Advanced characterization of PEMFCs using a two-phase time-dependent model

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Overview

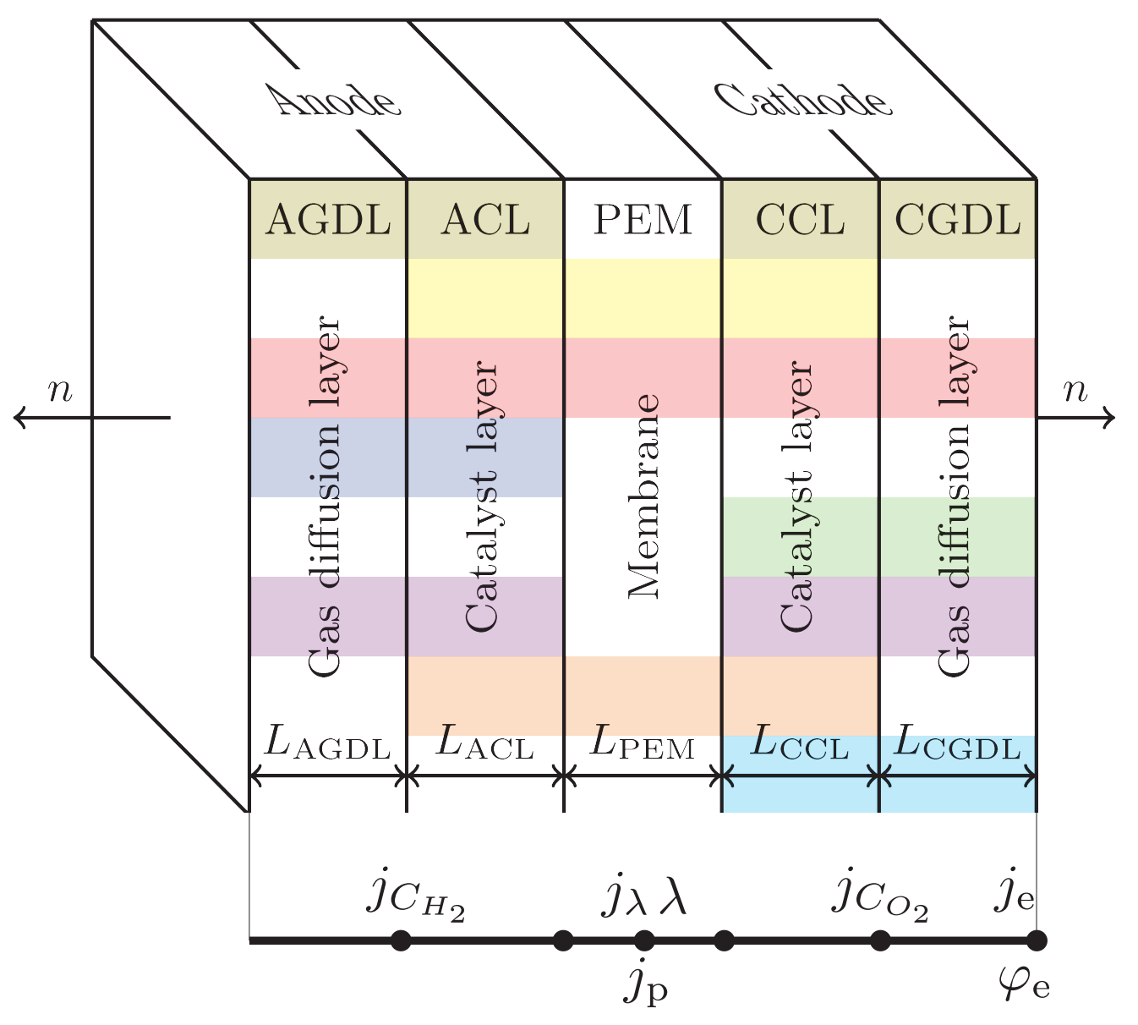
Recently, Vetter and Schumacher [2-3] showed that it is crucial to determine with high precision membrane properties as a function of hydration number. Here we:

- 1. Develop a non-isothermal, two-phase time-dependent PEM fuel cell model
- 2. Conduct classical EIS experiments using small input signals
  - 2.1 Analyze the response of current density
  - 2.2 Analyze the response inside the membrane and extract from it membrane properties, which is illustrated by the electro-osmotic drag coefficient
- 3. Analyze the non-linear, distorted response from larger input signals

1. Time-dependent PEMFC model

We build upon our previously developed steady-state PEFC model [1-2]:

- 1D through-plane, macro-homogeneous, non-isothermal, two phase
- Electrochemistry: Butler-Volmer equation
- Fully parameterized: Maxwell-Stefan diffusion, adsorption/desorption, condensation/evaporation, temperature/hydration dependence of properties, ...
- Coupled solution of 8 transport equations using COMSOL



1D model setup of a PEMFC in through-plane direction. Thickness of the different layers are L_{GDL}= 174.3 µm, L_{CL}=7.3 µm, L_{PEM}=25.4 µm. Boundary temperature is 70 °C and pressure is 1.5 bar. In the CL, ionomer volume fraction is 0.3 and tortuosity is 1.4. Pore tortuosity/Porosity is 2.96/0.7 in GDLs and 1.5/0.18 in CLs. Electron conductivity is 400 S/m. The double layer capacitance is 0.2 F/m².

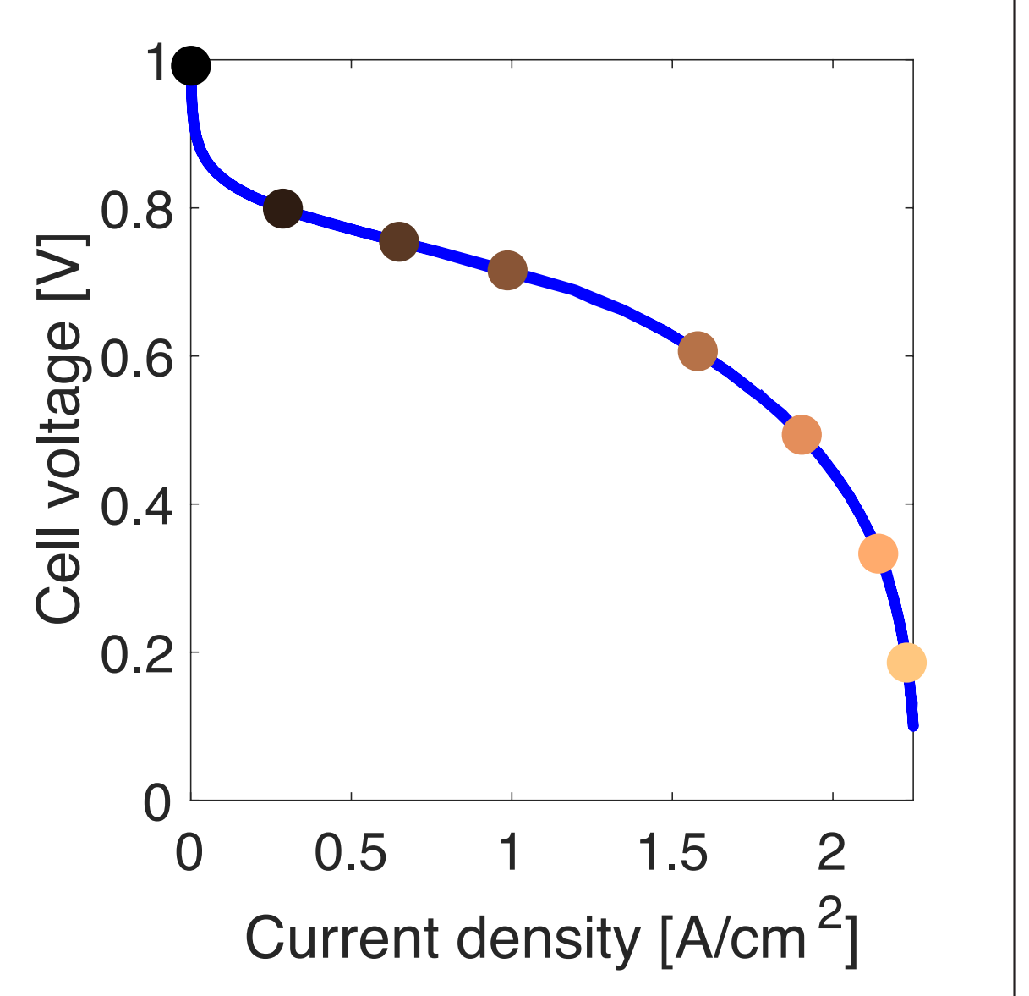
Measurement points

- Implementation of transient terms:

Electron transport	$a_{A,C}C_{DL}\frac{\partial\varphi_e}{\partial t}+\nabla\cdot j_e=S_e,\quad j_e=-\sigma_e\nabla\varphi_e$
Proton transport	$a_{A,C}C_{DL}\frac{\partial\varphi_p}{\partial t}+\nabla\cdot j_p=S_p,\quad j_p=-\sigma_p\nabla\varphi_p$
Heat conduction	$c_p\frac{\partial T}{\partial t}+\nabla\cdot j_T=S_T,\quad j_T=-k\nabla T$
Hydrogen diffusion	$(1-s)\epsilon_p C\frac{\partial y_X}{\partial t}+\nabla\cdot j_X=S_X,\quad \mathrm{X}=\mathrm{H_2},\mathrm{H_2O},\mathrm{O_2}$ $-C\nabla y_X=\sum_{Y\neq X}\frac{y_Y j_X-y_X j_Y}{\mathcal{D}_{X,Y}}$
Oxygen diffusion	
Water vapor diffusion	
Dissolved water	$\frac{\epsilon_i}{V_m}\frac{\partial\lambda}{\partial t}+\nabla\cdot j_\lambda=S_\lambda,\quad j_\lambda=-\frac{D_\lambda}{V_m}\nabla\lambda+\frac{\xi}{F}j_p$
Liquid water transport	$\frac{\epsilon_p}{V_w}\frac{\partial s}{\partial t}+\nabla\cdot j_s=S_s,\quad j_s=-\frac{D_s}{V_w}\nabla s\quad s=0.1$

2.1 Small-signal response: EIS

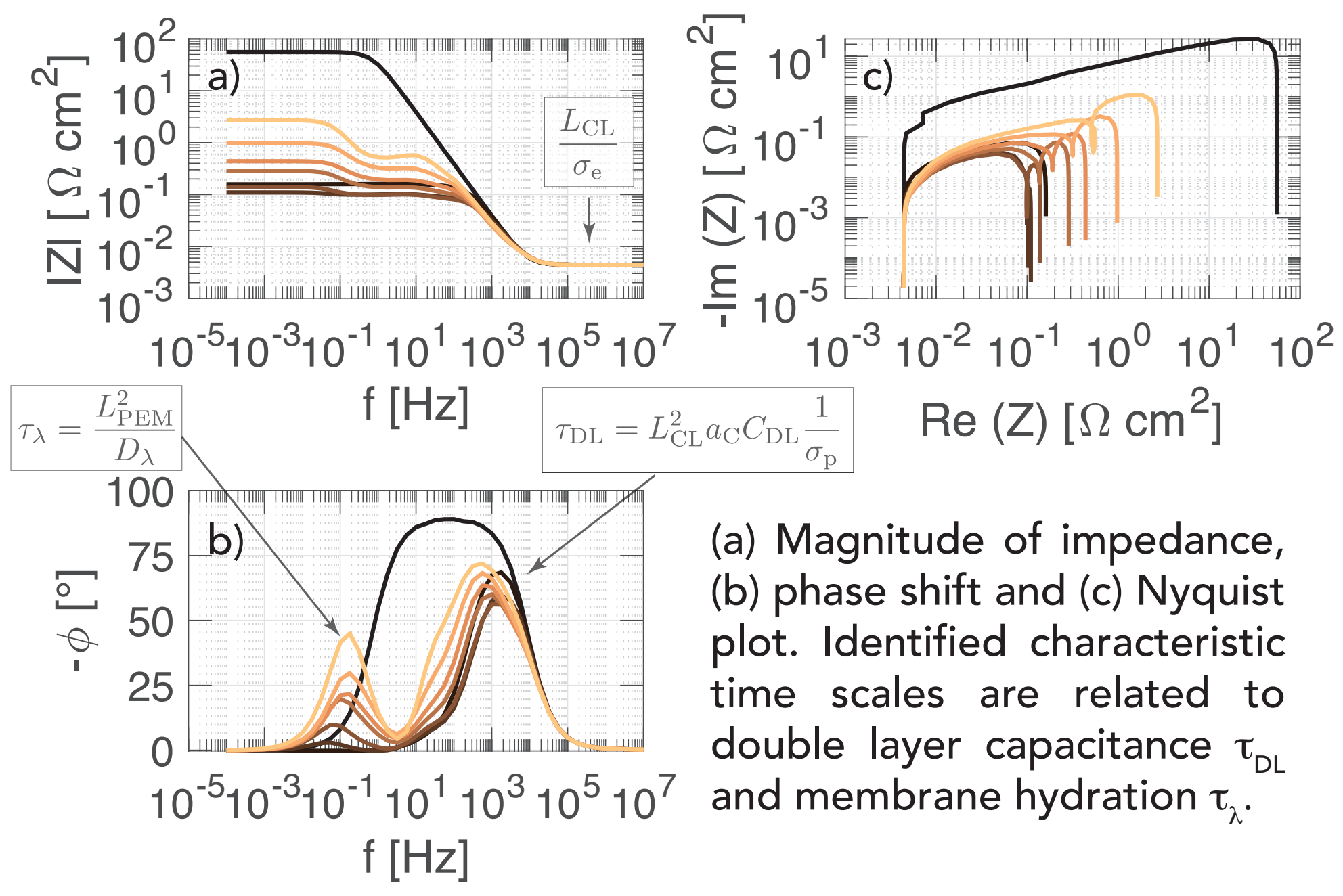
- Steady-state operating points:



Steady-state polarization curve. Colored circles indicate the operation cell voltage V_0 for EIS analysis.

- Classical EIS:

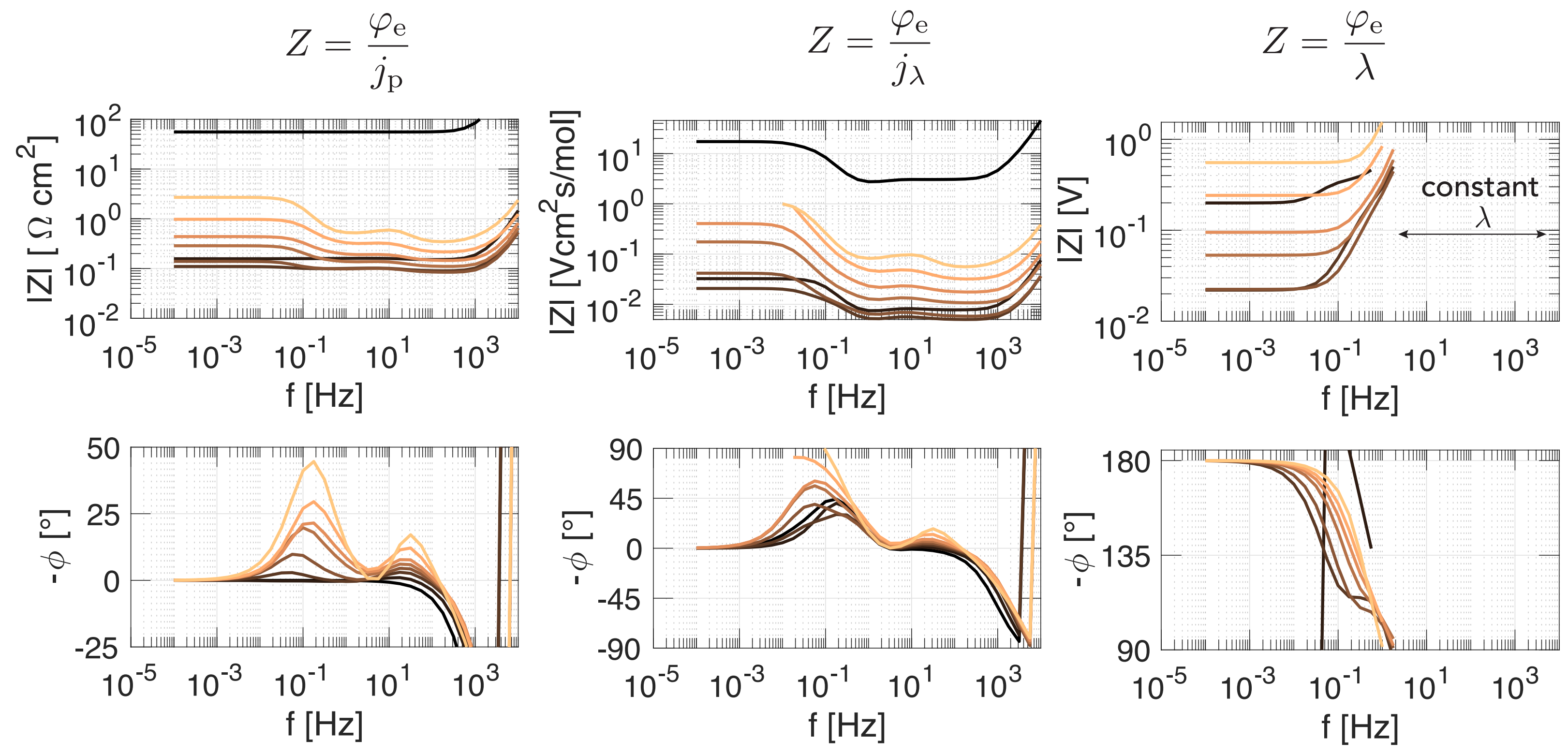
$$V=V_0+\Delta V\sin(2\pi ft),\quad \Delta V=1\mathrm{mV}\qquad Z=\frac{\varphi_e}{j_e}$$



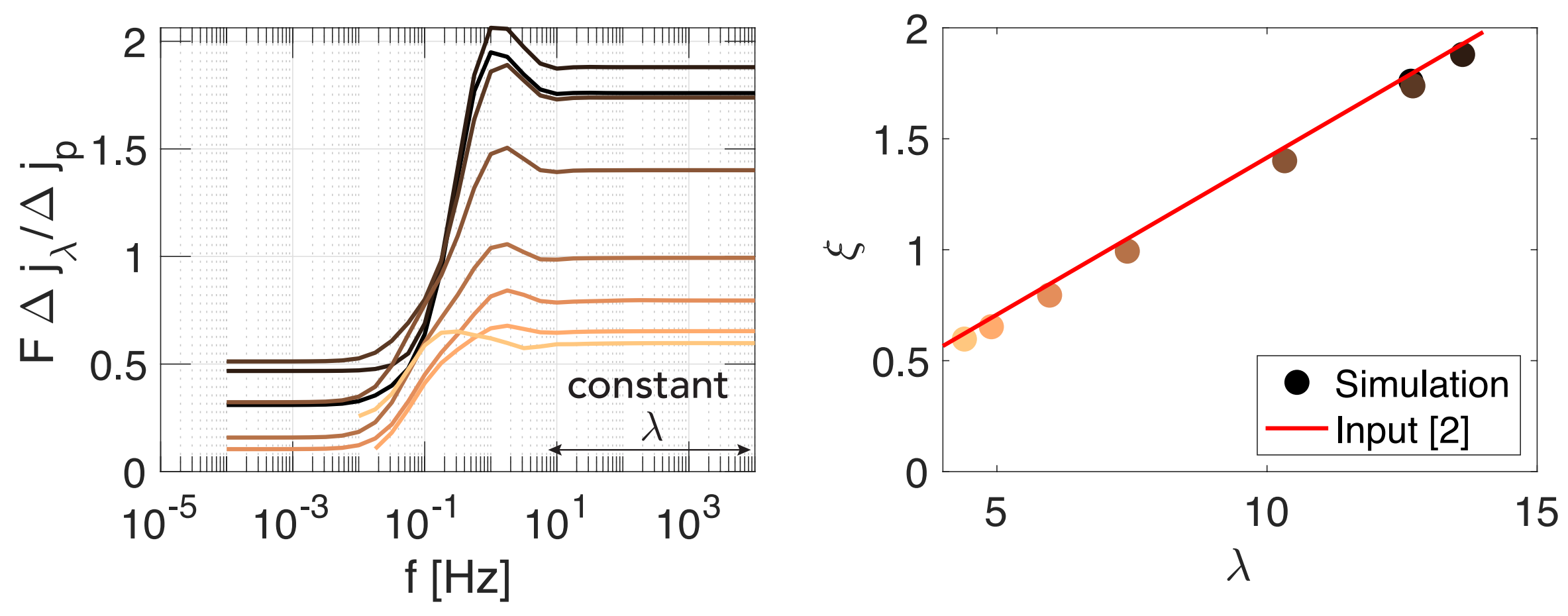
(a) Magnitude of impedance, (b) phase shift and (c) Nyquist plot. Identified characteristic time scales are related to double layer capacitance τ_{DL} and membrane hydration τ_λ.

2.2 Membrane properties

- Response inside the membrane:



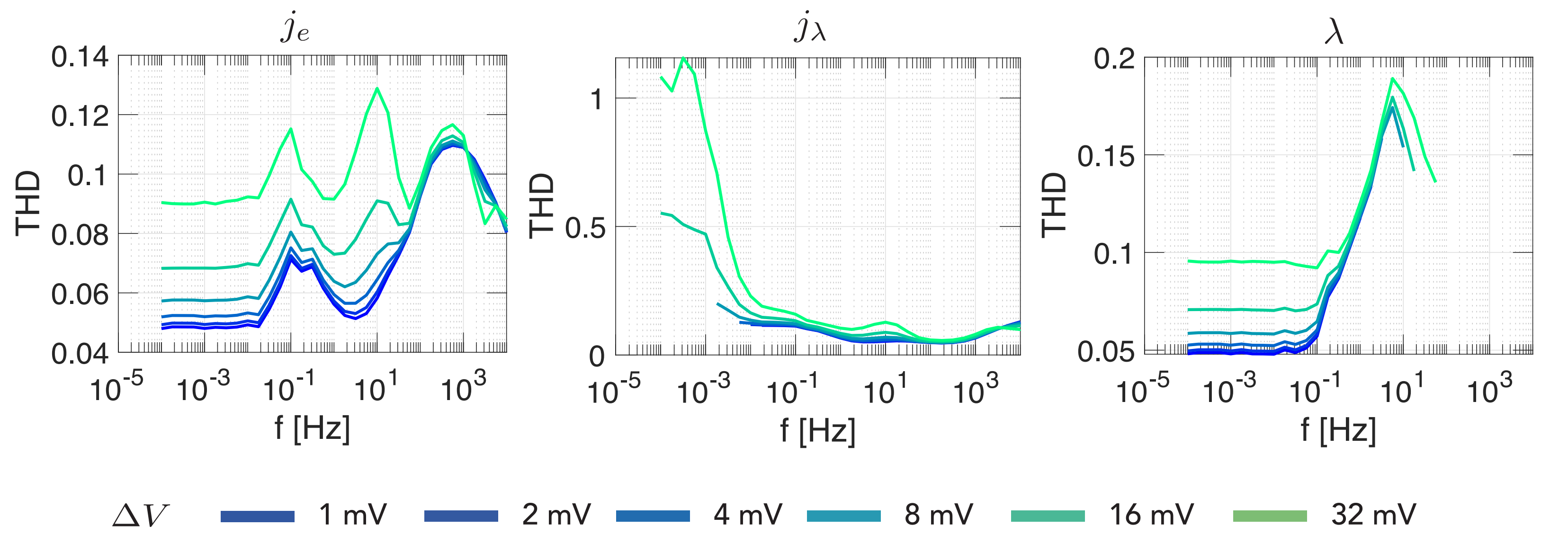
- Extraction of the electro-osmotic drag coefficient ξ:



3. Large-signal response

- Analysis of the response to input amplitudes from 1 mV to 32 mV
- Calculation of the total harmonic distortion (THD) with P_i being the power at the *i*-th harmonic of the input signal:

$$\mathrm{THD}=\sqrt{\frac{\sum_{i=2}^{10}P_i}{P_1}}$$



Conclusions

- Classical EIS detects electrical conductivity, polarization resistance and time scales related to double-layer capacitance and membrane hydration.
- Analyzing further the response inside the membrane allows extraction of the electro-osmotic drag coefficient.

Outlook:

- Rerun models by including liquid water saturation
- Utilize the large-signal response as on-board diagnostics
- Analyse the response from different inputs: temperature, gas pressure, ...

Acknowledgements

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References:

[1] Roman Vetter and Jürgen O. Schumacher, 2019, Free open reference implementation of a two-phase PEM fuel cell model, Comp. Phys. Commun., 234, 223-234, 10.1016/j.cpc.2018.07.023

[2] Roman Vetter and Jürgen O. Schumacher, 2018, Experimental parameter uncertainty in PEM fuel cell modeling. Part I: Scatter in material parameterization, submitted, arXiv:1811.10091

[3] Roman Vetter and Jürgen O. Schumacher, 2018, Experimental parameter uncertainty in PEM fuel cell modeling. Part II: Sensitivity analysis and importance ranking, submitted, arXiv:1811.10093