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Experimental and Numerical Investigation of the Low-Frequency Inductive Features in Differential PEMFCs: Ionomer Humidification and Platinum Oxide Effects

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The low-frequency inductive features in PEMFC are studied by differential measurements and numerical simulation. Systematic parameter variations are conducted and the discrepancies between the local polarization curve slopes and the capacitive loops of electrochemical impedance spectra (EIS) are evaluated to compute the inductive contributions. These contributions, primarily slow platinum oxide kinetics and ionomer humidification, are disentangled and we show that the latter is more relevant at medium to high currents, leaving mainly kinetics contributions of around 35 mV dec⁻¹ at small currents. We demonstrate that the inductivity reaches over 150 mV dec⁻¹ at high load and that it strongly depends on the current density (*j*) and on the relative gas humidity (*RH*), whereas temperature (*T*) and oxygen partial pressure (p_{O_2}) play a minor role. A new approach for modeling the combination of the oxygen reduction reaction and platinum oxidation leading to inductive loops is presented and integrated into a 1D through-plane model which we parameterize based on our large dataset. We present a comprehensive parameter study with this model. Its current version contains platinum oxide kinetics and electron, proton as well as oxygen transport and yields a good match with both steady-state and EIS data.

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The optimization of PEM fuel cells lifetime and costs in view of wide commercialization requires strong understanding of the membrane electrode assembly (MEA) performance signatures. Thus, in situ and in operando methods to characterize the physicochemical processes are strongly needed in the PEMFC development. In the past, mainly polarization curves complemented by electrochemical impedance spectroscopy (EIS) were employed as operando techniques. While steady-state polarization measurements are done by recording the cell voltage at different loads or vice-versa, the EIS technique uses a small sinusoidal current (galvanostatic) or voltage (potentiostatic) signal to record the system's response for a range of frequencies. However, polarization measurements alone are insufficient to separate the loss mechanisms and even though EIS is widely used in PEM characterization, it is still not fully understood. In Figs. 1a (Nyquist plot) and 1b (Bode representation) we show a representative EIS spectrum at high load and cold and dry conditions. There, the high-frequency (HF) inductive part due to the setup is visible below the axis intercept at approximately 10 kHz, which represents the Ohmic resistance (membrane and electronic resistance). The capacitive part that contains the proton transport resistance in the electrodes, charge transfer resistances and mass transport contributions is visible from approximately 10 kHz to 1 Hz. Recently, the distribution of relaxation times (DRT) was applied additionally to EIS to deconvolute the capacitive processes and generate better initial guesses for equivalent circuit model (ECM) fitting.¹ However, this method is also limited when the time constants in the system are very close or even overlap with each other. Thus, separating the reaction kinetics from oxygen and water transport processes happening at medium to low frequencies in PEMFC might be challenging under some conditions, making the analysis of EIS complex.

As can be seen in Fig. 1a, a low-frequency (LF) inductive loop is detected in EIS below 1 Hz. As a consequence, the axis intercept at approximately 1 Hz, which is typically used in EIS analyses, differs

from the actual differential resistance of the polarization curve (=local slope, black ellipse with red contour). This causes discrepancies between polarization-curve-based and EIS-based evaluation of the oxygen reduction reaction (ORR) Tafel slope $b_{\text{ORR}} = \partial \eta_{\text{ORR}} / \partial \ln j$, with *j* the current density and η_{ORR} the kinetics overpotential. This LF loop is still subject to research and has previously been attributed to side reactions and intermediates of the ORR, to platinum surface oxide (PtOx) formation and dissolution, to platinum poisoning by CO, or to changes in the ionomer hydration due to slow water dynamics, see the references in Table I.

However, to the best of our knowledge, there has been no attempt to quantify the contributions based on a consistent experimental dataset in combination with simulation since these effects were mostly treated separately in the past. Ionomer hydration effects were investigated by physical modeling by Kosakian et al.,¹⁷ by Kulikovsky¹⁸ and by Wiezell et al. in combination with humidity-dependent anode contributions.^{12–15} An EIS model containing platinum oxide effects was proposed early by Mathias et al.,⁶ though it was fed with constant parameters and validated only by a single experimental spectrum. Setzler et al. analyzed the LF inductive behavior and the discrepancy between steady-state polarization and capacitive EIS response for various operating conditions based on experimental data and physical cell modeling.⁹ Nevertheless, their platinum oxide kinetics were rather complex and their model did not match the experimental data at high loads. Also, their model did not predict an influence of water management on the LF inductive features, which is puzzling since most other comparable physical models do.^{14,16,17,29} Futter et al. proposed an along-the-channel model that takes into account both water management phenomena and platinum oxide effects on the LF inductive signatures, but they observed a large mismatch between experimental and numerical spectra at low frequencies.²⁹ Lately, Schiefer et al. managed to record EIS down to 5 mHz in a differential cell and used a negative DRT analysis to unravel two processes with separate time constants within the LF inductive loops of their spectra:³⁰ one process was dominant at high cell voltage and the other one at low humidity. They could however not unambiguously assign the time constants to physico-chemical processes.





Figure 1. (a) Nyquist plot of an EIS spectrum recorded at $j = 1 \text{ A/cm}^2$, RH = 30% and T = 50 °C (dry conditions) from 100 kHz to 10 mHz. Some frequencies are highlighted by the filled red symbols and the steady-state differential resistance is shown by the black ellipse with red contour. (b) Corresponding Bode diagram showing the real and imaginary parts over the frequency *f*. See Fig. S1 in the supplementary material for the corresponding EIS at hot and dry conditions.

Finally, Meyer and Zhao showed that they could control the size of their inductive loops by making the oxygen volume flow oscillate at the same frequencies as the current during galvanostatic EIS.³¹ The low-frequency limits of their spectra converged to the steady-state differential resistances of their polarization curves.

In this work, we aim at disentangling the different contributions of the LF inductive loop based on the extensive test run of our previous works.^{32,33} We evaluate the absolute values of the inductive contributions by subtracting the local slopes of the polarization curves (calculated by numerical derivation) from the low-frequency real-axisintercept of the capacitive EIS that occurs at approximately 1 Hz. With this knowledge and our previous study of the ionomer resistances,³² we separate the humidification from the PtOx contributions and parameterize a simple ORR model containing platinum poisoning effects that result in a low-frequency inductive loop. We integrate this mechanism into a simplified 1D through-plane MEA model which matches the experimental data well. Thus, this model goes beyond simple Tafel law kinetics in order to reconcile steady-state performance and EIS signatures of PEM fuel cells. We also use this model for an extensive parameter study (see Figs. S6 to S29 in the supplementary material).

Experimental

Setup and procedures.—We used Gore[®] PRIMEA[®] MEAs (W. L. Gore & Associates, Elkton, MD, USA) with 18 μ m membrane

thickness and loadings of 0.4/0.05 mg_{Pt} cm⁻² in the cathode/anode. They were sandwiched between Sigracet[®] 22BB gas diffusion layers (GDL) from SGL[®] Carbon and mounted in a 12 cm² differential cell setup from Baltic FuelCells (quickConnect[®]) with an equivalent clamping pressure of about 1.3 MPa. In this setup, the combination of high gas flow rates (differential conditions, cell inlet = cell outlet) and the flowfield structure on the cathode side with wide channels (channel/land ratio of approximately 0.7/0.3) leads to negligible inplane gradients during operation. We conditioned the cells in H₂/air configuration at $p_{total} = 1.5$ bar_a, RH = 100%, T = 50 ° C, and with H₂/air flows of 1300/2000 sccm, as described by Harzer et al.³⁴

The same full factorial test runs under H_2/O_2 and H_2/N_2 conditions to record polarization curves and EIS spectra as in our previous publications were used here.^{32,33} The parameter ranges are summarized in Table II. For our EIS measurements we chose 10 currents out of the 16, which lead to 1120 spectra. We set constant dry flow rates of 1300/2000 sccm in the anode/cathode at the system pressure $p_{\text{total}} = 1.5$ bar_a to get low pressure drops ($\Delta p < 100$ mbar) for all the conditions. The run was carried out in the order of increasing dew points and from high currents to low currents. Whenever adjusting the temperature or the dew point, the cell was stabilized in H₂/air at 0.7 V for 2 h. The currents at which we performed EIS were stabilized for at least 25 min prior to the measurement to ensure high measurement quality. We recorded most of our EIS in the range of f = 100 kHz to f = 100 mHz with 10 points per decade but some selected conditions were also recorded down to f = 10 mHz (see Fig. 1).

More information about our setup and tests and how we ensured good measurement quality (state-of-health checks and Kramers-Kronig analyses) is given in our previous publications.^{32,33}

Model

Model description.—In this work we aim at using a pragmatic approach for kinetics modeling and therefore propose a simple model based on two reactions. In the past, Setzler et al. published an extended ORR modeling approach and implemented it into a physical MEA model which yielded meaningful results, even though their spectra showed large deviations at high loads or low oxygen concentration.⁹ Further, their oxide growth model is quite complex and thus not suited for our applications since we want a model that can be parameterized with a minimal amount of simple in situ experiments. Our model resembles the one of Mathias et al.⁶ in the way that we also have a single step representing the slow platinum poisoning effect through oxides, even though we further simplify it by keeping only a single Tafel equation for the ORR rather than using a two-step mechanism with OH intermediates.

We model the ORR as a single non-reversible electron transfer step comparable to the well-known ORR Tafel approximation (only the cathodic branch), although containing the need for free platinum sites in the rate determining step:

$$\frac{n}{4}O_2 + nH^+ + ne^- + n_{\Box} \operatorname{Pt} - \Box \longrightarrow \frac{n}{2}H_2O + n_{\Box} \operatorname{Pt} - \Box \qquad [1]$$

where Pt- represents an active platinum site. The oxidation of the platinum surface is represented in a general way by

$$Pt_{n_{Pt}}OH_{(2-n_2)} + n_2H^+ + n_2e^- \rightleftharpoons H_2O + n_{Pt}Pt - \Box$$
 [2]

For simplicity, we will restrict our analysis in the following to the special case $n_2 = 1$. Based on the reaction given in Eq. 1 the rate of the ORR step ν_1 can be written as follows:

$$\nu_1 = k_1' [\mathcal{O}_2]^{\frac{n}{4}} [\mathcal{H}^+]^n \cdot \exp\left(\frac{-\Delta G_1^{\ddagger} - (1-\beta)nF\Delta\phi}{RT}\right) \theta_{\square}^{\frac{n}{\square}} \qquad [3]$$

with k'_{l} the rate constant, ΔG_{l}^{\ddagger} the Gibbs free energy of activation of the ORR step, $\Delta \phi = \phi_{e} - \phi_{p}$ the difference between the electrode

Table I. Overview of the most relevant literature regarding the low-frequency inductive loop and/or the bias between the slope of the polarization curve and the LF limit of the capacitive impedance.

Attributed physics	System/Model	Source/Year
Kinetics intermediates and/or platinum oxides	Half cells/ORR model Single cells Half cells/ORR and HOR model Single cells/OD cell model Single cells/ORR model Single cells and stacks/ECM modeling Single cells/1D cell model ORR model PEM stacks/ECM modeling	Antoine et al. ² /2001 Mathias et al. ³ /2006 Kuhn et al. ⁴ /2006 Roy et al. ⁵ /2007 Mathias et al. ⁶ /2008 Cruz-Manzo et al. ^{7,8} /2013 Setzler et al. ⁹ /2015 Kulikovsky ¹⁰ /2015 Giner-Sanz et al. ¹¹ /2018
Water and/or Ionomer dynamics	Single cells/1D model 2D along-the-channel 1-phase isothermal model Single cells/2D across-the-channel 1-phase non-isothermal model CCL model	Wiezell et al. ^{12–15} /2006-2012 Bao and Bessler ¹⁶ /2015 Kosakian et al. ¹⁷ /2020 Kulikovsky ¹⁸ /2022
Combined effects/Others	Single cells (CO poisoning) Segmented cell (water dynamics and along-the-channel effects) Segmented cell/2D along-the-channel model (along-the-channel effects) Single cells/ ECM modeling Single cells/ECM modeling (O2 transport effects in CCL) 2D along-the-channel 2-phase non-isothermal model (water dynamics and platinum oxides) Single cells/ECM modeling & negative DRT (water dynamics, kinetics intermediates, anode contribution) Single cells (concentration oscillations)	Wagner et al. ¹⁹ /2004 Schneider et al. ^{20–23} /2007-2008 Maranzana et al. ²⁴ /2012 Pivac et al. ^{25,26} /2016-2017 Pivac et al. ²⁷ & Meyer et al. ²⁸ /2018-2020 Futter et al. ²⁹ /2018 Schiefer et al. ³⁰ /2020 Meyer et al. ³¹ /2021

Table II. Values taken by the parameters during our experimental run.³³ The values for x_{O2} and *j* only apply for the test run in fuel cell mode.

Parameter	Values	
RH / %	{30, 40, 50, 60, 70, 80, 90, 100}	
T / °C	{50, 60, 70, 80}	
$x_{O_2}^{dry}$ or x_{O_2} / -	$\{1\}$ or $\{0.5, 0.25, 0.16\}$	
j / A/cm ²	$\{2, 1.5, 1, 0.5, 0.3, 0.2, 0.1, 0.05, 0.03, 0.02\}$	

and the electrolyte potentials, β the symmetry coefficient, *n* the number of transferred electrons, $[O_2]$ and $[H^+]$ the activity of oxygen and protons, respectively, and θ_{\Box} the fraction of platinum sites free from oxides. As we want to express the rate constant as a function of the overpotential $\eta = \Delta \phi - \Delta \phi_{eq}$, we introduce the equilibrium condition

$$\Delta\phi_{\rm eq} = -\frac{\Delta G_{\rm 1,ref}}{2F} - \frac{RT}{2F} \ln\left(\frac{[\rm H_2O]}{[\rm O_2]^{\frac{1}{2}}[\rm H^+]^2}\right)$$
[4]

with $\Delta G_{1,\text{ref}}$ the molar Gibbs free energy of reaction at standard conditions and [H₂O] the activity of water. With this, the reaction rate of the ORR can be rewritten as

$$\nu_{1} = k_{1} [\mathrm{H}^{+}]^{\beta_{n}} [\mathrm{O}_{2}]^{\frac{\beta_{n}}{4}} [\mathrm{H}_{2}\mathrm{O}]^{\frac{(1-\beta)n}{2}} \cdot \exp\left(\frac{-(1-\beta)nF}{RT}\eta\right) \theta_{\Box}^{n_{\Box}} \quad [5]$$

where k_1 is defined such that it includes constants and an Arrheniustype temperature dependency with the activation energy $E_{\text{act},1}$. Using a similar approach for the poisoning reaction, assuming $\beta_2 = 1/2$, introducing $\Delta G_{1,\text{ref}}$, and keeping both the cathodic and anodic branches, the reaction rate ν_2 can be expressed as follows:

$$\nu_{2} = k_{2}^{\prime} \left[\theta_{\Box}^{n_{\text{Pt}}}[\text{H}_{2}\text{O}] \exp\left(\frac{-\Delta G_{2}^{\ddagger} + \Delta G_{2,\text{ref}} + \frac{1}{2}F\Delta\phi}{RT}\right) - \left(\frac{1 - \theta_{\Box}}{n_{\text{Pt}}}\right) [\text{H}^{+}] \exp\left(\frac{-\Delta G_{2}^{\ddagger} - \frac{1}{2}F\Delta\phi}{RT}\right) \right]$$
[6]

where $\Delta \phi$ must again be substituted since we want to express the kinetics as a function of the overpotential η . Thus, we transform Eq. 6 by implementing Eq. 4 and rearranging to

$$\nu_{2} = k_{2} [\mathrm{H}^{+}]^{\frac{1}{2}} \left[\theta_{\Box}^{n_{\mathrm{Pt}}} [\mathrm{O}_{2}]^{\frac{1}{8}} [\mathrm{H}_{2}\mathrm{O}]^{\frac{3}{4}} \exp\left(\frac{F}{RT} \Delta U_{\mathrm{eq}}\right) \exp\left(\frac{F}{2RT} \eta\right) - \left(\frac{1-\theta_{\Box}}{n_{\mathrm{Pt}}}\right) [\mathrm{O}_{2}]^{-\frac{1}{8}} [\mathrm{H}_{2}\mathrm{O}]^{\frac{1}{4}} \exp\left(-\frac{F}{2RT} \eta\right) \right]$$
[7]

with $\Delta U_{\rm eq} = -\Delta G_{1,\rm ref}/(2F) + \Delta G_{2,\rm ref}/F$ the difference of the reference equilibrium potentials of both reactions. We neglect the temperature dependency of $\Delta U_{\rm eq}$ and handle it as a fitting parameter. From this point on we set the proton activity [H⁺] to unity. Further, we define the reaction rate constant k_2 as

$$k_2 = k_{2,\text{ref}} \exp\left[\frac{-E_{\text{act},2}}{RT} \left(1 - \frac{T}{T_{\text{ref}}}\right)\right]$$
[8]

even though we set $E_{\text{act},2} = 0 \text{ kJ mol}^{-1}$ in this study. According to this, $k_{2,\text{ref}}$ is the only fitting parameter in Eq. 8. In order to transform ν_2 from Eq. 7 to a current density j_2 , k_2 and therewith $k_{2,\text{ref}}$ are expressed in A/cm².

We convert the reaction rate from Eq. 5 to a current density and re-organize the coefficients in the following way:

$$j_1 = n \cdot \nu_1 = j_{c,eff}^0 \exp\left(\frac{-(1-\beta)nF}{RT}\eta\right)$$
[9]

where $j_{c,eff}^0$ is the effective or apparent exchange current density of the ORR which is given by

$$j_{\rm c,eff}^0 = rf \cdot j_{\rm c,ref}^0 \cdot [O_2]^{\gamma} \cdot [H_2 O]^m \cdot \theta_{\Box}^{\ n_{\Box}} \cdot \exp\left[\frac{-E_{\rm act,1}}{RT} \left(1 - \frac{T}{T_{\rm ref}}\right)\right] \quad [10]$$

with the roughness factor rf, the reference exchange current density $j_{c,ref}^0$, the activation energy $E_{act,1}$ and the exponents γ , m for the dependencies on the activities of the species. These parameters can be fitted independently of each other and allow therefore for more flexibility. In the steady-state, the coverage is constant in time, leading to

$$\frac{\partial \theta_{\Box}}{\partial t} = 0 \to \nu_2 = 0$$
[11]

Thus, the total current j equals the ORR current j_1 . With this, it is possible to write the equation of the steady-state coverage

$$\frac{\theta_{\Box}^{n_{\rm Pt}}}{1-\theta_{\Box}} = \frac{1}{n_{\rm Pt}} [O_2]^{-\frac{1}{4}} [H_2 O]^{-\frac{1}{2}} \exp\left(-\frac{F}{RT} \Delta U_{\rm eq}\right) \exp\left(-\frac{F}{RT} \eta\right)$$
[12]

and to discuss the asymptotic behavior of the model. In the low current limit ($j \rightarrow 0$, index "LC"), the denominator $1 - \theta_{\Box}$ of Eq. 12 approaches unity since the platinum surface is almost completely covered by oxides ($\theta_{\Box} \rightarrow 0$). By summarizing the first four terms of Eq. 12 in the constant C_1 and bringing the exponent $n_{\rm Pt}$ to the right side of the equation we get the approximation for the free platinum surface fraction:

$$\theta_{\Box}|_{j \to 0} = C_{1} \exp\left(-\frac{F}{n_{\rm Pt}RT}\eta\right)$$
[13]

This expression can be incorporated into the steady-state total current density equation which consists only in the ORR contribution and thus transforms to the low current form

$$j_{\rm LC} = C_2 \cdot \exp\left(-\frac{F}{RT}\left((1-\beta)n + \frac{1}{n_{\rm Pt}}\right)\eta\right)$$
[14]

In this case, the apparent steady-state Tafel slope b_{LC} is given by

$$b_{\rm LC} = -\frac{RT}{\left((1-\beta)n + \frac{1}{n_{\rm Pl}}\right)F}$$
[15]

In the opposite limit, at high current $(j \rightarrow +\infty)$, index "HC"), the electrode potential and the oxide coverage of the platinum surface decrease such as

$$\theta_{\Box}|_{j \to +\infty} = 1 \tag{16}$$

which means that the complete active platinum surface is available for the ORR, leading to the high current form

$$j_{\rm HC} = C_3 \cdot \exp\left(-\frac{(1-\beta)nF}{RT}\eta\right)$$
[17]

and thus to the apparent Tafel slope at high currents $b_{\rm HC}$

$$b_{\rm HC} = -\frac{RT}{(1-\beta)nF}$$
[18]

We see that Eqs. 15 and 18 only differ in the term $1/n_{\text{Pt}}$ which comes from the oxide formation and relaxation at low load and which we expect to cause the low-frequency inductive behavior of 30 mV dec⁻¹ to 50 mV dec⁻¹ that we observe experimentally (see below). At high load, where the apparent Tafel slope is solely influenced by the actual ORR step, this term disappears. This means that carrying out polarization and EIS measurements at small currents is enough to fix the product $(1 - \beta)n$ as well as n_{Pt} :

• $(1 - \beta)n \approx 0.66$ from the capacitive part of the EIS that represents -100 mV dec^{-1} to -120 mV dec^{-1} .

• $n_{\text{Pt}} \approx 2.5 - 3.3$ from the inductive part of the EIS that represents 30 mV dec⁻¹ to 50 mV dec⁻¹.

To compute polarization curves and EIS spectra and to fit the parameters of the model described above to our experimental data we built a simple 1D through plane performance model in the commercial software COMSOL Multiphysics (Version 6.0). The aim of this model is to propose an improved description of PEMFC performance and EIS compared to models containing Butler-Volmer or Tafel description of the ORR while still being easier to parameterize and to handle than complete MEA models which also solve energy and water management. The justification for not representing in-plane effects, i.e. along- and across-the-channel gradients, lies in the differential operating conditions and the test cell setup with wide gas channels on the cathode side (see the setup and procedures above). Variations of the cathode flow around our baseline conditions (see experimental) showed no influence on the cell response, thus we discarded along-the-channel effects. Small channel-land effects cannot completely be discarded, particularly at high cell currents where liquid water is present in the porous structures. However, the latter effects mainly affect oxygen transport which is represented in a simplified manner through effective diffusion coefficients in this 1D approach.

The model is represented schematically in Fig. 2a and contains three domains: the membrane (PEM), the cathode catalyst layer (CCL) and the cathode gas diffusion layer (CGDL). Neither the anode catalyst layer (ACL) nor the cathode gas channel (CGC) are modeled. Hence, the model reaches from the ACL/PEM boundary to the CGDL/CGC boundary. Four partial differential Eqs. are solved in the model: two Eqs. based on the current conservation and Ohm's law for the proton and for the electron potentials ϕ_p (PEM and CCL) and ϕ_e (CCL and CGDL), one equation for the free platinum surface fraction θ_{\Box} (only in the CCL), and one equation for the oxygen mole fraction x_{O_2} (CCL and CGDL) based on Fick's law of diffusion. These Eqs. were implemented as follows for the CCL:

$$\frac{C_{\rm dl}}{L_{\rm CCL}} \cdot \frac{\partial \Delta \phi}{\partial t} + \nabla (-\sigma_p \nabla \phi_p) = -\frac{n \cdot \nu_1 + \nu_2}{L_{\rm CCL}}$$
[19]

$$\frac{C_{\rm dl}}{L_{\rm CCL}} \cdot \frac{\partial \Delta \phi}{\partial t} + \nabla (-\sigma_e \nabla \phi_e) = \frac{n \cdot \nu_1 + \nu_2}{L_{\rm CCL}}$$
[20]

$$\frac{\Gamma}{L_{\text{CCL}}} \cdot \frac{\partial \theta_{\Box}}{\partial t} = -\frac{\nu_2 \cdot n_{\text{Pt}}}{L_{\text{CCL}} \cdot F}$$
[21]

$$\epsilon_{\rm p} C \frac{\partial x_{\rm O_2}}{\partial t} + \nabla (-CD_{\rm O_2} \nabla x_{\rm O_2}) = -\frac{n \cdot \nu_1}{L_{\rm CCL} \cdot 4 \cdot F}$$
[22]

Since the model is considered as being macro-homogeneous, the material properties are distributed homogeneously over the layer thicknesses and the source terms on the right side of the Eqs. need to be volumetric. In these equations, C_{dl} is the double layer capacitance in mF cm⁻², Γ the total quantity of surface platinum atoms in mol_{Pt}/cm²_{geo}, ϵ_p the porosity of the porous layer, *C* the total gas concentration in mol/m³ and D_{O_2} the effective diffusion coefficient of oxygen in m² s⁻¹. As can be seen, the mixed conductive nature of



Figure 2. (a) Schematic representation of our physical 1D through-plane model as implemented in COMSOL Multiphysics 6.0. The domains and corresponding physics plus external boundary conditions (black stars) are shown. (b) Exemplary distribution of the electrode potential ϕ_e , the electrolyte potential ϕ_p and the oxygen mole fraction x_{02} over the layer thickness for the baseline parameterization at RH = 80%, T = 80° C, $x_{02}^{dry} = 0.5$ and different cell currents. Model parameters are consistent with Table III, with one exception: The electrode conductivity $\sigma_{e,CCL}$ has been set unphysically low (5 S/m) to show its influence on the potential distribution. c) Corresponding distribution of the platinum oxide coverage in the CCL.

the electrode is modeled, which is necessary to reproduce experimental performance curves and EIS accurately. We set the electron conductivity very high to create only negligible losses (>500 S m⁻¹) and took the proton conductivities σ_p from our previous characterization study.³² The latter can be calculated based on the area specific resistances (*ASR*) shown in Fig. S4 and the layer thicknesses *L* given in Table III by $\sigma_p = L/ASR$.

So far, we did not model the water management (transport and ionomer hydration) explicitly in order to avoid too high complexity and only took the experimental data with high relative humidities for the parameterization and validation (see below). Particularly the EIS contributions of slow ionomer hydration/dehydration due to water management are not computed in the current model version. However, the impact of water management on the effective ionomer conductivities and thus on the performance is taken into account implicitly by employing the effective conductivities from our

Table III. Baseline parameters of the presented model.				
Design				
$L_{\rm PEM}$ (μ m)	18			
L_{CCL} (µm), ϵ_{p} (—)	13, 0.4			
L_{GDL} (μ m), ϵ_{p} (—)	180, 0.8			
$rf(m_{Pt}^2/m_{geo}^2)$	166			
$C_{\rm dl}$ & $C_{\rm dl,CV}$ (mF/cm ² _{geo})	30 & 50			
Operating conditions				
RH (%)	80			
<i>T</i> (° C)	80			
$x_{O_2}^{dry}$ (—)	1			
P (bar _a)	1.5			
Diffusion properties (at $T = 80$	° C)			
D_{O_2GDL} (cm ² /s)	$3.0 \cdot 10^{-2}$			
D_{O_2CCL} (cm ² /s)	$3.4 \cdot 10^{-4}$			
Kinetic properties				
	Tafel + PtOx	Tafel ³³		
n _{O2} (—)	0.5	0.5		
n (—)	2	2		
<i>n</i> _{Pt} (—)	2.5	—		
n_{\Box} (—)	1	—		
β (—)	0.66	0.5		
$\Gamma (\text{mol/cm}_{\text{geo}}^2)$	$1.44 \cdot 10^{-7}$	—		
$\Delta U_{\rm eq}$ (V)	0.42	_		
$j_{c,ref}^0$ (A/cm _{Pt} ²)	$1.92\cdot 10^{-6}$	$2.13 \cdot 10^{-8}$		
$k_{2,\text{ref}} (\text{A/cm}_{\text{geo}}^2)$	$7.07\cdot 10^{-7}$	-		
γ (—)	0.54	0.51		
<i>m</i> (—)	0.50	0.49		
$E_{\rm act,1}$ (kJ/mol)	60.5	68.7		
$E_{\rm act,2}$ (kJ/mol)	0	—		

experiments as functions of the gas channel relative humidity, the temperature and the current density. This means that no throughplane distribution of the conductivities is considered and especially that the membrane behaves like a purely Ohmic element (linear potential profile over the PEM). On this PEM layer, only the following equation is solved:

$$\nabla(-\sigma_p \nabla \phi_p) = 0$$
^[23]

Finally, on the GDL layer, electron and oxygen transport were computed respectively according to

$$\nabla(-\sigma_e \nabla \phi_e) = 0$$
 [24]

and

ŧ

$$\mathcal{E}_{\rm p}C\frac{\partial x_{\rm O_2}}{\partial t} + \nabla(-CD_{\rm O_2}\nabla x_{\rm O_2}) = 0$$
[25]

The external boundary conditions for our simulations were the following:

• Dirichlet boundary $\phi_e = \phi_p = 0$ V at the anode—membrane interface (ACL–PEM) as an approximation of the anode half-cell potential.

• Neumann boundary $j = j^{\text{setpoint}}$ at the cathode gas diffusion layer—cathode gas channel interface (CGDL—CGC) to match the current setpoints of our experiments. For the EIS calculations we used the dynamic Neumann boundary condition j = j(t) and for the cyclic voltammetry simulations we used the dynamic Dirichlet boundary condition U = U(t).

• Dirichlet boundary $x_{0_2} = x_{0_2}^{\text{setpoint}}$ at the CGDL—CGC interface representing the oxygen mole fraction in the gas channel to match our experiments.



Figure 3. (a) Time traces of a galvanostatic EIS simulation at *j*=0.1 A/cm², $T = 80 \degree$ C, RH = 80 % and $x_{02}^{dry} = 1$ for our baseline parameterization without considering mass transport contributions and setting $\sigma_{p,CCL} = 0.5 \text{ S/}$ m and $\sigma_{p,PEM} = 5 \text{ S/m}$. The excitation current (blue line, exponential step at $t = 10^{-15}$ s), the potential response for a Tafel law (dashed black line) and for our new model (solid red line) and the corresponding resistance assessment are shown. (b) Resulting EIS spectra in the Bode plot.

Computation of EIS and polarization curves.—Polarization curves were simulated galvanostatically to match the currents selected during our experiments. In Figs. 2b and 2c we show typical through-plane distributions of the field variables of our model for the different current setpoints. This was simulated with our baseline parameterization given in Table III at RH = 80%, T = 80 °C and $x_{O_2}^{dry} = 0.5$. Only the electronic conductivity $\sigma_{e,CCL}$ has been lowered in this example to show its influence on the potential distribution



Figure 4. (a) Time traces of a cyclic voltammetry simulation (potentiostatic ramp up and ramp down) at 100 mV/s, T = 50 °C and RH = 80 %. (b) Corresponding cyclic voltammogram in the representation *j* vs *U* (solid red line) and exemplary experimental CV (dashed black line). Hydrogen adsorption and the explicit dynamics of fast Pt oxidation effects are not modeled (see main text).

within the CCL. It can be observed that all the trends are linear within the PEM and the GDL layers; however, these trends are nonlinear within the mixed-conducting CCL because of the sources and sinks due to the ORR. It is also interesting to notice that at current densities above 0.5 A cm^{-2} in Fig. 2c the platinum oxide coverage drops toward zero at the PEM/CCL interface even though it remains almost as high as 50% at the CCL/CGDL interface. Thus, even at typical high current densities, the catalyst is not completely oxide free and the effective exchange current density and Tafel slope of the ORR are distributed inhomogeneously over the CCL. Note that this effect comes from the fact that all the kinetics locally depend on the difference between the electrolyte and the electrode potentials. Therefore, even if $\sigma_{e,CCL}$ is not lowered, the effect remains almost as pronounced as in Fig. 2c. In the latter more realistic case, the electrode potential is constant through the CCL but the electrolyte potential is still strongly inhomogeneous due to the relatively low ionomer conductivity of the CCL in comparison with its electronic conductivity.

EIS spectra were simulated by applying a small current step on top of the DC load as described by Bessler.³⁵ The steady-state solution of each DC load was computed before performing an exponential current step $j_{step} = 2 \text{ mA cm}^{-2}$ according to

$$j(t) = j_{\rm DC} + j_{\rm step} \cdot \left[1 - \exp\left(-\frac{t}{\tau}\right) \right]$$
[26]

with $\tau = 10^{-9}$ s. The simulated time window was defined from 10^{-15} s to 10^7 s with a logarithmic time step distribution with 10 points per decade. After the simulation, a point was added artificially at $t = 10^{15}$ s to slowly bring the system back to its original state. Then, the DC state was subtracted from the time trace of j(t) and $\phi_e(t)|_{\text{GDL/GC}} = U(t)$ as shown exemplarily in Fig. 3a (only displacement from steady-state point remaining) and the Fourier transform of

these signals into the frequency domain was computed, followed by complex division to obtain the impedance: 35

$$Z^*(\omega) = U^*(\omega)/j^*(\omega)$$
[27]

In the example shown in Fig. 3a, mass transport contributions were not taken into account and the protonic conductivities were set to $\sigma_{p,PEM} = 5 \text{ S m}^{-1}$ and $\sigma_{p,CCL} = 0.5 \text{ S m}^{-1}$. The associated impedance responses are shown in Figs. 3b (Nyquist) and 3c (Bode), where the red curves originate from our new kinetics model and the black curves come from a Tafel kinetics model for the ORR. It is apparent that in contrast to the Tafel kinetics, our new description leads to an inductive loop. Since both EIS spectra converge to the same value for $f \rightarrow 0$ Hz, the effective differential resistance (local slope of the polarization curve) of both models is equivalent. Regarding only the kinetics, both models yield approximately $b = -70 \text{ mV dec}^{-1}$:

• Tafel: high-frequency capacitive loop of -70 mV dec^{-1} .

• New kinetics with PtOx: high-frequency capacitive loop of -110 mV dec^{-1} to -100 mV dec^{-1} and low-frequency inductive loop of 30 mV dec⁻¹ to 40 mV dec⁻¹.

This step method to compute EIS has already been used in the PEMFC context by Kosakian et al.,¹⁷ who showed its equivalency to the sine wave technique that requires a complete transient study for each frequency of the spectrum and is therefore way more demanding for computational time. The Fourier transform of the non-equispaced signals in time (logarithmic distribution) was calculated by the method which was first proposed by Wiese and Weil and also used by Bessler and Kosakian et al. for instance (see the corresponding publications for more details^{17,35,36}).

Additionally, we carried out cyclic voltammetry (CV) simulations by ramping the voltage up and down at 100 mV s^{-1} (red curve) and recording the current response (blue curve) as shown exemplarily in Fig. 4a. Since we model neither hydrogen sorption nor desorption kinetics, only one oxidation and one reduction peak coming from the slow platinum oxidation kinetics can be seen above 0.5 V in the resulting simulated CV in Fig. 4b (red curve). Fast kinetics effects, i.e. features which are present in the capacitive loop of the EIS, are not disentangled and thus taken into account implicitly through the parameterization of the ORR step. We added an experimental CV for comparison (dashed black line) to point out the limitations of our model compared to other more sophisticated models that match the experimental CVs better;⁹ however, as shown in the results below, this model offers a good compromise between accuracy and simplicity as it is easier to parameterize than other literature models and fits both experimentally gathered steady-state polarization curves and EIS spectra well. Hence, it helps understanding the commonly known discrepancies between steadystate and dynamic performance signatures of PEM fuel cells.

Results and Discussion

Bias between steady-state and EIS evaluation.—In our previous work, we focused on the cathode kinetics which cause a major loss contribution at relevant operating points.³³ We parameterized models based on polarization curves that were corrected for the Ohmic contributions R_0 and R_p^{eff} and demonstrated that neither oxygen transport nor anode contributions significantly affect the characterization of the ORR at low current densities. Due to the sluggish kinetics of the ORR, the overpotentials are usually quite high even at low loads and thus simple Tafel kinetics are assumed to take place according to

$$\eta_{\text{ORR}} = -\frac{RT}{\alpha_c F} \cdot \ln \frac{j}{j_{c\,\text{eff}}^0}$$
[28]

where η_{ORR} is the kinetic overpotential, α_{c} the transfer coefficient (= $(1 - \beta)n$), j the current density and $j_{\text{c,eff}}^0$ the effective exchange



Figure 5. (a) Steady-State polarization curve with Ohmic corrections and corresponding ORR Tafel analysis. (b) Equivalent circuit model (ECM) of the cell in H₂/O₂ configuration. (c) Representative EIS spectrum measured at 0.3 A cm⁻² and corresponding Tafel slope resulting from $R_{\rm ct}$ (yellow box). (d) Tafel slope |b| over the relative humidity based on the slope of the polarization curve for $j \leq 0.2$ A cm⁻² (hollow symbols) and based on the slope obtained by the charge transfer resistance $R_{\rm ct}$ recorded at j = 0.1 A cm⁻² (full symbols).

current density. Our ORR parameterization was consistent with previous literature findings that were also based on steady-state investigations and we found $\alpha_c = 1$, leading to Tafel slopes $b = -RT/(\alpha_c F) \approx -70$ mV dec⁻¹. This is depicted in Fig. 5a, where the blue curve which is corrected for the ionomer contributions yields a slope of around -70 mV dec⁻¹ at small to medium current densities and slightly higher slopes at high current densities due to combined anode and oxygen transport contributions (see our previous publication³³).

Nevertheless, we pointed out that these kind of models show inconsistencies with EIS-based determination of the Tafel slope, which is directly linked to the charge transfer resistance R_{ct} by

$$\frac{\partial \eta_{\text{ORR}}}{\partial j} = -\frac{RT}{\alpha_{\text{c}}Fj} = \frac{b}{j} = -R_{\text{ct}}$$
[29]

EIS data usually yield slopes that are higher, which is also illustrated in Fig. 5: in Fig. 5b we show a transmission line model (TLM) that is typically used to evaluate the impedance response of PEM fuel cells under the assumption of negligible oxygen transport and anode resistance, thus that the impedance is dominated by the membrane and the cathode contributions. The parameters of this ECM can be fitted to match a low-current-density spectrum like the one shown exemplarily in Fig. 5c, measured from 100 kHz to 0.1 Hz and cut at 1 Hz. According to Eq. 29, the absolute Tafel slope |b| is obtained by multiplying the diameter of the semicircle in Fig. 5c ($\approx 160 \text{ m}\Omega \text{cm}^2$) with the current density (0.3 A cm⁻²) and results in 0.048 V·ln(10)·1000 = 111 mV dec⁻¹.

The bias between the slope of the corrected polarization curve and $R_{\rm ct}$ therefore represents around 30 to 40 mV dec⁻¹ at small current densities and is depicted depending on RH and T in Fig. 5d. Overall, these discrepancies can be explained by the presence of low-frequency inductive features occurring below 0.1 Hz that are not visible in the spectrum in Fig. 5c. In steady-state, the local slope of the polarization curve must equal the low-frequency impedance where the Nyquist plot intercepts the real axis (differential cell resistance, in theory when the frequency f converges to 0 Hz). However, as seen above in Fig. 1, the EIS spectra show lowfrequency inductive features besides the capacitive contributions at frequencies below 0.1 Hz, which has been demonstrated early by Mathias et al.³⁸ This proves that typical EIS investigations limited to frequencies above 0.1 Hz or 1 Hz in the literature are incomplete and that the equivalent circuit in Fig. 5b is unable to describe the whole frequency range of PEMFC operation. At higher current densities, this bias between steady-state polarization and capacitive EIS gets even larger and our findings are therefore in agreement with those of Schiefer et al.,³⁰ who reported inductive loops the size of up to 50%of the capacitive loops. Hence, the LF inductive behavior plays a major role in PEMFC performance and needs to be understood.

According to our summarized literature overview in Table I containing both experimental and theoretical studies, two explanations to the low frequency inductive behavior are prominent. On the one hand, slow ionomer humidification effects that decrease the ionomer resistance in course of increased water production when increasing the current may be responsible. On the other hand, nontrivial ORR kinetics with intermediates or platinum oxidation phenomena at high cathode half-cell potentials may be another source of LF inductivities. A large number of investigations have been carried out in the last 20 years and yet, to our knowledge, there has not been an attempt to properly apportion these contributions based on a combined experimental and numerical approach. In simulation studies, the inductive loops are mostly investigated with models containing either detailed cathode kinetics (ORR with intermediates and/or platinum oxide kinetics) or water dynamics effects. Some models consider both effects, but the validation to experimental data is often insufficient. This lack might be due to the difficulty of measuring EIS at frequencies as low as 100 mHz down



Figure 6. (a) Local slope of the polarization curve over the current density at RH = 30%, T = 80 °C and $\alpha_{O_2} = 1$ based on the numerical derivative of the polarization curve and based on the low-frequency *x*-axis intercept of the EIS spectra ($f \approx 1$ Hz). (b) Low-frequency inductive contribution $-R_{ind}$ over the current density at T = 80 °C and $x_{O_2} = 0.5$ for a variation of *RH*, computed for each condition by calculating the difference of the two curves shown exemplarily in (a). (c) Representation of the inductive contribution in mV/ dec over the current density *j* depending on the relative humidity and the oxygen concentration at T = 80 °C.

to 1 mHz because of instabilities in course of the long measurement durations.

Subramanian et al. managed to parameterize a simple steady-state model for the ORR extended by oxide coverage effects solely by fitting polarization data.³⁹ They stuck to their steady-state description of the potential-dependent change in the electrochemical surface area (ECSA) and did not investigate the dynamical cell response, even though their model would certainly yield inductive effects due to the PtOx kinetics. Moreover, such a parameterization is challenging, too, since in medium to high-loaded cathodes the halfcell potential is usually high in typical operating ranges and therefore a change in the apparent Tafel slope cannot be unambiguously discerned (see our previous publication³³). Meyer et al.³¹ recently showed that the size of the inductive loop during galvanostatic EIS can be controlled by provoking oscillations in the oxygen mass flow at the same frequencies as the current oscillations. They observed only small incomplete inductive semicircles during their normal EIS and were capable of getting completely closed loops by oscillating with the mass flow controllers: however, in our case we clearly see the inductive behavior even at the lowest currents (highest stochiometries $\lambda \gg 10$, differential conditions) and mass flow variations revealed no influence on the size of our inductive features. We thus discard this hypothesis and other along-the-channel effects and only investigate the two first assumptions in more detail in the next sections.

Evaluation of the low-frequency inductive loop.—To quantify the low-frequency inductive part of the EIS spectra we computed two quantities. The first one was the local slope of the steady-state polarization curve, obtained by numerical derivation and expressed in mV/dec by

$$\left| \frac{\partial U}{\partial \ln j} \right| = \left| \frac{\Delta U}{\Delta \ln j} \right| \cdot \ln(10) \cdot 1000$$
 [30]

The second was the low-frequency real-axis-intercept of the capacitive part of the EIS spectra (capacitive polarization resistance), where Im(Z)=0 and $f \approx 1$ Hz. Its equivalent local slope in mV/dec was computed via

$$\left| \frac{\partial U}{\partial \ln j} \right| = R_{\text{pol}} j \cdot \ln(10) \cdot 1000$$
 [31]

Figure 6a depicts these two quantities over the current density for hot and dry conditions with pure oxygen in the dry cathode gas $(T = 80^{\circ}, RH = 30\%$ and α_{O_2}). As can be seen, the capacitive part of the EIS yields higher slopes than the polarization curve derivative over the whole current density range. The amount of the discrepancies are however dependent on the operating conditions (see Fig. S2). The inductive contribution is then simply defined as the difference between the two corresponding polynomial fitting curves and can be expressed as a negative differential resistance in Ω cm² as shown in Fig. 6b. This simple and rapid technique gives the size of the inductive contribution but misses the frequency information, which is needed to determine the time constants of the processes. The parameter study in Figs. S6 to S29 shows the quantities that affect the time constant of the inductive loop caused by the PtOx kinetics according to our new model. Some of these parameters also strongly affect the performance and EIS response and can therefore be fitted, others are taken from the literature or estimated in order to give meaningful results (see parameterization below).

From Fig. 6b it gets clear that the behavior of the inductive contribution is non-linear with the current density and that there is a non-negligible dependency on the relative humidity, with low RH leading to higher LF inductivities even at the lowest load point. Figure 6c depicts the LF inductive contribution in terms of a slope in mV/dec and shows that there is no significant dependency on the oxygen partial pressure at small to medium current densities; at high currents, however, such a dependency can be observed as the inductive contribution slightly increases with decreasing oxygen partial pressure at both high and low humidity. This observation is discussed in more details below. Since the slope of the curves at dry conditions is higher than the slope of the curves at humid conditions, we speculate that all the curves merge at current densities even lower than 0.02 A cm^{-2} . Furthermore, this Fig. demonstrates that even though the inductive features are the smallest at low current densities, they decrease the local slopes of the polarization curve



Figure 7. (a) Low-frequency contribution of the membrane humidification dynamics over the current density for varying gas channel humidity levels at T = 80 ° C. (b) Same as in (a) but for the CCL humidification contribution. (c) Size of the low-frequency inductive contribution over the current density at T = 80 °C for wet (RH = 80 %, solid black line) and dry (RH = 30 %, dashed black line) conditions and corresponding corrections by the LF membrane contributions (blue lines) and by the LF membrane and CCL contributions (red lines).

by up to almost 50 mV dec⁻¹ depending on the operating conditions. Then, the inductive contribution increases with increasing current density. The lower the gas humidity and the oxygen partial pressure are, the faster the inductive loop increases with current density (higher slope of the curves in Fig. 6c at low *RH* and low p_{O_2}). Additional conditions can be found in the Figs. S2 and S3.

Based on the assumption that the overpotentials caused by proton transport in the membrane and in the cathode catalyst layer follow Ohms law, which is a sufficiently good compromise between complexity and accuracy, we have

$$|\eta_{\rm PEM}| = R_{\rm PEM} \cdot j$$
[32]

for the membrane, with η_{PEM} the potential drop caused by the membrane, R_{PEM} the high-frequency membrane resistance and *j* the cell current density. For the CCL we have

$$|\eta_{\rm CCL}^{\rm H^+}| = R_{\rm p}^{\rm eff} j$$
[33]

with $\eta_{\text{CCL}}^{\text{H}^+}$ the potential drop due to proton transport in the CCL and R_p^{eff} the effective CCL sheet resistance that follows $R_p^{\text{eff}} \approx (1/3) \cdot R_p$. The resistances R_{PEM} and R_p are inversely proportional to the conductivity of the corresponding layer.³² Considering the results of our previous publication³² we can compute the absolute value of the impedance caused by proton transport in the membrane according to

$$\left|\frac{\partial \eta_{\text{PEM}}}{\partial j}\right| = R_{\text{PEM}} + j \cdot \frac{\partial R_{\text{PEM}}}{\partial j}$$
[34]

It is important to note that the membrane resistance R_{PEM} is included in the high-frequency intercept R_{Ω} of the EIS spectra, which comprises also the electronic bulk and contact resistances of the setup. However, the latter contributions are assumed to be constant and do therefore not affect the derivative term (last term) in Eq. 34. Thus, we have

$$j \cdot \frac{\partial R_{\text{PEM}}}{\partial j} = j \cdot \frac{\partial R_{\Omega}}{\partial j}$$
[35]

which represents the contribution from the changing membrane resistance during operation caused by the production of water and thus ionomer hydration. In this work we do not attempt to quantify time constants for this process but assume that it entirely contributes to the evaluated LF inductive loop. Its inductive nature is confirmed by the fact that its sign is always negative in our case because the resistance R_{PEM} decreases with increasing current density. Moreover, this contribution is expected to appear at low frequencies in the EIS since it is linked to slow water management effects. With thicker membranes, however, the sign could supposedly become positive in some cases where the EOD contribution dries out the membrane at higher currents.

Taking the ionomer resistances as a function of the current density from our previous publication³² shown in Fig. S4, we can compute their derivatives numerically and determine the terms of Eq. 35. Then, based on these low-frequency (LF) terms we calculate equivalent Tafel slopes $b_{ionomer}^{LF} = j^2 \cdot (\partial R_\Omega / \partial j)$. These Tafel slopes contribute to the complete apparent Tafel slope of the polarization curve and can be presented in mV/dec as in Fig. 7a by calculating $j^2 \cdot |(\partial R_\Omega / \partial j)| \cdot \ln(10) \cdot 1000$. Therefore, these contributions are proportional to j^2 . We see that the low-frequency membrane contribution due to changes in the humidification is negligible at low current densities since it only gets visible above 0.2 A cm^{-2} for dry conditions. At RH = 30% we barely reach 30 mV dec⁻¹ at 1 A cm⁻² and at RH = 90% we do not see any contribution at all. Following the same logic for the proton resistance in the cathode catalyst layer we get

$$\frac{\partial \eta_{\text{CCL}}^{\text{H}^+}}{\partial j} = R_p^{\text{eff}} + j \cdot \frac{\partial R_p^{\text{eff}}}{\partial j}$$
[36]

The contribution of the second term of this equation to the apparent Tafel slope is illustrated as $j^2 \cdot |(\partial R_p^{\text{eff}}/\partial j) \cdot \ln(10) \cdot 1000|$ in Fig. 7b similarly to the membrane contribution $(\propto j^2)$. Even though this CCL

contribution is generally higher than the one of the membrane, it is still negligible below 0.2 A cm^{-2} at any conditions. Hence, even the sum of both ionomer hydration contributions remains very small at current densities below 0.2 A cm^{-2} . Especially the inductive loop of 30–40 mV dec⁻¹ at the smallest current density in Fig. 7c cannot be explained by such contributions. The diagrams corresponding to Figs. 7a and 7b for T = 50 °C can be found in Fig. S5.

The total LF inductive contribution over the current density (black curves) for dry (RH = 30%, dashed lines and hollow symbols) and wet (RH = 80%, solid lines and full symbols) conditions and the corresponding curves minus the ionomer hydration contributions are depicted in Fig. 7c. The blue curves with the square markers represent the total inductivity minus the membrane contribution, and the red curves with the diamond markers represent the total inductivity minus both membrane and CCL contribution. Thus the red curves supposedly contain mainly the LF inductivity caused by the PtOx kinetics, representing $30-40 \text{ mV} \text{ dec}^{-1}$ at very small currents. All the solid curves start with an almost completely flat slope at small currents and overlap over a wide range, highlighting again that the ionomer humidification does not significantly influence the LF inductive loop at humid conditions. Yet, the dashed curves have a steeper slope at small to medium current densities and begin diverging at $0.1 \,\mathrm{A}\,\mathrm{cm}^{-2}$, proving that ionomer humidification effects on the LF inductive features cannot be neglected at dry conditions. Since particularly the dashed red curve exhibits a small positive slope at low currents, we believe that another small humidity-dependent effect is contained in the LF inductive loop, which leads to the gap of 10 mV dec⁻¹ between the RH = 30% and the RH = 80% conditions. One explanation might be the presence of an additional ionomer humidification term coming from the transmission line structure of the CCL which is not considered in Eq. 36. Such a term was recently derived by Kulikovsky under the assumption that the CCL conductivity increases linearly with the current density.¹⁸ This term provoked an inductive contribution in mV/dec increasing linearly with *j*, in contrast to the second term of Eq. 36 which leads to a contribution proportional to j^2 as shown above.

Other humidity-dependent effects could also be envisaged, for example related to the humidification of the anode catalyst layer (ACL). Some authors assumed an influence of water activity on the anode reaction kinetics (HOR, hydrogen oxidation reaction),^{14,15} which would also lead to LF inductive effects. We could neither confirm nor deny the presence of such contributions from the ACL based on the current dataset. However, in our previous publication we showed that the anode contribution to the performance is generally very small,³³ therefore we do not believe that such contributions could be responsible for the gap observed between the wet and dry conditions.

Finally, as already mentioned for Fig. 6c, the wet and dry curves are very close to each other and might converge at very low current densities in Fig. 7c according to the trend. Since mainly PtOx kinetics contributions are present at such low load, this means that the relative humidity has only little or no influence at all on them, which is supported by our model (see Fig. S20). At higher current densities, both red curves eventually drop, which is linked to the decreasing presence of platinum oxides due to the lower cathode half-cell potentials.

Considering that the ORR follows simple Tafel kinetics in each point as in Eq. 28, the kinetics overpotential can be written in a simplified manner as

$$\eta_{\rm ORR} = b \ln \frac{j}{j_0}$$
[37]

where *b* is the Tafel slope, *j* the current density and j_0 the effective exchange current density. As explained above, Tafel kinetics with a constant intrinsic Tafel slope *b* do not lead to LF inductive processes in the EIS spectra. Thus, a model as ours that takes into account the slow poisoning effect of platinum oxide formation happening within

the CCL at high cell voltages is needed to investigate the LF contributions of the ORR kinetics. If one assumes that neither *b* nor j_0 are constant over the current density, the total impedance caused by the ORR can be written as

$$\frac{\partial \eta_{\text{ORR}}}{\partial j} = \frac{b}{j} + \frac{\partial b}{\partial j} \ln\left(\frac{j}{j_0}\right) - \frac{b}{j_0} \cdot \frac{\partial j_0}{\partial j}$$
[38]

where the first term b/j equals $-R_{\rm ct}$ which is the well-known charge transfer resistance from the Tafel law. The two other terms depend on the change in the Tafel slope and the exchange current density over the current density and can be determined by a more sophisticated model as presented in this work. In the next section, our model is parameterized and validated with experimental data and the behavior of $b_{\rm apparent}$ as well as $j_{0,\rm effective}$ is investigated for our baseline conditions.

Model parameterization and validation.—A complete variation of all the relevant model parameters and their influence on the steady-state polarization curves, the EIS response and the cyclic voltammetry is shown in Figs. S6 to S29 in the supplementary material and gives some deep insights into our model. The focus of this section, however, is the parameterization and validation. In Fig. 8 we depict the experimental and simulated Ohmic-contributions-corrected steady-state polarization curves used in the fitting procedure (Figs. a and c) and the respective simulated platinum oxide coverage (Figs. b and d). Here, no mass transport contributions were taken into account in the model and only currents up to $0.2 \,\mathrm{A}\,\mathrm{cm}^{-2}$ were used in the fitting procedure. Further, we did not consider low relative humidity conditions here since our model does not account for the water management effects discussed above. To simulate dry conditions accurately, a complete MEA model would be needed, which goes beyond the scope of this work. To summarize, we used both EIS and steady-state polarization data at RH = 80% and $j \le 0.2$ A cm⁻² to parameterize the model. We fixed the values of Γ and $k_{2,ref}$ by adjusting them to three requirements: (1) being physically meaningful (i.e. with the order of magnitude of Γ being in line with a Pt atomic surface density of $2.17 \cdot 10^{-9}$ mol/ cm_{Pt}^{2} ⁴²), (2) matching the 0.6 V shoulder in the experimental CV, (3) yielding a consistent time constant of the inductive process in the EIS (between 10 mHz and 1 Hz³⁰). However, based on this dataset we could not precisely determine the time constant and solely focused on the absolute contribution of the low-frequency inductive features as mentioned above. We thus considered all the fast capacitive kinetics effects equivalently in the parameterization of the ORR step and the slow inductive kinetics effects equivalently in the PtOx parameterization.

In Figs. 8a and 8b we show an oxygen mole fraction variation at $T = 50 \text{ }^{\circ}\text{C}$ and $T = 80 \text{ }^{\circ}\text{C}$ and in Figs. 8c and 8d a variation of temperature for $x_{O_2}^{dry} = 1$ and $x_{O_2} = 0.16$. The model matches the experimental points well for currents up to 0.5 A cm⁻² and the deviation gets only larger at higher currents, probably because of inaccuracies in the protonic loss correction as well as mass transport issues that were not accounted for. Further, even though the apparent Tafel slope increases continuously with increasing current density due to the decreasing oxide coverage, it is almost impossible to detect any change with the naked eve until corrected cell voltages of around 0.75 V (corresponding to remaining coverages of about 10% to 30%), which confirms that simple steady-state models with a single Tafel slope and exchange current density can easily fit such polarization data at low to medium current density. It is known, however, as mentioned previously, that simple Butler-Volmer and Tafel models cannot reproduce both the steady-state and the dynamic response observed in PEMFC as there are discrepancies in the resulting Tafel slopes between the polarization curves and the EIS response. Our new simple model aims at resolving this issue. Thus, we also computed EIS spectra for all the operating points to tune the parameters even further and improve results. As can be seen



Figure 8. (a) Experimental (symbols) and simulated (lines) polarization curves in the Tafel representation for a variation of x_{O_2} at T = 50 °C and T = 80 °C. (b) Corresponding curves of the platinum oxide coverage. (c) Experimental (symbols) and simulated (lines) polarization curves in the Tafel representation for a variation of T at $x_{O_2}^{dry} = 1$ and $x_{O_2} = 0.16$. (d) Corresponding curves of the platinum oxide coverage. All the data were gathered at RH = 80% and the simulations were carried out without considering mass transport contributions.

in Fig. 9, the simulated capacitive parts of the EIS spectra also match the experiments well up to 0.5 A cm^{-2} and deviations can only be observed above this current density as the simulated resistances seem to be too low.

Figure 10a displays the results of our parameterization for our baseline condition (RH = 80%, T = 80 ° C, $x_{O_2}^{dry} = 1$). The experimental R_{ct} was obtained by fitting a transmission line model (TLM) to our EIS as explained in our previous publication³³ and the corresponding $|R_{ind}|$ was obtained as explained above and shown in Fig. 6a. Model responses are represented by the solid lines and the dashed line represents the model results plus the low-frequency inductive contribution from the ionomer humidification effects determined in Fig. 7. The good agreement between model and experiment for both the high-frequency capacitive R_{ct} and the lowfrequency inductive $|R_{ind}|$ is emphasized in Fig. 10a. The match of the capacitive charge transfer resistance is good over the complete current density range and the match of the inductive part caused by the PtOx kinetics (solid line) is good for currents up to 0.5 A cm⁻⁻ Above these currents, the model prediction for the inductive contribution is slightly too small because of the other effects that are not taken into account including the slow ionomer humidification (see explanation above). We can take this effect into account nonetheless by adding it to the model prediction (dashed line, see the investigation of the ionomer behavior above). This yields better results at high current densities even though the match is not perfect, probably because of the decreasing accuracy in determining the ionomer contributions at high current densities caused by two reasons: the decreasing fitting quality and the increasing error of the numerical derivation due to the limited number of sampled load points. However, owing to the good agreement of this new simple model with our consistent dataset we can say that we made a step forward in reconciling steady-state and EIS signatures in PEM fuel cells.

Based on computed polarization curves corrected by the Ohmic contribution, $U_{jR-\text{free}} = f(j)$, an apparent differential Tafel slope of the cathode kinetics can be determined by numerical derivation according to

$$b_{\text{apparent}}| = \left| \frac{\partial U_{jR-\text{free}}}{\partial \ln j} \right|$$
 [39]

and given this apparent slope $b_{\rm apparent}$, the effective exchange current density of the ORR can be calculated using

I

$$i_{0,\text{effective}} = \frac{j}{rf} \cdot 10^{\left|\frac{\eta}{b_{\text{apparent}}}\right|}$$
[40]

These two quantities are depicted in Fig. 10b as functions of the current density *j* at our baseline conditions. As previously shown in the literature, for example based on microkinetic modeling of the ORR, both $|b_{apparent}|$ and $j_{0,effective}$ increase with increasing current density and thus decreasing cathode half-cell potential.⁴⁰ In our case, the absolute apparent Tafel slope curve starts between 60 and 70 mV dec⁻¹ at low load with a flat slope and tends to increase toward 90 mV dec⁻¹ while the slope gets steeper with increasing load. Comparably, the effective exchange current density increases by almost three orders of magnitude over the investigated current range, from 10^{-9} A/cm²_{Pt} to 10^{-6} A/cm²_{Pt}. For comparison, the effective exchange current density we found in our previous publication for the ORR based on the Tafel approximation lies at around $2.15 \cdot 10^{-8}$ A/cm²_{Pt}, with $\alpha_c = 1$ leading to |b| = 70 mV dec⁻¹ at T = 80 ° C. Such values are attained at approximately 0.2 A cm⁻² with our new model.

Mass transport contributions.—In this Section we took mass transport contributions into account through Fick's law of diffusion



Figure 9. Experimental (dots) and simulated (lines) EIS spectra at RH = 80%, T = 80 °C and $x_{O_2}^{dry} = 1$ for the cell currents shown in the polarization curves in Fig. 8. (a) and (d) Nyquist representations. (b), (c), (e) and (f) Bode representations. All the data were gathered at RH = 80% and the simulations were carried out without considering mass transport contributions.



Figure 10. (a) Experimental (symbols) and simulated (lines) charge transfer resistance R_{ct} and inductive contribution $|R_{ind}|$ over the current density *j* at RH = 80%, T = 80 °C and $x_{O2}^{dry} = 1$. The experimental R_{ct} was obtained by fitting EIS data to an equivalent circuit model and $|R_{ind}|$ was obtained as described in Fig. 6a. The lines correspond to our model without mass transport contributions and the dashed line was added including the ionomer contributions determined in Fig. 7. (b) Corresponding apparent Tafel slope |b| and effective exchange current density j_0 .

(see model description above) to further improve the match between the experiments and simulations. We focused on the T = 50 °C and T = 80 °C conditions and determined independent oxygen diffusion coefficients for the GDL and the CCL by fitting the high current density parts of the polarization curves at T = 80 °C and respecting the proportionality $D \propto T^{3/2}$:

•
$$T = 50$$
 ° C: $D_{O_2,GDL} = 2.6 \cdot 10^{-2} \text{ cm}^2 \text{ s}^{-1}$, $D_{O_2,CCL} = 2.8 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1}$
• $T = 80$ ° C: $D_{O_2,GDL} = 3.0 \cdot 10^{-2} \text{ cm}^2 \text{ s}^{-1}$, $D_{O_2,CCL} = 3.2 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1}$

These values lie in the same orders of magnitude as values determined previously in the literature for instance by Kulikovsky.⁴¹ The complete set of parameters of this enhanced model is depicted in Table III. As shown in Fig. 11, considering these mass transport features leads to simulated EIS that correspond better to the experiments at high currents as there are only small deviations even at $j \ge 0.5$ A cm⁻². Further, the polarization curves in Fig. 12a match the measurements well even at high current densities, pointing out again that this model is suited for modeling both steady-state performance and EIS features of PEM fuel cells despite its simplicity. Comparing the new oxide coverage in Fig. 12b with the previous, mass transport free coverage in Fig. 8b indicates that this parameter remains almost unaffected by the change in the model at small and medium loads. Differences can be observed at high currents since the oxide coverage is lower than before due to the lower cathode half-cell potential. This effect increases with decreasing oxygen partial pressure.

Finally, the EIS spectra of a p_{O_2} variation at j = 0.2 A cm⁻² in Fig. 13 highlight that even though it is impossible to probe partial pressure effects on the local slope of polarization data at such small current densities, EIS is capable of sensing these contributions. Our model containing mass transport contributions predicts an increasing capacitive loop with decreasing oxygen partial pressure due to the increasing oxygen mass transport resistance and is in accordance with the experimental data. Further, the model predicts a slightly lower inductive contribution at lower partial pressure, which is in



Figure 11. Experimental (dots) and simulated (lines) EIS spectra at RH = 80%, T = 80 °C and $x_{O_2}^{dry} = 1$ for the cell currents shown in the polarization curves in Fig. 8. (a) and (d) Nyquist representations. (b), (c), (e) and (f) Bode representations. All the data were gathered at RH = 80% and the simulations were carried out considering oxygen mass transport through GDL and CCL by Fick's law of diffusion.

agreement with our expectation because the half-cell potential gets lower with decreasing partial pressures and so does the oxide coverage. However, above $0.1 \,\mathrm{A \, cm^{-2}}$, the data in Fig. 6c show



Figure 12. (a) Experimental (symbols) and simulated (lines) polarization curves in the Tafel representation of a variation of x_{02} at T = 50 °C and T = 80 °C for RH = 80% considering mass transport contributions by Fick's law. (b) Corresponding curves of the platinum oxide coverage.

slightly higher inductive contributions at lower partial pressures, which is not linked to the platinum oxide kinetics and thus cannot be simulated by the model. Such behavior could probably be explained by a beneficial transport effect that is strongest at small partial pressures (not integrated in our model), for instance due to an improvement in the oxygen diffusion through a more humidified ionomer film. Pivac et al. investigated LF inductive features based on a specially developed equivalent circuit model (ECM) and stated that such an improvement in the transport properties of oxygen to the catalyst provoke LF inductive contributions.^{26,27} In principle, our new kinetics model can be integrated into a complete MEA simulation model to replace the typically used Butler-Volmer of Tafel approaches for the ORR kinetics. Such a model would allow to account for the most important effects including water management and local catalyst-near effects. Nevertheless, this would add much complexity as it would need additional comprehensive representations of the following effects: heat transport, water and proton transport within the ionomer phase, two-phase water flow within the porous media and catalyst-near transport effects through the ionomer/water film. Therefore, this would go beyond the scope of this work whose purpose of providing a simple model for the cathode reaction kinetics that represents a good compromise between complexity and accuracy is fulfilled.

Conclusions

In this work we investigated the low-frequency inductive phenomena in differential PEM fuel cells based on both a numerical simulation model and a large experimental dataset. The latter has been acquired by varying the operating conditions RH, T, p_{O_2} and j systematically and recording steady-state polarization curves as well as the corresponding EIS spectra. In the first part we explained that the discrepancies between the polarization curve slopes and the slopes from EIS based on the capacitive parts of the spectra are caused by the low-frequency inductive features (positive imaginary part) of 30 mV dec⁻¹ to over 200 mV dec⁻¹ depending on the operating conditions. Since measuring EIS at very low frequencies is very challenging and time-consuming, EIS spectra are typically recorded at frequencies higher than 0.1 Hz, thus missing these low-



Figure 13. Nyquist plot of a x_{O_2} variation at j = 0.2 A cm⁻², T = 80 °C and RH = 80%. The dots represent the measurement points and the lines the model results considering mass transport by Fick's law.

frequency inductive contributions. In order to explain them we summarized previous literature sources which allowed us to narrow down the possible interpretations to complex cathode kinetics involving intermediates or platinum oxidation, and slow water management dynamics that influence the ionomer hydration and thus its conductivity.

We calculated the absolute inductive contributions by subtracting the low-frequency real-axis-intercepts ($f \approx 1$ Hz) of the capacitive EIS from the local slopes of the polarization curves which we obtained by numerical derivation. Therewith, we investigated the influence of the operating conditions on the inductive loop in a full factorial fashion, which was done for the first time to our knowledge. We found that the size of the inductive loop strongly depends on the current density and the relative humidity; however, the effect of temperature and oxygen partial pressure is minor but not negligible. Thus, the inductive loop (in Ωcm^2) is largest at low load even though its influence on the slope of the polarization curve is proportional to the current density and therefore increases with increasing load. Further, decreasing the relative humidity increases the inductive loop and decreasing the oxygen partial pressure increases it at high current density. Based on our previous characterization of the ionomer resistances as a function of the current density depending on the relative humidity we could quantify the inductive contributions originating from slow ionomer hydration. We pointed out that these contributions play almost no role at all at wet conditions and are important only at medium to high currents at dry conditions. Hence, we could prove that the inductive effects at small current density come almost exclusively from ORR kinetics effects within the cathode electrode, even though we observed a small additional process of $\leq 10 \text{ mV dec}^{-1}$ at dry conditions that is not proportional to the current density.

Finally, we proposed a new approach to model the cathode kinetics following a single-step Tafel equation for the oxygen reduction reaction and an additional equation for the platinum oxidation reaction. The latter influences the effective exchange current density of the ORR step through the fraction of available platinum surface, therefore also affecting the apparent Tafel slope. We integrated this approach into a dynamic, isothermal, one-dimensional through-plane FEM model reaching from the anode side of the membrane to the cathode gas channel. By using the current-step method we got one complete EIS spectrum per computation and we simulated cyclic voltammetry responses by switching off the ORR and imposing a succession of voltage ramp up and ramp down. Based on this fast model we performed an extensive parameter study that helps understanding the influence of

each quantity on the steady-state and EIS response. We parameterized the model for high relative humidity conditions based on both polarization and EIS data and despite the good match between simulation and experiment over a wide range of operating conditions, the polarization curves showed deviations at high current densities. We attributed these deviations to oxygen transport in the porous media and minimized them by adding Fickian diffusion physics in the GDL and CCL. Our validation study based on this final model showed an improved match between simulation and experiment for both polarization curves and EIS spectra, highlighting that our model approach is well-suited for PEMFCs. According to this, we proposed a simple model which presents a good compromise between complexity, parameterability and accuracy and which brings the reconciliation of steady-state performance and EIS signatures in differential PEM fuel cells one step forward. In future works, this model could be complemented by ionomer hydration dynamics in order to simulate also dry conditions, or it may directly be integrated into complete MEA models in order to get even deeper and more precise insights into PEMFC performance.

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