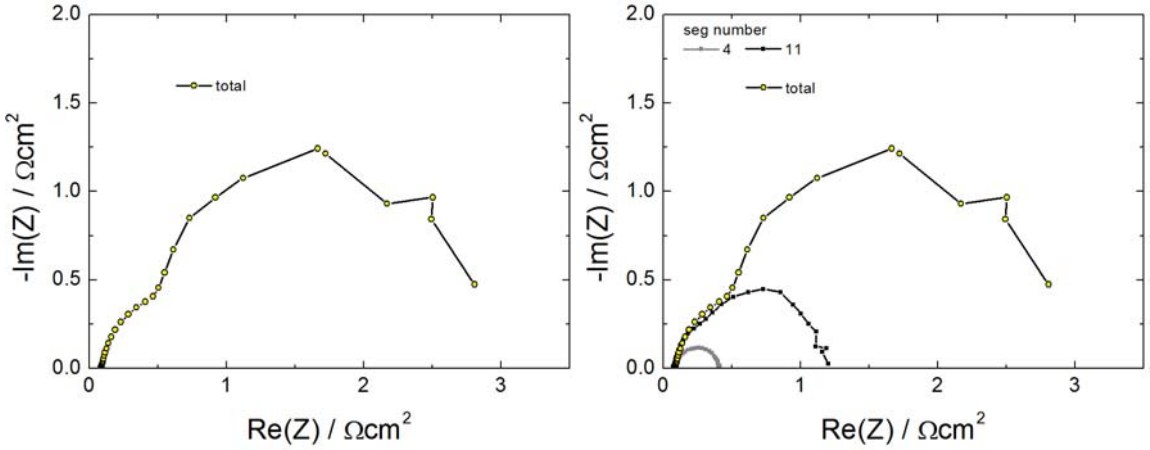

Fraunhofer ISE

Local analysis of the electrochemical impedance spectra

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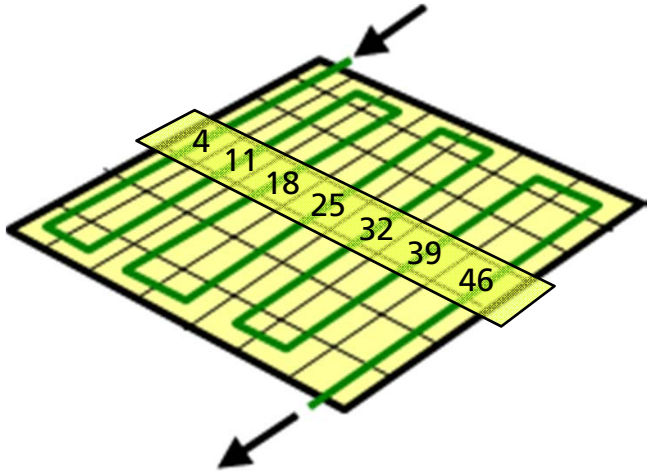

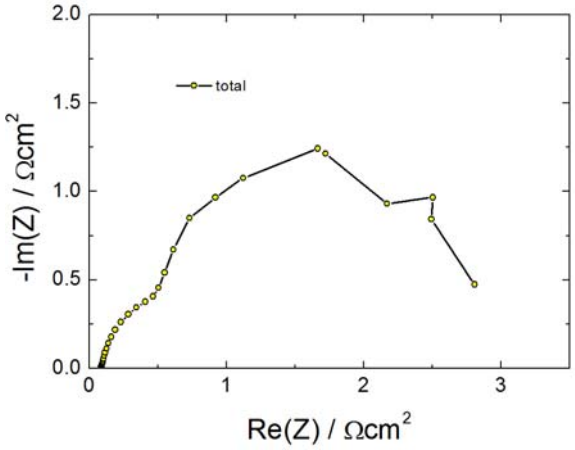

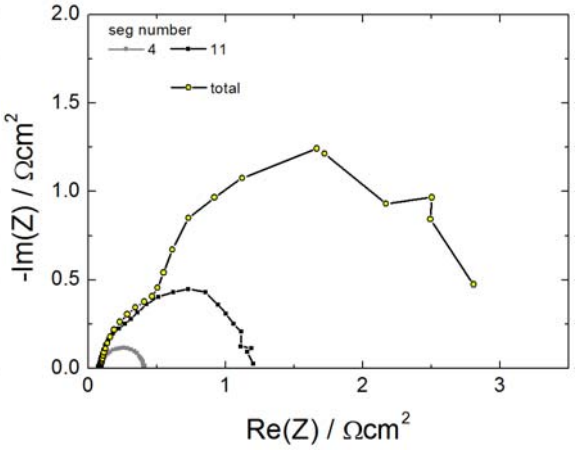

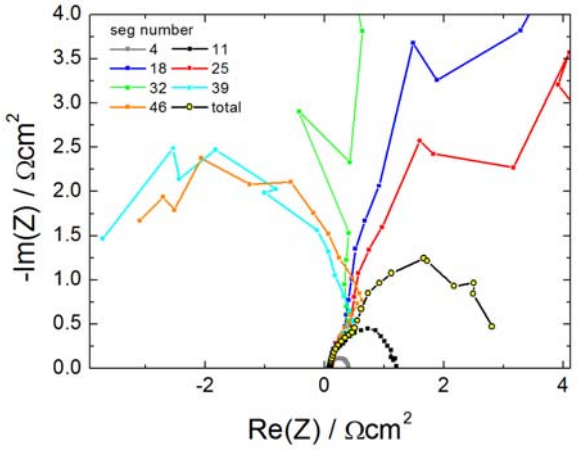

Fraunhofer ISE

First explanation was given by Schneider et al.[1]

1. I. A. Schneider, S. A. Freunberger, D. Kramer, A. Wokaun and G. G. Scherer, J. Electrochem. Soc. 2007 154(4): B383-B388
2. T. Jacobsen, P. V. Hendriksen, S. Koch, Electrochimica Acta 2008, 53(25): 7500–7508
3. A. A. Kulikovsky, *J. Electrochem. Soc. 2012 159(7): F294-F300*

Basic idea:

d.c. current per segment: $i_{seg} = i_0\, c \exp(\eta/b)$

a.c. current response: $\Delta i_{seg} = i_0 \exp(\eta/b)\,(\Delta c + c\,\Delta\eta/b) - C_{DL}\, d_t\Delta\eta$

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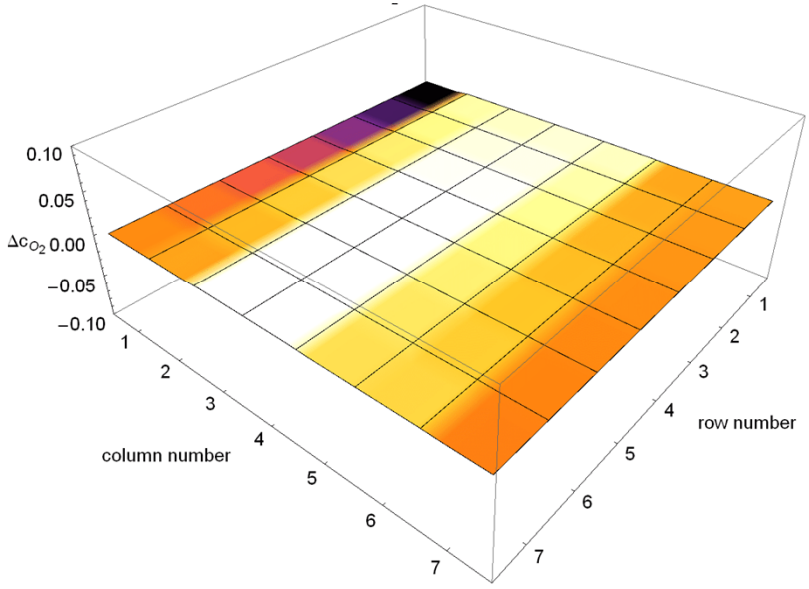
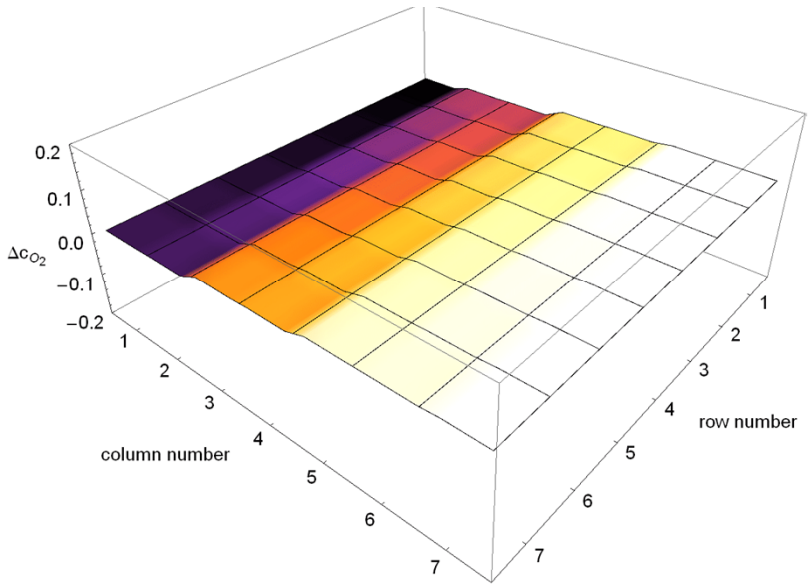
normed O_2 conc oscillation in channel



normed O_2 conc oscillation in CL



Fraunhofer ISE

EIS-Simulation by a simplified 2+1D model

GDL

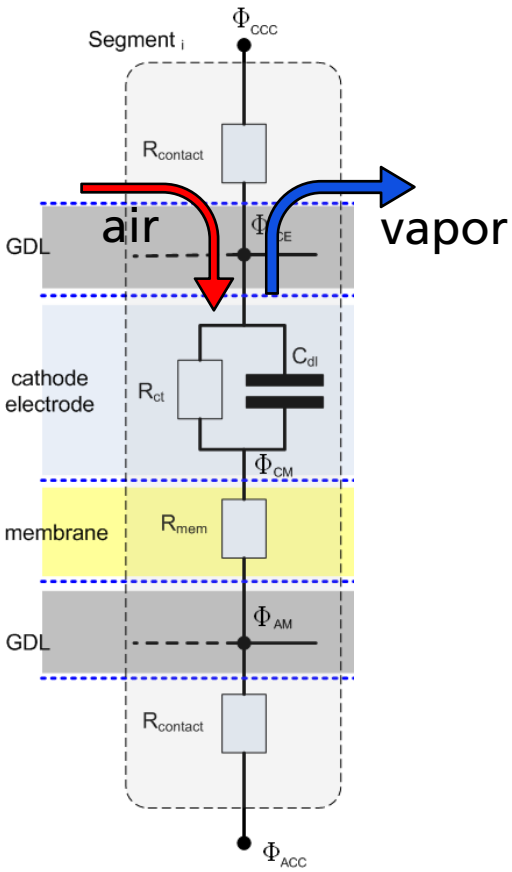
- Fick's diffusion of air and water vapor in GDL

CCL

- Tafel law describes charge transfer resistance
- Double layer charging

ACL

- Anode polarisation neglected



GDL

- Phase change of water in GDL
- Fickian diffusion approach for saturation

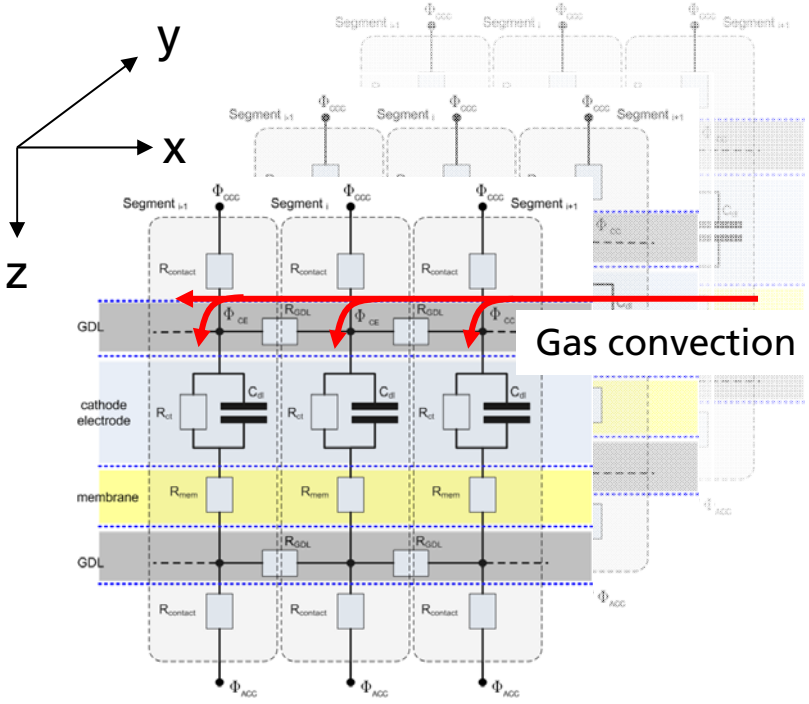
membrane

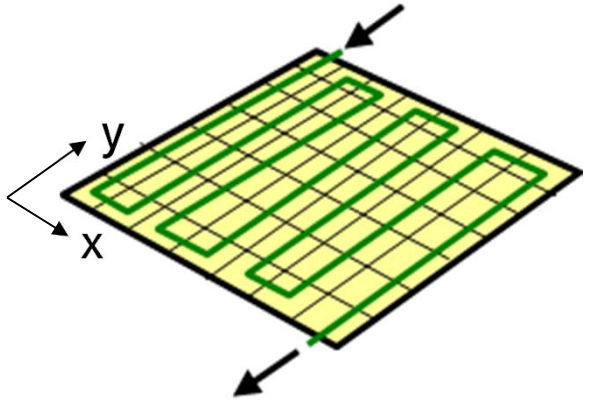
- Ohmic loss in membrane as a function of the water content

interfaces

- Contact resistance on cathode and anode

EIS-Simulation by a simplified 2+1D model





Fuel cell segments are coupled to nearest neighbors (x-y-direction) by

- Gas convection of air and vapor according to flow field pattern
- Cross current in GDL
- In-plane permeation of liquid water

Fraunhofer ISE

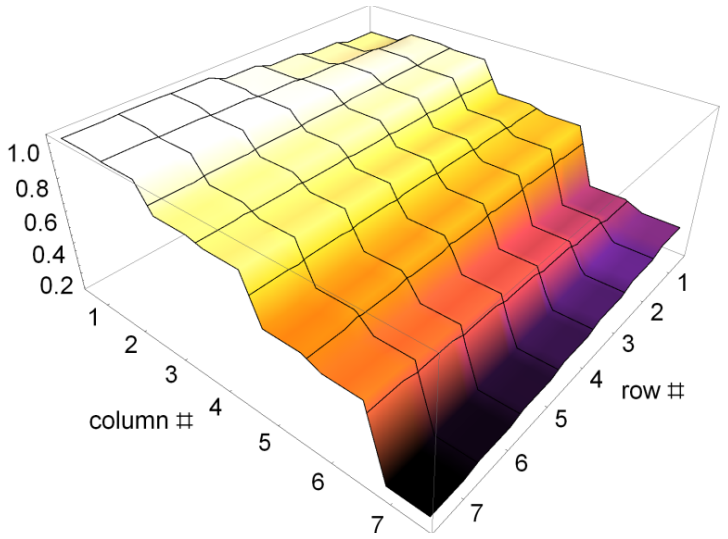
Simulation of the steady-state distributions

Current density distribution …

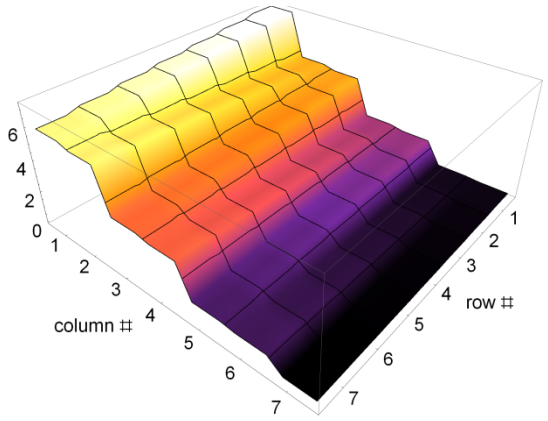
- depends mainly on oxygen concentration
- shows an effect of the non-optimal membrane hydration at the inlet region

Saturation distribution is a function of the vapor concentration and the water production

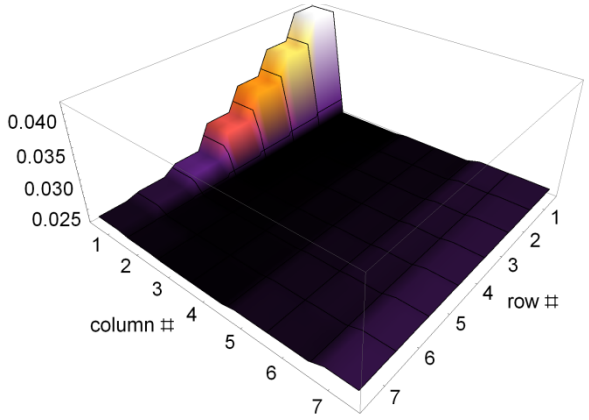
current density [Acm²]



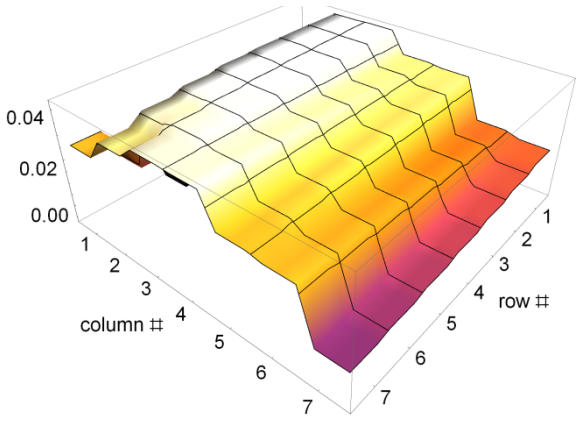
O_2 conc in CL [mol cm^{-3}]



R_{mem} [Ω cm²]



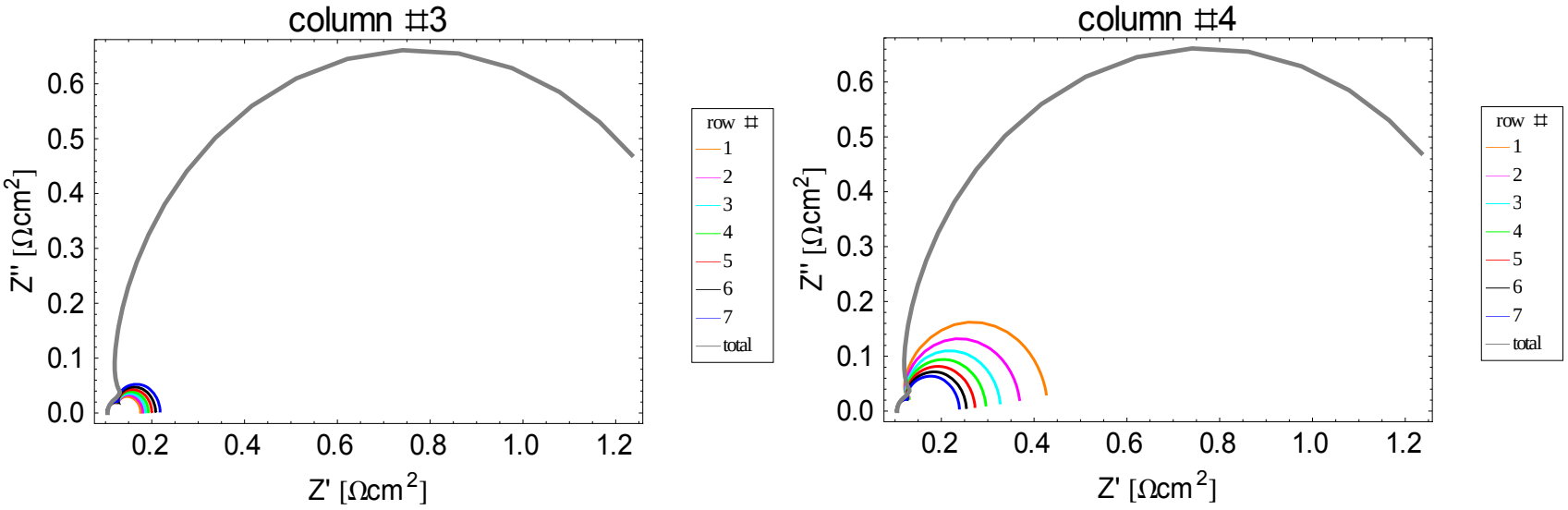
saturation [-]



Fraunhofer ISE

Simulation of the oxygen in-plane effects on local EIS

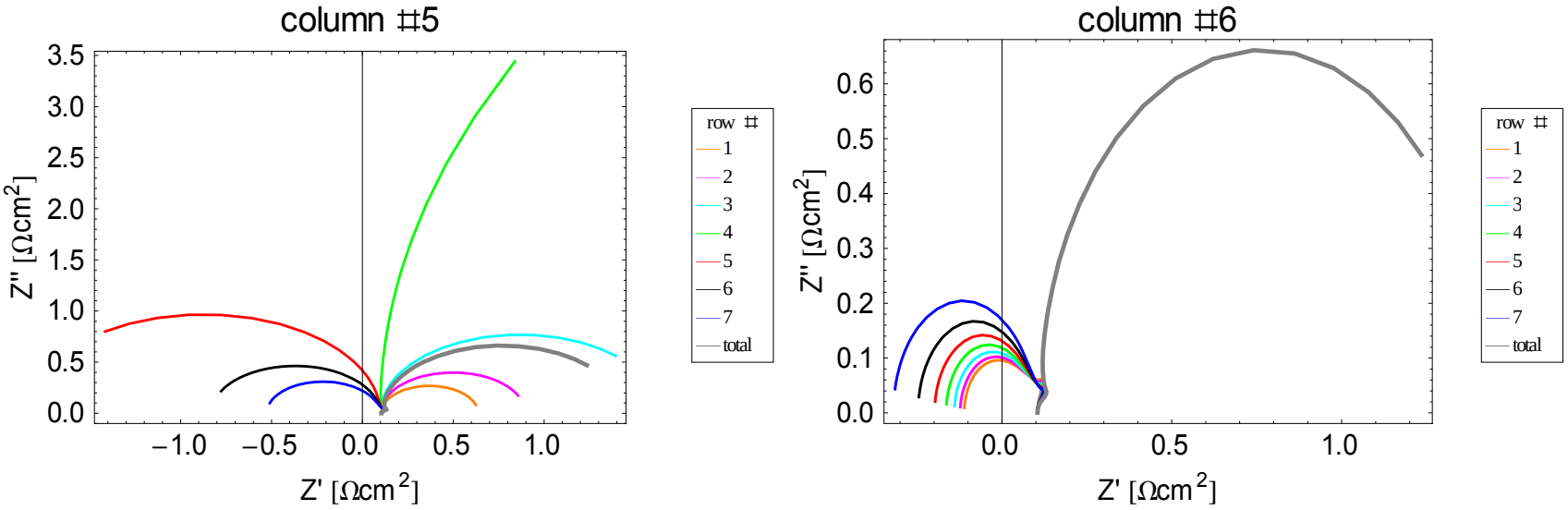
- Simulation results capture the measured characteristics
  - EIS near inlet is very small compared to the total impedance spectra
  - EIS increases along the channel



Fraunhofer ISE

Simulation of the oxygen in-plane effects on local EIS

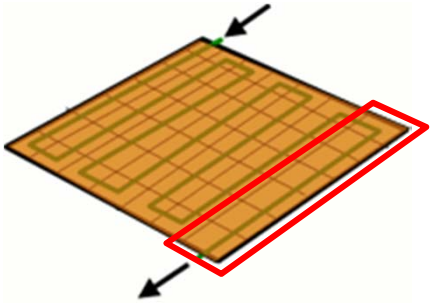
- Simulation results capture the measured characteristics
  - in column#5, some spectra are flipped into 2nd quadrant
  - in column#6, all spectra are flipped

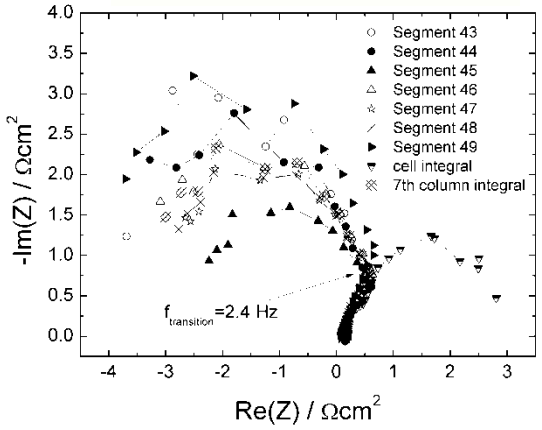


Fraunhofer ISE

Measured impedance characteristic by local perturbation

- MCCS has the capability to perturb specific segments
- Perturbation of the **whole** cell (all segments)



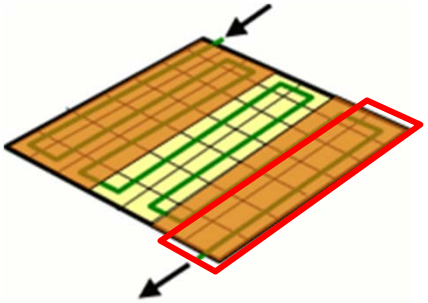


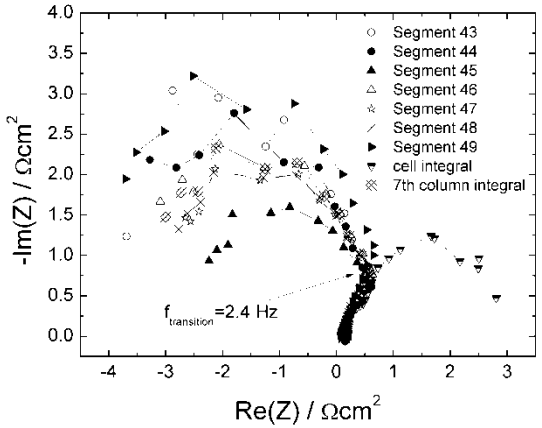
Fraunhofer ISE

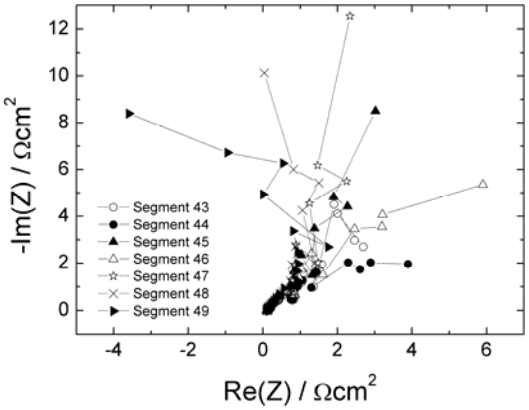
Measured impedance characteristic by local perturbation

- MCCS has the capability to perturb specific segments
- Perturbation of **col #1,2,3,6,7**

All segments of
col#7 are flipped



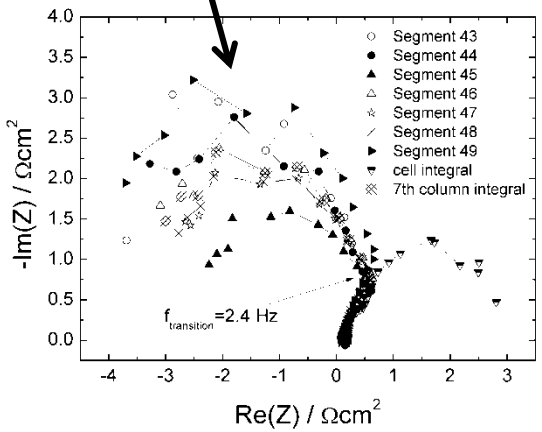




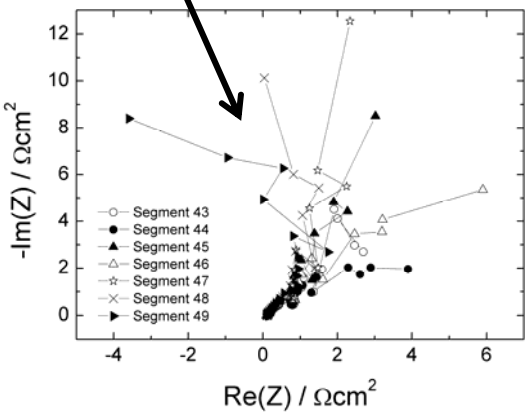
Measured impedance characteristic by local perturbation

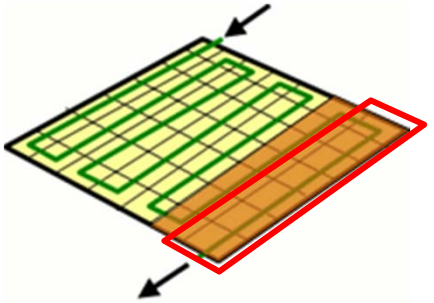
- MCCS has the capability to perturb specific segments
- Perturbation of **col #6,7**

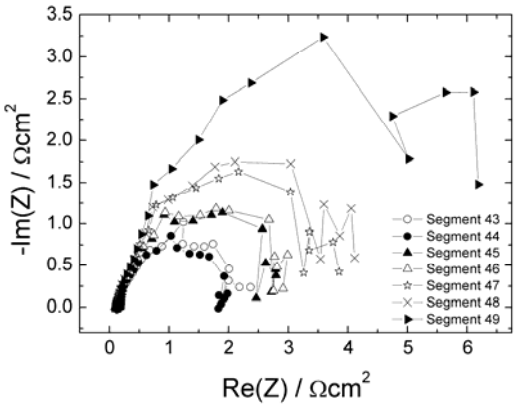
All segments of col#7 are flipped



Some segments of col#7 are flipped



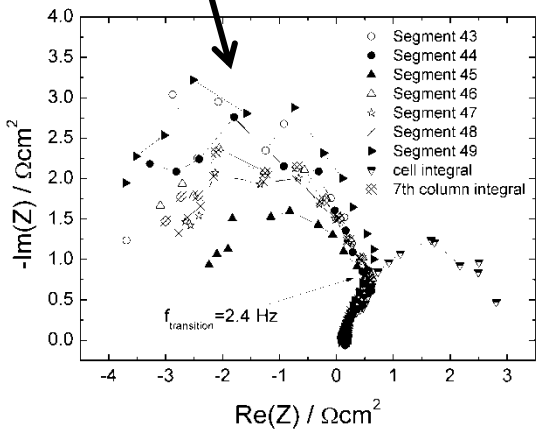




Measured impedance characteristic by local perturbation

- MCCS has the capability to perturb specific segments
- Perturbation of **col #6,7**

All segments of col#7 are flipped



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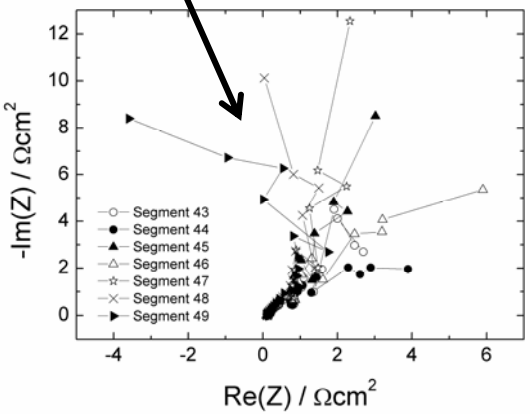
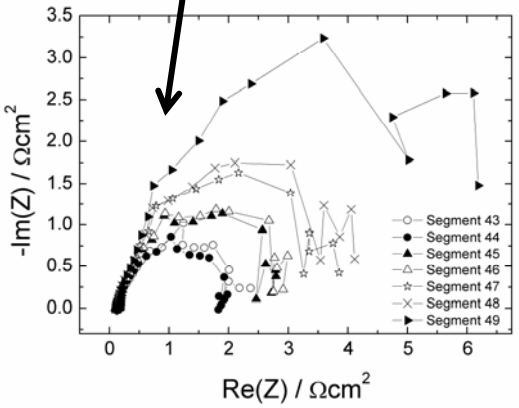


No segment of col#7 is flipped

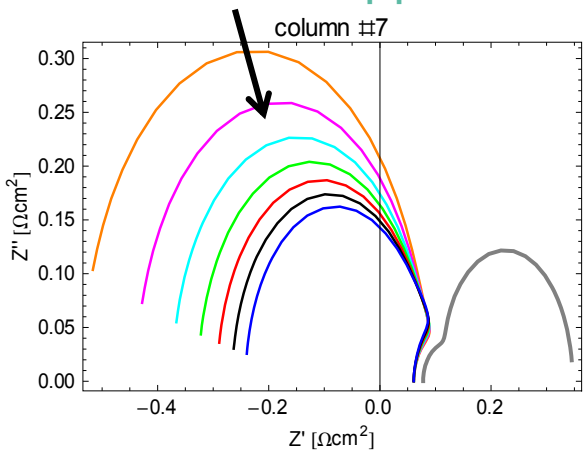


Simulated impedance characteristic by local perturbation

- The model can mimic the local perturbation experiment
- Perturbation of …

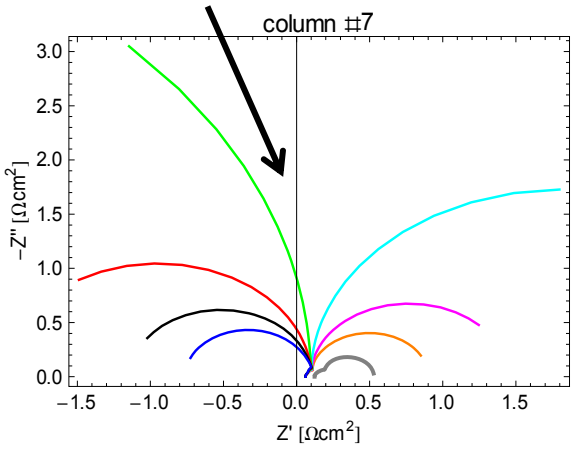
…the **whole** cell

All segments of col#7 are flipped



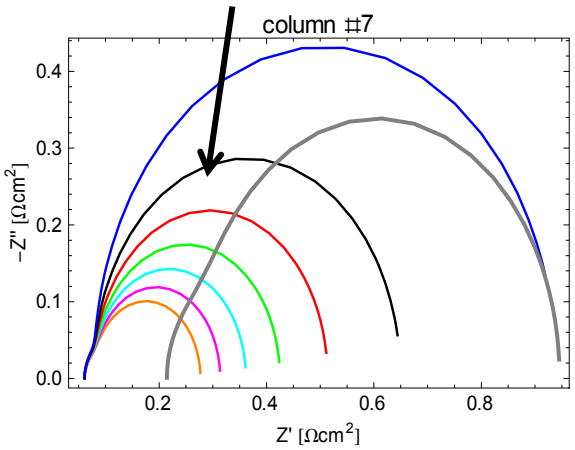
…**col #1,2,3,6,7**

Some segments of col#7 are flipped



…**col #6,7**

No segment of col#7 is flipped



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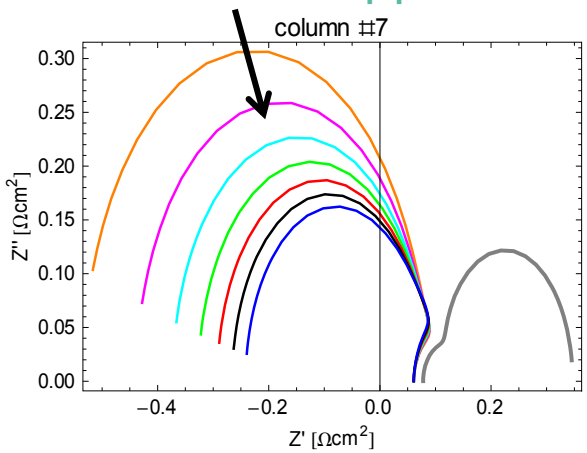
Simulated impedance characteristic by local perturbation

- The model can mimic the local perturbation experiment …
- … and shows qualitatively the same behavior

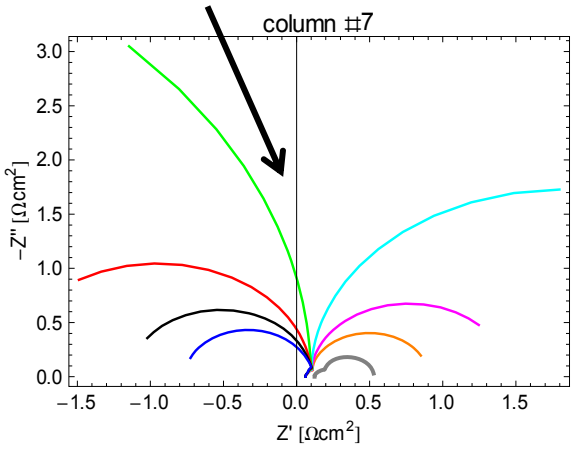
…the **whole** cell

All segments of col#7 are flipped



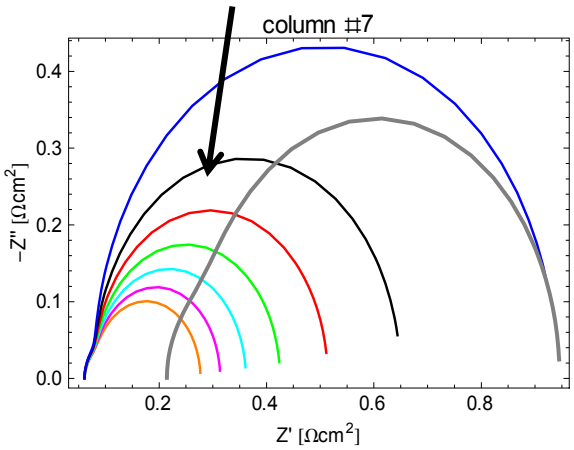
…**col #1,2,3,6,7**

Some segments of col#7 are flipped



…**col #6,7**

No segment of col#7 is flipped



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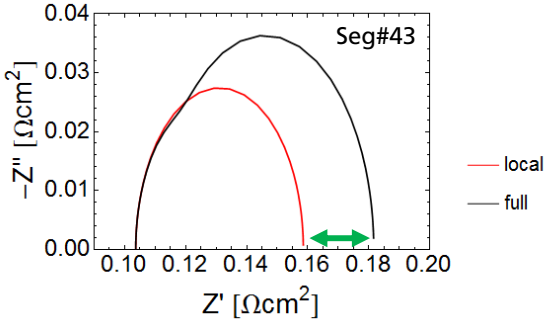
Stoichiometric impact on the local EIS

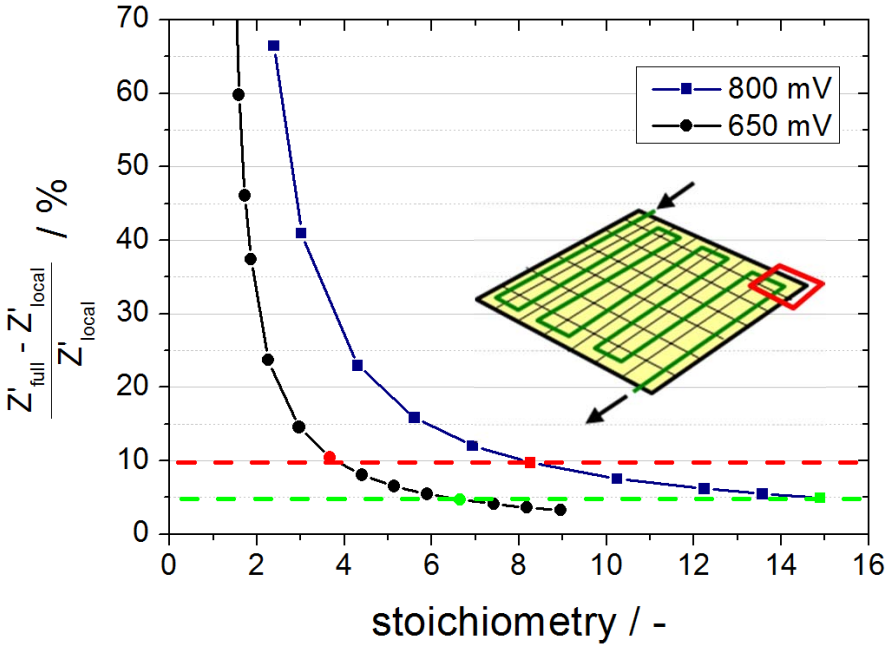
Comparison of full perturbation vs local perturbation @ low frequency (10mHz) shows…

- large deviance at $\lambda_{air} < 3$
- reduced artifact at high λ_{air}
  - error<5% @ $\lambda_{air} > 7$ @ 650mV
  - error<5% @ $\lambda_{air} > 15$ @ 800mV

→ High stoichiometry needed for analysing mass transport processes in the porous transport layers

→ Otherwise this effect has to be taken into account by modeling





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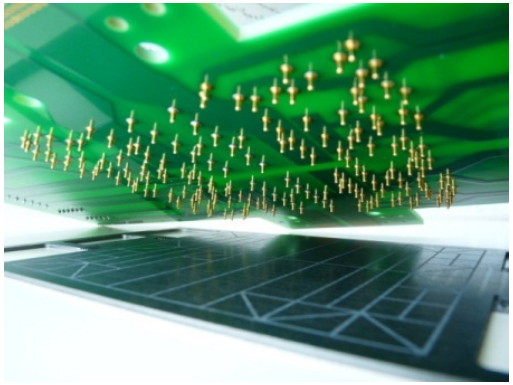
Conclusion and Outlook

- Spatially resolved characterization combined with modelling work can disclose inhomogeneity in the cell.
- The MCCS has a high capability to gain insights of what's going on in the cell (full perturbation, local perturbation, fast transient (talk: N. Zamel)).
- The interpretation of a impedance spectra that was not conducted with a very high stoichiometry is very complex.
- A simple 2+1D model is developed that shows qualitatively the right characteristics. Simulation time below <2sec.
- Model validation has to be done. Maybe CL has to be resolved.

Conclusion and Outlook

- The MCCS has been upgraded with additional high-power potentiostats to a total current of 790A
- Cells with several 100cm^2 active area can be characterized



Thank You Very Much for Your Attention!

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