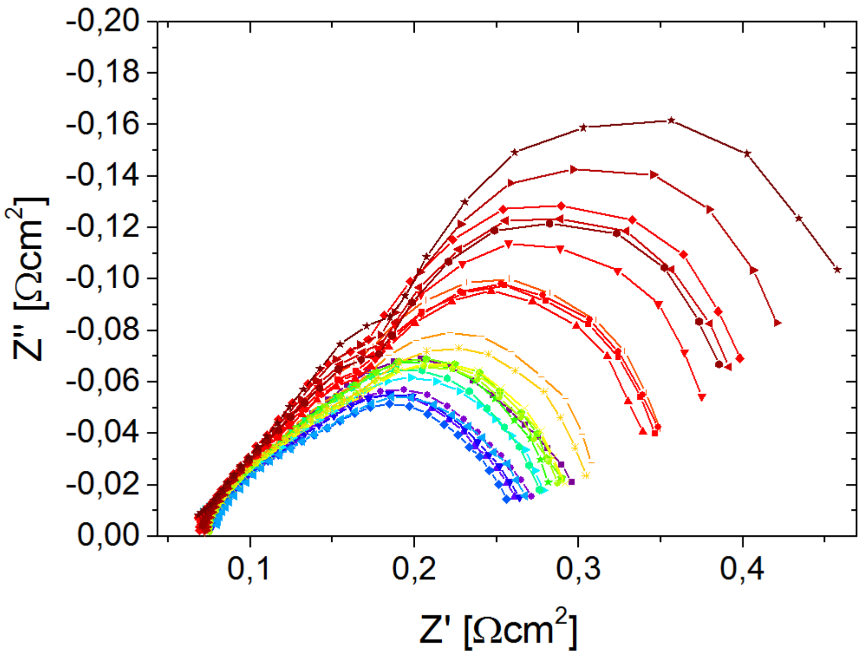
CHARACTERIZATION OF PEM FUEL CELLS BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY



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Fraunhofer-Institut für Solare Energie Systeme ISE

Heraeus-Seminar: Next generation polymer membrane fuel cells

2.-5. July 2017

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AGENDA

- Motivation: What can impedance spectra tell us?
- Characteristics of EIS and their interpretation
    - High frequency resistance (HFR)
    - 45°-branch at high frequencies
    - Charge transfer resistance
    - Mass tansport resistance
- Differential cell measurements vs. „normal“ stoichiometric measurements
    - Channel impedance
- Conclusion

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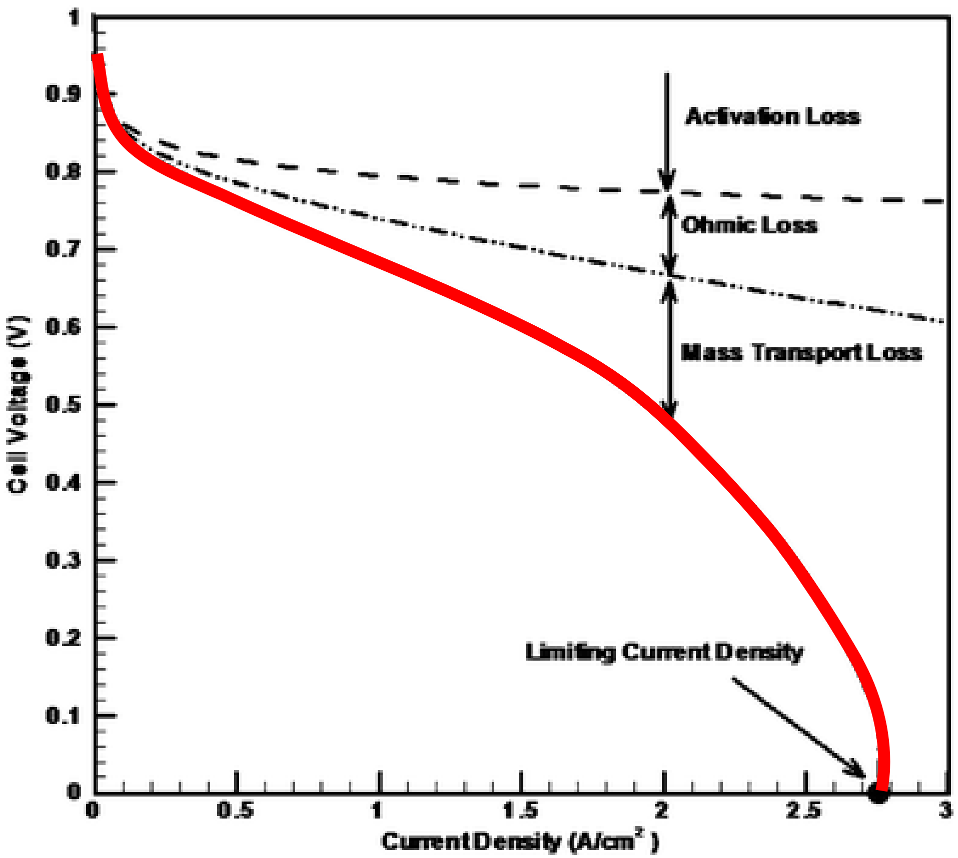
Interpretation of typical polarization curve

- PolCurve shows voltage at specific current
  - Voltage loss breakdown is of interest
- EIS can discriminate different loss mechanisms
  - if processes occure at different time constants



Mukerjee et al., Energy Environ. Sci., 2011, **4**, 346-369

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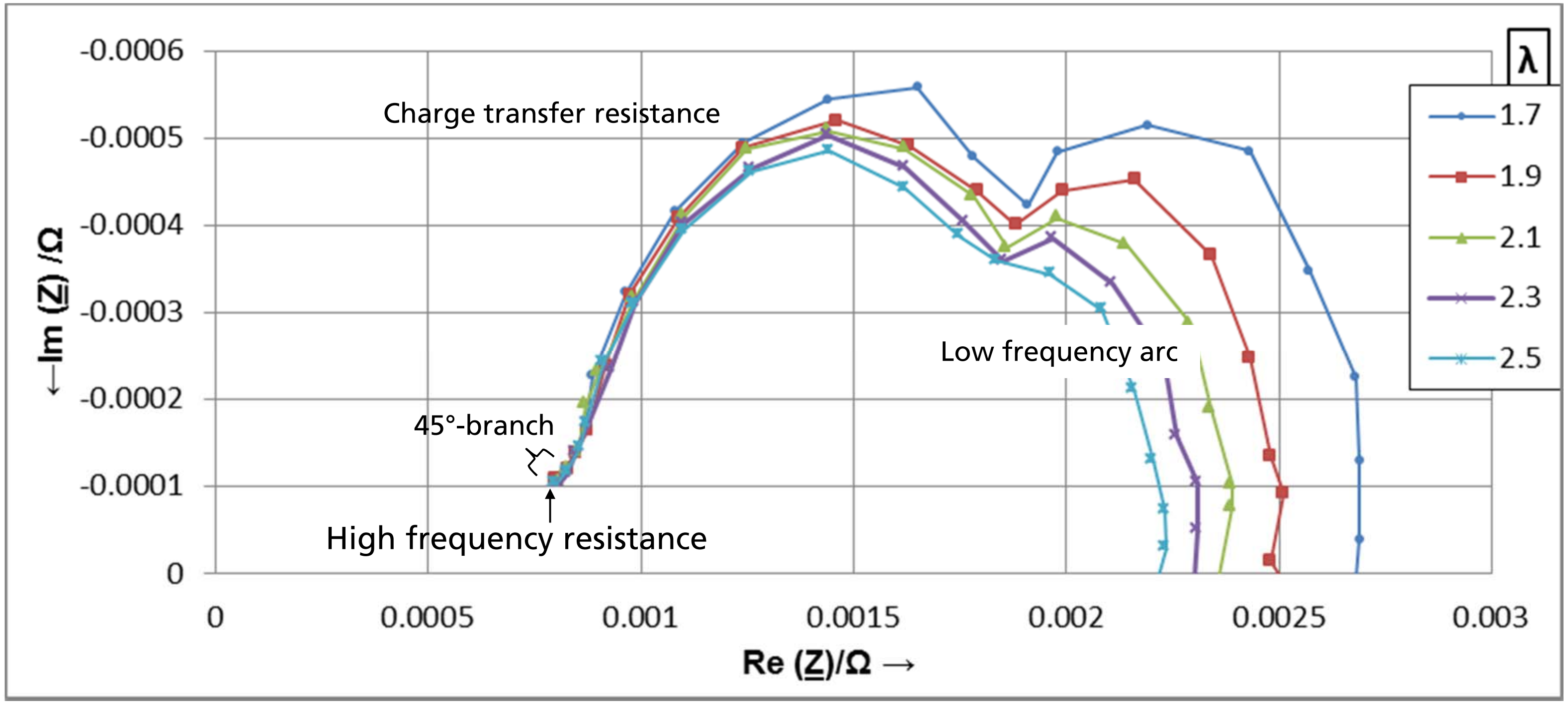
Typical impedance spectrum of a PEMFC stack

- Question: What can we learn from such spectra?



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High frequency resistance

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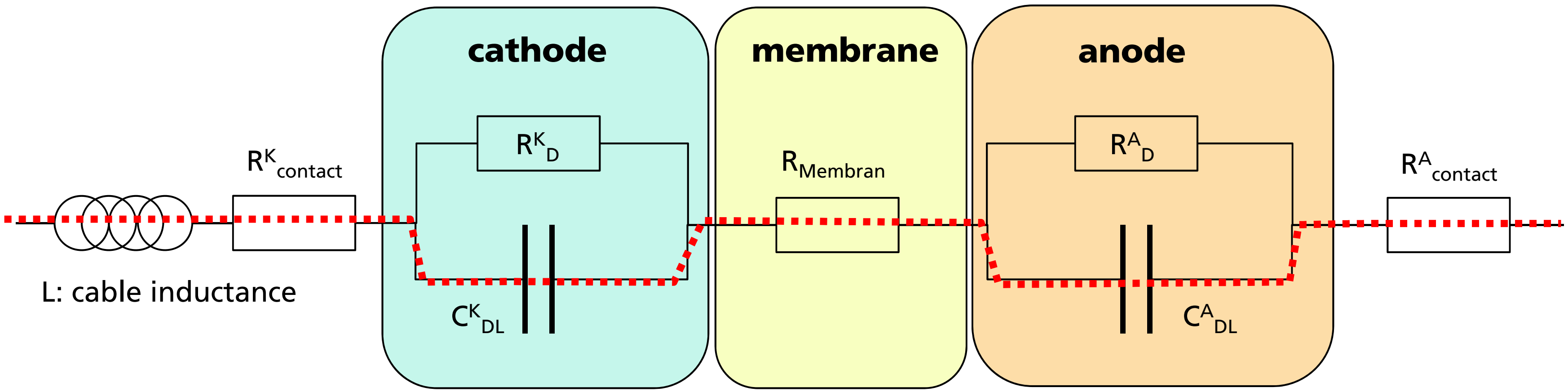
High frequency resistance (HFR)



$$Z_{FC}(\omega \rightarrow \infty) = i\omega L_{cable} + R^K{}_{contact} + R_{membrane} + R^A{}_{contact}$$

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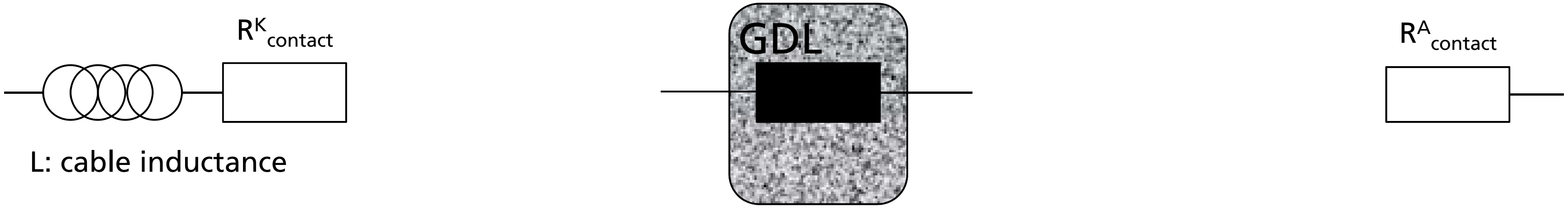
Der Hochfrequenzwiderstand (HFR)



$$Z_{blank}(\omega \rightarrow \infty) = i\omega L_{cable} + R^K_{contact} + R^A_{contact} + R_{GDL}$$

$$Z_{FC}(\omega \rightarrow \infty) - Z_{blanc}(\omega \rightarrow \infty) = R_{membrane} - \cancel{R_{GDL}}$$

negligible or known

From HFR or conductivity, the membrane water content λ can be determined

$$\sigma = (0.514 * \lambda - 0.326) e^{1268\left(\frac{1}{303} - \frac{1}{T}\right)}$$

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45°-branch and charge transfer resistance

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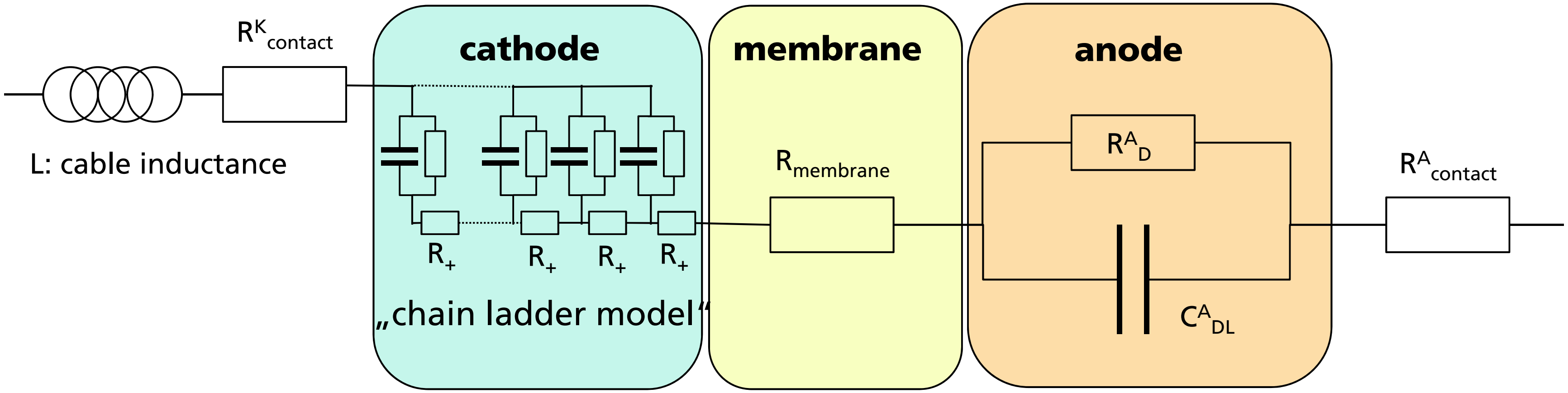
45°-branch @ high frequency



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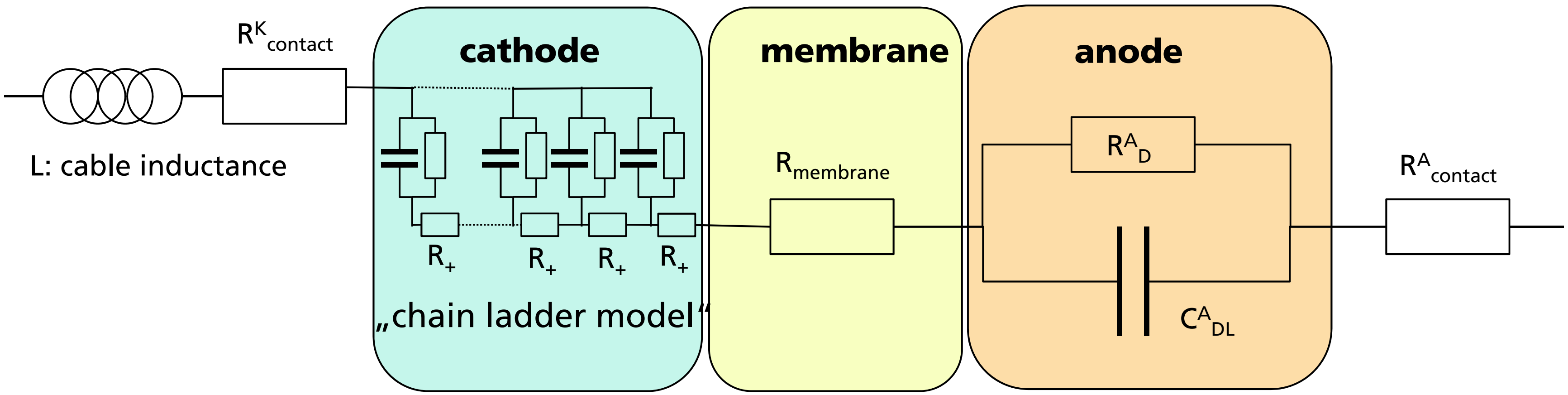
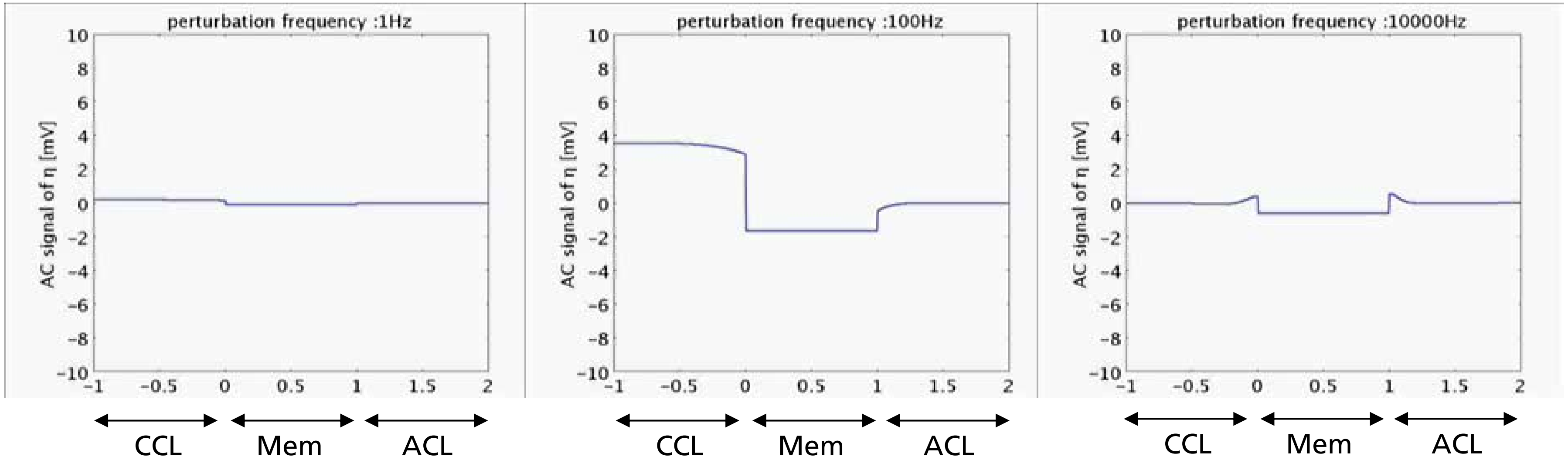
45°-branch @ high frequency





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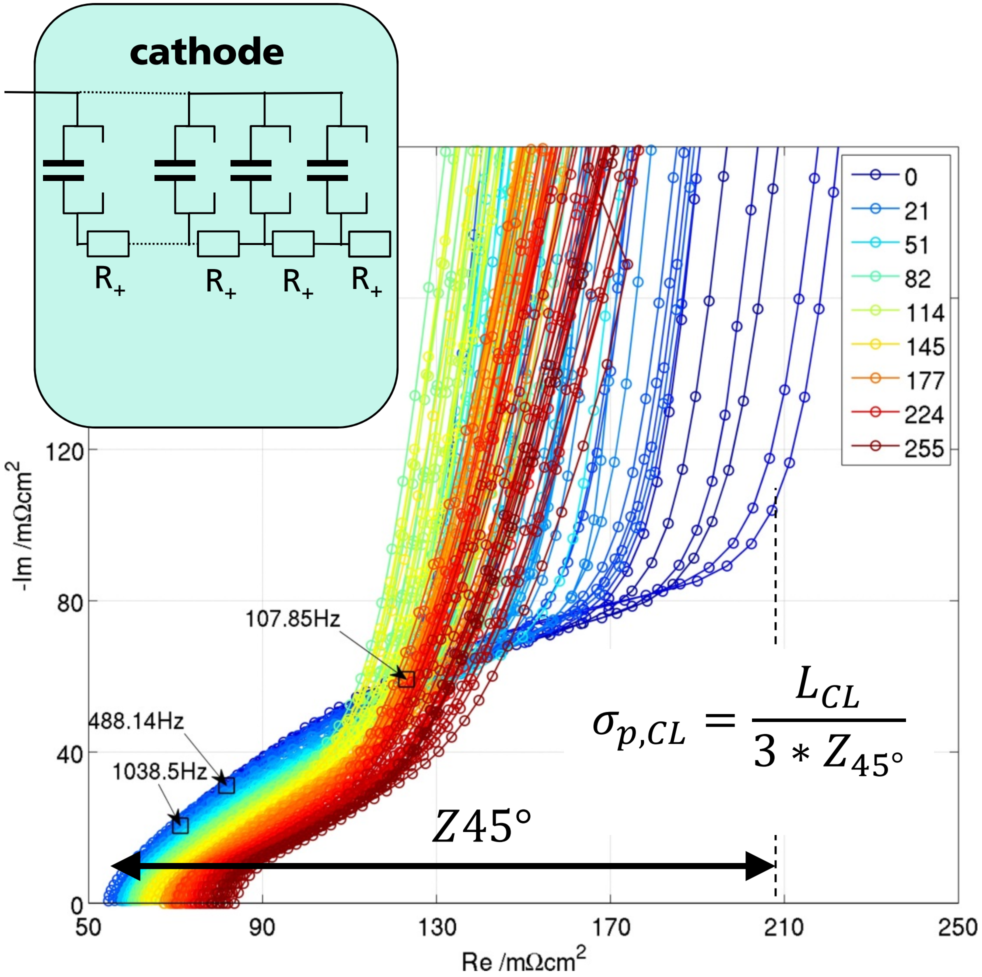
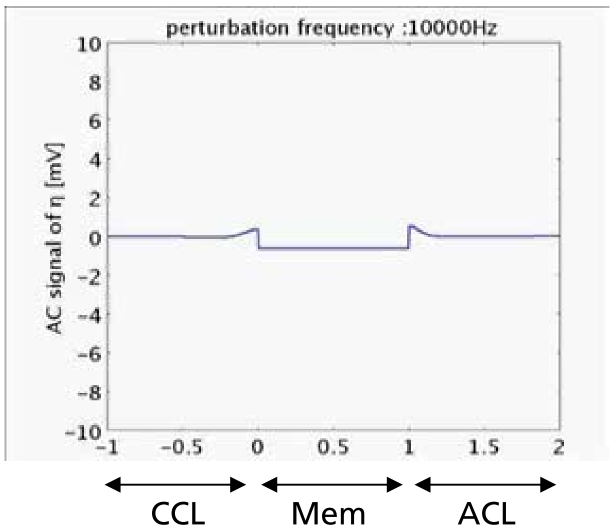
45°-branch @ high frequency



Example:

- EIS @ N_2/H_2
- Protonic resistance of CL



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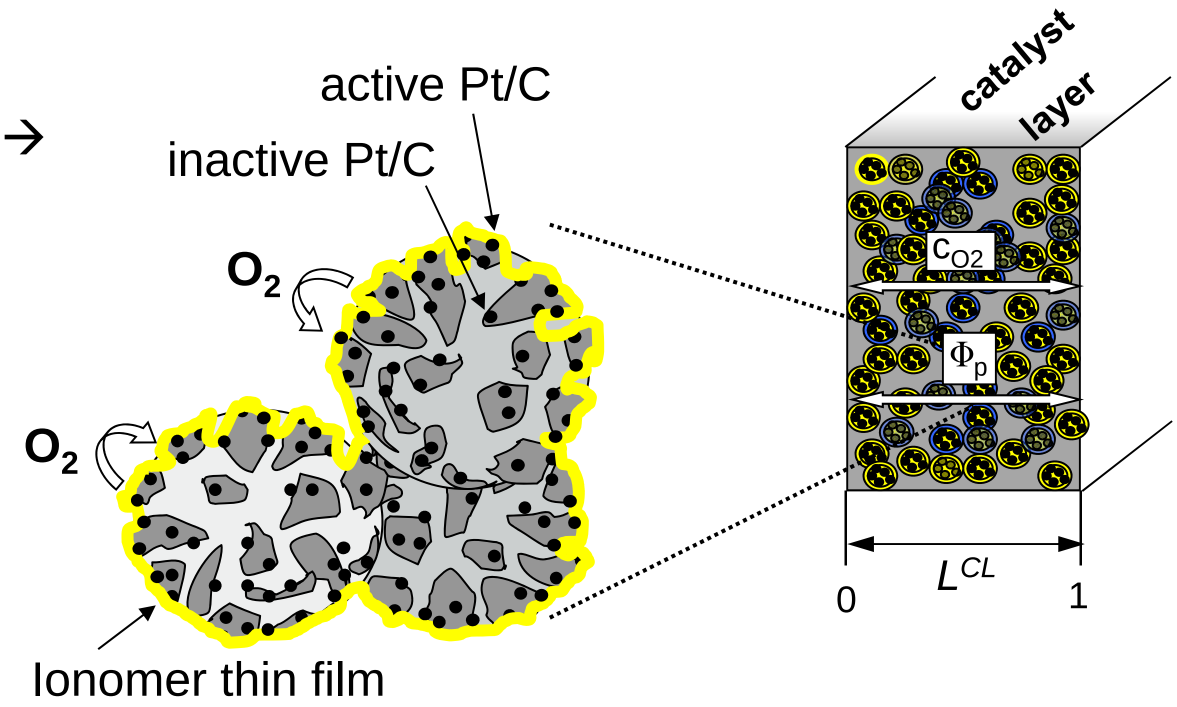
45°-branch @ high frequency
Inhomogeneous CL properties

- Agglomerate model
- Oxygen transport in CCL → concentration gradient dependent on D_{eff}
- Proton transport in CCL → overpotential gradient dependent on σ_{eff}



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D. Gerteisen, Journal of The Electrochemical Society, **162** (14) F1431-F1438 (2015)
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1D cathode model

- Charge balance equation & boundary conditions

$$l_{CL}{}^{2} C_{DL} \frac{\partial(\Phi^{p} - \Phi^{e})}{\partial t} - \frac{\partial}{\partial x}\left(\sigma \frac{\partial \Phi^{p}}{\partial x}\right) = -l_{CL}{}^{2} \Lambda\, j_{gen}^{a}$$

$$\frac{\partial \Phi^{p}(0)}{\partial x} = 0 \qquad \Phi^{p}(1) = 0$$

- Mass balanance equation & boundary conditions

$$l_{CL}{}^{2} \varepsilon_{CL}^{eff} \frac{\partial c_{O2}}{\partial t} - \frac{\partial}{\partial x}\left(D_{O2}^{eff} \frac{\partial c_{O2}}{\partial x}\right) = -l_{CL}{}^{2} \frac{\Lambda}{4\,F} j_{gen}^{a}$$

$$c_{O2}(0) = c_{O2}^{GDL} \qquad \frac{\partial c_{O2}(1)}{\partial x} = 0$$

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1D cathode model

- Differential equation system after perturbation, linearization and Laplace transformation

$$l_{CL}{}^2 C_{DL}\, s\,(\overline{\Phi^p} - \overline{\Phi^e}) - \frac{\partial}{\partial x}\left(\sigma \frac{\partial \overline{\Phi^p}}{\partial x}\right) = -l_{CL}{}^2 \Lambda\, \overline{j_{gen}^a}$$

$$l_{CL}{}^2 \varepsilon_{CL}^{eff}\, s\, \overline{c_{O2}} - \frac{\partial}{\partial x}\left(D_{O2}^{eff} \frac{\partial \overline{c_{O2}}}{\partial x}\right) = -l_{CL}{}^2 \frac{\Lambda}{4\,F} \overline{j_{gen}^a}$$

$$\overline{\Phi^p}(1) = \frac{\partial \overline{\Phi^p}(0)}{\partial x} = \frac{\partial \overline{c_{O2}}(1)}{\partial x} = \overline{c_{O2}}(0) = 0$$

$$Z = \frac{\overline{\Phi^e}}{\sigma \frac{\partial \overline{\Phi^p}(1)}{\partial x}}$$

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What happens for inhomogeneous CL properties?

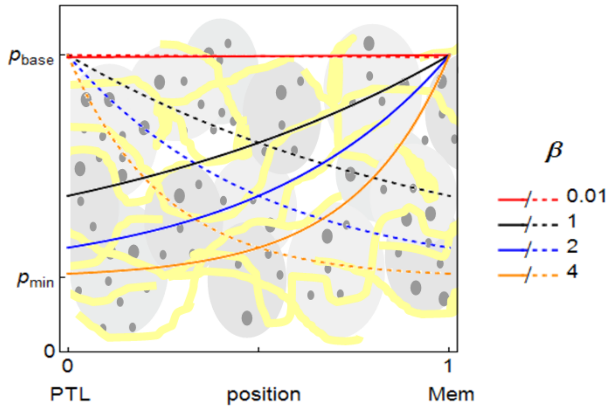
- Differential equation system after perturbation, linearization and Laplace transformation

$$l_{CL}{}^2 C_{DL}\, s\,(\overline{\Phi^p}-\overline{\Phi^e})-\frac{\partial}{\partial x}\left(\sigma\frac{\partial\overline{\Phi^p}}{\partial x}\right)=-l_{CL}{}^2\Lambda\,\overline{j^a_{gen}}$$

$$l_{CL}{}^2 \varepsilon_{CL}^{eff}\, s\,\overline{c_{O2}}-\frac{\partial}{\partial x}\left(D_{O2}^{eff}\frac{\partial\overline{c_{O2}}}{\partial x}\right)=-l_{CL}{}^2\frac{\Lambda}{4\,F}\overline{j^a_{gen}}$$

$$\overline{\Phi^p}(1)=\frac{\partial\overline{\Phi^p}(0)}{\partial x}=\frac{\partial\overline{c_{O2}}(1)}{\partial x}=\overline{c_{O2}}(0)=0$$

$$Z=\frac{\overline{\Phi^e}}{\sigma\frac{\partial\overline{\Phi^p}(1)}{\partial x}}$$



$$p(y)=p_{base}(\alpha+(1-\alpha))e^{-\beta*\tilde{y}}$$

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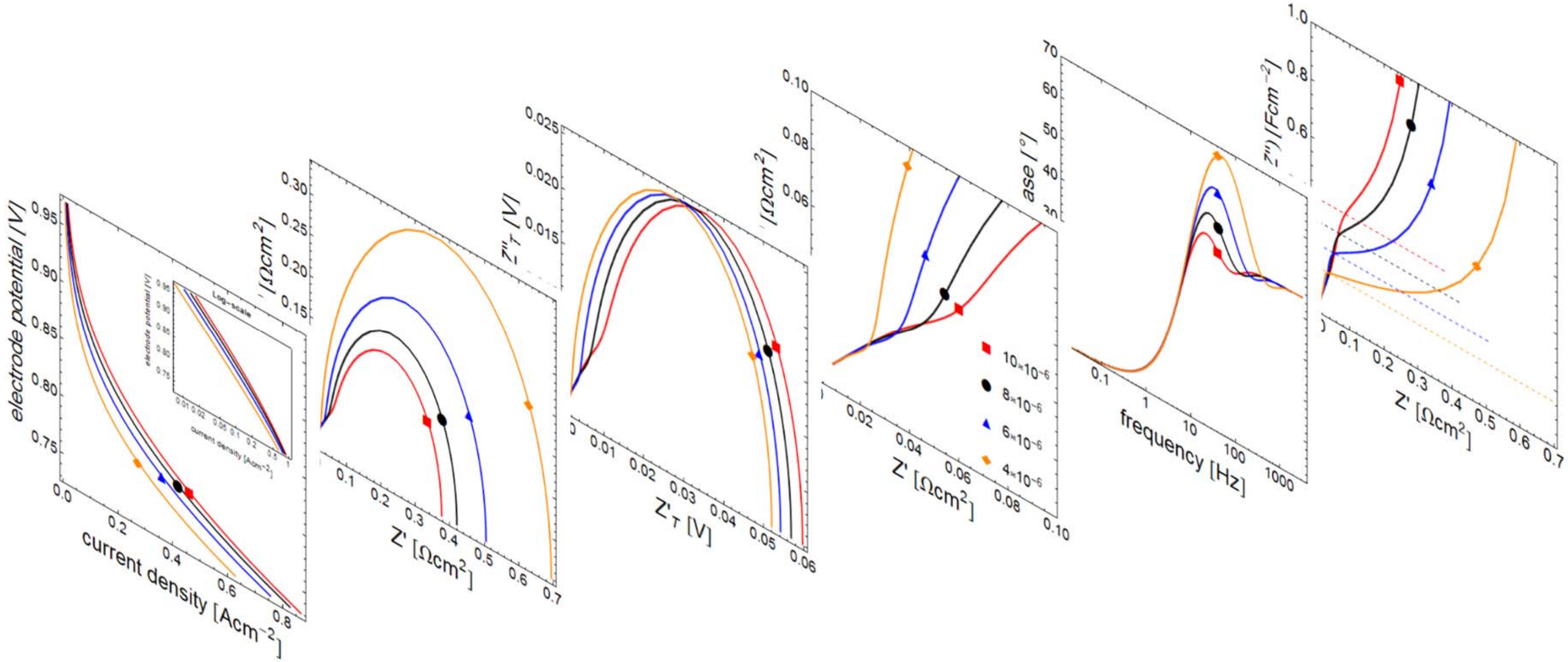
Variation of catalyst layer thickness

- Homogeneous CL properties !!



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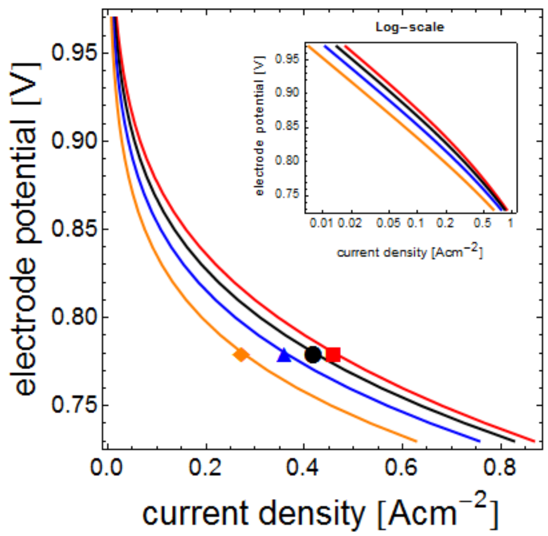
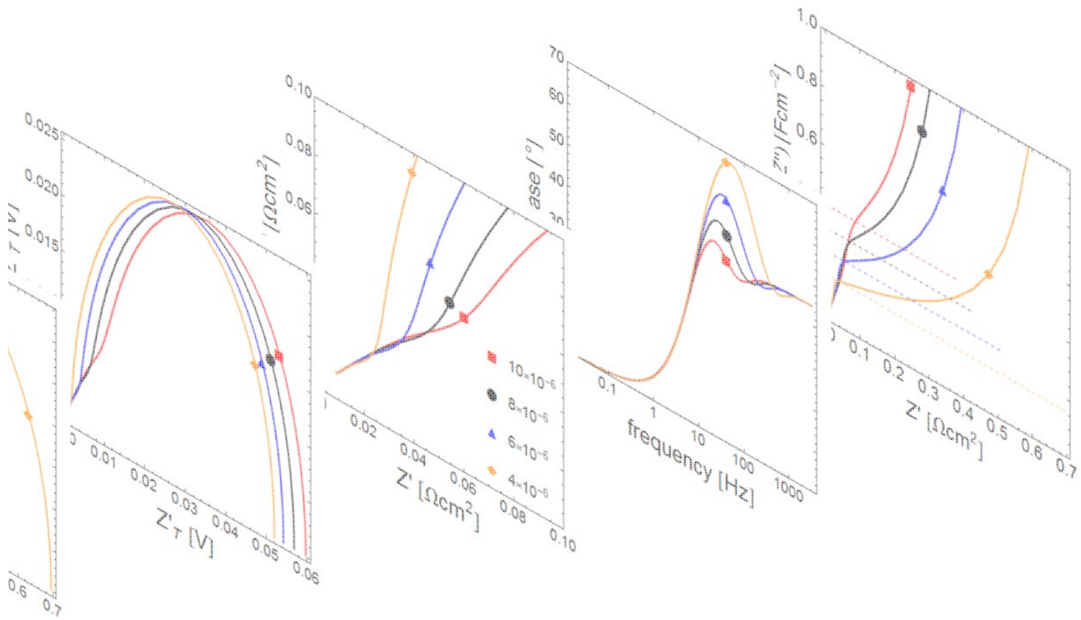
Variation of catalyst layer thickness

- Polarization curve
  - Doubling of Tafel slope for thicker CL at lower current density





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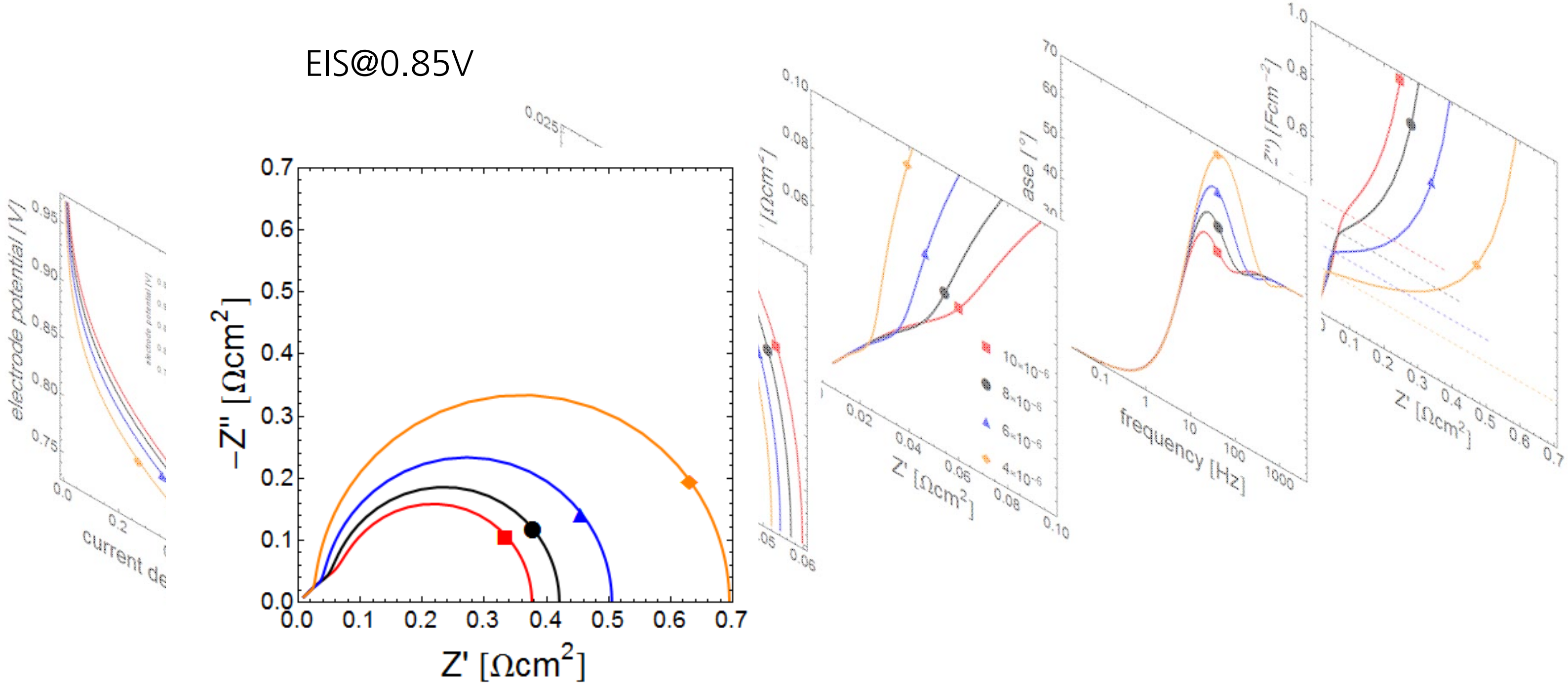
Variation of catalyst layer thickness

- Impedance spectra as Nyquist-Plot
  - R_{CT} increases with lowering the CL thickness

EIS@0.85V



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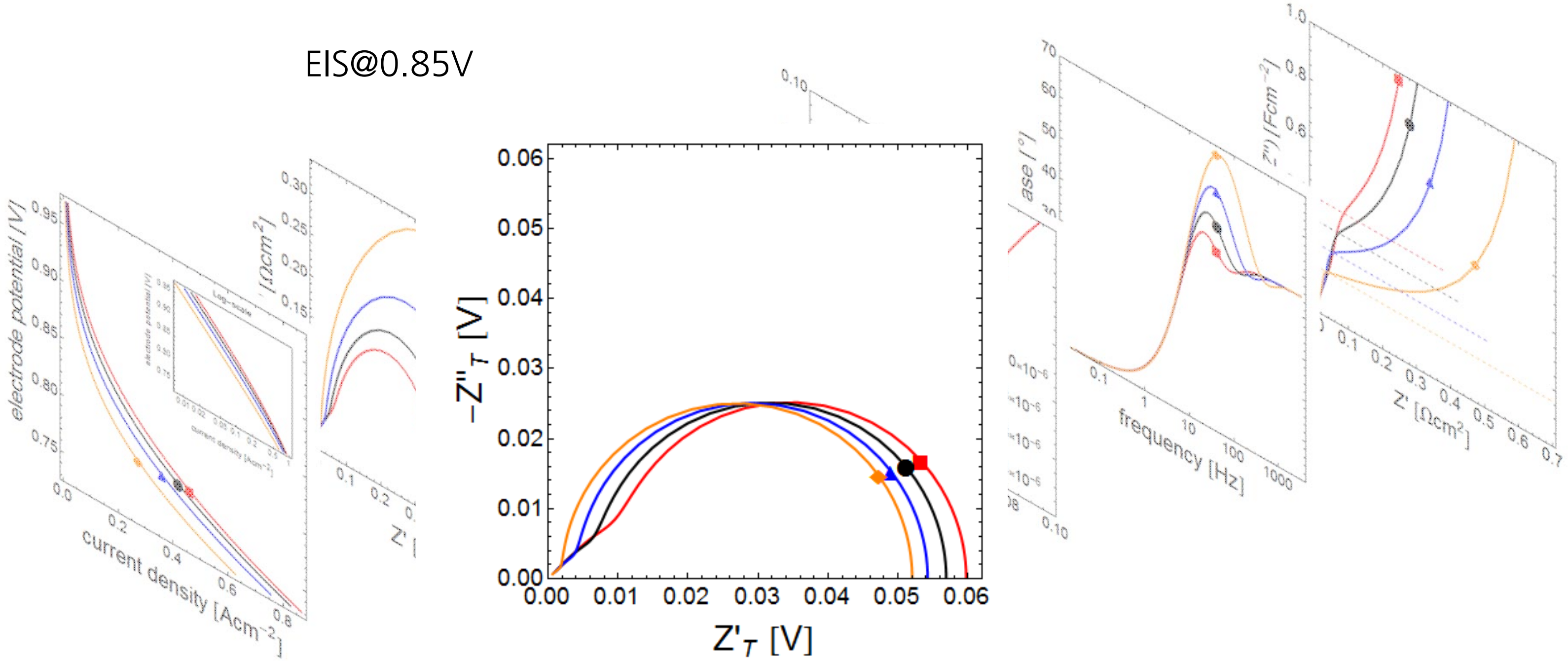
Variation of catalyst layer thickness

- Tafel-Impedance as Nyquist-Plot → $Z_T = i_{steady\text{-}state} * Z$
  - Identical height → Tafel slope identical
  - Shift to higher real part due to larger 45° branch (scales with thickness)

EIS@0.85V



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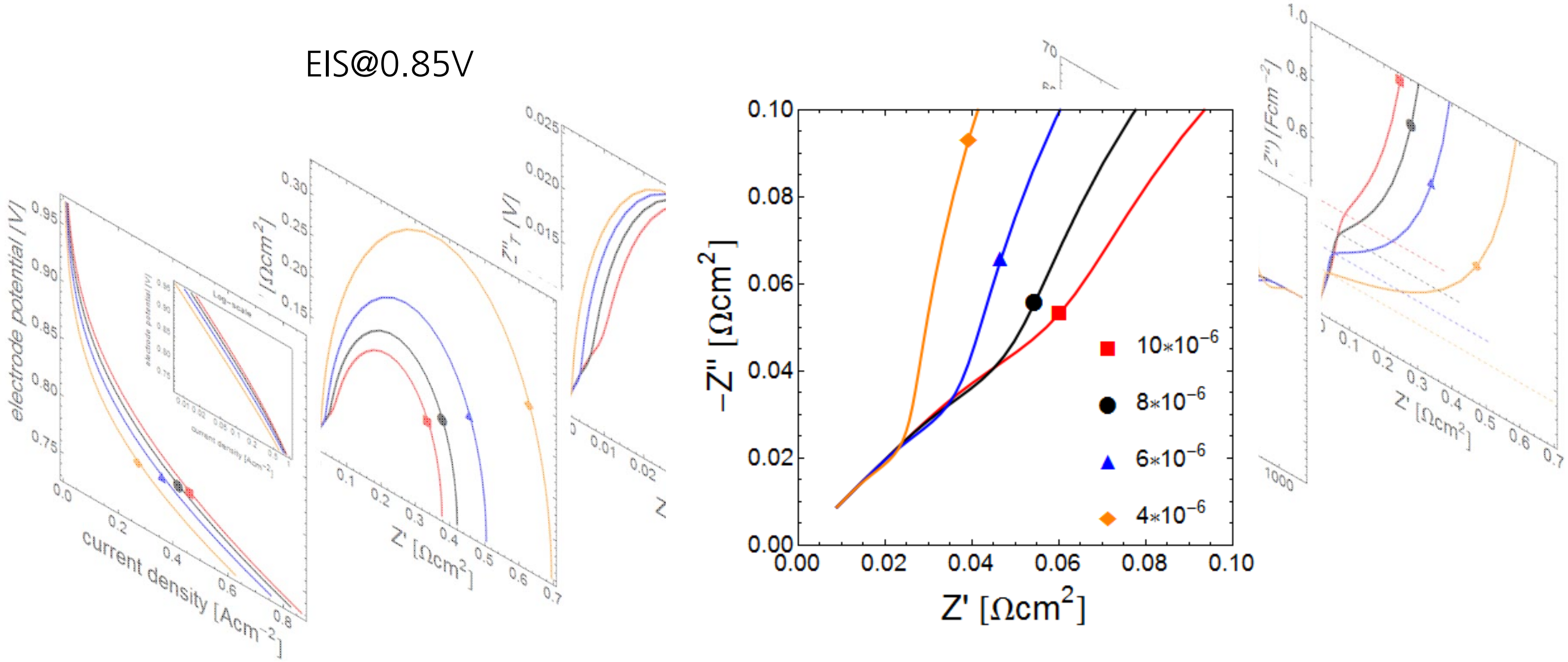
Variation of catalyst layer thickness

- Impedance as Nyquist-Plot at high frequencies
  - Linear branch
  - Thicker CL layer = longer branch

EIS@0.85V



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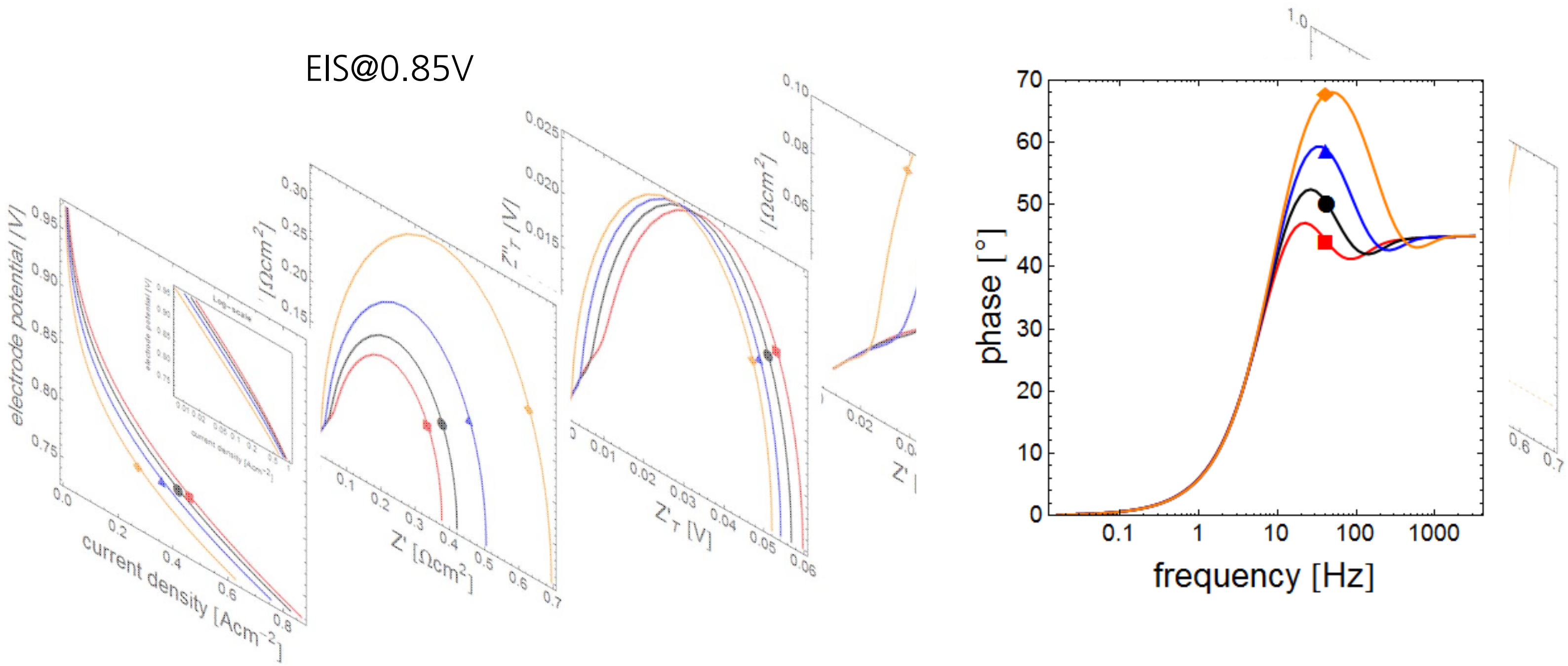
Variation of catalyst layer thickness

- Impedance as Bode-Plot (only phase)
  - Linear branch shows 45°-phase



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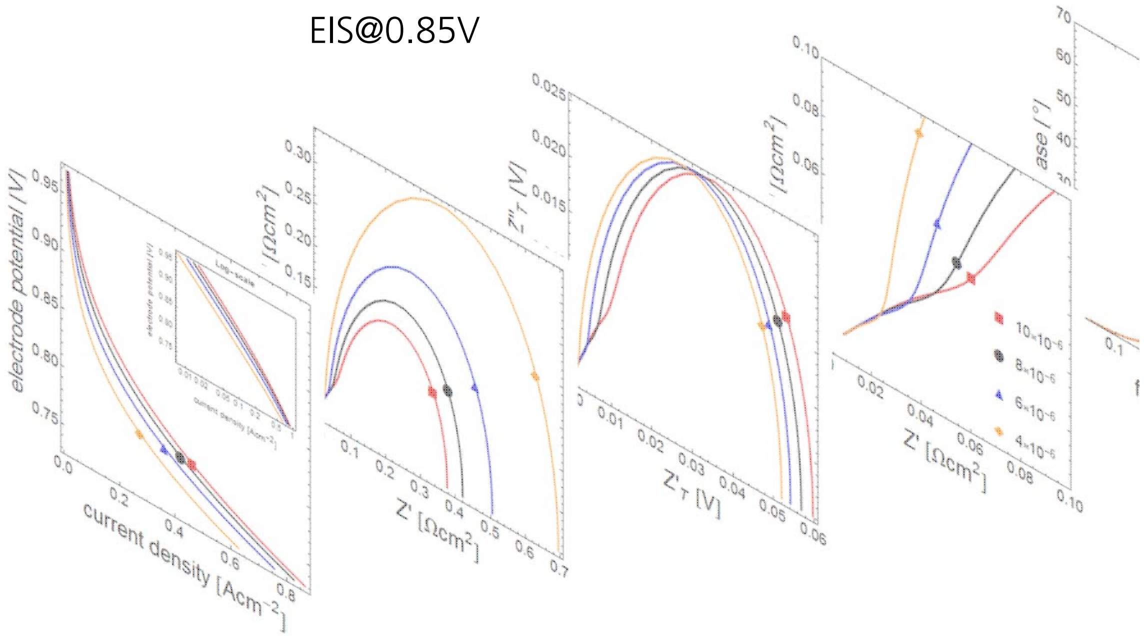
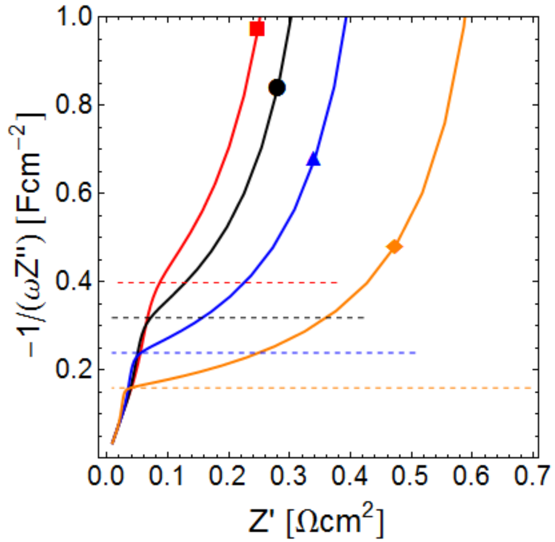
Variation of catalyst layer thickness

- Capacity-Plot (1/ωZ'' vs Z')
  - When the perturbation completely penetrates the CL, the curve deviates from the linear branch





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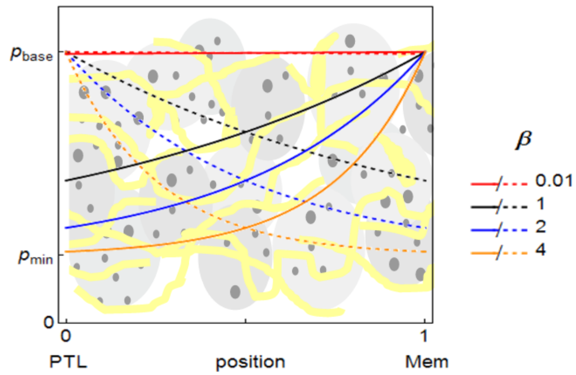
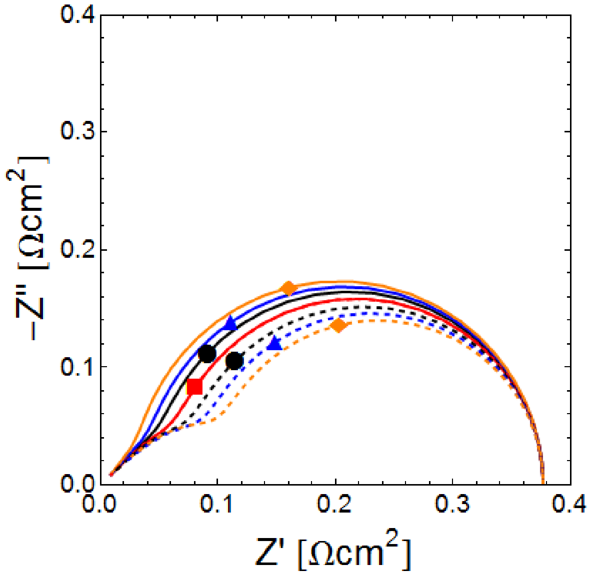
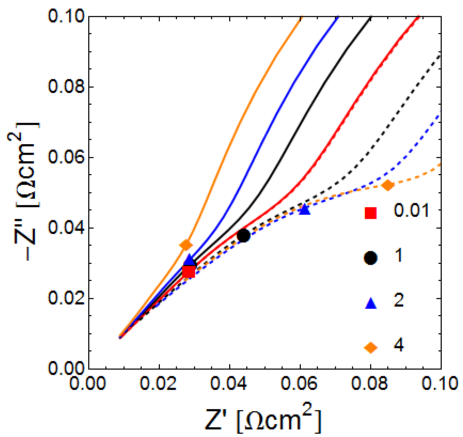
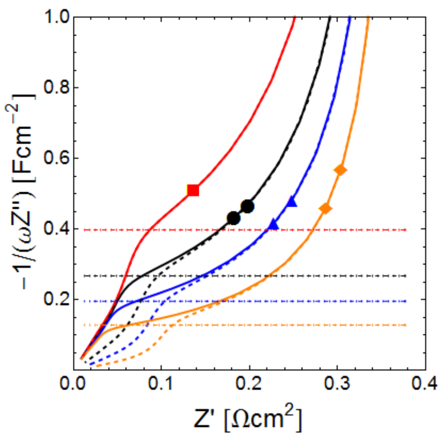
Distributed double-layer capacitance

- Impedance spectrum
  - No impact on LFR → no charging currents at steady-state
  - Depressed impedance arc









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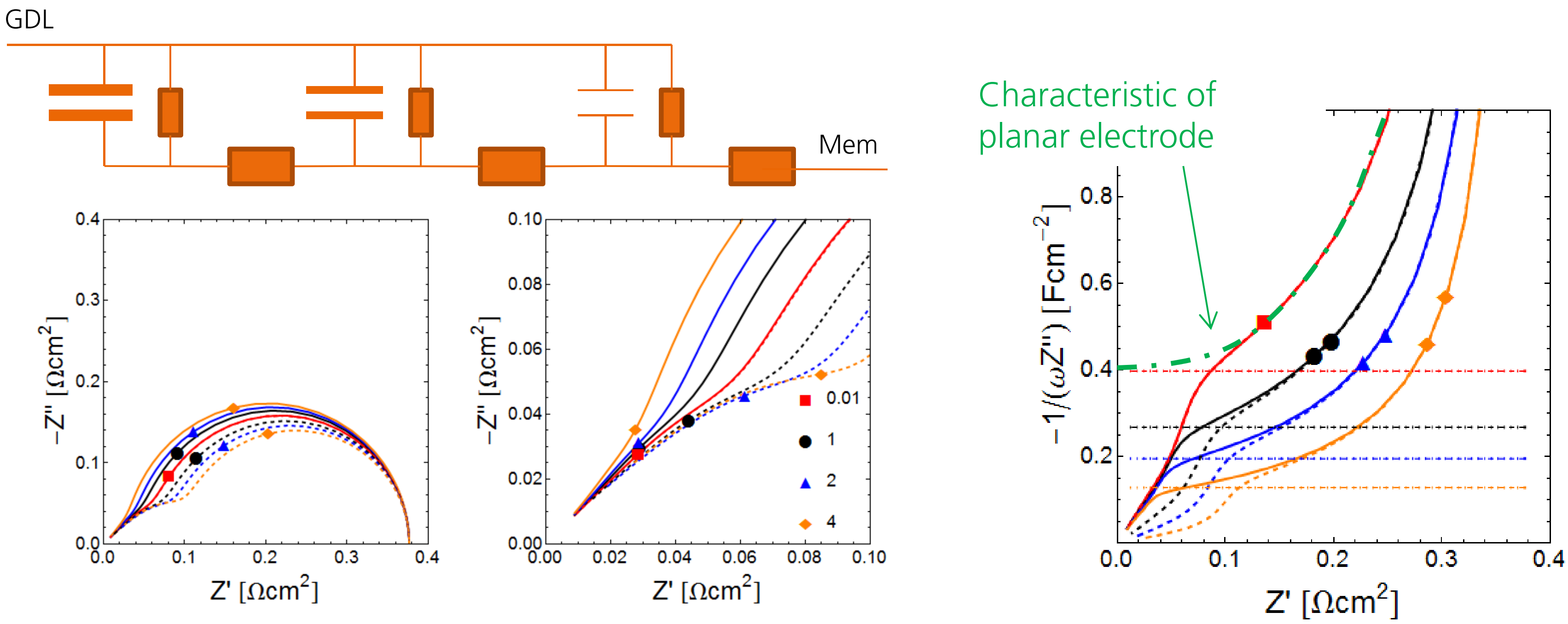
Distributed double-layer capacitance

- Capacity-Plot ($1/\omega Z''$ vs Z')
  - Turning point still defines the total electrode double-layer capacity
  - Convex shape in the high frequency range



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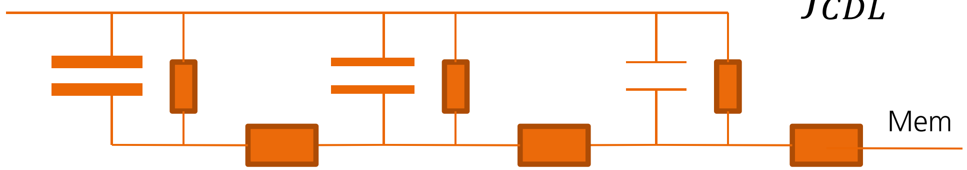
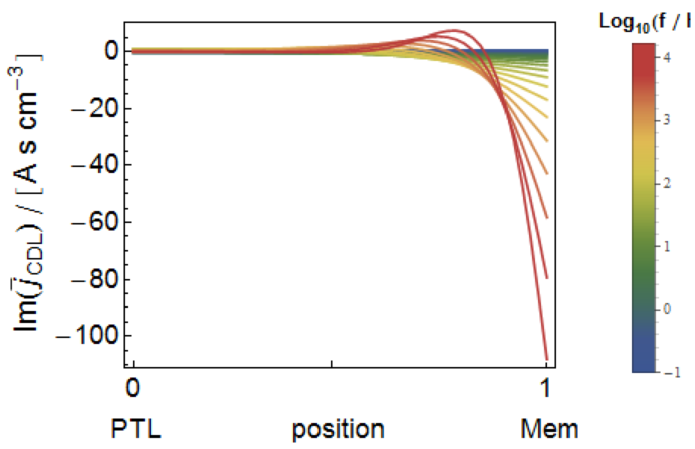
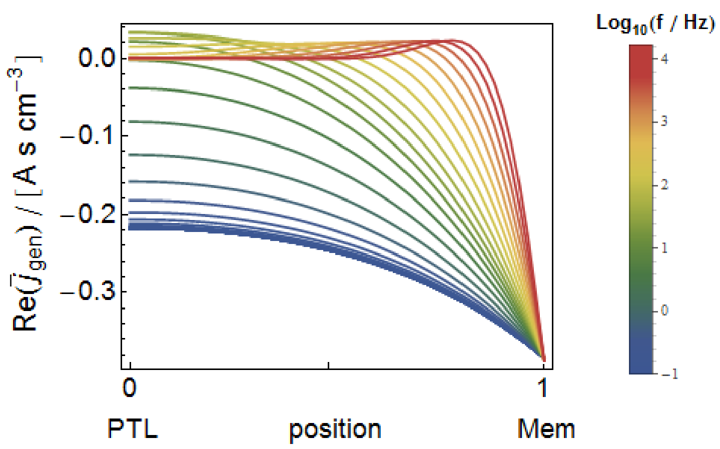
Distributed double-layer capacitance

- Penetration depth

$$\underbrace{{l_{CL}}^2 C_{DL}\, s\, (\overline{\Phi^p} - \overline{\Phi^e})}_{j^*_{CDL}} - \frac{\partial}{\partial x}\left(\sigma \frac{\partial \overline{\Phi^p}}{\partial x}\right) = \underbrace{-{l_{CL}}^2 \Lambda\, \overline{j^a_{gen}}}_{j^*_{gen}}$$







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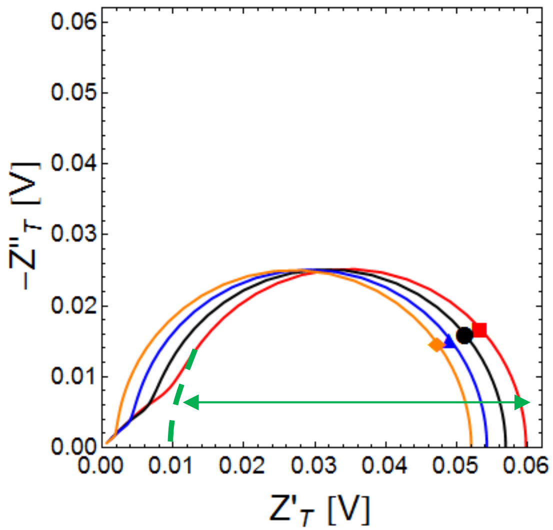
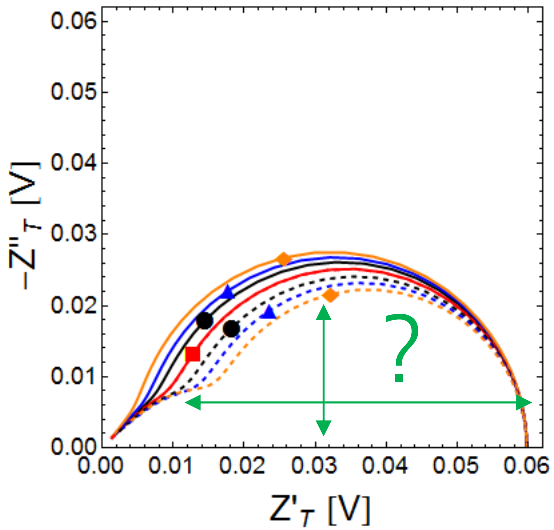
Distributed double-layer capacitance

- Tafel impedance
  - Tafel slope can not be extracted easily by the height or diameter of the spectra





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Decreasing double-layer capacitance and protonic conductivity profile towards membrane

- Theoretical consideration
  - Derivation of divergence leads to additional term

$$l_{CL}{}^{2} C_{DL}\, s\, (\overline{\Phi^p} - \overline{\Phi^e}) - \frac{\partial}{\partial x}\left(\sigma \frac{\partial \overline{\Phi^p}}{\partial x}\right) = -l_{CL}{}^{2} \Lambda\, \overline{j_{gen}^{a}}$$

$$\underbrace{l_{CL}{}^{2} C_{DL}\, s\, (\overline{\Phi^p} - \overline{\Phi^e})}_{j^*_{CDL}} - \underbrace{\left(\frac{\partial}{\partial x}\sigma\right)\left(\frac{\partial \overline{\Phi^p}}{\partial x}\right)}_{j^*_{para-Profile}} - \underbrace{\sigma\left(\frac{\partial^2 \overline{\Phi^p}}{\partial x^2}\right)}_{j^*_{divergence}} = \underbrace{-l_{CL}{}^{2} \Lambda\, \overline{j_{gen}^{a}}}_{j^*_{gen}}$$

New Term

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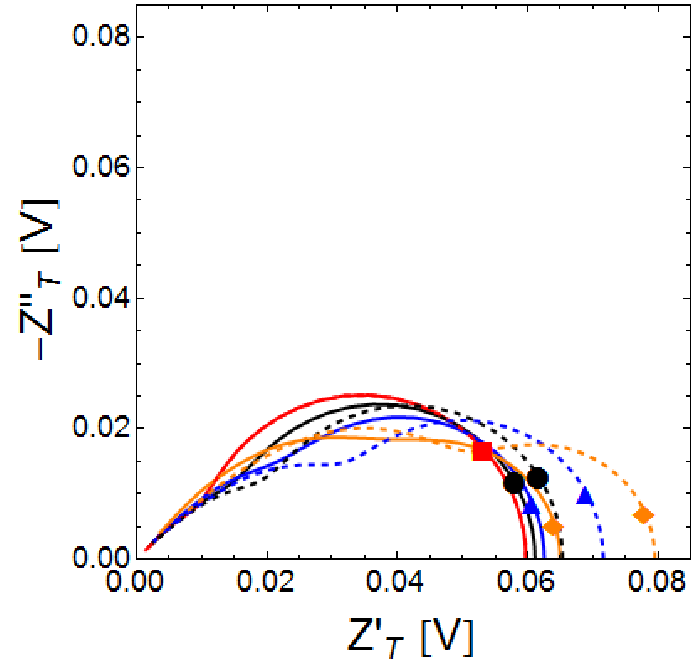
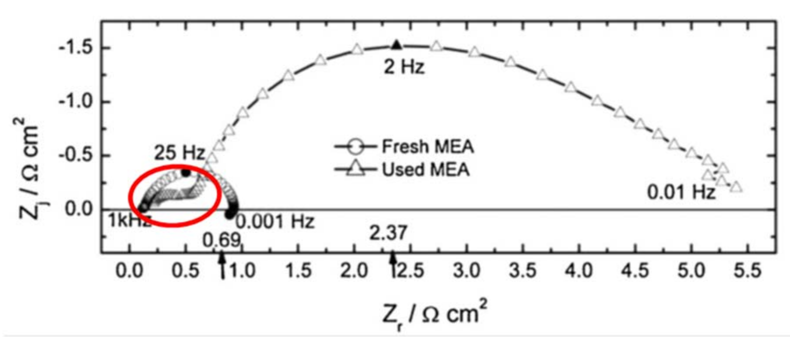
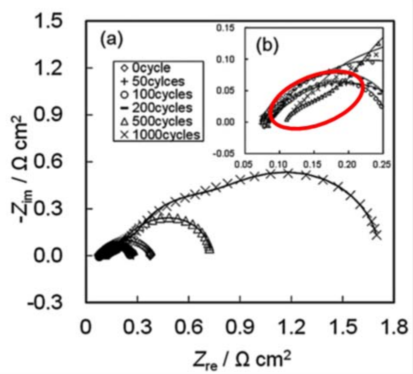
Decreasing double-layer capacitance and protonic conductivity profile towards membrane

- Tafel impedance
  - Dependent on the parameter profile the spectra separates into a low and high frequency arc.





S.K. Roy, H. Hagelin-Weaver, M.E. Orazem, Journal of Power Sources 196 (2011)



H. Nara, S. Tominaka, T. Momma, T. Osaka, Journal of The Electrochemical Society 158 (2011)

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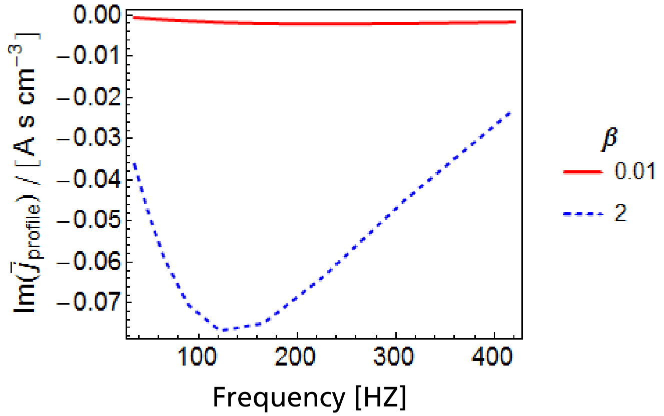
Origin of the separation into high/loe frequency arc

- Comparison between homogeneous (solid) and non-homogeneous CL-properties: $\boldsymbol{\beta_\sigma} = \boldsymbol{\beta_{CDL}} = \mathbf{2}$ (dashed)
- Charge balance equation

$$l_{CL}{}^2 C_{DL}\, s\, (\overline{\Phi^p} - \overline{\Phi^e}) - \underbrace{\left(\frac{\partial}{\partial x}\sigma\right)\left(\frac{\partial \overline{\Phi^p}}{\partial x}\right)} - \sigma\left(\frac{\partial^2 \overline{\Phi^p}}{\partial x^2}\right) = -l_{CL}{}^2 \Lambda\, \overline{j_{gen}^a}$$

→ Additional term shows minimum, which is responsible for the separation



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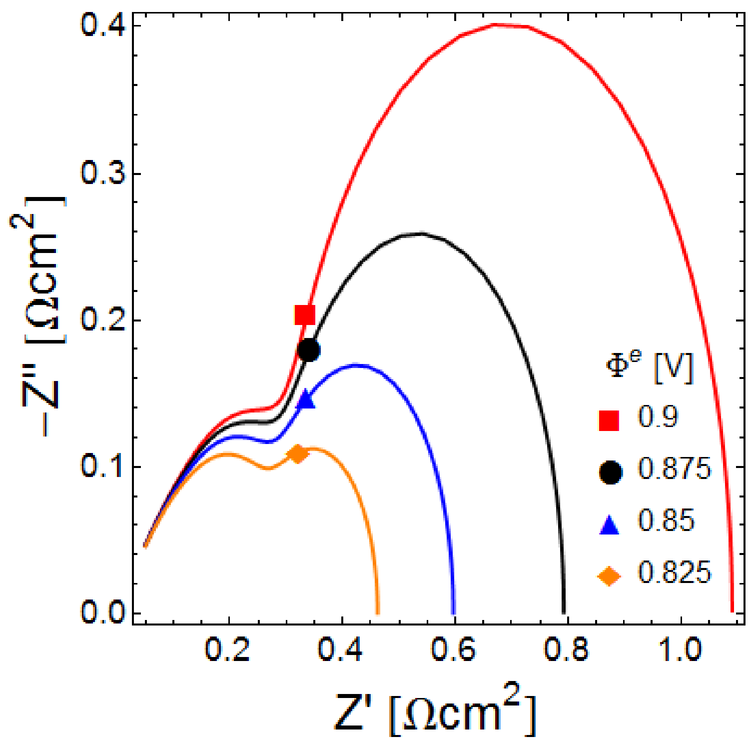
Impact of the electrode potential on the low frequency arc

- Distributed double-layer capacitance
  $p(y) = p_{base}(\alpha + (1-\alpha)e^{-\beta*\tilde{y}})$
- Low frequency arc decreases with decreasing potential
  - Charge transfer resistance
  - No mass transport resistance



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Low frequency arc

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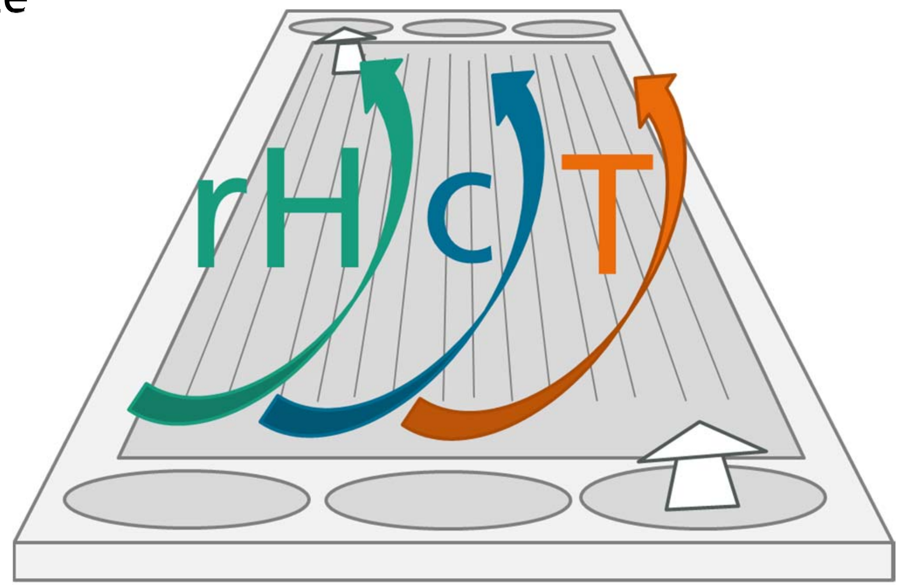
Impedance measurement at „normal" flow conditions

- What means „normal" in this context?
  - Non-excessive stoichiometry
  - Inhomogeneous conditions over active area
  - Cell with technical relevant size
  - Real stack hardware



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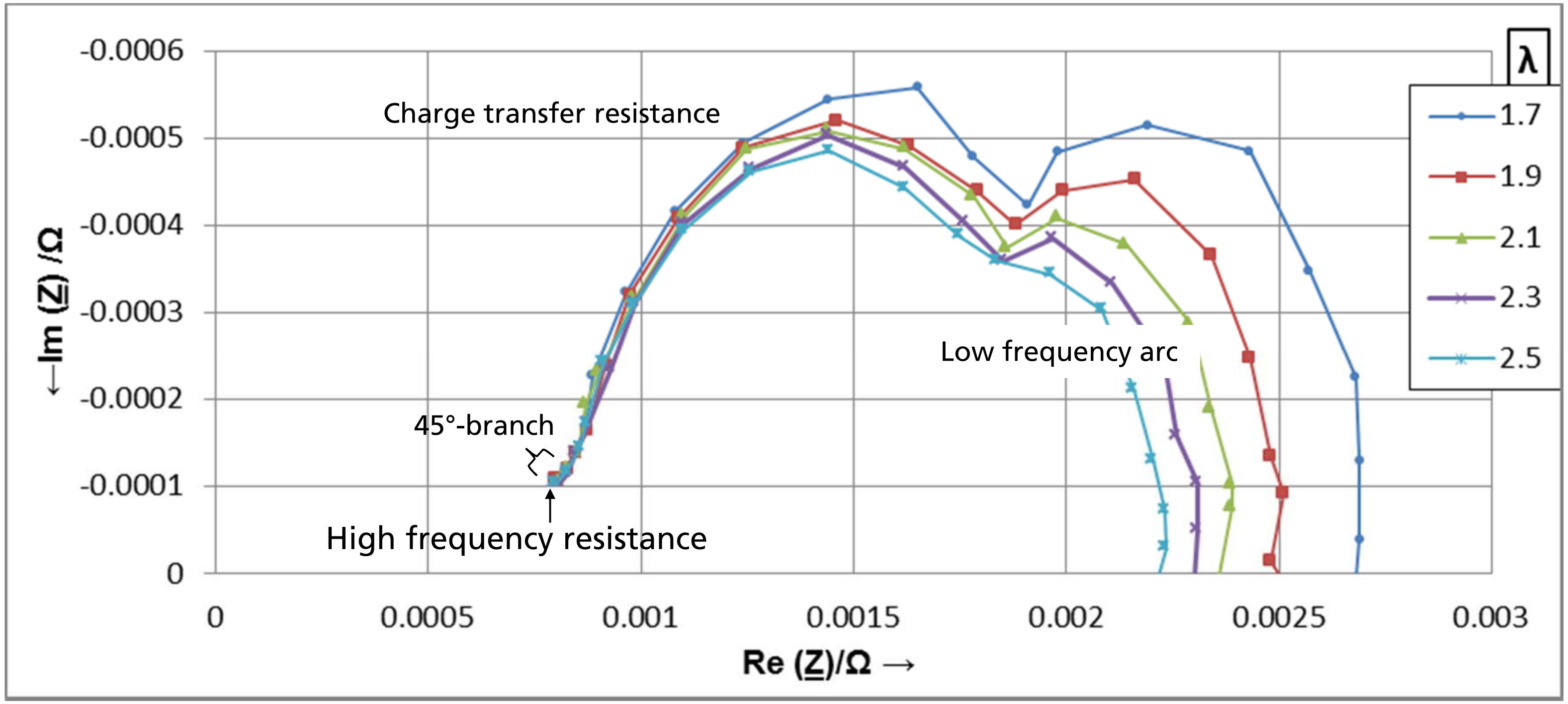
How to interprete the low-frequency arc at „normal“ flow conditions

- Large impact on flow conditions → in-plane effects have to be considered



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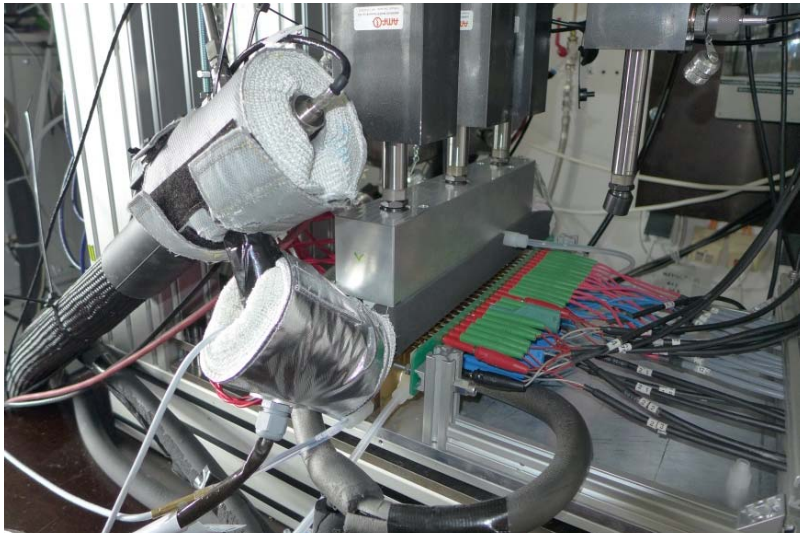
Low-frequency arc:
Insights by spatially resolved EIS measurements

- Multi-Channel-Characterization-System (MCCS)

- Segmented Along-the-channel-Cell



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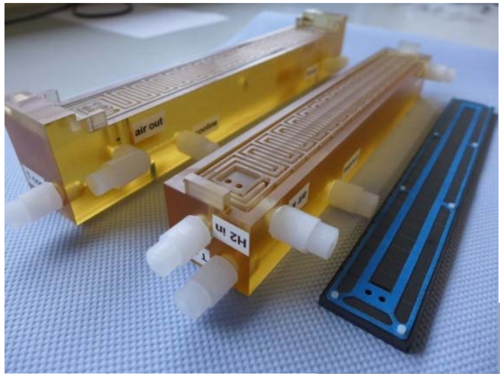
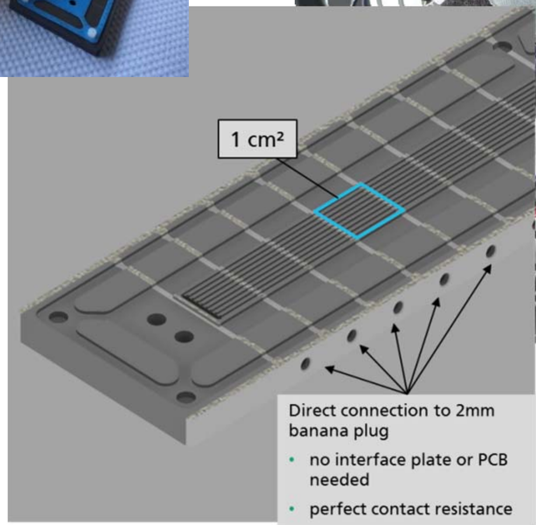
Low-frequency arc:
Insights by spatially resolved EIS measurements

- Segmented Along-the-channel-Cell





- 25 segments
- Size: 1 cm^2
- 9 Channel á 25cm length
- Land/channel width 0.45/0.55mm

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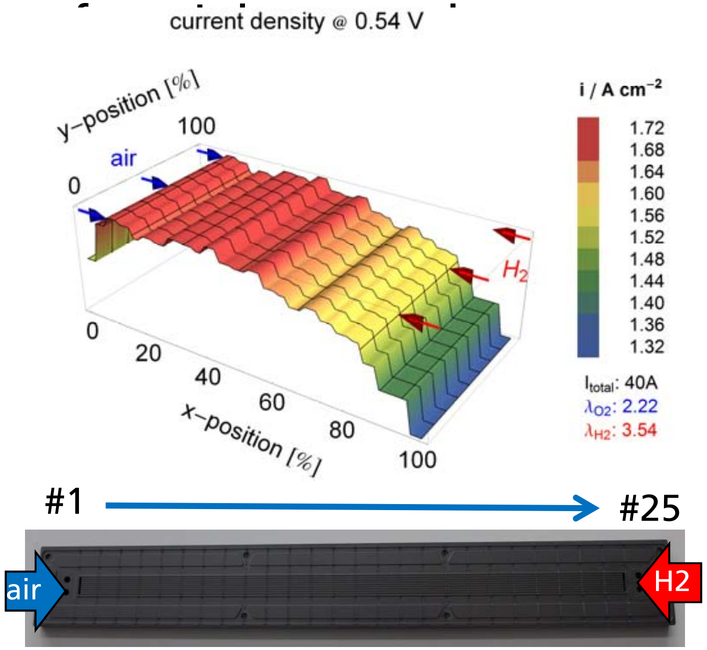
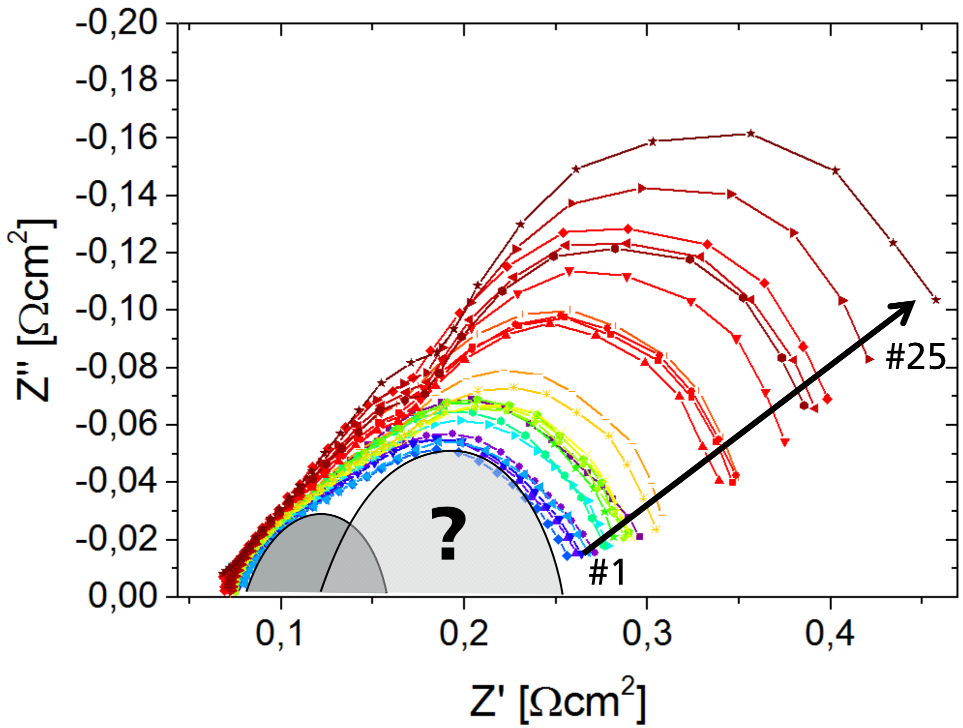
Current distribution and evolution of impedance spectra downstream the channel

- Current generation decreases from inlet to outlet (I_{total}=40A)
- Low frequency arc increases





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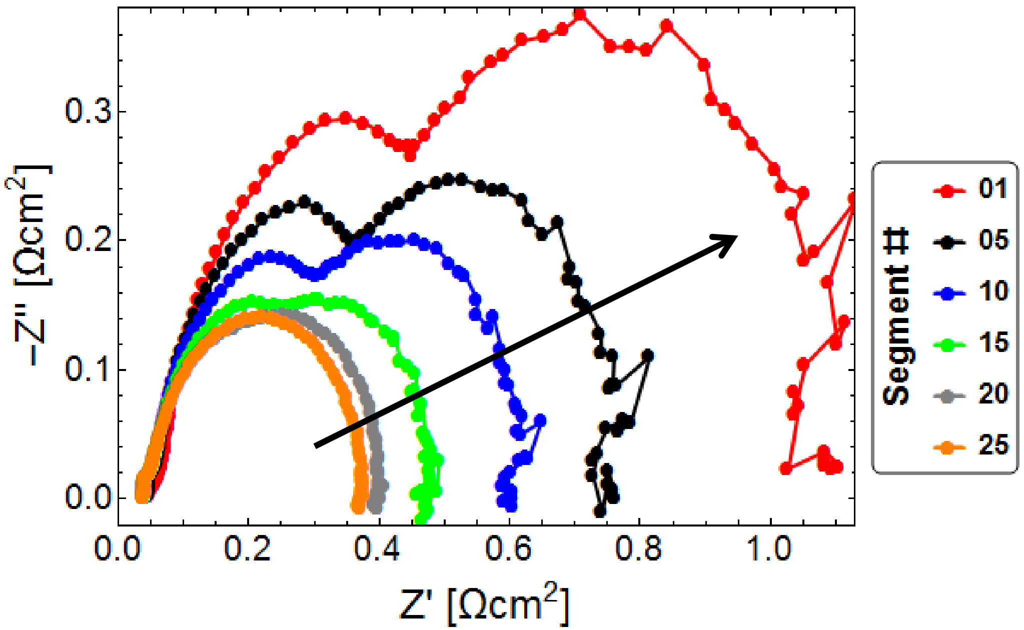
Current distribution and evolution of impedance spectra downstream the channel

- EIS @ low current density (I_{total}<3A)
- Even at low current density values and „normal“ flow conditions a low-frequency arc appears



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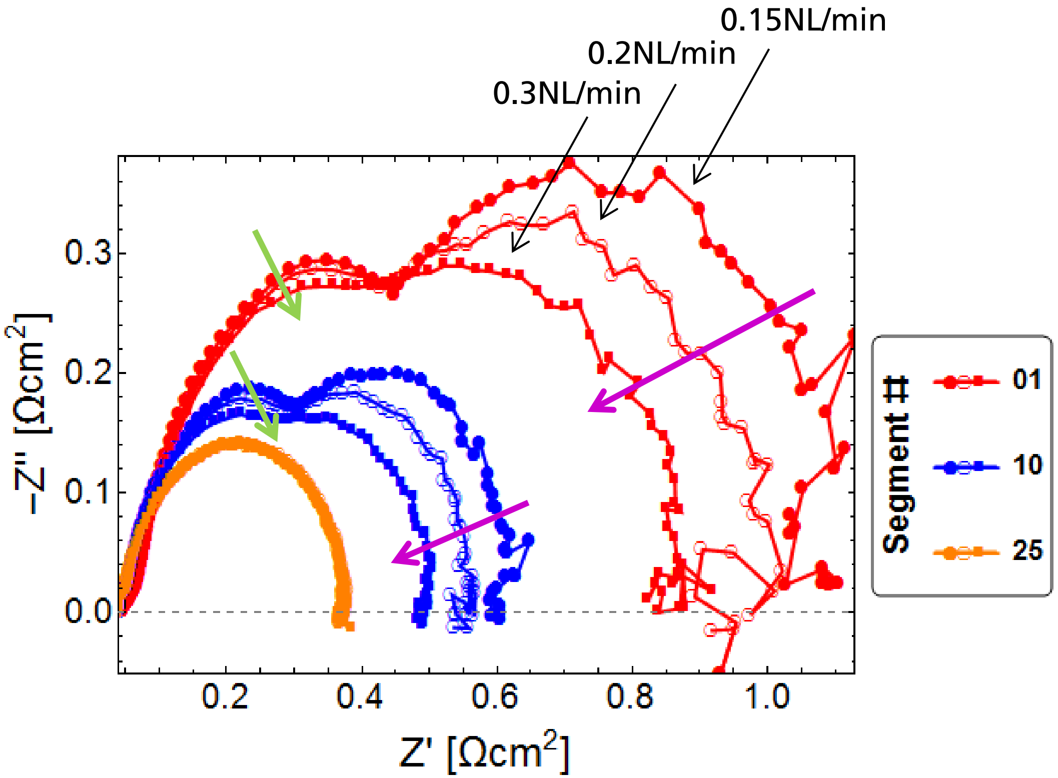
Current distribution and evolution of impedance spectra downstream the channel

- Even at low current density values and „normal“ flow conditions a low-frequency arc appears
- Increasing flow rate
  - Does not impact air inlet segment
  - Has a small impact on the high frequency arc
  - Effects strongly the low-frequency arc



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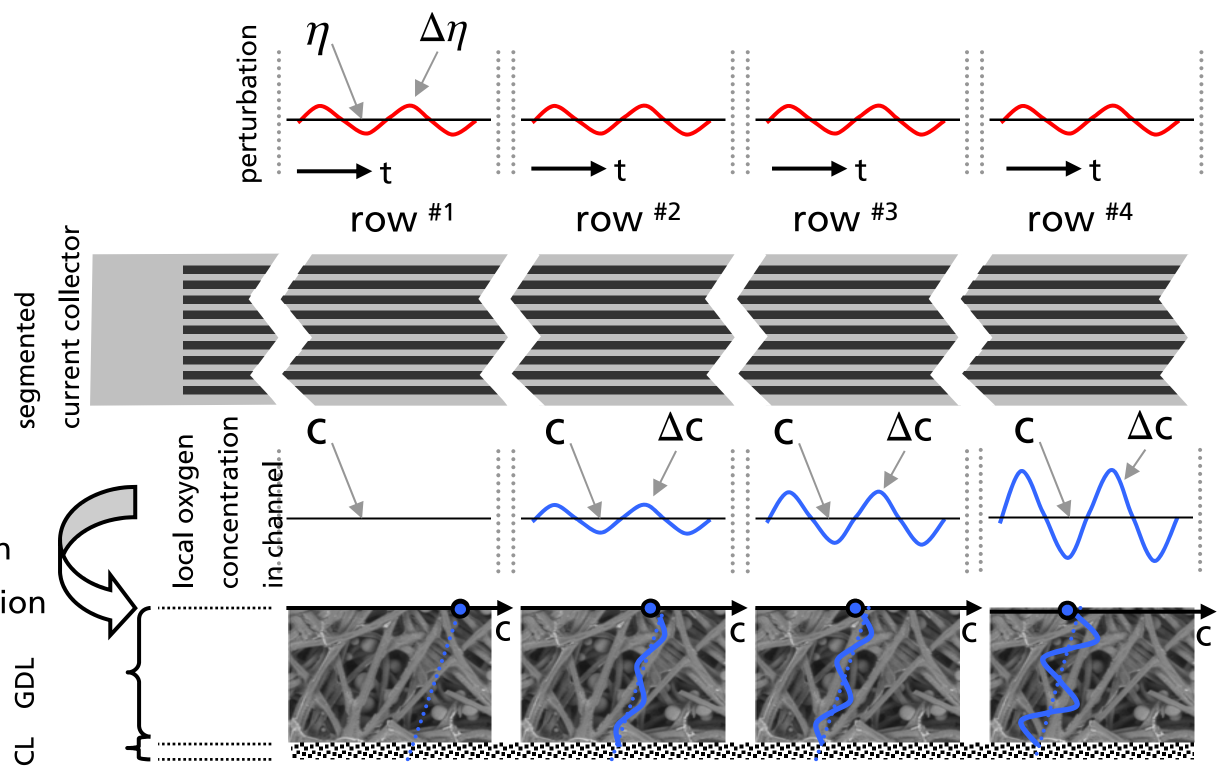
What is the origin of the low-frequency arc?



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

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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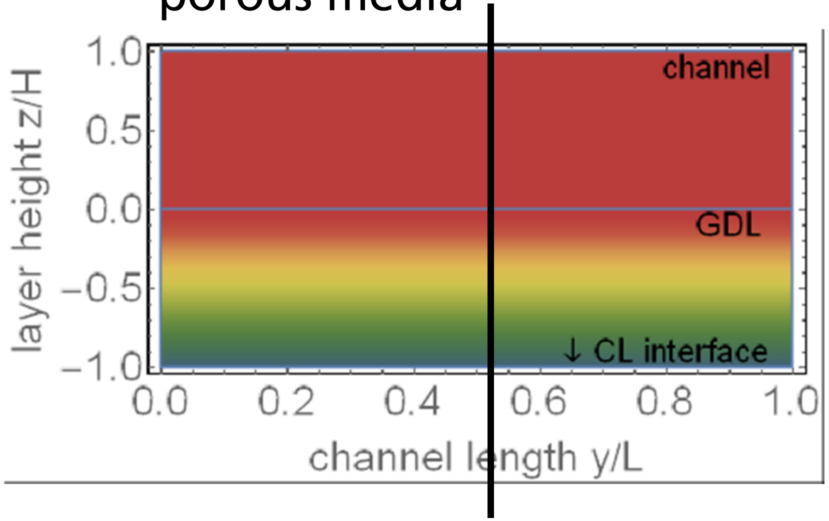
What is the origin of the low-frequency arc?

- Differential cell
  - High stoichiometry → no concentration gradient
  - Oscillating concentration in porous media



Fix boundary condition for oxygen concentration

→ Warburg impedance

1D-cut is representative for whole cell

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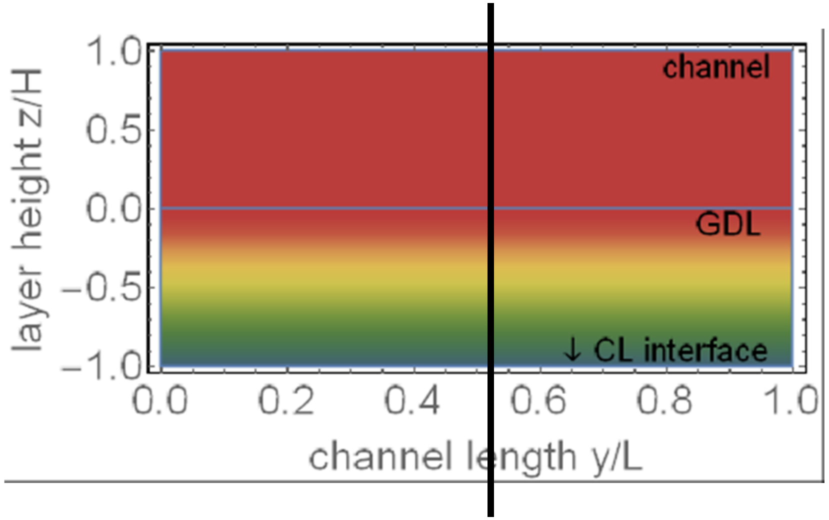
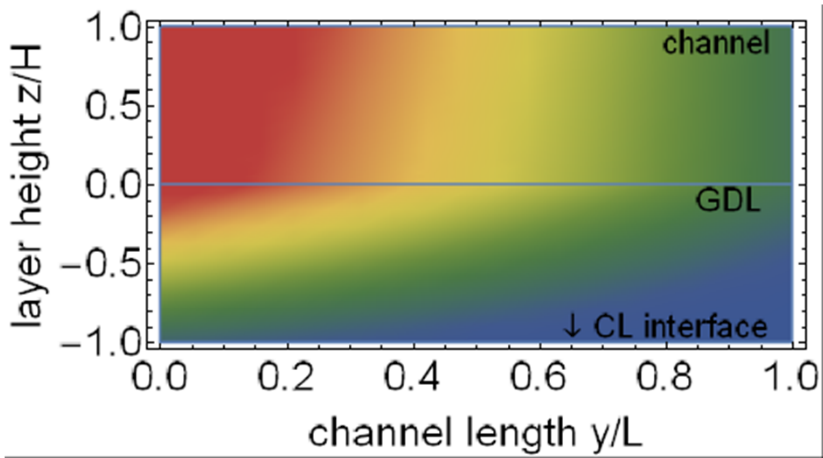
What is the origin of the low-frequency arc?

- Differential cell



- Non-differential cell
  - „normal" stoichiometry → concentration gradient present
  - c_{O_2} oscillates also in-plane



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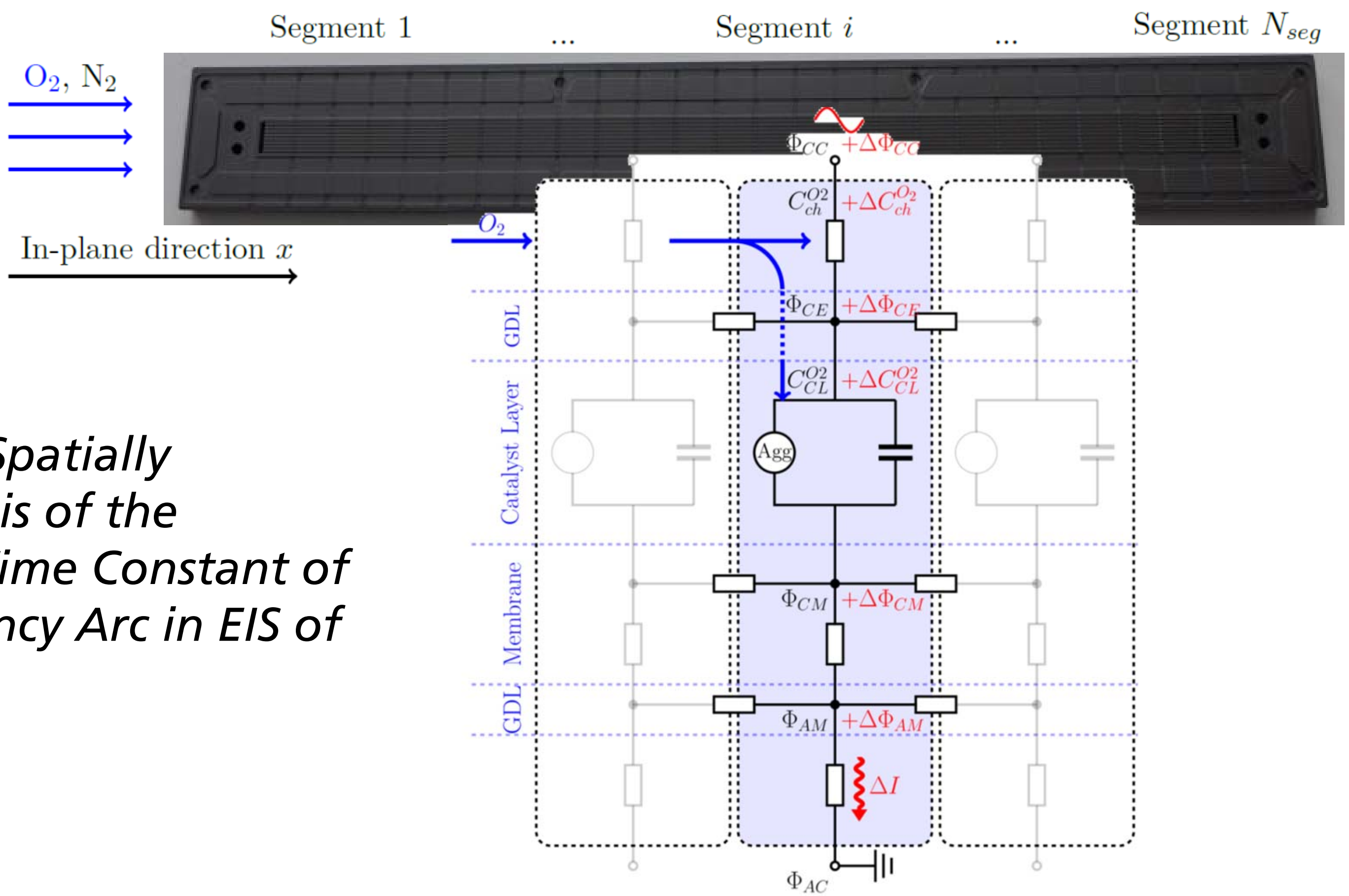
Numerical model available that acounts for the oxygen dynamics in through- as well as in-plane direction



- See poster:

Scherzer et al., *Spatially Resolved Analysis of the Characterisitic Time Constant of the Low-frequency Arc in EIS of PEMFC*

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Analytical cathode EIS model developed by Kulikovsky et al. for small current density values

- Negligible steady-state gradients in the CCL
  - <= 100mA/cm²

$$J \ll \min\left\{ j_p = \frac{\bar{\sigma}_p b}{l_t}, \quad j_{ox} = \frac{4FD_{ox}c_1}{l_t} \right\}$$

- Faradaic and proton transport impedance
  - $J_{0,1}$: Bessel function 1th/2nd

$$Z_{ct+p} = \frac{l_t}{\sigma_p}\left(\frac{2}{\beta\zeta}\right)\frac{J_1(\zeta)Y_0(\phi) - J_0(\phi)Y_1(\zeta)}{J_0(\phi)Y_0(\zeta) - J_0(\zeta)Y_0(\phi)}$$

$$\phi = \exp\left(\frac{\beta}{2}\right)\zeta, \quad \zeta = \frac{2}{\beta}\sqrt{-\frac{j_0 l_t}{\sigma_0 b} - \mathrm{i}\frac{\omega C_{dl} l_t^2}{\sigma_0}}$$

- Impedance due to oxygen transport in CCL

$$Z_{ox} = \frac{b\left(1 - \tilde{Z}_W\right)}{j_0\left(\tilde{Z}_W - \frac{\omega^2}{\omega_{ct}^* \omega_0^*} + \mathrm{i}\omega\left(\frac{1}{\omega_{ct}^*} + \frac{1}{\omega_0^*}\right)\right)\left(1 + \frac{\mathrm{i}\omega}{\omega_{ct}^*}\right)}$$

$$\omega_0^* = \frac{j_0}{4Fc_1 l_t}, \quad \omega_{ct}^* = \frac{j_0}{C_{dl} b l_t} \qquad \tilde{Z}_W = \frac{\tanh\left(\sqrt{(j_0 + \mathrm{i}4Fc_1 l_t \omega)/j_{ox}}\right)}{\sqrt{(j_0 + \mathrm{i}4Fc_1 l_t \omega)/j_{ox}}}$$

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Analytical cathode EIS model developed by Kulikovsky et al. for small current density values

- Impedance due to oxygen transport in GDL and channel

$$Z_{gdl+c} = -\frac{l_t/\sigma_0}{\varphi \sin \varphi} \left(\frac{c_1^0 \tilde{\eta}_1^1}{c_1^1 \tilde{j}_0} \varphi^2 - 1 \right)^{-1}$$

Perturbation amplitude of the oxygen concentration at the GDL/CL interface, which is a function of position

- Derivation of the different impedance contribution can be found in

T. Reshetenko and A. Kulikovsky. Impedance spectroscopy study of the PEM fuel cell cathode with nonuniform nafion loading. *J. Electrochem. Soc.*, 164:E1–E6, 2017. doi: 10.1149/2.0041711jes.

A. A. Kulikovsky. A simple physics–based equation for low–current impedance of a PEM fuel cell cathode. *Electrochimica Acta*, 196:231–235, 2016. doi: 10.1016/j.electacta.2016.02.150.

A. Kulikovsky and O. Shamardina. A model for PEM fuel cell impedance: Oxygen flow in the channel triggers spatial and frequency oscillations of the local impedance. *J. Electrochem. Soc.*, 162:F1068–F1077, 2015. doi:10.1149/2.0911509jes.

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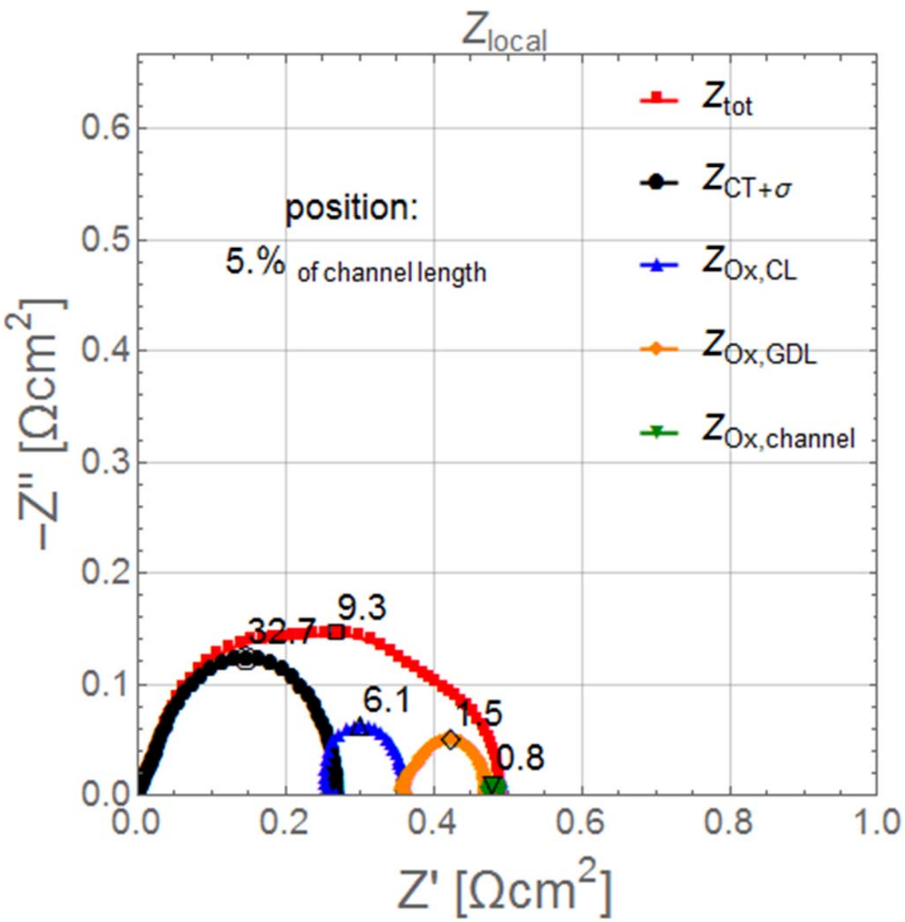
Some examples of the spatially resolved EIS model according to Kulikovsky et al.

- Impact of position
  - Increase of impedance spectra is dominated by channel impedance



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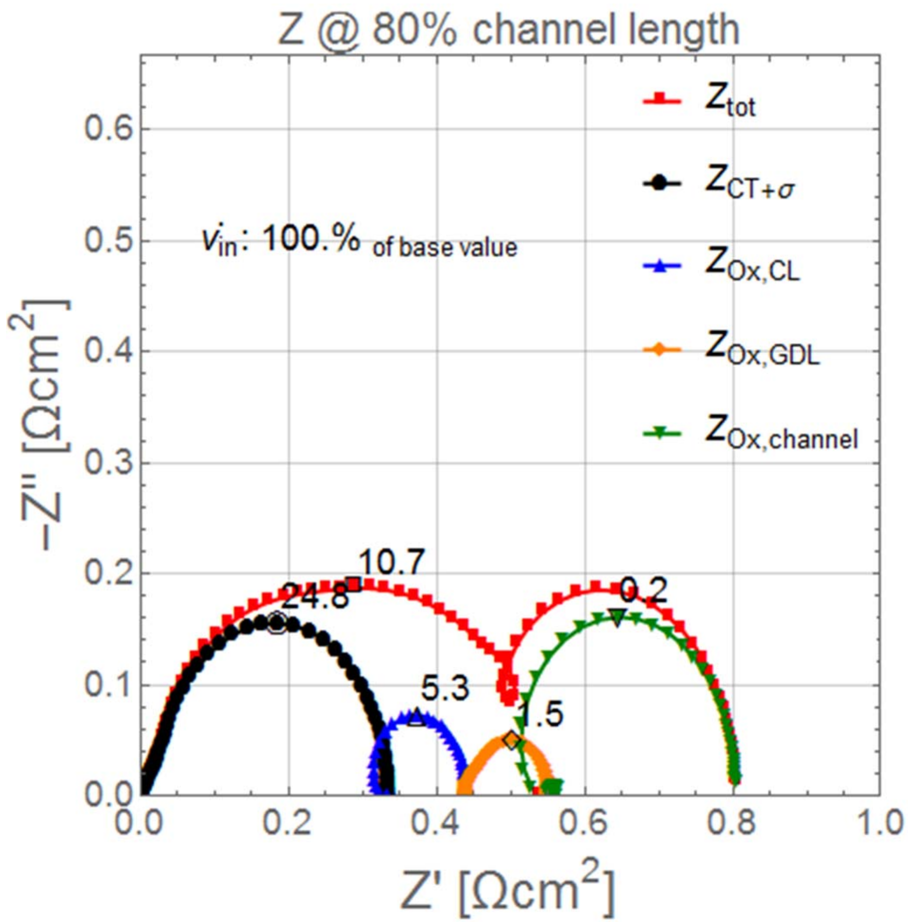
Some examples of the spatially resolved EIS model according to Kulikovsky et al.

- Impact of the flow rate / gas velocity
  - Inlet flow rate dominates the channel impedance
  - Small impact on high frequency arc (similar to experiement)



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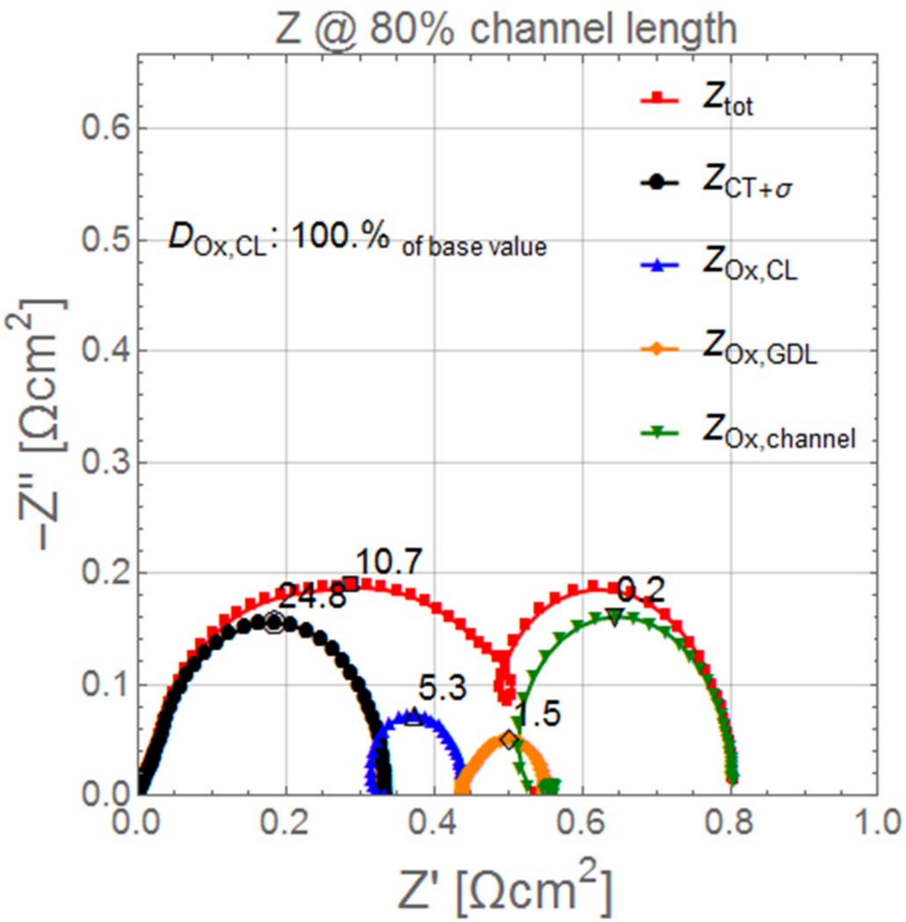
Some examples of the spatially resolved EIS model according to Kulikovsky et al.

- Impact of oxygen diffusivity in CCL
  - only $Z_{ox,CL}$ is changing



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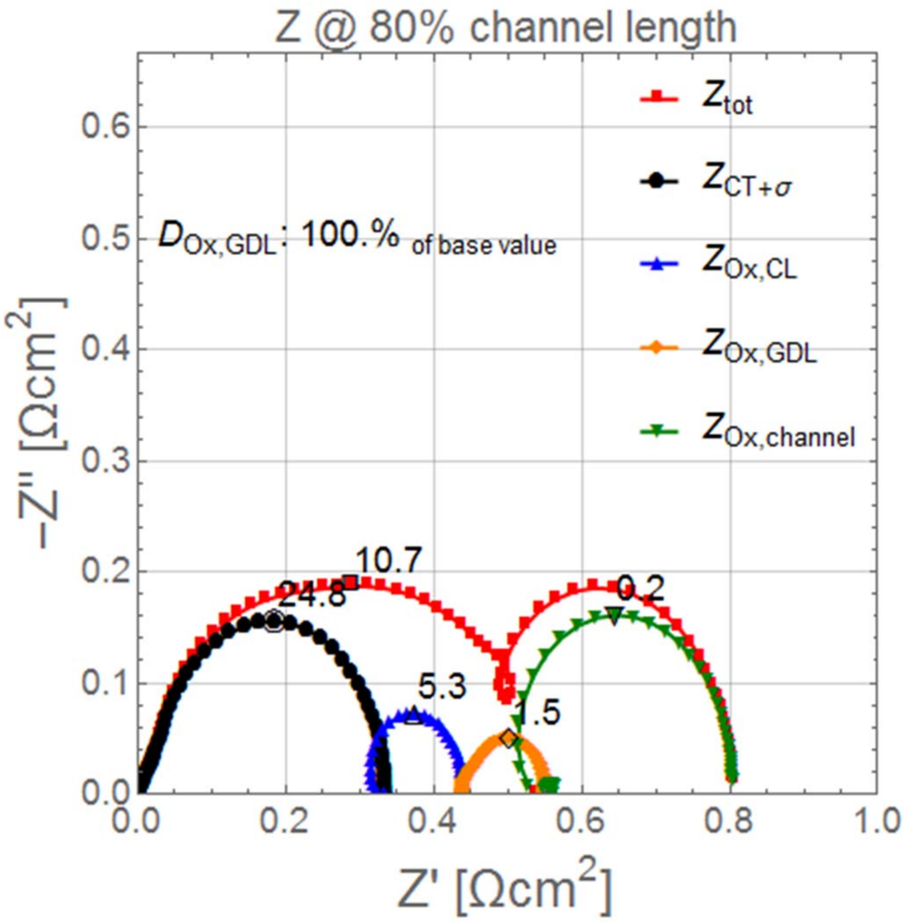
Some examples of the spatially resolved EIS model according to Kulikovsky et al.

- Impact of oxygen diffusivity in GDL
  - all mass transport related impedances are affected



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Conclusion

- Impedance spectroscopy is a powerfull characterization method for analysing fuel cells
- Dependent on the cell hardware and operating conditions, the spectrum shows different features that has to be interpreted carefully
  - Inhomogeneous catalyst layer properties can result in non-expected characteristics
  - In-plane effects have to be considered in non-differential cell measurements
- By means of spatially resolved EIS measurements the mass transport impedances can better get extracted

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Thank You Very Much for Your Attention!

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