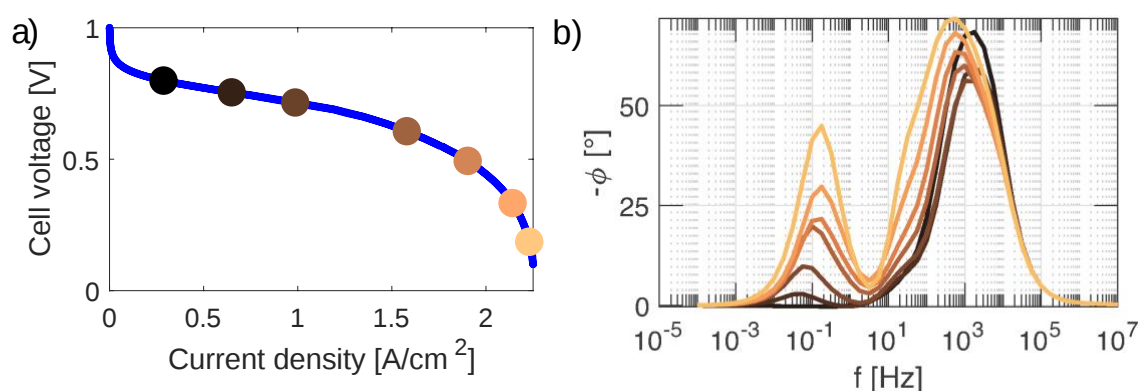




Final report dated 31 August 2019

ACTIF

Advanced Characterisation of Fuel Cell Stacks for Automotive Applications



The figure shows parts of the results of an electrochemical impedance spectroscopy study, conducted at different operation points along a steady-state polarisation curve (a). The peaks of the phase shifts in the frequency spectrum (b) provides information of the characteristic time-scales of the governing process in a fuel cell.

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Date: 31 August 2019

Location: Bern

Subsidiser:

Swiss Federal Office of Energy SFOE
Energy Research and Cleantech Section CH-3003 Bern
CH-3003 Bern
www.bfe.admin.ch

Subsidy recipients:

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SFOE contract number: SI/501764-01

All contents and conclusions are the sole responsibility of the authors



Summary

The project ACTIF was funded by the SFOE between September 2018 and August 2019. During the project duration, we have developed a time-dependent numerical model of a polymer electrolyte fuel cell (PEFC). This model solves for the transport of the gas species, liquid water, charge, heat and the electrochemical reactions. It includes a detailed parameterization of material properties of the gas diffusion layers, the electrodes, the membrane, and the interfaces between these layers.

We demonstrated the capability of this new model to characterize the transient behaviour of PEFCs. In time-dependent jump experiments, we analyzed the characteristic time scale of the physical and electrochemical processes. In cyclic voltammetry experiments, we identified membrane hydration as the main cause of the simulated hysteresis. The model was further applied to study the response to sinusoidal perturbations of the steady state. We conducted a classical electrical impedance study, where we analyzed the small-signal response of electric current density. From this analysis, we inferred the electrical conductivity and time scale of double-layer capacitance and membrane hydration. The extension of the response analysis to protonic and dissolved water flux demonstrates the possibility to extract crucial parameters such as the electro-osmotic drag coefficient as a function of dissolved water content. Furthermore, we analyzed the total harmonic distortion of the large-signal response. This additionally provides the characteristic time scale of gas diffusion.

Besides the development of the time-dependent PEFC model, we improved our physical model with respect to the transport of gas species. We updated our website [isomorph.ch](http://www.isomorph.ch) by making it more attractive to potential academic and industry partners. Simulation results were presented to the Swiss company GreenGT, which served as a basis for a fruitful discussion about future collaborations.

Main findings

- Development of a parameterized, time-dependent polymer electrolyte fuel cell model
- Demonstration of its potential to characterize fuel cells in numerical experiments
- National cooperation with GreenGT
- Demonstration and promotion of computational solutions for fuel cells and flow batteries on www.isomorph.ch



Contents

1	Introduction	6
1.1	Background and current situation	6
1.2	Purpose of project	6
1.3	Objectives	6
2	Procedures and methodology	7
2.1	Model setup	7
2.2	Properties of porous media	8
2.3	Electrochemical reaction	10
2.4	Time-dependent conservation laws	10
2.5	Treatment of phase changes	14
2.6	Definition of source terms	16
2.7	Boundary and initial conditions	18
2.8	Numerical implementation in COMSOL and MATLAB	18
2.9	Model development: gas transport equation	19
3	Results and discussion	22
3.1	Time-dependent jump and cyclic voltammetry experiments	22
3.2	Response to sinusoidal perturbations of the steady state	28
3.3	Improvement of isomorph.ch	32
4	Conclusions	32
5	Outlook and next steps	32
6	National and international cooperation	33
6.1	International cooperation	33
6.2	National cooperation with GreenGT	33
7	Publications and conferences	33
	References	34
A	Appendices	38
A.1	Financial report	38



Abbreviations

ACL	Anode catalyst layer
ACTIF	Advanced characterisation of fuel cell stacks for automotive applications
AGDL	Anode gas diffusion layer
CCL	Cathode catalyst layer
CGDL	Cathode gas diffusion layer
CL	Catalyst layer
EIS	Electrochemical impedance spectroscopy
FCEV	Fuel cell electric vehicle
GDL	Gas diffusion layer
HOR	Hydrogen oxidation reaction
ICP	Institute of Computational Physics
MEA	Membrane-electrode assembly
ORR	Oxygen reduction reaction
PEFC	Polymer electrolyte fuel cell
PEM	Polymer electrolyte membrane
ZHAW	Zurich University of Applied Sciences



1 Introduction

1.1 Background and current situation

In the framework of the Swiss Federal Councils Energy Strategy 2050, the Swiss Federal Assembly passed a total revision of the energy act, demanding drastically reduced CO₂ emissions for private and commercial road vehicles under a very steep gradual increase in monetary sanctions for excess emissions. Our vision is to contribute to reaching this ambitious goal by pushing the advent of fuel cell technology as a competitive and zero-emission electrical power supply. Low-temperature PEFCs have the potential to replace fossil fuels by pure hydrogen, thus leading to a substantial decarbonization of the transport sector. However, the market deployment of fuel cell electric vehicles (FCEVs) requires the improved efficiency, reduced costs and greater durability. This can be achieved only through the implementation of advanced characterization techniques of PEFC. A good understanding of the time-dependent behavior of PEFC is indispensable to improve the performance and durability of fuel cells. The reason is that operating conditions change rapidly during system start-up/shut-down and power demand variations. During these changes, different processes are active leading to the degradation of the fuel cell components. This results in a deterioration of the performance and, hence, in a reduction of the fuel cell life time.

The project ACTIF was planned as a French-German-Swiss initiative for research collaboration on fuel cells and hydrogen for automotive application. The Institute of Computational Physics (ICP, ZHAW) received funding from the SFOE. German partners applied for funding within NIP2 (National Innovation Programme for Fuel Cells and Hydrogen Technology). French partners applied for funding at Direction Générale de l'Énergie et du Climat. Beginning of year we were notified that these applications were not successful. As this was defined as a no-go criteria in the contract with the SFOE, the project was cut short in August 2019. Here we report about the progress in the Swiss part of the project.

1.2 Purpose of project

Regarding the three main challenges of improving efficiency, increasing lifetime and reducing costs on the stack level, the overall goal of the project ACTIF was to develop innovative methods for time-dependent characterization of automotive fuel cell stacks and, thereby, to optimize operation strategies.

The Swiss part of the project is based on the development of a steady-state computational PEFC model in our group at the ICP of ZHAW. This development lead to an advanced parameterization of the most important physical and electrochemical processes that control the water and thermal management, and hence, the performance of PEFC. Uncertainties in the experimentally determined materials parameterization was shown to seriously affect the prediction of the fuel cell performance (Vetter & Schumacher 2018, 2019). While this model development was essential to create a reliable baseline parameterization for PEFC simulation, it lacks the capability to study time-dependent processes.

1.3 Objectives

The main objective is to develop a time-dependent PEFC model, which can be used for the advanced characterization of PEFCs. Its capability to identify characteristic time scale is demonstrated in simulated voltammetry and time-dependent jump experiments as well as in classical electrochemical



impedance spectroscopy (EIS). The classical EIS technique is extended to include the analysis of additional parameters, which allows to characterize membrane properties. Further insights into the fuel cell is sought by conducting a large-signal response analysis.

Besides these scientific objectives, our goal is to improve the website isomorph.ch on which we offer our computational solutions to potential academic and industrial partners.

2 Procedures and methodology

2.1 Model setup

We extend our previously developed one-dimensional, macro-homogeneous, steady-state two-phase model of a membrane-electrode assembly (MEA) in through-plane direction (Vetter & Schumacher 2018, 2019). This model consists of five layers (Fig. 1). A polymer electrolyte membrane (PEM) is situated in the middle, which consists of the proton-conducting ionomer Nafion. The anode and cathode catalyst layers (ACL and CCL), which sandwich this membrane, contain an electron-conducting carbon matrix and an ionomer phase. The outer gas diffusion layers (AGDL and CGDL) are made of hydrophobized carbon paper. Note that anode and cathode micro-porous layer could be added to this setup.

We model the coupled charge, heat and mass transport processes by solving for the conservation of electrons (electron potential ϕ_e), protons (proton potential ϕ_p), heat (temperature T), dissolved water (λ , defined as the number of water molecules per acid group), liquid water (pore saturation s), water vapor (y_{H_2O}), hydrogen (y_{H_2}) and oxygen (y_{O_2}) in the respective model domains as shown in Fig. 1.

We follow most of the baseline parameterization of Vetter & Schumacher (2018) with some simplifications. General model parameters are given in Table 2.

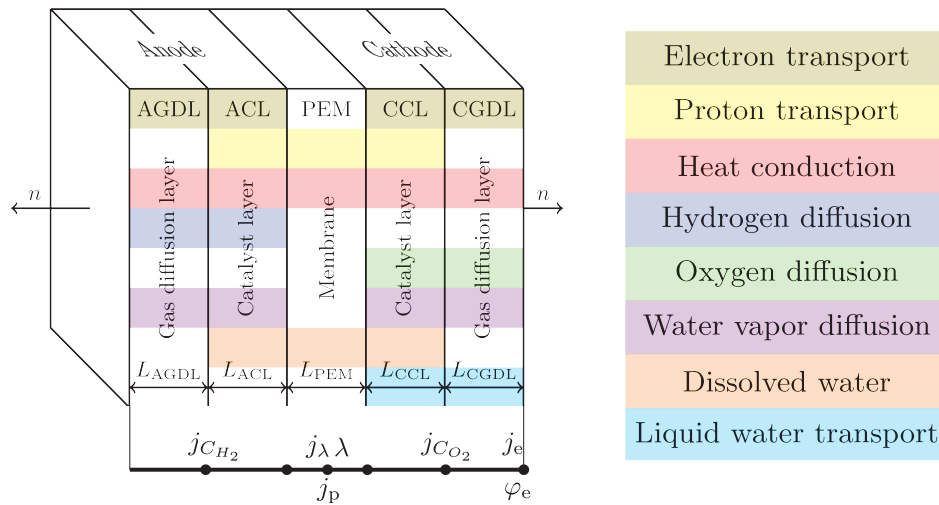


Figure 1: 1D model setup of a PEFC in through-plane direction.



Table 1: Domain dependent material and through-plane transport parameters.

Symbol	Explanation	Unit	AGDL & CGDL	ACL & CCL	PEM
L_0	Uncompress. layer thickness	μm	190 [1]	10	25.4 [2]
ε_c	Compressive strain		0.0828 [11]	0.2715 [11]	0
L	Compressed layer thickness	μm	174.27 [11]	7.29 [11]	25.4
ϵ_i	Ionomer volume fraction	–		0.3	1
τ_i	Ionomer tortuosity	–		1.4 [13]	1
τ_p	Pore tortuosity	–	2.96 [11]	1.5	
$\epsilon_{p,0}$	Uncompress. porosity	–	0.75 [12]	0.4 [3]	
ϵ_p	Compress. porosity	–	0.70 [11]	0.18 [11]	
σ_e	Electron conductivity	S/m	450 [9]	390 [10]	

[1] SGL 24 BA SGL (2009), [2] Nafion NR211 Nafion (2016), [3] Bernardi & Verbrugge (1992), [4] Khandelwal & Mench (2006), [5] Litster et al. (2013), [6] Babu et al. (2016), [7] (El-kharouf et al. 2012), [8] Yi & Van Nguyen (1999), [9] SGL 28 AA compressed by 1 MPa (Schweiss et al. 2016), [10] catalyst layer with $\epsilon_i = 0.3$ (Gode et al. 2003), [11] evaluated at $P_{cl} = 1$ MPa, [12] Kumbur et al. (2007), [13] Babu et al. (2016)

To account for the effects of clamping pressure on the computational domain, the GDL and CL thicknesses are modeled as a function of pressure. Given the compressive strain ε_c , one can write

$$L = L_0(1 - \varepsilon_c), \quad (1)$$

where L_0 denotes the thickness of the uncompressed layer (Table 1). The relationship between strain and applied clamping pressure P_{cl} for GDLs is (Kumbur et al. 2007)

$$\varepsilon_c^{\text{GDL}} = -0.0083 \left(\frac{P_{cl}}{1 \text{ MPa}} \right)^2 + 0.0911 \left(\frac{P_{cl}}{1 \text{ MPa}} \right). \quad (2)$$

Vetter & Schumacher (2018) fitted the following two-parameter function to the compressive strain of the CL reported by Burheim et al. (2014):

$$\varepsilon_c^{\text{CL}} = 0.422 \left(1 - \exp \left[-\frac{P_{cl}}{0.970 \text{ MPa}} \right] \right). \quad (3)$$

The membrane thickness is held constant, assuming for simplicity that swelling and compression cancel one another.

2.2 Properties of porous media

The anode and cathode layers are modeled as porous media, which is characterized by the average specific pore surface area density a_p^{GDL} , porosity ϵ_p and tortuosity τ_p .

2.2.1 Average specific pore surface area density

Vetter & Schumacher (2018) fitted a quadratic polynomial to the data of Kumbur et al. (2007) to obtain the average specific pore surface area density

$$\frac{a_p^{\text{GDL}}}{1 \text{ m}^2/\text{cm}^3} = -1.96 \left(\frac{P_{cl}}{1 \text{ MPa}} \right)^2 + 8.18 \left(\frac{P_{cl}}{1 \text{ MPa}} \right) + 23.4. \quad (4)$$



Table 2: Domains independent material and through-plane transport parameters.

Symbol	Explanation	Value
T_B	Boundary temperature	70 K
P_B	Boundary pressure	1.5 bar
RH	Relative humidity	1
P_{cl}	Clamping pressure	1 MPa
M_w	Molar mass of water	18.015 g/mol
ρ_c	Critical density	332 kg/m ³
T_c	Critical temperature	647.96 K
P_c	Critical pressure	22.064 MPa
σ_e	Electron conductivity	400 S/m
C_{DL}	Double layer capacitance	0.2 F/m ²
k	Thermal conductivity	0.6 W/(m K)
c_p	Heat capacity	$4 \cdot 10^6$ J/(m ³ K)

Vetter & Schumacher (2018) set $a_p^{CL} = a_p^{GDL}$. For the membrane, $a_p^{PEM} = 210 \text{ m}^2/\text{cm}^3$ (Divisek et al. 1998).

2.2.2 Porosity

For the porosity of the GDLs, Kumbur et al. (2007) proposed the relationship

$$\epsilon_p^{GDL} = \epsilon_{p,0}^{GDL} \left(\frac{0.9}{1 + \epsilon_c^{GDL}} + 0.1 \right) \quad (5)$$

where $\epsilon_{p,0}^{GDL}$ is the porosity of the uncompressed GDL (Table 1). (Vetter & Schumacher 2018) assumed that only the pore space of the CLs is compressed, which yields

$$\epsilon_p^{CL} = \frac{\epsilon_{p,0}^{CL} - \epsilon_c^{CL}}{1 - \epsilon_c^{CL}} \quad (6)$$

where $\epsilon_{p,0}^{CL}$ is the porosity of the uncompressed CL (Table 1).

2.2.3 Tortuosity

The relationship between through-plane pore tortuosity and applied clamping pressure, Vetter & Schumacher (2018) used a parabolic least-squares fit to experimental data for SGL 24 DA by Flückiger et al. (2008), reading

$$\tau_p^{GDL} = -17.3 (\epsilon_p^{GDL})^2 + 18.8 \epsilon_p^{GDL} - 1.72, \quad (7)$$

whereas the tortuosity of the CLs is assumed constant as $\tau_p^{CL} = 1.5$ (Babu et al. 2016, Litster et al. 2013) due to the apparent absence of published measurement data on its compression dependence. The ionomer tortuosity is given in Table 1.



2.3 Electrochemical reaction

In the CLs, the two phase potentials φ_e and φ_p coexist and define the total Galvani potential difference $\Delta\varphi = \varphi_e - \varphi_p$. Using the reversible half-cell potentials

$$\begin{aligned}\Delta\varphi_A^0 &= -\frac{T\Delta S_A^{\text{ref}}}{2F} - \frac{RT}{2F} \ln \left[\frac{p_{\text{H}_2}}{P_{\text{ref}}} \right] \\ \Delta\varphi_C^0 &= -\frac{\Delta H^{\text{ref}} - T\Delta S_C^{\text{ref}}}{2F} + \frac{RT}{4F} \ln \left[\frac{p_{\text{O}_2}}{P_{\text{ref}}} \right]\end{aligned}\quad (8)$$

the anode and cathode activation overpotentials are defined as

$$\eta_A = \Delta\varphi - \Delta\varphi_A^0 \quad \text{and} \quad \eta_C = \Delta\varphi_C^0 - \Delta\varphi. \quad (9)$$

ΔH^{ref} is the standard enthalpy of formation of liquid water, ΔS_A^{ref} and ΔS_C^{ref} the half-reaction entropies, F Faraday's constant, R the gas constant, P_{ref} the reference pressure, $p_{\text{H}_2} = y_{\text{H}_2}P$ the partial pressure of hydrogen, and $p_{\text{O}_2} = y_{\text{O}_2}P$ that of oxygen. We describe the reaction kinetics with the Butler–Volmer equation, which leads to the definition of the electron and proton production rates

$$\begin{aligned}S_A &= j_A^0 a_A (1-s) \left(\exp \left[\frac{\alpha_A F \eta_A}{RT} \right] - \exp \left[-\frac{\tilde{\alpha}_A F \eta_A}{RT} \right] \right), \\ S_C &= j_C^0 a_C (1-s) \left(\exp \left[\frac{\alpha_C F \eta_C}{RT} \right] - \exp \left[-\frac{\tilde{\alpha}_C F \eta_C}{RT} \right] \right),\end{aligned}\quad (10)$$

where $j_{A,C}^0$ is the exchange current density, $a_{A,C}$ is the reactive (electrochemical) surface area density and $(1-s)$ is a correction factor for site blockage by liquid water. $\alpha_{A,C}$ ($\tilde{\alpha}_{A,C}$) are the forward (backward) half-reaction transfer coefficients. The exchange current density can be written as (Neyerlin et al. 2006, 2007)

$$\begin{aligned}j_A^0 &= j_{A,\text{ref}}^0 \left(\frac{p_{\text{H}_2}}{P_{\text{ref}}} \right)^{\delta_A} \exp \left[\frac{E_A}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right], \\ j_C^0 &= j_{C,\text{ref}}^0 \left(\frac{p_{\text{O}_2}}{P_{\text{ref}}} \right)^{\delta_C} \exp \left[\frac{E_C}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right],\end{aligned}\quad (11)$$

where $j_{A,C,\text{ref}}^0$ are the exchange current densities at reference conditions ($P_{\text{ref}} = 1 \text{ atm}$ and $T_{\text{ref}} = 353.15 \text{ K}$), $\delta_{A,C}$ the kinetic reaction orders and $E_{A,C}$ the half-reaction activation energies.

The electrochemical parameters of the model are summarized in Table 3.

2.4 Time-dependent conservation laws

In general, we assume that diffusion is the governing mass transport mechanism. Convection is neglected and isobaric conditions are assumed (i.e., $\nabla P = 0$).



Table 3: Electrochemical model parameters.

Symbol	Explanation	Value	Source
a_A	Reactive surface area of ACL	$14 \text{ m}_{\text{Pt}}^2/\text{cm}^3$	Flückiger (2009)
a_C	Reactive surface area of CCL	$28 \text{ m}_{\text{Pt}}^2/\text{cm}^3$	Flückiger (2009)
E_A	Activation energy of ACL	16 kJ/mol	Neyerlin et al. (2007)
E_C	Activation energy of CCL	67 kJ/mol	Neyerlin et al. (2006)
$j_{A,0,\text{ref}}$	Ref. exchange current density of ACL	$0.54 \text{ A/cm}_{\text{Pt}}^2$	Neyerlin et al. (2007)
$j_{C,0,\text{ref}}$	Ref. exchange current density of CCL	$2.47 \times 10^{-8} \text{ A/cm}_{\text{Pt}}^2$	Neyerlin et al. (2006)
$\alpha_A, \tilde{\alpha}_A$	Transfer coefficients of ACL	0.5	Neyerlin et al. (2007)
$\alpha_C, \tilde{\alpha}_C$	Transfer coefficients of CCL	1	Neyerlin et al. (2006)
δ_A	Kinetic reaction order of HOR	0	Neyerlin et al. (2007)
δ_C	Kinetic reaction order of ORR	0.54	Neyerlin et al. (2006)
ΔH^{ref}	Reference molar enthalphy	-285.83 kJ/mol	Chase (1998)
ΔS_A^{ref}	Molar reaction entropy of ACL	0.104 J/mol K	Lampinen & Fomino (1993)
ΔS_C^{ref}	Molar reaction entropy of CCL	-163.3 J/mol K	Lampinen & Fomino (1993)

2.4.1 Electron and proton transport

Conservation of electrons and protons is described as (Ong & Newman 1999)

$$\begin{aligned}
 a_{A,C} C_{\text{DL}} \frac{\partial \varphi_e}{\partial t} + \nabla \cdot j_e &= S_e, \quad j_e = -\sigma_e \nabla \varphi_e \\
 a_{A,C} C_{\text{DL}} \frac{\partial \varphi_p}{\partial t} + \nabla \cdot j_p &= S_p, \quad j_p = -\sigma_p \nabla \varphi_p
 \end{aligned} \tag{12}$$

with t is time, j_e , σ_e (Table 2) and S_e are the current density, conductivity and source of electrons. Similarly, j_p , σ_p and S_p are the current density, conductivity and source of protons, respectively. The accumulation term includes the double-layer capacitance C_{DL} (Table 2).

To describe the proton conductivity, we use the percolation model by Weber & Newman (2003) as

$$\sigma_p = M_i \sigma_0(T) \max \{f_w - f_0, 0\}^\beta \tag{13}$$

with $f_0 = 0.06$ is the percolation threshold, $\beta = 1.5$, $\sigma_0 = 50 \text{ S/m} \times \exp[E_\sigma / R(1/303.15 \text{ K} - 1/T)]$ and $E_\sigma = 15 \text{ kJ/mol}$. The water volume fraction in the hydrated ionomer is given by

$$f_w = \frac{\lambda V_w}{\lambda V_w + V_m}, \tag{14}$$

where $V_m = \frac{\text{MW}}{\rho_m}$ is the acid equivalent volume of the ionomer (ρ_m is the density, MW is the equivalent mass of the ionomer). $V_w = \frac{m_w}{\rho_w}$ is the molar volume of liquid water, where m_w is the molar mass of water. The water density ρ_w is given at standard atmospheric pressure by (Wagner & Pruss 1993)

$$\rho_w = \rho_c \left(1 + 1.9927\hat{T}^{1/3} + 1.0997\hat{T}^{2/3} - 0.51084\hat{T}^{5/3} - 1.7549\hat{T}^{16/3} - 45.517\hat{T}^{43/3} - 674694\hat{T}^{110/3} \right) \tag{15}$$

with $\hat{T} = 1 - T/T_c$ and ρ_c given in Table 2.

The microstructure factor of the ionomer M_i is given by Holzer et al. (2017) as

$$M_i = \epsilon_i / \tau_i^2, \tag{16}$$



where ϵ_i is the ionomer volume fraction (Table 1).

2.4.2 Heat transport

The heat transport equation is defined as

$$c_p \frac{\partial T}{\partial t} + \nabla \cdot j_T = S_T, \quad j_T = -k \nabla T, \quad (17)$$

where c_p is the isobaric heat capacity, S_T is the heat source and j_T is the heat flux governed by heat conduction with the thermal diffusivity k (Table 2).

2.4.3 Dissolved water transport

Following Gerteisen et al. (2009), the time-dependent evolution of λ is governed by

$$\frac{\epsilon_i}{V_m} \frac{\partial \lambda}{\partial t} + \nabla \cdot j_\lambda = S_\lambda, \quad j_\lambda = -\frac{D_\lambda}{V_m} \nabla \lambda + \frac{\xi}{F} j_p, \quad (18)$$

where S_λ is the source term. The first term of the dissolved water flux j_λ describes back diffusion due to a moisture gradient with D_λ being the effective water diffusivity. The second term represents the electro osmotic drag of traveling protons through the membrane with ξ being the electro-osmotic drag coefficient. Thermo-osmosis is neglected here for simplicity in contrast to Vetter & Schumacher (2018). The water diffusivity in the ionomer is taken from Vetter & Schumacher (2019) who fitted the experimental data from Mittelsteadt & Staser (2011) with

$$D_\lambda = 10^{-6} \text{cm}^2/\text{s} \times M_i \frac{3.842\lambda^3 - 32.03\lambda^2 + 67.74\lambda}{\lambda^3 - 2.115\lambda^2 - 33.013\lambda + 103.3} \exp \left[\frac{E_d}{R} \left(\frac{1}{353.15 \text{ K}} - \frac{1}{T} \right) \right] \quad (19)$$

with the activation energy (Vetter & Schumacher 2018)

$$E_d = (38.0f_w^2 - 47.9f_w + 29.2) \frac{\text{kJ}}{\text{mol}}. \quad (20)$$

The electro-osmotic drag coefficient follows the the linear approximation of Springer et al. (1991):

$$\xi = \xi_l \frac{\lambda}{\lambda_l}. \quad (21)$$

Weber & Newman (2004) suggested to use the Arrhenius equation

$$\xi_l = 2.55 \exp \left[\frac{E_\xi}{R} \left(\frac{1}{303.15 \text{ K}} - \frac{1}{T} \right) \right] \quad (22)$$

with an activation energy of $E_\xi = 4 \text{ kJ/mol}$ to model the temperature dependence of ξ_l .

2.4.4 Liquid water transport

Liquid water is assumed only to be present on the cathode side of the PEFC. The conservation of liquid water modeled with Darcy's law, i.e.,

$$\frac{\epsilon_p}{V_w} \frac{\partial s}{\partial t} + \nabla \cdot j_s = S_s, \quad j_s = -\frac{D_s}{V_w} \nabla s \quad (23)$$



The diffusion coefficient D_s is defined as

$$D_s = \frac{K_{\text{abs}} K_{\text{rel}}}{\mu} \frac{\partial p_c}{\partial s}. \quad (24)$$

For μ , the dynamic viscosity of liquid water, we use the internationally recommended correlation at 1 bar up to 110 °C (Huber et al. 2009):

$$\mu = \left(280.68 \bar{T}^{-1.9} + 511.45 \bar{T}^{-7.7} + 61.131 \bar{T}^{-19.6} + 0.45903 \bar{T}^{-40} \right) \mu\text{Pa s} \quad (25)$$

with $\bar{T} = T/300$ K. For $\partial p_c / \partial s$, the layer's differential relationship between capillary pressure and saturation, we use the van Genuchten law, which Gostick et al. (2009) have found to apply to many common GDLs as

$$\frac{\partial p_c}{\partial s} = \frac{p_b}{lm} \left(s_w^{-1/m} - 1 \right)^{1/l-1} s_w^{-1/m-1}, \quad s_w = \frac{1-s}{1-s_{\text{im}}} \quad (26)$$

with the following parameters for the secondary water injection curve of compressed SGL carbon paper: $m = 0.6$, $l = 100$, a breakthrough pressure of $p_b = 1.07$ bar, and an immobile saturation of $s_{\text{im}} = 0.08$ (Gostick et al. 2009).

Mualem's model is used for the saturation-dependent relative hydraulic permeability K_{rel} (Zamel et al. 2011), reading

$$K_{\text{rel}} = (1 - s_w)^2 \left(1 - s_w^{1/m} \right)^{2m} + 10^{-6}, \quad (27)$$

where the small offset serves to bypass numerical difficulties under dry conditions, i.e., to avoid that $K_{\text{rel}} \rightarrow 0$ as $s \rightarrow s_{\text{im}}$.

K_{abs} is the porous medium's intrinsic (absolute) hydraulic permeability. We use the semi-heuristic Carman–Kozeny equation for fibrous porous media, as it proved to work well for carbon paper (Gostick et al. 2006):

$$K_{\text{abs}}^{\text{GDL}} = \frac{\epsilon_p^3 d_f^2}{16 k_K (1 - \epsilon_p)^2} \quad (28)$$

where $d_f = 8.0 \mu\text{m}$ and $k_K = 4.54$ are the fiber diameter and the Kozeny constant for a SGL 24 BA (Gostick et al. 2006). A constant value of $K_{\text{abs}}^{\text{CL}} = 0.1 \mu\text{m}^2$ (Yi & Van Nguyen 1999) is assumed for the CLs.

2.4.5 Gas transport

The ideal gas law is assumed to hold, such that the partial pressures are given by $p_X = y_X C R T$, $X = \text{H}_2, \text{O}_2, \text{H}_2\text{O}, \text{N}_2$, where y_X are the mole fractions of the gas species and C is the total interstitial gas concentration. Following Vetter & Schumacher (2018), the transport of gas species is given by an in-series combination of the transport resistances of the Maxwell–Stefan model and Knudsen diffusion:

$$(1-s)\epsilon_p C \frac{\partial y_X}{\partial t} + \nabla \cdot j_X = S_X, \quad (29)$$

$$-C \nabla y_X = \sum_{Y \neq X} \frac{y_Y j_X - y_X j_Y}{\mathcal{D}_{X,Y}} + \frac{j_X}{D_{K,X}}, \quad (30)$$

where $\mathcal{D}_{X,Y}$ denote the effective binary diffusivities and $D_{K,X}$ the effective Knudsen diffusivities in the porous layers. The inert nitrogen is not explicitly modeled on the cathode side because it follows from the requirement that $\sum_X y_X = 1$.



An accurate way to estimate the effective binary diffusion coefficients $\mathcal{D}_{X,Y}$ is given by Chapman–Enskog kinetic gas theory (Bird et al. 2002, Green & Perry 2008). Assuming the ideal gas law, they can be calculated as

$$\mathcal{D}_{X,Y} = M_p \frac{3}{8} \sqrt{\frac{RT}{2\pi} \left(\frac{1}{m_X} + \frac{1}{m_Y} \right)} \frac{k_B T}{P \sigma_{X,Y}^2 \Omega_{X,Y}} \quad (31)$$

where k_B is the Boltzmann constant, m_X denotes the molar mass of substance X , and

$$M_p = \frac{\epsilon_p}{\tau_p^2} (1 - s)^\phi \quad (32)$$

is the microstructure factor of the pores, with compression-dependent porosity ϵ_p and pore tortuosity τ_p . For the saturation exponent ϕ , we use $\phi^{\text{GDL}} = 3$ (Hwang & Weber 2012) and $\phi^{\text{CL}} = 1.5$ (Fathi et al. 2017). A curve fit of the collision integral $\Omega_{X,Y}$ is given by Neufeld et al. (1972)

$$\Omega_{X,Y} = \frac{1.06036}{(T^*)^{0.15610}} + \frac{0.19300}{\exp[0.47635T^*]} + \frac{1.03587}{\exp[1.52996T^*]} + \frac{1.76474}{\exp[3.89411T^*]} \quad (33)$$

where $T^* = k_B T / \epsilon_{X,Y}$. For non-polar gases, the combining rules $\sigma_{X,Y} = (\sigma_X + \sigma_Y)/2$ and $\epsilon_{X,Y} = \sqrt{\epsilon_X \epsilon_Y}$ can be used, where σ_X and ϵ_X are the Lennard–Jones collision diameters and potential depths, respectively, which are tabulated in the literature (Berendsen et al. 1981, Bird et al. 2002, Hirschfelder et al. 1967). For inter-diffusion of a polar and a non-polar gas, modified theories with increased complexity exist, such as the one by Brokaw (1969). For simplicity it is assumed here that Chapman–Enskog theory also applies with sufficient accuracy for humid gases, i.e., that the dipole moment of water molecules can be neglected.

Assuming cylindrical pores with effective average pore radius r_p , the Knudsen diffusivities $D_{K,X}$ are given by Knudsen (1909)

$$D_{K,X} = \frac{8r_p}{3} \sqrt{\frac{RT}{2\pi m_X}}. \quad (34)$$

To account for pore narrowing by liquid water, we adopt the quadratic law $r_p = r_{p,\text{dry}} s_w^2$, which fits the data by Hutzenlaub et al. (2013) well, where s_w is the reduced wetting phase saturation as defined in Eq. 26. The following dry radii are used: $r_{p,\text{dry}}^{\text{GDL}} = 15 \mu\text{m}$ for a SGL 24 BC Wood et al. (2006) and $r_{p,\text{dry}}^{\text{CL}} = 20 \text{ nm}$ for a Nafion/carbon black CL (Ono et al. 2013).

2.5 Treatment of phase changes

2.5.1 Adsorption of water vapor and desorption of dissolved water

Within the CLs, water is absorbed by the ionomer phase and desorbed again back to vapor in a relatively sluggish process. In order to account for this interfacial mass transfer resistance across the entire CL thickness, the sorption source terms are modeled as

$$S_{\text{ad}} = \begin{cases} \gamma_a(\lambda_{\text{eq}} - \lambda)/V_m & \text{if } \lambda < \lambda_{\text{eq}} \text{ (absorption)} \\ \gamma_d(\lambda_{\text{eq}} - \lambda)/V_m & \text{if } \lambda > \lambda_{\text{eq}} \text{ (desorption)} \end{cases} \quad (35)$$

where $\gamma_{a,d} = k_{a,d}/L_{\text{CL}}$ are the absorption and desorption rates with L_{CL} the catalyst layer thickness. $k_{a,d}$ are the ab-/desorption mass transfer coefficients. Following Ge et al. (2005), they are defined as



$$\begin{aligned} k_a &= 1.14 \cdot 10^{-3} \text{cm/s} \times f_w \times \exp \left[\frac{20 \frac{\text{kJ}}{\text{mol}}}{R} \left(\frac{1}{353.15 \text{ K}} - \frac{1}{T} \right) \right] \\ k_d &= 4.59 \cdot 10^{-3} \text{cm/s} \times f_w \times \exp \left[\frac{20 \frac{\text{kJ}}{\text{mol}}}{R} \left(\frac{1}{303.15 \text{ K}} - \frac{1}{T} \right) \right] \end{aligned} \quad (36)$$

The equilibrium hydration number λ_{eq} of the membrane is defined as

$$\lambda_{\text{eq}} = s\lambda_l + (1-s)\lambda_v \quad (37)$$

where λ_l and λ_v denote the hydration number when the membrane is liquid-equilibrated and vapor-equilibrated, respectively. λ_v depends on the water activity a as

$$\lambda_v = \lambda_m \frac{Ka}{1-a} \frac{1 - (n+1)a^n + na^{n+1}}{1 + (K-1)a - Ka^{n+1}} \quad (38)$$

where K denotes the ratio of the absorption equilibrium constant of the first layer to that of the subsequent layers, determining the shape of λ_v at low relative humidity. n is the number of adsorbed layers, governing the increase of water uptake at high relative humidity. The water vapor activity is calculated as

$$a = \frac{y_{\text{H}_2\text{O}}}{y_{\text{sat}}} = \frac{p_{\text{H}_2\text{O}}}{P_{\text{sat}}} \quad (39)$$

The saturation pressure is calculated as

$$P_{\text{sat}} = P_c \exp \left[\frac{T_c}{T} \left(-7.8595\hat{T} + 1.8441\hat{T}^{1.5} - 11.787\hat{T}^3 + 22.681\hat{T}^{3.5} - 15.962\hat{T}^4 + 1.8012\hat{T}^{7.5} \right) \right] \quad (40)$$

with $\hat{T} = 1 - T/T_c$, where P_c and T_c are the critical pressure and temperature of water given in Table 2, respectively (Wagner & Pruss 1993). The water loading at monolayer coverage λ_m can be estimated by Thampan et al. (2000)

$$\lambda_m = \frac{a_{\text{p}}^{\text{PEM}}}{A_w} \frac{V_m}{N_A} \quad (41)$$

where the area occupied by each adsorbed water molecule on the pore surface is approximately given by Emmett & Brunauer (1937)

$$A_w = \sqrt{3} \left(\frac{V_w}{2N_A} \right)^{2/3} \quad (42)$$

N_A is the Avogadro constant. Fitting equation 38 with experimental data, Vetter & Schumacher (2018) obtained for the model parameters $n=12.8$ and $K = 92$. The liquid-membrane water is defined as

$$\lambda_l = \lambda_m n. \quad (43)$$

2.5.2 Evaporation of liquid water and condensation of water vapor

The phase change between vapor and liquid water is modeled as

$$S_{\text{ec}} = \begin{cases} \gamma_e(y_{\text{H}_2\text{O}} - y_{\text{sat}})C & \text{if } y_{\text{H}_2\text{O}} < y_{\text{sat}} \text{ (evaporation)} \\ \gamma_c(y_{\text{H}_2\text{O}} - y_{\text{sat}})C & \text{if } y_{\text{H}_2\text{O}} > y_{\text{sat}} \text{ (condensation)} \end{cases} \quad (44)$$



in which $y_{\text{sat}} = P_{\text{sat}}/P$ denotes the saturation mole fraction of water vapor with P_{sat} the saturation pressure. We use the Hertz–Knudsen equation in the form proposed by Wu et al. (2009) to define the evaporation/condensation rates $\gamma_{\text{e,c}}$:

$$\begin{aligned}\gamma_{\text{e}} &= \Gamma_{\text{e}} \Gamma_{\text{s}} a_{\text{p}} s \sqrt{\frac{RT}{2\pi m_{\text{w}}}} \\ \gamma_{\text{c}} &= \Gamma_{\text{c}} \Gamma_{\text{s}} a_{\text{p}} (1 - s) \sqrt{\frac{RT}{2\pi m_{\text{w}}}} x\end{aligned}\quad (45)$$

with the interfacial area accommodation coefficient at the liquid vapor interface $\Gamma_{\text{s}} = 0.1$, the evaporation coefficient $\Gamma_{\text{e}} = 0.0005$ (at 1 bar given in Marek & Straub 2001), and the condensation coefficient $\Gamma_{\text{c}} = 0.006$ (at 1 bar given in Marek & Straub 2001).

2.5.3 Latent heat

The molar latent heat of water condensation H_{ec} used in Eq. 51 is parameterized as

$$H_{\text{ec}} = 52.51 \exp \left[0.261\tilde{T} - 0.044\tilde{T}^2 - 0.0044\tilde{T}^3 \right] \frac{\text{kJ}}{\text{mol}} \quad (46)$$

with $\tilde{T} = \ln [1 - T/T_{\text{c}}]$. This is a global least-squares fit to the tabulated data from Haynes et al. (2017). The latent heat of water sorption can be written as

$$H_{\text{ad}} = H_{\text{ec}} + H_{\text{mix}} \quad (47)$$

Vetter & Schumacher (2018) proposed a parameterization of H_{mix} based on the measurements on Nafion 115 by Wadsö & Jannasch (2013)

$$H_{\text{mix}} = \left(a_1 \exp [-b_1 \lambda] + a_2 \lambda \exp [-b_2 \lambda^2] \right) \frac{\text{kJ}}{\text{mol}} \quad (48)$$

with temperature-dependent coefficients and least squared residuals for

$$\begin{aligned}a_1 &= -107.5\bar{T}^2 + 253.9\bar{T} - 138.7 \\ a_2 &= 106.8\bar{T} - 102.4 \\ b_1 &= 2.006\bar{T}^2 - 4.365\bar{T} + 2.931 \\ b_2 &= 108.7\bar{T}^2 - 262.8\bar{T} + 159.5\end{aligned}\quad (49)$$

where $\bar{T} = T/300 \text{ K}$.

2.6 Definition of source terms

2.6.1 Electron and proton source

The source of electrons and protons are defined as

$$S_{\text{e}} = \begin{cases} 0 & \text{in AGDL} \\ -S_{\text{A}} & \text{in ACL} \\ S_{\text{C}} & \text{in CCL} \\ 0 & \text{in CGDL} \end{cases}, \quad S_{\text{p}} = \begin{cases} S_{\text{A}} & \text{in ACL} \\ 0 & \text{in PEM} \\ -S_{\text{C}} & \text{in CCL} \end{cases} \quad (50)$$



2.6.2 Heat source

Heat is generated by Joule heating, charge transfer resistance, Peltier heating and latent heat by the phase changes:

$$S_T = \begin{cases} j_e^2/\sigma_e & \text{in AGDL} \\ j_e^2/\sigma_e + j_p^2/\sigma_p + (\Pi_A + \eta_A)S_A + H_{ad}S_{ad} & \text{in ACL} \\ j_p^2/\sigma_p & \text{in PEM} \\ j_e^2/\sigma_e + j_p^2/\sigma_p + (\Pi_C + \eta_C)S_C + H_{ad}S_{ad} + H_{ec}S_{ec} & \text{in CCL} \\ j_e^2/\sigma_e & \text{in CGDL} \\ & + H_{ec}S_{ec} \end{cases} \quad (51)$$

where $\Pi_{A,C} = -\Delta S_{A,C}^{\text{ref}} T/2F$ are the Peltier coefficients of the half-reactions.

2.6.3 Dissolved water source

The source term for dissolved water content consists of an adsorption/desorption source term S_{ad} in both CL and an additional reaction term in the CCL:

$$S_\lambda = \begin{cases} S_{ad} & \text{in ACL} \\ 0 & \text{in PEM} \\ S_{ad} + \omega S_C/2F & \text{in CCL} \end{cases} \quad (52)$$

with $\omega = 0.5$ being the mass fraction of water produced in dissolved water rather than in liquid form. Following Vetter (2018), we assume that water is produced in equal shares in liquid and dissolved form in the CCL.

2.6.4 Liquid water source

The source term for liquid water saturation consists of an evaporation/condensation source term S_{ad} and an additional reaction term in the CCL:

$$S_s = \begin{cases} S_{ec} + (1 - \omega)S_C/2F & \text{in CCL} \\ S_{ec} & \text{in CGDL} \end{cases} \quad (53)$$

2.6.5 Gas source

The source terms

$$S_{H_2} = \begin{cases} 0 & \text{in AGDL} \\ -S_A/2F & \text{in ACL} \end{cases} \quad (54)$$

$$S_{O_2} = \begin{cases} -S_C/4F & \text{in CCL} \\ 0 & \text{in CGDL} \end{cases} \quad (55)$$



account for reactant consumption, whereas

$$S_{\text{H}_2\text{O}} = \begin{cases} 0 & \text{in AGDL} \\ -S_{\text{ad}} & \text{in ACL} \\ -S_{\text{ec}} - S_{\text{ad}} & \text{in CCL} \\ -S_{\text{ec}} & \text{in CGDL} \end{cases} \quad (56)$$

accounts for the phase transitions from vapor to liquid or dissolved water and back.

2.7 Boundary and initial conditions

The boundary conditions are the same as in Vetter & Schumacher (2018) except that electrical and thermal contact resistances are neglected to simplify the model. Furthermore, we apply time-dependent boundary conditions.

Initial values of the dependent variables are chosen in consistent manner with the boundary conditions at the outer GDL surfaces.

2.8 Numerical implementation in COMSOL and MATLAB

We implemented the time-dependent PEFC model in COMSOL Multiphysics 5.3a. Based on previous work, we have developed an automatic model generator using MATLAB and COMSOL's LiveLink for MATLAB. This work flow allows for modular model building. For example, one can choose between stationary and dynamic mode or activate/deactivate a governing equation.

2.8.1 Spatial discretization

The model is discretized in space with finite elements. 80 elements are symmetrically distributed per model layer with a higher resolution approaching the layer boundaries. The distribution method is arithmetic with an element ratio of 4.

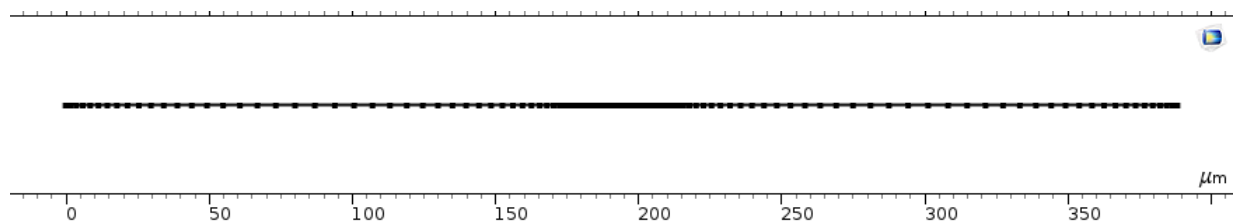


Figure 2: 1D mesh generated by Comsol.

2.8.2 Time discretization

The equations are discretized using the backward differentiation formula (BDF) method, with the maximum and minimum order of 5 and 1, respectively, and an event tolerance of 0.01. The initialisation is consistently chosen to be back-ward Euler.



2.8.3 Solver

The solution of a steady-state study serves as an initial condition for the time-dependent study. Generally, we use the direct solver MUMPS to obtain a fully coupled solution. In the stationary solver, we use non-linear Newton iterations (automatic, maximum number of iterations is 25). Iterations are terminated when the tolerance reaches a factor of 1. In the time-dependent solver, we use non-linear Newton iterations (constant, maximum number of iterations is 40). Iterations are terminated when the tolerance reaches a factor of 1.

2.9 Model development: gas transport equation

The equations for the gas transport in Vetter & Schumacher (2018, 2019) were reviewed to ensure that the sum of all gas mole fractions is equal to 1. We reformulated the equations for the gas transport in the anode and cathode by taking into account gas convection and a different treatment of Maxwell-Stefan multicomponent diffusion equations. Note that the results presented in this report have been obtained without considering these model developments.

The general transport equation for a gas mixture with N species in a porous media with liquid water is defined for each species i within the gas phase as:

$$\frac{\partial}{\partial t} [(1-s)\epsilon_p \rho_{\text{gas}} \omega_i] + \nabla \cdot [\rho_{\text{gas}} \omega_i u_{\text{gas},i}] = R_i, \quad (57)$$

- $\rho_{\text{gas}} = \sum_{i=1}^N \rho_{\text{gas},i}$ is the intrinsic density of the gas phase,
- $w_i = \frac{\rho_{\text{gas}}}{\rho_{\text{gas},i}}$ [-] is the mass fraction of each individual species in the gas phase, with $\sum_{i=1}^N \omega_i = 1$,
- R_i [kg/m³·s] is the mass source term
- $u_{\text{gas},i}$ is the velocity of gas species i .

By defining the mass flux relative to the mass average velocity u as the diffusive mass flux $j_{\text{gas},i} = \rho_{\text{gas},i}(u_{\text{gas},i} - u_{\text{gas}})$ (with $\sum_{i=1}^N j_{\text{gas},i} = \sum_{i=1}^N \rho_{\text{gas},i} u_{\text{gas},i} - u_{\text{gas}} \sum_{i=1}^N \rho_{\text{gas},i} = 0$), equation 57 becomes:

$$\frac{\partial}{\partial t} [(1-s)\epsilon_p \rho_{\text{gas}} \omega_i] + \nabla \cdot [\rho_{\text{gas}} \omega_i u_{\text{gas}} + j_i] = R_i, \quad (58)$$

with u_{gas} [m/s] is the barycentric velocity defined as $u_{\text{gas}} = \frac{\sum_{i=1}^N \rho_{\text{gas},i} u_{\text{gas},i}}{\sum_{i=1}^N \rho_{\text{gas},i}} = \frac{\sum_{i=1}^N \rho_{\text{gas},i} u_{\text{gas},i}}{\rho_{\text{gas}}} = \sum_{i=1}^N \omega_i u_{\text{gas},i}$

Equation 57 is summed up to account of for conservation of the whole gas mass

$$\frac{\partial}{\partial t} [(1-s)\epsilon_p \rho_{\text{gas}}] + \nabla \cdot [\rho_{\text{gas}} u_{\text{gas}}] = \sum_{i=1}^N R_i. \quad (59)$$



The diffusive mass flux $j_{\text{gas},i}$ is calculated using the Maxwell-Stefan equation following Curtiss & Bird (1999) while ignoring thermal diffusion and Knudsen diffusion

$$j_{\text{gas},i} = -\rho_{\text{gas}}\omega_i \sum_{\beta=1}^N \mathbb{D}_{i,\beta} d_{\beta}. \quad (60)$$

d is the diffusive driving flux defined as

$$d_i = \nabla y_i + \frac{1}{P_{\text{gas}}}(y_i - w_i)\nabla P_{\text{gas}}. \quad (61)$$

$y_i = \frac{\omega_i}{M_i} M_n$ and M_i is the molar fraction and molar mass of each species, respectively. $M_n = \frac{1}{\sum_i^N \frac{\omega_i}{M_i}}$ is the mean molar mass. The density is defined assuming the ideal gas law as

$$\rho_{\text{gas}} = \frac{M_n P_{\text{gas}}}{RT}, \quad (62)$$

where T is the temperature.

The multicomponent Fick diffusivities $\mathbb{D}$ are defined via the binary diffusion coefficients $\mathcal{D}$ following Curtiss & Bird (1999) as

$$\mathcal{D}_{\alpha\beta} = -\frac{y_{\alpha}y_{\beta}}{\omega_{\alpha}\omega_{\beta}} \frac{\sum_{\gamma \neq \alpha} \mathbb{D}_{\alpha\gamma} (\text{adj} B_{\alpha})_{\gamma\beta}}{\sum_{\gamma \neq \alpha} (\text{adj} B_{\alpha})_{\gamma\beta}} \quad (63)$$

where $(B_{\alpha})_{\gamma\beta} = -\mathbb{D}_{\beta\gamma} + \mathbb{D}_{\alpha\gamma}$. $\mathbb{D}$ is symmetric and obey the relationship $\sum_{\alpha} \omega_{\alpha} \mathbb{D}_{\alpha\beta} = 0$. For the binary system on the anode side, $\mathbb{D}$ is defined as

$$\mathbb{D}_{H_2H_2O} = -\frac{\omega_{H_2}\omega_{H_2O}}{y_{H_2}y_{H_2O}} \mathcal{D}_{H_2H_2O}, \quad (64)$$

$$\mathbb{D}_{H_2H_2} = \frac{\omega_{H_2}^2}{y_{H_2}y_{H_2O}} \mathcal{D}_{H_2H_2O}, \quad (65)$$

$$\mathbb{D}_{H_2OH_2O} = \frac{\omega_{H_2}^2}{y_{H_2}y_{H_2O}} \mathcal{D}_{H_2H_2O}, \quad (66)$$

and for the ternary system on the cathode side as

$$\mathbb{D}_{N_2N_2} = \frac{\frac{(\omega_{O_2} + \omega_{H_2O})^2}{y_{N_2}\mathcal{D}_{O_2H_2O}} + \frac{\omega_{O_2}^2}{y_{O_2}\mathcal{D}_{N_2H_2O}} + \frac{\omega_{H_2O}^2}{y_{H_2O}\mathcal{D}_{N_2O_2}}}{\frac{y_{N_2}}{\mathcal{D}_{N_2O_2}\mathcal{D}_{N_2H_2O}} + \frac{y_{O_2}}{\mathcal{D}_{N_2O_2}\mathcal{D}_{O_2H_2O}} + \frac{y_{H_2O}}{\mathcal{D}_{N_2H_2O}\mathcal{D}_{O_2H_2O}}}, \quad (67)$$

$$\mathbb{D}_{O_2O_2} = \frac{\frac{(\omega_{N_2} + \omega_{H_2O})^2}{y_{O_2}\mathcal{D}_{N_2H_2O}} + \frac{\omega_{N_2}^2}{y_{N_2}\mathcal{D}_{O_2H_2O}} + \frac{\omega_{H_2O}^2}{y_{H_2O}\mathcal{D}_{N_2O_2}}}{\frac{y_{N_2}}{\mathcal{D}_{N_2O_2}\mathcal{D}_{N_2H_2O}} + \frac{y_{O_2}}{\mathcal{D}_{N_2O_2}\mathcal{D}_{O_2H_2O}} + \frac{y_{H_2O}}{\mathcal{D}_{N_2H_2O}\mathcal{D}_{O_2H_2O}}}, \quad (68)$$

$$\mathbb{D}_{H_2OH_2O} = \frac{\frac{(\omega_{N_2} + \omega_{O_2})^2}{y_{H_2O}\mathcal{D}_{N_2O_2}} + \frac{\omega_{N_2}^2}{y_{N_2}\mathcal{D}_{O_2H_2O}} + \frac{\omega_{O_2}^2}{y_{O_2}\mathcal{D}_{N_2H_2O}}}{\frac{y_{N_2}}{\mathcal{D}_{N_2O_2}\mathcal{D}_{N_2H_2O}} + \frac{y_{O_2}}{\mathcal{D}_{N_2O_2}\mathcal{D}_{O_2H_2O}} + \frac{y_{H_2O}}{\mathcal{D}_{N_2H_2O}\mathcal{D}_{O_2H_2O}}}, \quad (69)$$

$$\mathbb{D}_{N_2O_2} = -\frac{\frac{\omega_{N_2}(\omega_{O_2} + \omega_{H_2O})}{y_{N_2}\mathcal{D}_{O_2H_2O}} + \frac{\omega_{O_2}(\omega_{N_2} + \omega_{H_2O})}{y_{O_2}\mathcal{D}_{N_2H_2O}} - \frac{\omega_{H_2O}^2}{y_{H_2O}\mathcal{D}_{N_2O_2}}}{\frac{y_{N_2}}{\mathcal{D}_{N_2O_2}\mathcal{D}_{N_2H_2O}} + \frac{y_{O_2}}{\mathcal{D}_{N_2O_2}\mathcal{D}_{O_2H_2O}} + \frac{y_{H_2O}}{\mathcal{D}_{N_2H_2O}\mathcal{D}_{O_2H_2O}}}, \quad (70)$$



$$\mathbb{D}_{N_2H_2O} = -\frac{\frac{\omega_{N_2}(\omega_{O_2}+\omega_{H_2O})}{y_{N_2}\mathcal{D}_{O_2H_2O}} + \frac{\omega_{H_2O}(\omega_{N_2}+\omega_{O_2})}{y_{H_2O}\mathcal{D}_{N_2O_2}} - \frac{\omega_{O_2}^2}{y_{O_2}\mathcal{D}_{N_2H_2O}}}{\frac{y_{N_2}}{\mathcal{D}_{N_2O_2}\mathcal{D}_{N_2H_2O}} + \frac{y_{O_2}}{\mathcal{D}_{N_2O_2}\mathcal{D}_{O_2H_2O}} + \frac{y_{H_2O}}{\mathcal{D}_{N_2H_2O}\mathcal{D}_{O_2H_2O}}}, \quad (71)$$

$$\mathbb{D}_{O_2H_2O} = -\frac{\frac{\omega_{O_2}(\omega_{N_2}+\omega_{H_2O})}{y_{O_2}\mathcal{D}_{N_2H_2O}} + \frac{\omega_{H_2O}(\omega_{N_2}+\omega_{O_2})}{y_{H_2O}\mathcal{D}_{N_2O_2}} - \frac{\omega_{N_2}^2}{y_{N_2}\mathcal{D}_{O_2H_2O}}}{\frac{y_{N_2}}{\mathcal{D}_{N_2O_2}\mathcal{D}_{N_2H_2O}} + \frac{y_{O_2}}{\mathcal{D}_{N_2O_2}\mathcal{D}_{O_2H_2O}} + \frac{y_{H_2O}}{\mathcal{D}_{N_2H_2O}\mathcal{D}_{O_2H_2O}}}. \quad (72)$$



3 Results and discussion

3.1 Time-dependent jump and cyclic voltammetry experiments

3.1.1 Analysis of transients in time-dependent jump experiments

In this section, we show the results of jump experiments, which we have conducted to identify the characteristic time scales of each governing process in a PEFC.

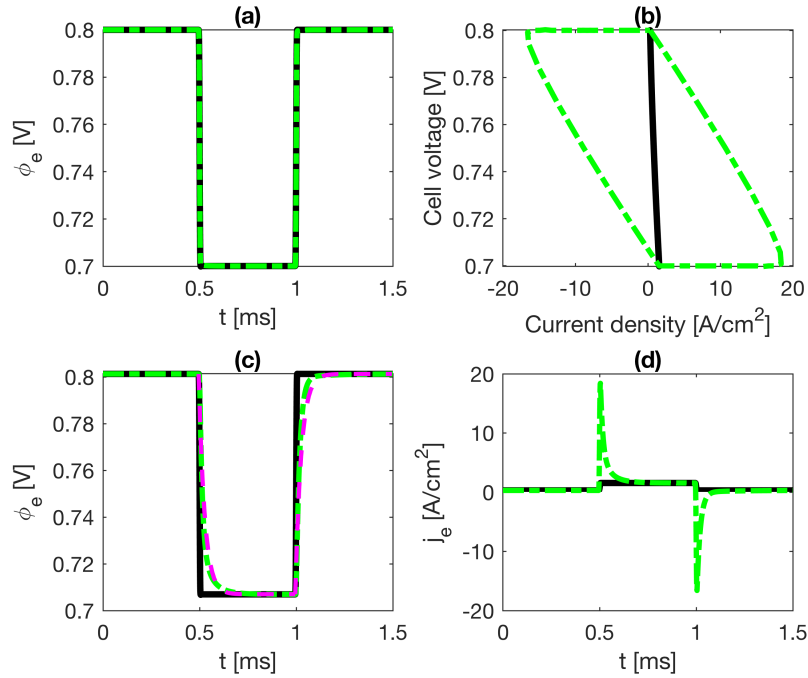


Figure 3: Results of voltage jump experiments. Green curves depict the time-dependent solution, whereas the steady-state solution is shown for reference in black. a) Electric potential and b) polarization curve, evaluated at the right model boundary. c) Electric potential at the boundary between CCL and PEM. The transient can be approximately fitted with a curve using a time constant $\tau_{DL} = 30 \mu s$ (magenta line). (d) Current density at the boundary between CCL and CGDL.

Electron and proton transient following a voltage jump We conducted voltage jump experiments by applying a change in electric potential from 0.8 to 0.7 V within $10 \mu s$ at the outer AGDL surface (Figure 3a). We solved for the transport of electrons and protons only and kept the other variables constant at $T = 70^\circ C$, $\lambda = 14$, $s = 0.1$, $y_{H_2O} = RHP_{sat}(T)/P_B$, $y_{H_2} = 1 - y_{H_2O}$, and $y_{O_2} = \alpha_{O_2}(1 - y_{H_2O})$. Furthermore, for simplicity, we used a homogeneous proton conductivity $\sigma_p = 10 S/m$ in the following analysis.

The time-dependent polarization curve (green) is clearly different from the steady-state solution (black) (Figure 3b), which is due to the following considerations. In the time-dependent simulation,



the electric potential in the catalyst layer evolves smoothly from the initial steady-state value to the new steady-state value (Figure 3c). The theoretical time scale of this transient process related to the electrochemical double layer is given in Wang & Wang (2005) as

$$\tau_{DL} = L_{CL}^2 a_C C_{DL} \cdot \left(\frac{1}{\sigma_e} + \frac{1}{\sigma_p} \right). \quad (73)$$

This can be used for the analytical solution (magenta) in the form of $\phi_e = U_{1,2} \pm \Delta U \exp\left(-\frac{t}{\tau_{DL}}\right)$ (Figure 3c), where the indices 1 and 2 stands for the value before and after the first step change, respectively. The slow response in the catalyst layer results in a gradient in electric potential from the model boundary to the catalyst layer (Figure 3c). Therefore, the step decrease (increase) in cell voltage leads to an immediate increase (decrease) in the current density (Figures 3d, 3b), which is followed by a transient evolution towards the new steady-state value. The peak in maximum current density depends on the duration Δt of the voltage step (Figure 3a). For sufficiently fast steps compared to τ_{DL} , the peak value of current density approaches $\frac{\sigma_e \Delta U}{L_{CGDL}}$, which yields the electric current density across the gas diffusion layer resulting from the voltage difference equal to the step change ΔU .

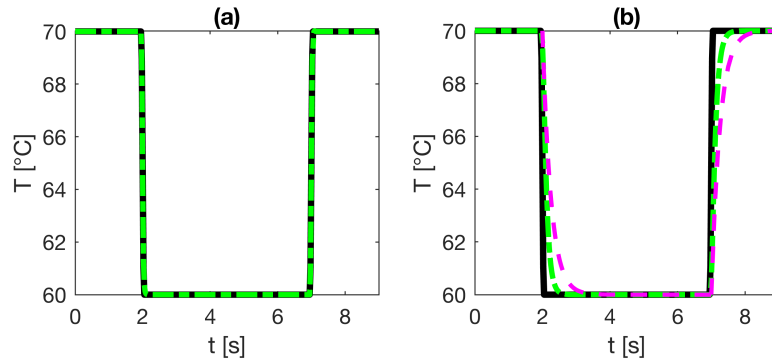


Figure 4: Results of temperature jump experiments. (a) Temperature at the outer AGDL surface, and (b) temperature in the center of the model. Black curve represents the steady-state solution, green curve the time-dependent solution. The dashed magenta line in (b) represents the analytical solution following the temperature step change: $T/K = T_{1,2} \pm \Delta T \cdot \exp\left(-\frac{t}{\tau_T}\right)$.

Temperature transient In a further experiment, we simulated only the heat transport equation with all other variables being constant. A temperature step increase and decrease applied at the outer AGDL and CGDL surfaces (Figure 4 a) results in a transient response (Figure 4 b). The characteristic time scale for the transient response can be calculated as

$$\tau_T = \frac{L^2 c_p}{k} \quad (74)$$

where L is half of the model length. For the given parameter set, $\tau_T = 0.252$ s (Figure 4 b). It should be noted, however, that in fuel cell experiments a longer temperature transient is expected. This is due the larger heat capacity of bipolar plates, which is neglected in our current PEFC model.

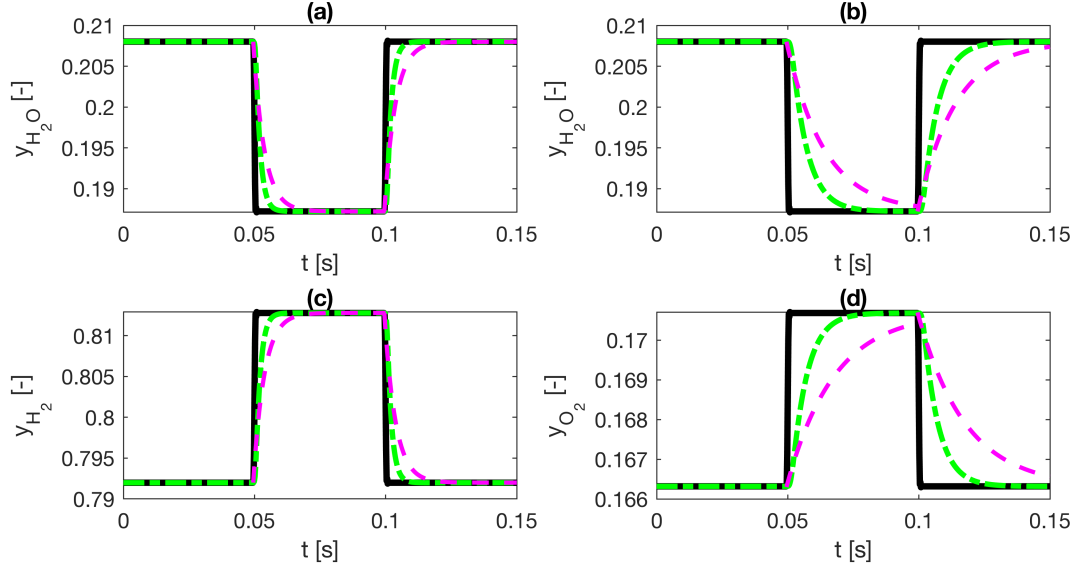


Figure 5: Results of gas humidity jump experiments on short time-scales. The black curve represents the steady-state solution, the green curve the time-dependent solution and the magenta curve shows a theoretical approximation. Evolution of (a) water vapor and (c) hydrogen concentrations on the anode side, (b) water vapor and (d) oxygen concentrations on the cathode side, evaluated at the respective boundaries between PEM and CLs.

Gas transport transient following a humidity jump To analyze transients of the gas transport, we applied a step change in relative humidity (RH) on the AGDL and CDGL outer surfaces. The resulting transient in gas concentrations in the AGDL and CL are shown in Figure 5. The gas transients on the cathode side are longer (time scale 0.015 s) than on the anode side (time scale 0.005 s), because of the smaller diffusion coefficients on the cathode side. The time scales can be computed as

$$\tau_g = \frac{(1-s)\epsilon_p L_{\text{AGDL}}^2}{D_F}, \quad (75)$$

where D_F is effective Fickian diffusion coefficient, which can be calculated from equation 30.

Dissolved water transient following a humidity jump To analyze transients of dissolved water, we applied a step change in relative humidity (RH) on the AGDL and CDGL outer surfaces, resulting in a step change in water vapor content (Figure 6a). The resulting transient in dissolved water content is shown in Figure 6b. The characteristic time-scale considering diffusion only is

$$\tau_\lambda = \epsilon_i \frac{L_{\text{PEM}}^2}{D_\lambda} \quad (76)$$

This yields around 3.2 seconds using an approximate value for the diffusion coefficient. The corresponding approximated curve has a shorter transient response than the simulated one (Figure 6b). In addition to diffusion, adsorption and desorption in the CLs prolongs the transient response. Simulations with different sorption rates shows that for increasing sorption rates the simulated curve converges towards the approximated curve with the characteristic time scale (Figure 7). Furthermore,



for decreasing sorption rates it becomes evident that the desorption process is shorter than the adsorption process as the desorption mass transfer coefficient is larger than the adsorption coefficient (see Equation 36). Thus, the transient response of the dissolved water content is due to a combination of diffusion and adsorption/desorption.

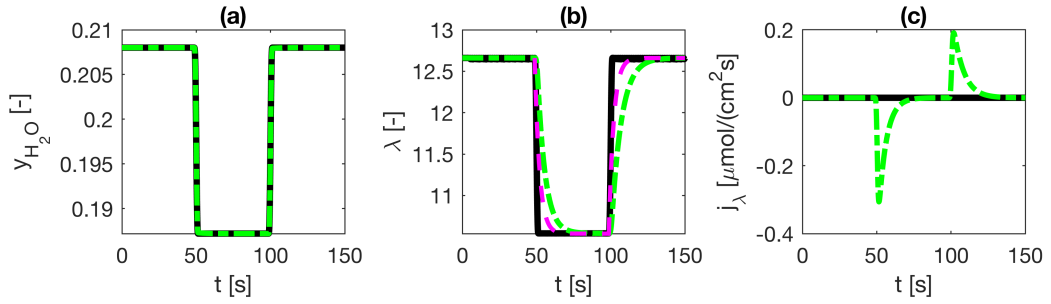


Figure 6: Results of humidity jump experiments on longer time scales. The black curve represents the steady-state solution, the green curve the time-dependent solution. Evolution of (a) water vapor concentration at the outer AGDL surface, (b) membrane hydration and (c) dissolved water flux in the center of the membrane. The magenta curve shows the theoretical approximation with τ_λ as the characteristic time scale.

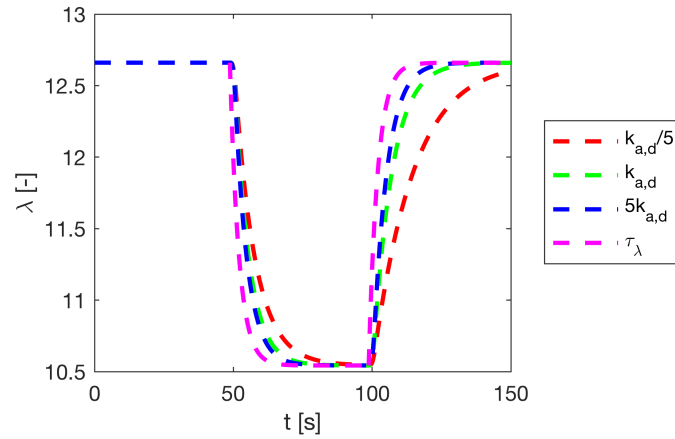


Figure 7: Comparison of models with different adsorption/desorption mass transfer coefficients $k_{a,d}$ with respect to Figure 6b.

Liquid water transient To analyze the transient of liquid water transport in the AGDL, we apply a step change of liquid water at the outer AGDL surface (Figure 8a). We solve for the transport of liquid water only. Following the step change, s evolves towards a new steady state value (Figure 8b) with a time constant of

$$\tau_s = \frac{\epsilon_p L_{AGDL}^2}{D_s}, \quad (77)$$

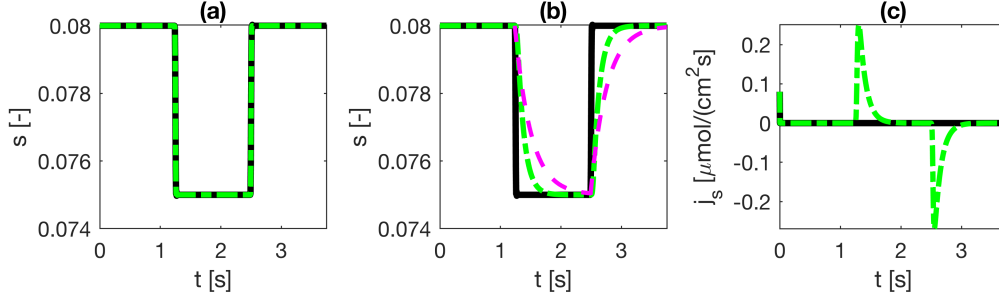


Figure 8: Step change of s at the outer AGDL surface (a). Response of (b) s and (c) j_s at the boundary between ACL and AGDL. The black curve represents the steady-state solution, the green curve the time-dependent solution, the magenta curve the analytic solution with the characteristic time τ_s .

where $D_s = 8 \cdot 10^{-4} \text{cm}^2/\text{s}$ in the AGDL, leading to $\tau_s = 0.26 \text{s}$. The simulated transient approximately the theoretical curve of $s(t) = s_{1,2} \pm \Delta s \cdot \exp(-t/\tau_s)$ (Figure 8b).

3.1.2 Cyclic voltammetry: role of membrane hydration

Following Gerteisen et al. (2009), we conducted the simulation of a cyclic voltammetry experiment. In this experiment, the cell voltage was decreased from 0.9 V to 0.06 V and then increased back to 0.9 V. The sweep rate is 0.1 V/s, leading to a cycle duration of 16.8s. To reduce the complexity of the simulation, we keep the liquid water content constant at $s = 0.1$.

Figure 9 shows the results for three cases. In the first case (black curve), the system of conservation equations are solved under the steady-state assumption, that is, the time-dependent accumulation terms in the conservation equations are omitted. The phases of voltage decrease and increase are indistinguishable. The second case (blue curve) represents the time-dependent solution for electron, proton, dissolved water, gas and heat transport. In this case, the voltage-current density curve follows a different path during voltage decrease than during voltage increase. This clear hysteresis effect is similar to the experiments conducted in Gerteisen et al. (2009). The third case (magenta line) with only the time-dependent solution for the dissolved water transport, leads to almost the same solution as in the second case. This demonstrates that the membrane (de-) hydration is the main cause for this hysteresis effect. As demonstrated in the previous section, the membrane (de-)hydration (i.e., diffusion and ad-/desorption phase change) has the longest time-scale in the order of 5 seconds. Therefore, the transient process of membrane (de-) hydration is slower than the voltage change. In contrast, the other transient processes are faster than the applied voltage change.

3.1.3 Convergence tests

We conducted a numerical convergence analysis to test the stability of our model. Therefore, we systematically varied the number of elements N_x per domain and the maximum computational time step Δt_{max} . For both numerical parameters, the polarization curve from Section 3.1.2 converges with increasing spatio-temporal resolution (Figure 10).

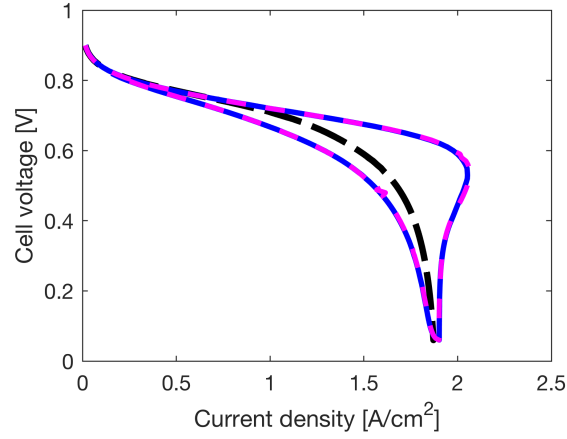


Figure 9: Simulation of a cyclic voltammetry experiment. Liquid water transport is not accounted for in this simulation. The black curve represents the solution under steady-state assumption. The blue curve represents the solution with accumulation terms in the conservation equations for electron, proton, dissolved water, gas and heat transport. The dashed magenta curve shows the results for a simulation with the accumulation term being only activated for dissolved water transport.

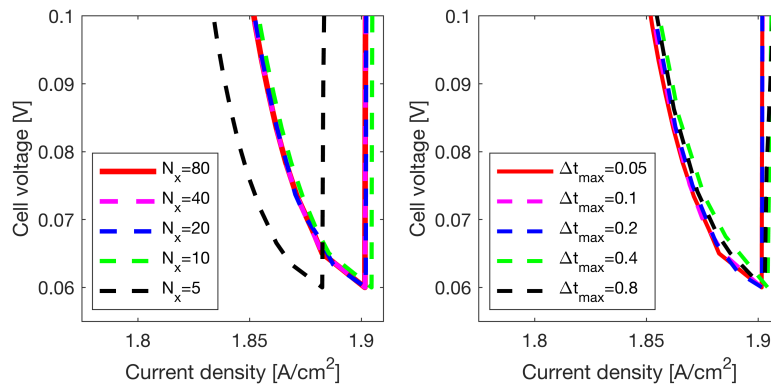


Figure 10: Results of the convergence analysis. Zoom into low cell voltage of the polarization curve. Convergence with (a) number of elements N_x per domain and (b) with maximum computational time step $\Delta t_{\max}$.



3.2 Response to sinusoidal perturbations of the steady state

3.2.1 Classical EIS analysis

EIS is an excellent diagnostic tool of the PEFC health (Gomadam & Weidner 2005). The reason is that this technique is capable of separating the response of the various processes happening simultaneously in PEFCs. Therefore it is capable of measuring the individual transport properties and, hence, the impedance of different PEFC parts.

As in a classical EIS analysis, a sinusoidal perturbation of amplitude ΔV is applied to a steady-state voltage V_0 to vary the voltage V at the boundary between GDL and GC/bipolar plate as

$$V = V_0 + \Delta V \sin(2\pi ft). \quad (78)$$

where f is the frequency and t is time. ΔV needs to be small enough so that the response is linear, and, hence, EIS analysis can be applied. Here we choose $\Delta V = 1$ mV.

The simulated response signal is first resampled and then fitted to a sinusoidal function in the form of

$$g_R(t) = A_R + B_R \cos(2\pi ft) + C_R \sin(2\pi ft) \quad (79)$$

From this function, the phase of the response signal is calculated by using the four quadrant inverse tangent

$$\alpha_R = \text{atan}\left(\frac{C_R}{B_R}\right) \cdot 180/\pi \quad (80)$$

where $\alpha_I = 90^\circ$. The magnitude of the response signal is

$$\Delta H = \sqrt{B_R^2 + C_R^2} \quad (81)$$

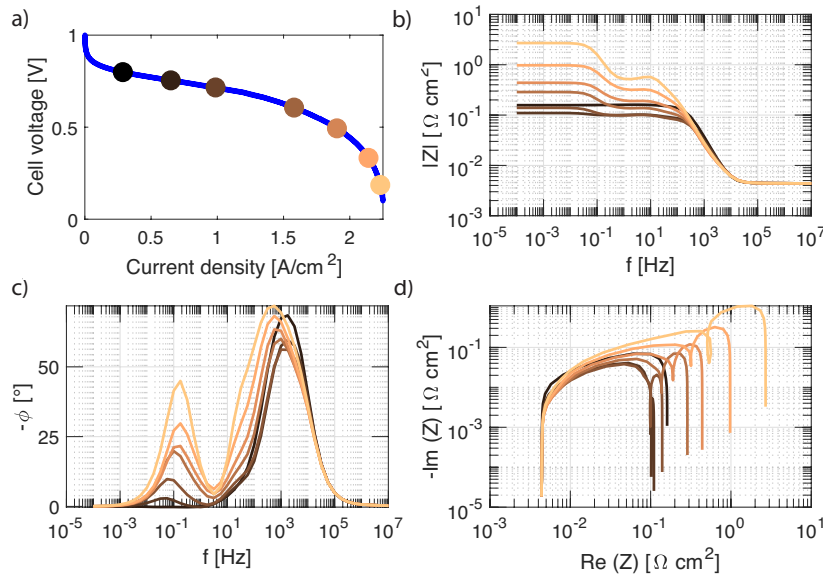


Figure 11: (a) Steady-state polarization curve. Colored circles indicate operating points V_0 at different voltages for the EIS analysis in (b-d). (b) Magnitude of impedance Z , (c) phase shift ϕ and (d) Nyquist plot.



From these values, the phase shift is calculated as

$$\phi = \alpha_R - \alpha_I \quad (82)$$

and the magnitude of impedance Z as

$$Z = \frac{\Delta V}{\Delta H}. \quad (83)$$

In classical EIS analysis and in this section, the response is taken to be the current density j_e , which is measured at the boundary between GDL and GC/bipolar plate (Figure 1). Different operating points in terms of V_0 are chosen from the steady-state polarisation curve (Figure 11 a).

In the high frequency range, Z is the smallest (Figure 11 b). In this range, the response in current density reaches its maximum, because the change in voltage at the boundary is too fast to lead to a change in voltage in the catalyst layer due to the double-layer capacity. Thus, there is a linear change in voltage from the CL/GDL boundary to the GDL/bipolar plate boundary ($\Delta j_e = \sigma_e \frac{\Delta V}{L_{GDL}}$), which is independent from the reference voltage V_0 . Hence, the high-frequency impedance is equal to

$$Z_{HF} = \frac{L_{GDL}}{\sigma_e} \quad (84)$$

and the phase difference is zero (Figure 11 c).

When the frequency is reduced, Z increases and the phase difference between the voltage and current density reaches a maximum. The reason is that the frequency approaches the time-scale of the double layer capacity, which is defined as

$$\tau_{DL} = \frac{a_p C_{DL} L_{CL}^2}{\sigma_p}. \quad (85)$$

There is a change in the location of the peak with V_0 , because the steady-state σ_p inside the membrane decreases due to the decrease in dissolved water with increasing current density.

When the frequency is further reduced, there is another step increase in Z and a second peak in ϕ . This is due to the time-scale of water diffusion inside the membrane, which is defined as

$$\tau_\lambda = \frac{L_{PEM}^2}{D_\lambda} \quad (86)$$

The phase difference and the impedance increase with decreasing V_0 (thus increasing current densities), for which the steady-state impedance increases.

3.2.2 Additional response analysis

In addition to the electric current density, we analysed the response of further quantities measured in the center of the membrane:

- Protonic current density j_p
- Dissolved water λ and its flux j_λ

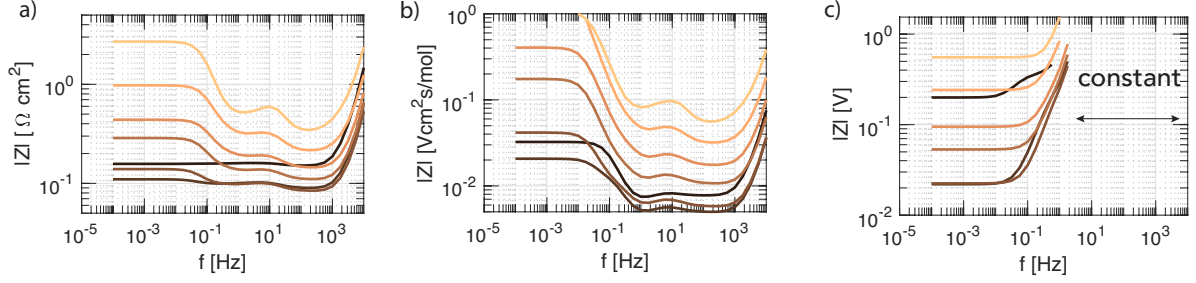


Figure 12: Membrane response for a) protonic current density $Z = \frac{\Delta V}{\Delta j_p}$, b) dissolved water flux: $Z = \frac{\Delta V}{\Delta j_\lambda}$, and c) dissolved water: $Z = \frac{\Delta V}{\Delta \lambda}$. Line colors correspond to different V_0 shown in Figure 11 a.

The result is shown in Figure 12. The impedance for the response of λ cannot be calculated for high frequencies, because λ stays constant due the inertia of the double-layer capacity.

The constant λ at high current densities can be used to determine the electro-osmotic drag coefficient. Let us remmember the equation for the dissolved water flux:

$$j_\lambda = -\frac{D_\lambda}{V_m} \nabla \lambda + \frac{\xi}{F} j_p \quad (87)$$

For the change at high frequencies, this becomes:

$$\Delta j_\lambda = -\Delta \frac{D_\lambda}{V_m} \nabla \lambda + \frac{\xi}{F} \Delta j_p \quad (88)$$

Since $\nabla \lambda$ does not change,

$$\xi_{\text{approx}} = F \frac{\Delta j_\lambda}{\Delta j_p}. \quad (89)$$

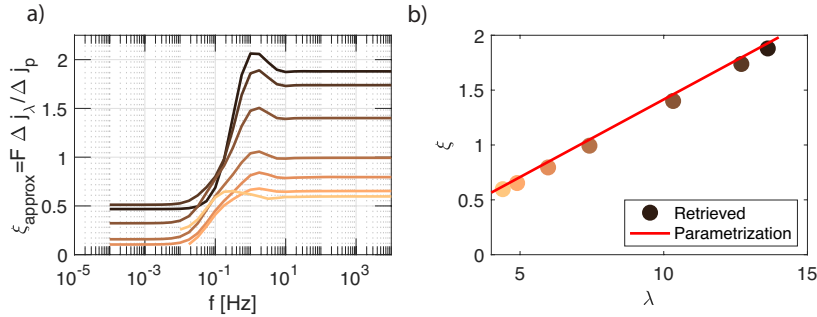


Figure 13: a) $F \frac{\Delta j_\lambda}{\Delta j_p}$ as a function of frequency. At high frequencies, this corresponds to the electro-osmotic drag coefficient ξ . (b) ξ as a function of λ , measured at high $f = 5 \cdot 10^3 \text{ Hz}$. The red curve corresponds to Equations 90-91. Colors correspond to different V_0 shown in Figure 11 a.



This approximation approaches a constant value at high frequencies (Figure 13 a). This value corresponds for different V_0 and, hence, for different λ to the input parameterization (Figure 13 b):

$$\xi = \xi_l \frac{\lambda}{\lambda_{\text{eq,liq}}} \quad (90)$$

$$\xi_l = \xi_{\text{ref}} \exp \left(\frac{E_\xi}{R} \left(\frac{1}{303.15 \text{ K}} - \frac{1}{T} \right) \right) \quad (91)$$

with T is the temperature, $\xi_{\text{ref}} = 2.5$ is the reference electro-osmotic drag coefficient, $E_\xi = 4 \text{ kJ/mol}$ is the activation energy and $\lambda_{\text{eq,liq}}$ is the equilibrium dissolved water content.

3.2.3 Total harmonic distortions

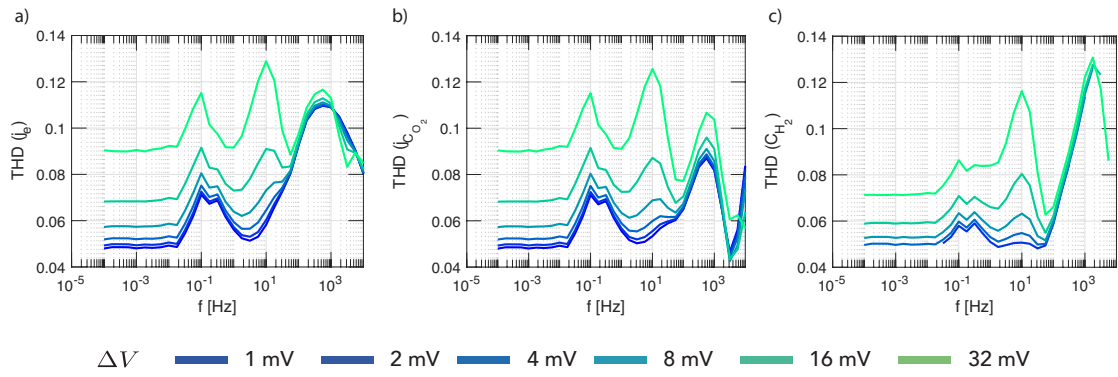


Figure 14: Total harmonic distortion, analysed at $V_0 = 0.35 \text{ V}$ with amplitudes ΔV from 1 to 32 mV for (a) electric current density j_e , (b) flux of oxygen concentration C_{O_2} and c) flux of hydrogen concentration C_{H_2} .

To analyse the response to larger input signals, ΔV is systematically increased from 1 mV to 32 mV at $V=0.35 \text{ V}$. The non-linear response is evaluated in terms of the total harmonic distortion (THD), which is defined as

$$\text{THD} = \sqrt{\frac{\sum_{i=2}^{10} P_i}{P_1}}, \quad (92)$$

with P_i being the estimate of the power at the frequency of i -th harmonic of the input signal. This estimate is obtained via discrete fourier analysis using the MATLAB function 'periodogram'. The larger the power of the higher harmonics, the more is the response distorted (i.e. different from a pure sinusoidal response).

In low frequency range between $10^{-4} - 10^{-2} \text{ Hz}$, THD is flat and increases with ΔV (Figure 14 a-c). The response becomes more distorted due to the non-linearity of governing processes. The already known characteristic time scales at 0.1 Hz and 1 kHz are also visible in the THD analysis. In addition, a peak in THD at a frequency of around 10 Hz becomes apparent for larger ΔV . We related this peak to the characteristic time-scale of oxygen diffusion.



Note that this peak is not detectable in the classical EIS analysis (Figure 11-12). This shows that the large signal response can be used to extend the characterization of fuel cells.

3.3 Improvement of isomorph.ch

For future collaborations, we restructured our webpage www.isomorph.ch, on which we advertise our computational solutions for PEM fuel cells. The solutions include the free- and open-source Master MEA model ([link](#)) and the parameterized MEA model ([link](#)). The steady-state

4 Conclusions

We have developed a numerically stable time-dependent PEFC model and demonstrated its capability to characterize PEFCs in a number of numerical experiments. In simulated jump experiments, we showed that this model is capable of analyzing transients of governing processes. Furthermore, we identified membrane hydration (water ad-/desorption and diffusion) as the main cause of the hysteresis observed in cyclic voltammetry experiments. The model was further applied to study the response to sinusoidal perturbations of the steady state. We conducted a classical electrical impedance study, where we analyzed the small-signal response of electric current density. From the analysis, we inferred the electrical conductivity and polarization resistance of the cell. Furthermore, we identified the time scales of double-layer capacitance and membrane hydration. The extension of the response analysis to protonic and dissolved water flux demonstrates the possibility to extract the electro-osmotic drag coefficient as a function of dissolved water content. We computed the large signal response by calculating the total harmonic distortion. This allowed to identify the time scale of gas diffusion.

Furthermore, we improved our physical model with respect to gas transport. Second, we updated the website isomorph.ch making it more attractive to potential academic and industry partners.

5 Outlook and next steps

The time-dependent modeling and simulation of proton exchange membrane fuel cells is an important working field to improve operational strategies for fuel cell systems and to monitor the state-of-health of a fuel cell.

The Institute of Computational Physics aims at providing computational solutions to simulate the time-dependent response of fuel cells to research institutes and partners from industry. We planned the following steps to achieve this goal:

- A computationally efficient version of the time-dependent PEFC model will be created by means of model order reduction.
- Degradation mechanism will be incorporated into the model.
- To validate the models, time-resolved simulation results will be compared to measurement data of fuel cell stacks, amongst others at the company GreenGT.
- We will promote the time-dependent model on isomorph.ch to make it available to industry. Therefore, a pricing scheme and a suitable software license will be worked out.



6 National and international cooperation

6.1 International cooperation

The project was terminated prematurely as the German and French partners did not receive any funding. A Go-NoGo criterion was agreed in the research contract for this case.

6.2 National cooperation with GreenGT

For automotive application, we are collaborating with the Swiss company GreenGT. During the course of the project we had fruitful discussions with Jean-Marc Le Canut, Julien Roussel and Jean Francois Weber at GreenGT. We presented our simulation results and discussed the future collaboration within the ACTIF project.

7 Publications and conferences

We presented our results with the following contributions at conferences:

- **Experimental parameter uncertainty in PEM fuel cell modeling.** 8th International Conference on Fundamentals and Development of Fuel Cells. 12.02-14.02.2019, Nantes, France. doi: <https://digitalcollection.zhaw.ch/handle/11475/15710>.
- **Advanced characterization of polymer electrolyte fuel cells using a two-phase time-dependent model.** 16th Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies. 12.03-13.03.2019, Braunschweig, Germany. <https://doi.org/10.21256/zhaw-2790>



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A Appendices

A.1 Financial report

ZHAW-ICP received 80'000 CHF of funding from SFOE in 2018. The hours worked by ZHAW-ICP for the project and the costs calculated according to the personnel costs are shown in the table. The total personnel costs amount to 54'853 CHF. It has been agreed between SFOE and ZHAW-ICP that SFOE will cover 70% of the personnel costs, that is, 38'397 CHF of personnel costs, and 38'612 CHF including travel expenses. The 41'388 CHF grant not used for the project will be refunded to the SFOE by ZHAW-ICP.

ICP WiMa			ICP Jürgen Schumacher		
CHF/h		65	CHF/h		115
CHF/Monat	CHF	9'880	CHF/Monat	CHF	17'480

Personnel costs	2018		2019		Total		Contribution of SFOE (70% of personnel costs)
	Work hours		Work hours		work hours		
ICP WiMa	176.4	CHF 11'466	552.49	CHF 35'912	728.89	CHF 47'378	CHF 33'164.50
ICP Schumacher	6	CHF 690	59	CHF 6'785	65	CHF 7'475	CHF 5'232.5
Total					793.89	CHF 54'853	CHF 38'397.00
	Non-personnel costs						
Total							

Figure 15: Overview on working hours of ICP-ZHAW and associated costs.