Simulative Investigation on Local Hydrogen Starvation in PEMFCs: Influence of Water Transport and Humidity Conditions

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Durability targets of automotive polymer electrolyte membrane fuel cells (PEMFCs) could be crucially threatened by local hydrogen starvation, typically induced by local blockage of gas channels. To gain a deep insight on the evolving of such starvation events and related carbon corrosion losses, we have developed a numerical model with transient nature that includes detailed transport phenomena and electrochemistry. Special focus is on water transport and sensitivity of relative humidity (RH) on both anode and cathode sides, whose influences were commonly neglected in starvation-related modeling studies. Utilizing the model, we show the dominating effect of in-plane hydrogen convection within the anode gas diffusion layer, which is again determined by the accumulation of other gas species including water vapor. We demonstrate how this is again linked with the water management throughout the fuel cell. Furthermore, water transport is shown to affect local current density and membrane oxygen permeability, both being critical influential factors regarding the severity of a local starvation event. The developed model is validated by conducting transient current density distribution measurements. As RH levels are crucial operational conditions within automotive PEMFCs, this work serves as useful input towards development of future operation strategies for better PEMFC durability.

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List of symbols

Symbol	Unit (SI)	Latin symbols:	Meaning
c	mol m^{-3}		Concentration
d	m		Thickness (through-plane)
D	$\text{m}^2 \text{s}^{-1}$		Diffusion coefficient
E^0	V vs RHE		Standard equilibrium potential
E^{ac}	J mol^{-1}		Activation energy
$ECSA$	$\text{m}^2 \text{kg}^{-1}$		Electrochemical active surface area (of Pt)
EW	kg mol^{-1}		Equivalent weight (of ionomer)
F	C mol^{-1}		Faraday's constant (96485 C mol^{-1})
i	A m^{-2}		(Area-specific) Current density
i_0	A m^{-2}		Exchange current density
i_V	A m^{-3}		Volumetric current density
j	$\text{mol m}^{-2} \text{s}^{-1}$		Species flux
K	m^2		Permeability (in the GDL)
K_{memb}	$\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$		Gas permeability in the membrane
L	kg m^{-2}		Loading (of Pt in the CL)
M	kg mol^{-1}		Molar mass
p	Pa		Pressure
r	—		Mass ratio
R	$\text{J mol}^{-1} \text{K}^{-1}$		Ideal gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$)
R_{ct}	Ωm^2		Contact resistance
rf	—		Roughness factor (of Pt)
S_ϕ			Generalized source term
t	s		Time
T	K		Temperature
t_{depl}	s		Initial depletion time
$\vec{u}$	m s^{-1}		Velocity
x	m		In-plane coordinate (normal to the flow field)
y	m		Through-plane coordinate

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(Continued).

Greek symbols		
Symbol	Unit	Meaning
α	—	Charge transfer coefficient
γ	—	Reaction order (apparent)
Γ	—	Generalized diffusion coefficient
ε	—	Porosity
η	V	Over-potential (apparent)
θ	—	Langmuir adsorption term
λ	—	Ionomer water content
μ	Pa s	Dynamic viscosity
ν	—	Volume fraction
ξ	—	Electro-osmotic drag coefficient
ρ	kg m ⁻³	Density
ρ_{stacking}	m ³ kg ⁻¹	Stacking density of carbon (in the catalyst layer)
σ	S m ⁻¹	Specific conductivity (electric or protonic)
ϕ	—	Relative humidity (RH)
ϕ_e	V	Electric potential
ϕ_p	V vs RHE	Protonic potential
Φ	—	Generalized solution variable

For the past decade, fuel cell electric vehicles (FCEVs) have been gaining increasing significance in the automobile industry, alongside with the first stages of commercialization achieved by Toyota, Honda and Hyundai.^{1–3} The performance requirement during the whole lifetime of a FCEV poses stringent durability targets on its core component, the polymer electrolyte membrane fuel cell (PEMFC). However, degradations within PEMFCs occur via a variety of mechanisms and the durability issue still remains one hurdle towards more wide-spread commercialization of FCEVs.^{1,4,5}

Among the various conditions that may lead to degradation mechanisms in the fuel cell, hydrogen starvation belongs to the most critical and harmful ones,^{1,4,6} with its consequence being irreversible carbon corrosion (carbon oxidation reaction, COR) in the catalyst layer (CL):^{7,8}

The loss of carbon support causes detachment and electric isolation of Pt particles, ultimately reducing the electrochemical active area of the CL and adding kinetic losses to the fuel cell.^{9–11} Besides, mass transfer in the PEMFC worsens due to porosity decay, ionomer redistribution and decreasing hydrophobicity within the CLs.^{6,12–14} Possible collapse of CL porous structure further exacerbates the issue.^{1,15,16} As a result, small extent of carbon weight loss (in the order of 5%–10%) can already lead to deterioration of the fuel cell performance and the failure in meeting the PEMFC durability target.^{17–19}

Hydrogen starvation events can generally be subdivided into overall/gross starvation,^{12,20,21} local hydrogen starvation, and startup/shutdown (SUSD) related events.^{22,23} Among them, we focus on the local hydrogen starvation, which occurs as a consequence of improper gas supply on the anode side due to e.g. liquid water blockage, even when the overall H₂ stoichiometry on the cell level is sufficient.^{4,18} When certain part of the fuel cell has no access to H₂, corrosion reactions can occur via the well-known reversed decay mechanism, originally published by Reiser et al.⁷ Local hydrogen starvation events are of primary concern due to the frequent occurrence of anode flooding^{24–26} and the difficulty in the detection of such events.^{18,22,27} For instance, they cannot be detected via cell voltage monitoring, in contrary to global starvation events.²⁷ As a result, local hydrogen starvation may potentially induce severe damage within the PEMFC catalyst layer, before any counter-measures are taken. These degradation effects have also been demonstrated for automotive conditions by several studies.^{15,25,28}

In the literature, one may find several numerical models with focus on local hydrogen starvation in a PEMFC. Meyers et al.⁸

presented the first model to demonstrate how carbon corrosion can be induced by local maldistribution of hydrogen. There, it was already noticed that the COR current is limited by the oxygen crossover during such events. Starting from then, steady-state models have been developed by several authors, focusing on sensitivity analysis of local starvation (e.g. influence of the cell voltage, oxygen permeability and COR kinetics),^{22,24,29–31} coupling of the starvation event with transport phenomena,^{24,30,31} as well as the investigation of transition between the starved and the normal operating region.^{24,32,33}

However, steady-state models cannot resolve the temporal development of the local starvation event. For instance, it shall be expected that blockage in the anode and carbon corrosion do not take place simultaneously, since H₂ is still temporarily available within the starved region for a short time span. Therefore, dynamic information is valuable towards understanding and mitigation of the local starvation and its related corrosion issue. Gu et al.³⁴ developed the first two-dimensional transient model, where they implemented species, electron, proton transport phenomena combined with detailed electrochemistry. Additionally, they conducted parametric studies with respect to length scale of the starved region, the N₂ content as well as operational current density, to name a few. Recently, Chen et al.³⁵ presented another transient model with respect to local hydrogen starvation, with the focus on along-the-channel profiles of hydrogen and current density within a dead-ended anode fuel cell.

Despite the significant progress in the modeling studies, little attention has been paid to water transport phenomena and the effect of humidity on the local starvation event. It is widely known that both strong influential factors, namely COR kinetics and oxygen permeation through the membrane, are highly dependent on the local relative humidity (RH).^{36,37} Experimentally, especially in dead-ended anode PEMFCs, water transport is also generally recognized as critical influential factor in determining H₂ starvation events.^{38–40} Furthermore, water transport and local humidity affect several other transport properties within the PEMFC, such as gas diffusivity and proton conductivity.⁴¹ Contrary to general numerical PEMFC models where water and humidity receive great attention,^{41–44} in most of the starvation modeling studies, RH was either neglected or set to an arbitrary constant value of 100% throughout the computational domain,^{17,34} very likely due to modeling limitations and computational restrictions.

To our best knowledge, only three of the existing local starvation modeling studies had implemented water transport and/or local RH dependence.^{24,31,35} In all three studies, membrane water sorption equilibrium as well as water transport mechanisms through the

Figure 1. Two-dimensional computational domain in this study, including anode GDL (GDL substrate and MPL) and the catalyst-coated membrane (CCM, consists of anode catalyst layer (ACL), membrane and cathode catalyst layer (CCL)), sizes not drawn to scale. Thicknesses of individual layers are marked. Two directions, namely through-plane (y) and in-plane normal to the flow field (x), are taken into consideration. Anode flow field is simplified as a boundary condition, certain length of which is blocked and allows no gas exchange. The left boundary of the domain represents the center of the blockage (starvation center).

membrane (being electro-osmotic drag and back diffusion) are implemented. Ohs et al. and Yang et al.^{24,31} have additionally implemented RH dependency of O_2 permeability and COR kinetics. However, none of the studies presented the distribution of water within the computational domain nor its possible influence on the H_2 transport and the development of the local starvation event. Additionally, RH remained as one single input parameter within the studies, leaving its sensitivity towards the electrochemistry uninvestigated.

In the present study, we develop a two-dimensional numerical model of transient nature to simulate local hydrogen starvation induced by blockage in the flow field. To investigate the influence of water transport and the local RH on the starvation event, we implement water transport via gas and ionomer phase, alongside with mass transport, charge transport and electrochemical reactions. With the number of solution variables included, the computational complexity is increased, and numerical stability of the model is reduced. We tackle this issue by justifying and applying the simplifications of quasi-stationarity and quasi-one-dimensionality within the domain of catalyst-coated membrane (CCM). Utilizing the developed model, we investigate the dynamic response of a PEMFC during a local hydrogen starvation event, with respect to gas and current density distribution as well as carbon corrosion amount. We show how the convective transport of hydrogen and the accumulation of other anode gas species (i.e. N_2 , water vapor) within the anode gas diffusion layer (GDL) determines the dynamic development of starvation and carbon corrosion. With parametric variation of anode/cathode RH settings within the fuel cell, we demonstrate their impact on the first occurrence of reversed current and the carbon loss over time. Additionally, the numerical model is validated via dynamic current density distribution (CDD) measurement within an automotive fuel cell, where part of the anode flow field is blocked using a special two-component replication material. Experimental observations under two different RH conditions verify the predicted trend of the model.

Modeling Details

Computational domain.—Figure 1 illustrates the two-dimensional (2D) computational domain in the present study. The y coordinate corresponds to the through-plane (TP) direction, normal to the fuel cell active area; whereas the x coordinate the in-plane (IP) direction, perpendicular to the gas flow directions of the PEMFC

flow field. Here, we focus on this IP direction since it represents a local starvation event where several parallel gas channels are blocked by liquid water. The same geometry was used by Gu et al. and Yang et al.^{24,34} Constant gas channel composition over the domain is assumed (same relative position in all gas channels).

As shown in Fig. 1, part of the flow field is set as blocked. The blockage is assumed perfect, allowing no gas to pass through. Its length amounts to 20 mm (across the channels, $0 < x < 20$ mm), which was suggested by Gu et al.³⁴ as the minimum distance to induce carbon corrosion. It shall be noted that even greater sizes of liquid water blockage are possible during automotive operation of PEMFCs, e.g. reported by Lochner et al.²⁵ Total domain length in x is kept to twice the blockage length, which ensures that the right end of the domain ($x = 40$ mm) is in normal operation and free from influence of the blockage.

In TP direction, the domain includes anode GDL (including the substrate and the micro-porous layer (MPL)) and the catalyst-coated membrane (CCM, consisting of anode catalyst layer (ACL), membrane and cathode catalyst layer (CCL)). Figure 1 additionally summarizes their individual thicknesses.

It shall be noted here that during a local H_2 starvation event, current reversal may occur, where locally the PEMFC anode becomes by definition the cathode with reduction reaction, vice versa for the cathode. Strictly speaking, we would have to use terms like hydrogen electrode (negative electrode) and oxygen electrode (positive electrode). However, to enhance readability, we still apply the terms “anode” and “cathode” (as well as abbreviations such as ACL or CCL), where anode and cathode always refer to the hydrogen electrode and the oxygen electrode, respectively, as it would be the case under normal PEMFC operation.

Modeling simplifications.—The following simplifications are made during the modeling with the aim to reduce computational cost and increase numerical stability of the model, while keeping the limitations of the model at minimum. In the Supplementary Material, we present the justifications/rationale of these simplifications.

- 1) Temperature of the domain is taken as constant and given as parameter input.
- 2) Two-phase phenomena are not considered.
- 3) Effect of the flow field ribs (structures supporting the GDL) with respect to their blockage of the gas transport is not implemented.

- 4) The CCM is considered quasi-stationary and quasi-one-dimensional (quasi-1D). We discuss and justify this critical simplification in section “Justification of simplifications in sub-model III.”
- 5) Macro-homogeneous model of the CL:⁴⁵ transport resistance of gases through the ionomer and carbon primary pores is neglected.
- 6) Variables on the cathode side of the CCM are constant and uniform (Oxygen gas, RH, total pressure, electric potential). Influence of cathode GDL is neglected.
- 7) Gaseous water and ionomer solved water are in equilibrium within CLs, described by the sorption isotherm.⁴⁶
- 8) In the CLs, the Wilke formula is applied as an approximation for multi-component diffusion.⁴⁷
- 9) Pt-related electrochemistry reactions (e.g. Pt dissolution) are not considered.
- 10) Electrochemistry is not influenced by carbon loss. This effect is planned to be investigated in a follow-up study.
- 11) Dynamic charging of electrochemical double-layer within the CLs and its possible influence on the protonic potential is neglected.
- 12) No hydrogen crossover through the membrane is simulated.

Sub-models and transport phenomena.—Based on the aforementioned simplifications, we separate the model into three sub-models, accounting for different time (transient, stationary or quasi-stationary) and location dependency (2D or quasi-1D) of various transport phenomena occurring in various PEMFC layers. Sub-model I calculates the transient species transport via convection and multi-component diffusion in the anode GDL, while sub-model II deals with the stationary electron transport in the GDL. These two sub-models (modeling equations, boundary conditions) are elaborated in the Supplementary Material.

Sub-model III is the core part of the model, accounting for the transport phenomena within the CCM domain (ACL, membrane, CCL). This includes the following five solution variables:

- Hydrogen concentration, c_{H_2} ;
- Oxygen concentration, c_{O_2} ;
- Electric potential, or sometimes referred to as the solid potential, ϕ_e ;
- Protonic potential, or sometimes referred to as the membrane potential, the electrolyte potential or the solution potential, ϕ_p ;
- Water concentration (gas or ionomer phase), c_{H_2O} .

Justification of simplifications in sub-model III.—As mentioned in section “Modeling simplification” under No. 4), transport of all five variables is considered quasi-one-dimensional and quasi-stationary. The former means that the in-plane (x) gradient terms in the transport equations are neglected, although the resulting 1D differential equation system is still solved at multiple x -coordinates. Analogously, quasi-stationarity means that the unsteady terms in the transport equations are omitted, while the solution of the stationary differential equation is still updated over time.

The simplification allows major order reduction of the mathematical model. As shown in Eq. 2, the general 2D transport, represented by a partial differential equation (PDE) system, is reduced to several ordinary differential equation (ODE) systems, within which only the TP coordinate (y) remains as the independent variable:

$$\varepsilon \frac{\partial \Phi}{\partial t} = \Gamma_x \frac{\partial^2 \Phi}{\partial x^2} + \Gamma_y \frac{\partial^2 \Phi}{\partial y^2} + S_\Phi \xrightarrow{\text{Simplification}} 0 = \Gamma \frac{\partial^2 \Phi(x, t)}{\partial y^2} + S_\Phi \quad [2]$$

Here, Φ represents a general variable (e.g. c_{H_2} , ϕ_e) and is in general a function of position (x, y) and time t . Γ_x and Γ_y are the

generalized diffusive coefficients (e.g. diffusion coefficient for c_{H_2} , specific electric conductivity for ϕ_e) and S_Φ the respective source term. $\Phi(x, t)$ on the right hand side of the equation indicates that the quasi-1D and quasi-stationary approach does not eliminate x and t dependence of Φ , but omits their gradient terms in the transport equation.

The simplification of quasi-one-dimensionality (omitting ∂x term in Eq. 2) is based on the aspect ratio of the CCM domain. The length scale of the blockage area (IP, x) is in the order of 10–20 mm, whereas the CCM thickness (TP, y) is around 20 μm (see Fig. 1), giving an aspect ratio of 500–1000. For an isotropic material ($\Gamma_x \approx \Gamma_y$), in order to make the two second derivative terms comparable, the IP gradient must be 500–1000 times greater than its TP counterpart. This is extremely unlikely for all the variables considered in the CCM domain. Nevertheless, it shall be noted that for the protonic potential ϕ_p , a sharp drop occurs in the transition region between H_2 -available and H_2 -depleted region, which has also been reported by the literature.^{24,32,33} As a result, there is a certain IP flow of protonic current in the transition region which partially violates the simplification, leading to over-estimation of ϕ_p gradient in this particular region using the current model. However, the affected transition region is known to have a length in the range of 2 mm,^{24,32,33} which is relatively small compared to the dimension studied (20 mm). In addition, the CCM thickness in the present study is less than those in the aforementioned studies (e.g. 10 μm membrane compared to 25 μm in Refs. 24, 32, 33; 3 μm ACL compared to 10 μm in Ref. 24), significantly weakening the effect of the IP protonic current. Furthermore, in the literature reporting this transition length, a sharp H_2/O_2 front is usually assumed.^{32,33} In the current model, it can be shown that there exists a certain transition region of H_2 concentration (around 5 mm, see section “In-plane gas distribution”), which at least partially compensates the transition length of the protonic potential.

Since the effect of dynamic charging or discharging of the double-layer capacitance is neglected (simplification 11)), electron and proton transport in the CCM is stationary (no ∂t term in Eq. 2).

Quasi-stationarity (omitting ∂t term in Eq. 2) of the mass transport is based on the characteristic time scale of transport within the CCM compared to the one within the GDL. The characteristic time (t_c) in Eq. 3 gives a rough estimation of how long it takes for a dynamic variation within a certain domain to reaches its steady state.

$$t_c = \frac{\varepsilon d^2}{D} \quad [3]$$

Here, d denotes the length scale of the domain and D the effective diffusion coefficient. Since we focus on the TP transport through the CCM, d is the thickness of the individual layer. The time scale d^2/D is well-known in transport phenomena (e.g. in Refs. 48, 49) and was applied in starvation modeling studies.^{8,9} The porosity ε accounts for the lower “storage” possibility of gases in the porous domain, which allows a quicker equilibrating of concentration variations. A derivation of Eq. 3 may also be found in the Supplementary Material.

Utilizing the equation, one may show that t_c in the CCM are orders of magnitudes smaller than in the GDL (see Table SII (available online at stacks.iop.org/JES/168/074504/mmedia) for a detailed listing). The longest time scale of gas transport within the CCM is O_2 through the cathode CL (14.5 μs), which is still about factor 40 smaller than the shortest time scale in the anode GDL (>600 μs for H_2). Thus, any disturbance and equilibrating of concentrations within the CCM is “instantaneous” if observed on the GDL time scale. As for the membrane, its porosity is negligible for the gas components, giving a characteristic time close to zero. This justifies the quasi-stationary simplification in the model.

Solution variables, source terms.—Table I summarizes the solution variables as well as their corresponding generalized diffusive term and source term for their use in Eq. 2. All source

Table I. Solution variables (Φ) in the CCM and their corresponding generalized diffusive coefficients (Γ) and source terms (S_Φ). For gas concentrations, Γ is the effective diffusion coefficient (D); for potentials, Γ is the specific conductivity (σ). All source terms are related to volumetric current densities (i_v) of the four possible electrochemical reactions in the domain: hydrogen oxidation reaction (HOR), oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and carbon corrosion reaction (COR). F is the Faraday constant (96485 C mol⁻¹).

Φ	Γ	S_Φ	Notes on S_Φ
c_{H_2}	D_{H_2}	$-i_{v,\text{HOR}}/(2F)$	Consumption by HOR
c_{O_2}	D_{O_2}	$(i_{v,\text{ORR}} + i_{v,\text{OER}})/(4F)$	Consumption by ORR, production by OER
ϕ_e	σ_e	$-(i_{v,\text{HOR}} + i_{v,\text{ORR}} + i_{v,\text{OER}} + i_{v,\text{COR}})$	Total current
ϕ_p	σ_p	$i_{v,\text{HOR}} + i_{v,\text{ORR}} + i_{v,\text{OER}} + i_{v,\text{COR}}$	Total current
$c_{\text{H}_2\text{O}}$	$D_{\text{H}_2\text{O}}$	$-(i_{v,\text{ORR}} + i_{v,\text{OER}} + i_{v,\text{COR}})/(2F)$	Production, consumption by ORR, OER, COR

terms are related with electrochemistry which is described in very detail in the Supplementary Material.

Modeling of water transport and RH dependencies.—Water transport (water vapor and ionomer-solved water) within the CCM is solved using one single variable (water concentration $c_{\text{H}_2\text{O}}$, in mol m⁻³), see also Table I. As shown in Eq. 4, in both CLs, $c_{\text{H}_2\text{O}}$ is defined in the gas phase and is proportional to the RH (denoted by ϕ in equations); whereas in the membrane, $c_{\text{H}_2\text{O}}$ denotes water concentration in the ionomer phase, which relates with the widely used membrane water content (λ , mol water per mol sulfonate ion, dimensionless) by the dry ionomer density (ρ_{ionomer} , in kg m⁻³) and the ionomer equivalent weight (EW, in kg mol⁻¹). Due to its presence in different phases, $c_{\text{H}_2\text{O}}$ does not obey continuity on the interface CL/membrane. Instead, the membrane sorption equilibrium in the form of $\lambda = f(\phi)$ is used to couple the two concentrations on the interface (see Eq. S46).

$$c_{\text{H}_2\text{O}} = \begin{cases} \frac{p_{\text{H}_2\text{O}}}{RT} = \phi \frac{p_{\text{sat}}}{RT}, & \text{in CLs} \\ \lambda \frac{\rho_{\text{ionomer}}}{\text{EW}}, & \text{in the membrane} \end{cases} \quad [4]$$

Due to the presence of additional electro-osmotic drag (EOD) flow that is not directly influenced by the gradient of water concentration, the general transport Eq. 2 needs modification for the water transport:^{41,50}

$$0 = -\frac{\partial}{\partial y} \left(-D_{\text{H}_2\text{O}} \frac{\partial c_{\text{H}_2\text{O}}}{\partial y} + \xi \frac{i}{F} \right) + S_{\text{H}_2\text{O}} \quad [5]$$

Where the terms in the parentheses denote the water flux as the sum of concentration-induced flux (first term) and the additional EOD flux (second term). ξ is the EOD coefficient and i the local current density (in y direction).

Since the local water content (or RH) has significant influence on several transport and kinetics parameters in sub-model III, we implement the following dependencies as listed in Table II.

Further details of the water transport modeling can be found in the Supplementary Material.

Simulation schemata and coupling of sub-models.—Table III summarizes the characteristics of the three sub-models. Based on this, we develop the simulation schemata, illustrated in Fig. 2. In general, (quasi-)stationary sub-models II/III are run after each time step of transient sub-model I. Since sub-model III is quasi-1D, we choose a number of sampling points along the x -coordinate (IP direction) and solve the 1D transport on all of the points. The interim results can then be interpolated back to 2D and applied in sub-models I/II.

As shown in Fig. 2, after each time step of sub-model I, hydrogen and water partial pressure are evaluated on every x -sample point and applied as inputs to sub-model III. Additionally, the CCM model

requires the electric potential (ϕ_e) on the anode side. This is evaluated by sub-model II, which needs inputs of current densities from sub-model III. Thus, an iteration between the two sub-models is necessary (loop in Fig. 2).

Besides the coupling of the sub-models and the iteration loop, sub-model III still requires the cell voltage as an additional input (boundary condition for ϕ_e on the cathode side). This value is unknown *a priori* if the cell is operated in galvanostatic mode (i.e. controlling overall current of the cell). In the present study, we apply a semi-galvanostatic condition by constraining the current density at the right end of the domain ($x = 40$ mm, refer to Fig. 1) at a fixed value (1 A cm⁻², see Table IV). Thus, an extra iteration loop is required to determine the cell voltage, which we elaborate in the Supplementary Material (see also Fig. S1). This boundary condition is of advantage as it requires minimum amount of iterations to find the cell voltage, while being a good approximation of the “overall” galvanostatic condition, since the starvation area typically constitutes only a small fraction within the fuel cell active area. A similar condition was also applied by Chen et al. for the starvation modeling.³⁵

Implementation and parameter settings.—All sub-models including their coupling were coded within MATLAB® 2015b, utilizing built-in solvers for PDE (parabolic and pdenonlin) and ODE systems (bvp4c, same as in Ref. 41). The triangular mesh necessary for the finite-element based PDE solvers was created automatically and possessed around 6000 triangles. The time step of the transient simulation was generally set to 0.5 ms with the exception of some stiff cases (0.2 ms for case No. 6–9, numbering see Table V). In the Supplementary Material, we provide mesh independent studies which justify the application of the present settings of the mesh and the time step.

Additionally, the Supplementary Material provides an elaboration of solver setup, numerical settings, and model initialization related to the present model.

The chosen operational conditions as well as critical material properties within the PEMFC are listed in Table IV as modeling parameters.

Table V lists different simulation cases for the parametric study, where we investigate the influences of the following parameters on the dynamic development of a local H₂ starvation event:

- Dry N₂ volume fraction (i.e. N₂/(H₂+N₂)) in the anode channel (0%–10%)
- RH in the anode channel (30%–90%)
- Cathode RH (30%–90%)

For cases 1–4, we chose slightly different humidity (70%/80%) on both sides, which approximately balances EOD and water diffusion flux across the CCM, giving a relatively small net water flux towards the anode GDL.

We define case No. 3 as the simulation base case where we show the overall observations during the modeled local starvation event (section “Overall observations in the base simulation case”).

Table II. Summary of sub-model III parameters with dependency on the water concentration (also relative humidity ϕ , and membrane water content λ) implemented. All units are in or converted to SI.

Parameter	Symbol	Unit	Dependency	Notes
CL proton conductivity	$\sigma_{p,CL}$	$S\ m^{-1}$	$\sigma_{p,CL} = 2.23 \cdot \phi^{2.84}$	34
Membrane proton conductivity	$\sigma_{p,memb}$	$S\ m^{-1}$	$\sigma_{p,memb} = \max\{0.002305\lambda^3 - 0.1053\lambda^2 + 1.782\lambda - 4.631, 0.6\}$	Cubic fit from internal data 37, at 353 K ^{a)}
Membrane oxygen diffusivity	$D_{O_2,memb}$	$m^2\ s^{-1}$		
			$D_{O_2,memb} = RT(4.78 \cdot 10^{-15} + 4.72 \cdot 10^{-14} v_{H_2O})$	
			$v_{H_2O} = \frac{\lambda \cdot 18 \cdot 10^{-6}}{\lambda \cdot 18 \cdot 10^{-6} + EW/\rho}$	
CL gas diffusivity (H_2 or O_2)	$D_{i,CL}$	$m^2\ s^{-1}$	Wilke formula (Supplementary Material)	
Membrane water diffusivity	D_{H_2O}	$m^2\ s^{-1}$	$D_{H_2O} = \frac{3.842\lambda^3 - 32.03\lambda^2 + 67.74\lambda}{\lambda^3 - 2.115\lambda^2 - 33.013\lambda + 103.37} 10^{-10}$	41, at 353 K
EOD coefficient	ξ	—	$\xi = \begin{cases} 1, & \lambda \leq 14 \\ 0.1875\lambda - 1.625, & \lambda > 14 \end{cases}$	51, 52
OER volumetric current density	$i_{V,OER}$	$A\ m^{-3}$	Reaction order of water: $\phi^{0.88}$	34
COR volumetric current density	$i_{V,COR}$	$A\ m^{-3}$	Reaction order of water: $\phi^{1.0}$	36
a) Gas permeability (in unit of $mol\ cm^{-1}\ s^{-1}\ kPa^{-1} = 0.1\ mol\ m^{-1}\ s^{-1}\ Pa^{-1}$) is usually reported by the literature which relates the molar flux with pressure gradient. An effective diffusivity in the membrane (here $D_{O_2,memb}$) can be obtained by multiplying the gas permeability with RT , since the pressure gradient relates to the concentration gradient by this factor ($\nabla p = \nabla c \cdot RT$).				

Table III. Summary of considered transport phenomena, geometric domain, time and position dependence, inputs/outputs for the three sub-models used in the simulations. Sub-models I/III are coupled via distribution of H_2O/H_2 partial pressures (p) and fluxes (j); sub-models II/III are coupled via distribution of electric potential (ϕ_e) and current density (i).

	Sub-model I	Sub-model II	Sub-model III
Transport of	$H_2, N_2, H_2O(g)$	e^-	H_2, O_2, e^-, H^+, H_2O
Domain	Anode GDL	Anode GDL	CCM
Time dependence	Dynamic	Stationary	Quasi-stationary
Position dependence	2D	2D	Quasi-1D
Required inputs on the GDL/CCM interface	$j_{H_2O}(x), j_{H_2}(x)$	$i(x)$	$\phi_e, p_{H_2O}, p_{H_2}$
Outputs on the GDL/CCM interface	$p_{H_2O}(x), p_{H_2}(x)$	$\phi_e(x)$	i, j_{H_2O}, j_{H_2}

Figure 2. Flowchart illustrating the basic simulation procedure under given cell voltage. Sub-model I calculates the transient mass transport in the GDL, sub-model II the stationary electron transport in the GDL, and sub-model III the quasi-stationary transports/electrochemistry in the CCM. An iteration procedure is required between sub-model II and III to obtain the correct distribution of electric potential (ϕ_e) and current density on the GDL/CCM interface.

Table IV. Parameters related to material properties or operational conditions within the PEMFC as well as their values chosen in the model. Additional non-critical parameters may be found in the Supplementary Material.

Parameter	Symbol	Value	Unit	Notes, Source, Rationale
Temperature	T	Operational conditions 353	K	Standard in PEMFC
Current density (in the normal region)	i_{normal}	1.0	A cm^{-2}	Standard operation point in PEMFC
Hydrogen partial pressure in the anode flow field	$p_{\text{H}_2,0}$	100	kPa	Standard in PEMFC
Air partial pressure in the cathode flow field	$p_{\text{e,a,dry}}$	100	kPa	O ₂ pressure is therefore 21 kPa
Porosity	ε_{GDL}	Anode GDL 0.4	—	Ref. 53
Permeability	K_{GDL}	$1 \cdot 10^{-12}$	m^2	Ref. 34
In-plane electric conductivity	$\sigma_{\text{TP,GDL}}$	$1.65 \cdot 10^4$	S m^{-1}	Ref. 53
Through-plane electric conductivity	$\sigma_{\text{TP,GDL}}$	200	S m^{-1}	Ref. 53
Porosity	ε_{CL}	CL 0.5	—	Estimation based on Ref. 54, details in the Supplementary Material
Density of dry ionomer	ρ_{ionomer}	$2 \cdot 10^3$	kg m^{-3}	state-of-the-art
Ionomer equivalent weight	EW	800	g mol^{-1}	state-of-the-art
Electric conductivity	$\sigma_{\text{e,CL}}$	100	S m^{-1}	Ref. 34

Table V. Parameters variations investigated in the present study.

Parametric study	Case No.	Anode dry N ₂ fraction (partial pressure)	RH anode/cathode	Blockage length
Study 1: N ₂ percentage in the anode channel	1	0%	70%/80%	20 mm
	2	2% (2.04 kPa)	70%/80%	20 mm
	3	5% (5.26 kPa)	70%/80%	20 mm
	4	10% (11.11 kPa)	70%/80%	20 mm
Study 2: RH in the anode channel	5	5% (5.26 kPa)	30%/90%	20 mm
	6	5% (5.26 kPa)	50%/90%	20 mm
	7	5% (5.26 kPa)	70%/90%	20 mm
	8	5% (5.26 kPa)	80%/90%	20 mm
	9	5% (5.26 kPa)	90%/90%	20 mm
Study 3: RH on the cathode	10	5% (5.26 kPa)	90%/30%	20 mm
	11	5% (5.26 kPa)	90%/50%	20 mm
	12	5% (5.26 kPa)	90%/70%	20 mm

Experimental

In this section, we seek to validate the numerical model by monitoring transient current density distributions (CDDs) over an automotive membrane electrode assembly (MEA) upon start of a local starvation event. To prove the RH dependency predicted by the model, the validation test is conducted with two extreme RH conditions on both sides, similar to the abovementioned sensitivity study (see also Table V, RH anode/cathode: 90%/30% and 30%/90%). It is worth noting that we focus explicitly on the dynamic current response and the RH dependency, as these two aspects represent the most critical and novel part of the present modeling study.

Material preparation.—PEMFCs of automotive size (active area 285 cm²) with flow fields developed in INSPIRE funded project⁵⁵ were used for the validation experiment. Commercial GDLs 29BC and 22BB (SGL Carbon) were applied on the anode and the cathode side, respectively. Preparation of the CCM was done in-house by the decal transfer method,⁵⁶ where the necessary electrodes were manufactured according to the authors' previous publication.⁵⁷ Hereby, the ACL comprises 30 wt% Pt/C with a Pt loading of 0.05 mg cm⁻², which gives an anode thickness of around 3.7 μm. The CCL is composed of 35 wt% Pt/C with a Pt loading of 0.21 mg cm⁻² and possesses a thickness of around 10.5 μm. The applied membrane has a thickness of 15 μm (M775.15, Gore).

To trigger the local hydrogen starvation reproducibly, a specific part of the anode flow field was manually blocked using a two-component silicon-based universal replication material (Repli-Set F5, Struers). This material is typically used to replicate miniature shapes with high resolution and can thus be fit into the gas channels with little coverage over the rib area. It shall be noted that covering the ribs with the replication material would obstruct the electrical contact between the metallic bipolar plate (BPP) and the GDL, falsifying current density measurements. This was explicitly avoided during the application procedure and the electrical contact was confirmed by measuring the through-plane resistance of BPP in the blocked region using a multimeter. Figure S13 shows a photo of the blocked channels.

The blockage was set close to the anode inlet (see also Fig. S14), since the anode gas composition (i.e. H₂/N₂ partial pressure, RH) plays an important role during the starvation event (refer to modeling section "Sensitivity of anode nitrogen content" and "Sensitivity of anode RH") and is only explicitly known near the inlet.

Current density distribution measurement.—A commercial current scan shunt (CSS) sensor plate (S++ Simulation Services) was applied to monitor the transient development of the current density distribution (CDD) over the cell. It consists of 18 × 34 segments for the 285 cm² active area. The resolution of the measurement is around

100 ms in time and in the order of 10 mA cm⁻² in current. Test setup of the CSS is similar to what was reported by Haase et al.⁵⁸ (schematic can be taken from Fig. S14). It shall be already mentioned here that while the CSS is meant to measure the current density distribution at the CCM, it is inevitable that the current is redistributed in-plane via the GDLs and the metallic BPP, a fact widely known in the literature and also referred to as the lateral current.^{58–60} Using a similar setup, Haase et al. demonstrated an equalizing effect while comparing expected CDD in the CCM to the CDD measured by CSS (Fig. 8 in the respective publication).⁵⁸ This partially results from the automotive setup, where the BPPs had been designed in such a way to distribute the current as uniformly as possible. Nonetheless, it shall be emphasized that the redistribution does not alter the qualitative shape of the CDD,⁵⁸ and is not expected to have any influence on the time scale of the measured transient, as none of the GDLs nor the BPP has electrical capacity for storage of electrons (same as the GDL within sub-model II, where the governing equation of electron transport is stationary per definition).

Fuel cell operation.—The tests were performed within a single cell test station (HORIBA FuelCon GmbH), where the anode reactant was either hydrogen (99.999% purity) with 2000 nccm, or a mixture of hydrogen and nitrogen (1600 nccm H₂ + 400 nccm N₂). Cathode reactant was 11000 nccm of compressed air, where this high flow minimizes the RH variance in the cathode channels. Detailed rationale of the flow settings shall be referenced to the Supplementary Material. A cell temperature of 80 °C was kept throughout the experiment, corresponding to the modeling condition (see Table IV). Back pressure on both anode and cathode sides was set to a relatively low value of 1.2 bara to encourage local starvation (as the hydrogen partial pressure at the start of the starvation event is reduced). Two distinct RH conditions were investigated (RH anode/cathode either 90%/30%, or 30%/90%), which corresponds to the two extreme conditions investigated by the modeling sections (see Table V).

Prior to the testing, the MEA was held at open circuit voltage (OCV) for 30 min to ensure that the membrane humidification has reached equilibrium. The test sequence thereafter can be taken from Table VIII, where for each operating point, the current density was first switched from zero (OCV) to 0.5 A cm⁻², held for certain time where the current response was monitored by the CSS, and switched back to OCV. It shall be noted that the holding time at 0.5 A cm⁻² for operating points I–IV (i.e. 10 s for anode with N₂, 150 s for anode with pure H₂) was optimized in such a way that the complete transient can be recorded without introducing significant degradation to the MEA that would affect later operating points. For the last point (No. V), on the other hand, the holding time was prolonged to 90 min to induce significant carbon corrosion within the starved region, so that the degradation effects can be observed in the ex situ performance determination and post-mortem analysis (see sections below).

To ensure reproducibility of the test, the same test sequence was repeated once applying a second automotive MEA with similar characteristics.

Localized performance determination.—For a qualitative confirmation of localized degradation, the MEA was subjected to spatially-resolved characterization (MS2 Engineering und Anlagenbau GmbH)^{61,62} after its operation during the validation experiment (end-of-life: EOL). The measuring device enables localized measurement of cyclic voltammetry (CV) or polarization curve on given segments of the MEA (active area per segment around 4 cm², see location matrix in Figs. 9 and S14). All measurements were conducted under 60 °C cell temperature with back pressures of 1.5 bara and 79% RH (dew point: 55 °C) on both anode and cathode sides. Flows on both anode and cathode sides were set to 1000 nccm (differential flows). Note that no blockage was applied during this EOL performance determination.

Localized H₂/air polarization curve was measured dynamically (scanning rate at 25 mV s⁻¹) between 0.9 V (or 0.85 V if the local OCV is lower than 0.9 V) and 0.2 V cell voltage. The CV measurement was conducted under H₂/N₂ environment with a scan rate of 25 mV s⁻¹ between 0.075 V and 0.8 V (vs RHE). Thereafter, the charge of the H_{upd} area can be evaluated and used to estimate the localized electrochemical active surface area.

The four following segments on the MEA were investigated: E2 (under the blockage); H2, K2 (downstream of the blockage); K5 (neither blockage nor downstream = reference segment).

Post-mortem analysis.—The EOL MEA was additionally subjected to post-mortem analysis to investigate the localized cathode thickness reduction. For this purpose, cross-sections were prepared from the MEA segments E2, K2 and K5 using a Cryo Cross section Polisher (JEOL IB-19520CCP), where the CCM thicknesses and morphology were subsequently analyzed using digital 3D-light microscopy (Keyence VHX-6000).

Results and Discussion

Overall observations in the base simulation case.—First, we examine the base simulation case (No. 3 in Table V), i.e. with 5% N₂ (100 kPa H₂, 5.26 kPa N₂) and 70% RH (33.0 kPa water vapor) in the anode flow field and 80% RH (37.7 kPa water vapor) on the cathode. As in all other cases, the temperature is kept constant at 353 K, while the current density is fixed to 1.0 A cm⁻² (10⁴ A m⁻²) at the right end of the domain ($x = 40$ mm). The present case gives an overview of the temporal and spatial development of a local H₂ starvation event with respect to H₂ and current density distribution. Utilizing the results, we explain the electrochemistry as well as the in-plane convection phenomenon, the latter playing a critical role during the local starvation event.

In-plane gas distribution.—Figure 3 illustrates the profile of gas partial pressures, the total pressure and the current density on the anode MPL/CL interface along the IP direction (x) at four different physical times (1 ms, 250 ms, 500 ms, 2500 ms). At time zero, the blockage within the flow field ($0 < x < 20$ mm) is set, “triggering” the local starvation event.

By comparing the hydrogen pressure profiles over time, one may identify that initial depletion of H₂ occurs around 250 ms at the starvation center ($x = 0$). Simultaneously, the local current density drops towards zero, ultimately reaching negative values where the reverse decay mechanism sets in (see Fig. 3b). Further discussions in the following section “Electrochemistry and carbon corrosion”. Starting from this “initial depletion time” (t_{depl}), the hydrogen depletion area grows, eventually reaching its maximum (at around 2500 ms) where the starvation event reaches its “steady state.”

During the whole development process after t_{depl} , there exists a certain transition region of H₂ partial pressure between the “fully starved region” (no H₂ present) and the “normal region” (H₂ pressure

Figure 3. (a) Profile of hydrogen (p_{H_2}), nitrogen (p_{N_2}) and water vapor partial pressure ($p_{\text{H}_2\text{O}}$) as well as total pressure (p_{total}) and current density (i) on the anode MPL/CL interface in the simulation base case (case No. 3 in Table V) at different physical times of 1 ms, 250 ms, 500 ms and 2500 ms. Anode gas composition in the flow field: 100 kPa H₂, 5.26 kPa N₂ (5% dry percentage), 33.0 kPa H₂O (70% RH). Cathode gas composition: 79 kPa N₂, 21 kPa O₂, 37.7 kPa H₂O (80% RH). Total domain length is 40 mm, where region between 0 and 20 mm (marked by grey dotted lines in the figures) is blocked, allowing no gas to be exchanged between GDL and flow field. Left end of the domain ($x = 0$) represents the starvation center. Current density is fixed to 1.0 A cm⁻² at the right end of the domain ($x = 40$ mm). Temperature is fixed to 353 K in the whole domain. (b) The zoomed-in version (0–4 mm as marked by the blue circle) of the current density distribution near to the starvation center at 500 ms, where reversed current takes place. Blue dashed auxiliary line shows zero current.

close to anode flow field). It can be observed that this transition region has a size of approximately 5 mm. This presence of this transition cannot be represented by the “classic modeling approach” of local

Figure 4. Schematic illustration of the mechanism of in-plane convection during dynamic development of a blockage-induced local H_2 starvation event. Two stages of development can be distinguished: “Beginning,” where local over-consumption of H_2 leads to low local total pressure and induces strong convection; and “End,” where N_2 accumulation gradually blocks H_2 convection and induces its depletion. Blue and purple color indicate H_2 and N_2 , respectively. Dashed lines represent diffusive flows and solid lines convective ones (lightness of colors indicates the strength of H_2/N_2 convective transport).

hydrogen starvation by separating the domain into a normal H_2 cell and an abnormal air cell (e.g. in models of Refs. 7, 22, 32, 63).

Alongside with the current density profile, profiles of N_2 and water vapor also show clear relationship with the different starvation level as well as similar transitions. Partial pressure of water vapor grows from around 33.3 kPa (70.7% RH) in the normal region to 37.7 kPa (80.0% RH) in the fully starved region. This “water plateau” completely resembles the cathode setting (80% RH) which shall be explained by the near-zero local current density. Since practically neither water production nor EOD through the CCM takes place, water diffusion sets in as the only water transport mechanism through the CCM and balances the concentration on both sides.

In the fully starved region, N_2 builds up towards 86 kPa at 250 ms and further to 92 kPa at 500 ms, close to replacing H_2 completely (which was 100 kPa at time zero). It shall be noted that the local N_2 pressure is not only significantly higher than the anode channel (around 5 kPa), but also exceeds cathode level (79 kPa), thus indicating a different source than diffusion or membrane permeation. With the blocked region showing overall lower total pressure, the explanation lies in the strong in-plane convection within the GDL.

Figure 4 illustrates the role of IP convection during a local H_2 starvation event as well as its mechanism. At beginning of the blockage, H_2 in the influenced region is over-consumed, where not enough gas (N_2 or water vapor) can “fill the gap” immediately. Thus, the total pressure decreases as can be clearly observed in Fig. 3. The resulting great IP pressure gradient within the GDL (its maximum being around 10 kPa over the distance of a mere 20 mm, yielding a gradient of 0.5 kPa mm^{-1} , refer to profile at 250 ms in Fig. 3) induces strong convection. It shall be emphasized that this convection is not related to the pressure drop along the gas channel(s). The latter is also considerably smaller, typically in the order of 0.01 kPa mm^{-1} .

This IP convection, being considerably more efficient than diffusion, brings fresh H_2 from the normal region and delays the

starvation (combined convective and diffusive transport of H_2 are represented in Fig. 4 by blue arrows). In the literature, similar convective H_2 transport phenomenon is sometimes referred to as the “vacuum effect.”^{64,65} The presence of this “across-the-channel” convection due to channel blockage is further confirmed by the study of Kulkarni et al.,⁶⁶ who investigated a 40 mm-wide fuel cell geometry without primary flow field (thus, the size of the “blockage” is same as in the present study). In their three-dimensional simulation with 1 mm bypass on both sides of the domain (act as two open channels), they demonstrated significant IP gas velocities from both sides towards the domain center, which dominate over the along-the-channel convection in most of the areas.

While the abovementioned convection phenomenon brings H_2 from the flow field to the GDL region under blockage, some N_2 is also transferred in the same direction as a consequence of N_2 presence (5%) in the anode flow field (purple arrows in Fig. 4, which also indicate that diffusive transport of N_2 towards the channel is insufficient to counteract this convection). Since N_2 cannot be consumed under the blocked region, it gradually accumulates and eventually cuts down H_2 convection (Fig. 4: “End,” where the lighter blue arrows indicate lesser convective transport of H_2). While H_2 transport increasingly relies on inefficient diffusion (blue dashed arrow), sufficient amount of H_2 cannot be supplied towards center of starvation and H_2 depletion eventually occurs as the consequence.

Similar influence of N_2 on H_2 starvation was observed in an experimental study by Meyer et al.,⁴⁰ who presented the so-called “nitrogen blanketing effect” in a dead-ended anode fuel cell, where the accumulation of N_2 in the center of the cell had led to local H_2 shortage and local retraction of current densities. While Meyer et al. also showed that MEA slightly dries out in the same region (contrary to what we observe from Fig. 3a), it has to be noted that the water management in their study differs strongly from ours. In the dead-ended anode operation, water in the MEA is almost solely from water production, which is directly coupled with the current density, whereas in our case, water is also primarily fed as gas humidification.

This concept of H_2 convective transport and influence of N_2 were also demonstrated by the simulative study of Yang et al.²⁴

The dominating effect of convection necessitates its implementation during the modeling of local starvation. Nonetheless, it can be observed that this convection phenomenon is “only” significant during the dynamic development of the local starvation. Once the steady state of starvation is reached (2500 ms profile in Fig. 3), total pressure in normal and blocked regions is approximately balanced, leaving diffusion as the main means of mass transport. The same was observed by Gu et al.,³⁴ who suggested that the convection flows became insignificant at steady state of starvation.

Electrochemistry and carbon corrosion.—As mentioned in section “Simulation schemata and coupling of sub-models,” a semi-galvanostatic condition was modeled by constraining the current density at the right end of domain ($x = 40 \text{ mm}$) to 1.0 A cm^{-2} . The corresponding cell voltage amounts to 0.671 V.

In the fully starved region, a maximum reversed current of -1.60 mA cm^{-2} (note the milli-) takes place as the consequence of the reversed decay mechanism. As suggested in the literature, this reversed current is mainly determined by the oxygen crossover through the membrane.^{8,31,34} Therefore, the reversed current is also practically constant over the depletion region. Over this region, the local average protonic potential in the ACL amounts to -0.764 V (thus, the local anode potential is 0.764 V vs RHE). A tiny difference between protonic potentials in ACL and CCL ($-81 \mu\text{V}$) is present due to the finite protonic conductivity of the membrane and the very small magnitude of reversed current density. Due to the extremely low protonic potential in the CCM, the cathode potential (difference of the electric and protonic potential in the CCL) is elevated to 1.435 V vs RHE, high enough to induce a COR current of 1.53 mA cm^{-2} . This accounts for 95.7% of the total reversed current, with the rest being OER contribution. The ratio agrees well with the results from Mittermaier et al. at high RHs.³⁶

Figure 5. Temporal development of carbon loss amount due to carbon corrosion reaction during the simulated base case of local H_2 starvation event (anode channel composition 5% N_2 in H_2 , RH 70%; cathode RH 80%). Unit is given in mass per length since a third dimension of the MEA (flow field direction) is not included by the 2D model. The right axis shows the equivalent fraction of carbon lost from the CCL, based on a carbon loading of $67 \mu\text{g mm}^{-2}$ in the blockage region (0.33 mg cm^{-2} area loading on a length of 20 mm).

The reversed current here is somewhat higher than what was reported in the literature for local starvation cases (e.g. 0.48 mA cm^{-2} in Ref. 34; $\sim 1 \text{ mA cm}^{-2}$ in Ref. 24). This shall be explained by the relatively low membrane thickness applied in the model ($10 \mu\text{m}$, see Fig. 1), compared to the literature ($18 \mu\text{m}$ in Ref. 34; $25 \mu\text{m}$ in Ref. 24). The gas permeability relation is also different among the models which may also contribute to this discrepancy.

At the same time, the higher reversed current also leads to more elevated COR over-potential and cathode potential. With similar cell voltage, this would mean a higher anode potential (or lower protonic potential in the CCM), which is also observed here (ca. 764 mV vs RHE, compared to ca. 540 mV in Ref. 31, ca. 700 mV in Ref. 24). This agrees with the observation from Ohs et al.,³¹ who suggested that the protonic potential is lower if membrane permeation is enhanced.

The total carbon loss during the local starvation event can be evaluated by numerically integrating the local volumetric COR current densities ($i_{V,\text{COR}}$, output from sub-model III) with respect of CCL thickness, domain length and time span. Converting the value to mass of carbon yields Fig. 5. As expected, the carbon loss remains practically zero prior to the initial depletion time. Thereafter, corrosion starts with an initial low rate, indicating a small area under the influence of reversed current. The gradual development of depletion area leads to an increasing slope of the curve. After around 2 s, the slope reaches its maximum and remains approximately constant, corresponding to the steady state of starvation. Normalizing the carbon loss mass with the MEA carbon loading within the blockage region yields a loss fraction of around 0.02% after 3 s (see right axis in Fig. 5).

The carbon loss fraction may seem low at a first glance. However, it shall be considered that the local hydrogen starvation is hard to detect within a PEMFC stack.^{18,22,27} If the error remains, it would take approximately 8 min to reach 5% local carbon loss (considering that the slope remains constant), which probably leads considerable performance loss to the MEA within this area. Likewise, it will take only 250 times of the three-second incident to reach the same effect. The problem could, however, be strongly mitigated if a local starvation event would never exceed the initial depletion time. Below this threshold, the MEA will still suffer certain temporary performance loss, yet no significant irreversible degradation will take place. Thus, in the following, we investigate

Figure 6. Initial depletion time (time where the current density at the starvation center drops below zero) and carbon lost after 1 s or 2 s (normalized with the total carbon loading in the blockage region: $6.7 \cdot 10^{-5} \text{ kg m}^{-1}$) in dependence on the dry N_2 fraction in the anode flow field. All four cases run under same anode H_2 partial pressure (1 bar), anode/cathode RH (70%/80%). Logarithmic scale is applied for the left axis due to considerably longer time for the 0%-case (pure H_2 in the flow field) to reach initial depletion.

how this critical time is influenced by some operational parameters such as the anode nitrogen content and anode/cathode RH.

Sensitivity of anode nitrogen content.—The convection mechanism explains why N_2 accumulation plays a deciding role during the local H_2 starvation event. Generally, N_2 is present in the anode flow field within an automotive PEMFC due to its permeation from the cathode side and the anode gas recirculation. It has been shown that even with pure H_2 feed and 90% H_2 utilization, N_2 can accumulate up to $>20\%$ within the channel, depending on the purge rate during recirculation.⁶⁷ It shall be expected that an increase in nitrogen content in the anode flow field will lead to an accelerated N_2 accumulation under the blockage area, which in turn exacerbates the local starvation. In contrary, if the anode operates under pure H_2 , the only N_2 source in the anode becomes the N_2 permeation through the CCM from the cathode, resulting in delay on H_2 depletion. In this section, we confirm this using the present model.

As described in Table V (cases No. 1–4), we vary the dry N_2 content in the anode flow field between 0, 2%, 5% and 10%, while keeping the partial pressures of H_2 and water vapor constant. Here, we evaluate the severity of the local starvation event via two aspects: the initial depletion time t_{depl} , where the current density at the starvation center becomes negative; and the carbon loss amount within a time frame of 1 s or 2 s. Figure 6 shows results plotted against the set N_2 fractions.

It is evident that the initial depletion occurs sooner with higher N_2 content, as it is expected from the N_2 accumulation mechanism. This dependency is the strongest with low N_2 content: a 2% N_2 content already speeds up the depletion to a factor of over ten compared to pure H_2 case (6.6 s and 0.52 s). It can be deduced that N_2 accumulation occurs to a considerably higher rate via convection than via permeation from the cathode (the only possibility in the pure H_2 case). Similar differences in time scales were observed by Gu et al.,³⁴ who compared local starvation event under pure H_2 and under 30% N_2 content, showing that the time scale of the latter is reduced by around factor 20.

While the initial depletion takes place only around 90 ms later for the 5%– N_2 case compared to the 10%– N_2 one, the latter shows almost double the carbon loss after 1 s. This indicates that a higher N_2 content triggers an additional quicker development after a prompt first formation of fully starved region.

Table VI. Sensitivity of starvation severity towards RH (water vapor content) or N₂ content in the anode flow field.

Change	70% RH → 30% RH (−18.9 kPa H ₂ O)	5% N ₂ → 10% N ₂ (+5.85 kPa N ₂)
Condition	5% N ₂ , 90% RH cathode	70%/80% RH anode/cathode
Initial depletion time in s	0.23 → 0.15 (−35%)	0.26 → 0.17 (−35%)
Carbon loss 1 s (fraction)	$3.52 \cdot 10^{-5} \rightarrow 4.83 \cdot 10^{-5}$ (+37%)	$2.91 \cdot 10^{-5} \rightarrow 5.65 \cdot 10^{-5}$ (+94%)
Carbon loss 2 s (fraction)	$1.36 \cdot 10^{-4} \rightarrow 1.58 \cdot 10^{-4}$ (+16%)	$1.16 \cdot 10^{-4} \rightarrow 1.64 \cdot 10^{-4}$ (+41%)
Reversed current in mA cm ^{−2}	−1.804 → −1.797 (−0.4%)	−1.598 → −1.598 (±0%)

Sensitivity of anode RH.—As shown in the last sections, N₂ accumulation within the anode GDL plays a dominating role during a local H₂ starvation event. In this section, we investigate whether the other gas species available on the anode side, namely water vapor, has similar effects in determining the severity of the local starvation.

Figure 7a compares the severity of local starvation event among various simulation cases while keeping the cathode RH settings constant (90% RH) and varying the anode RH settings in the flow field (30%–90% RH). Overall, it can be observed that a wetter anode flow field (higher partial pressure of water) leads to milder starvation issue, reflected by a delayed initial depletion time and the lower amount of carbon loss after 1 s or 2 s. The trend seems to be opposite to the one of N₂ content, where an increase leads to more severe starvation issue.

In terms of the initial depletion time, a decrease of anode RH from 70% to 30% (decrease of 18.9 kPa) reaches about the same accelerating effect as increasing the N₂ content from 5% to 10% (increase of 5.85 kPa) under the given simulation settings, as shown in Table VI. Despite this similar shifting of the corrosion start, the carbon losses after 1 s/2 s show weaker sensitivity towards water vapor than towards nitrogen gas. This indicates that water vapor does not accelerate the development of the fully starved region as N₂ does.

Table VI additionally shows that the reversed current is practically independent of the RH setting in the anode flow field, which may seem counter-intuitive since the COR kinetics and the O₂ permeation is strongly RH-dependent. However, as explained for the base simulation case (section “In-plane gas distribution”), in the fully starved region, the RH on the anode side approaches the cathode RH setting (here constant 90%). Thus, independent of RH within anode flow field, the CCM has an approximately 90% RH level locally, explaining the observed sensitivity of the reversed current.

To help explain the discrepancies between the effects of the two gas species, we analyze the profiles of gas concentrations in the extreme case with 30% RH in the anode channel (case No. 5, cathode RH at 90%), shown in Fig. 7b. The settings in this case represent the anode inlet of a fuel cell under counter-flow, where the cathode is close to its respective outlet and has a very high RH.

Here, it can be observed that water vapor accumulates rapidly as soon as the blockage is set (profile at 1 ms already shows considerably higher level of $p_{\text{H}_2\text{O}}$ in the blockage region). At the early stage of starvation event, this water vapor accumulation leads to an increase of total pressure in the blockage region, blocking convective transport of hydrogen towards this specific region. Eventually, accumulation of water vapor reaches its maximum (about 42 kPa, corresponds to 90% RH and the cathode setting) and total pressure falls back due to excessive H₂ consumption, resuming the H₂ convection as in the base case. In other words, the applied low water content in the anode flow field leads to an early accumulation of water vapor within the anode GDL, which cuts out H₂ supply for a short period of time and accelerates its initial depletion.

To this point, it becomes clear that the dynamic development of local hydrogen starvation depends on to what degree other gas species (being N₂ or water) can accumulate within the anode GDL and cut down excessive convective supply of H₂. This also underlies

Figure 7. Sensitivity analyses of anode RH settings. (a) Initial depletion time (time where the current density at the starvation center drops below zero) and carbon loss after 1 s or 2 s (normalized with the total carbon loading in the blockage region: $67 \mu\text{g mm}^{-1}$) in dependence on the RH setting in the anode flow field. All four cases run under same dry gas composition in the anode flow field (H₂ 1 bar, 5% N₂ in H₂) as well as RH setting on the cathode (90%). (b) Profiles of hydrogen (p_{H_2}), nitrogen (p_{N_2}) and water vapor partial pressure ($p_{\text{H}_2\text{O}}$) as well as total pressure (p_{total}) and current density (i) on the anode MPL/CL interface in simulation case No. 5 (see Table V).

the difference observed within the two sensitivity analyses. While N_2 can practically accumulate freely (permeation across the CCM is too weak to balance both sides), water vapor is constrained by its equilibrium with the cathode via water transport mechanism through the CCM. The saturation also limits its level on both sides. As a result, water accumulation within the anode GDL is rather temporary and N_2 takes over as soon as the “water maximum” is reached. This explains the previous observation that the anode RH setting only influences the initial depletion, yet has less effect on the development of the fully starved region.

As it can be observed from Fig. 7b, the local water accumulation under the blockage has also certain influence on the local current density. In fact, the maximum local current density takes place in the blocked region (where hydrogen pressure has not significantly dropped) rather than in the normal operating region (H_2 rich). The local maximum is linked to the significantly higher level of anode RH in the blockage area than in the normal area, which leads to locally wetter CCM and less protonic resistances (cathode RH and cell voltage is constant over the whole domain).

Undesirably, this local “overshooting” of current density results in higher consumption rate of the remaining hydrogen in the region and therefore also contributes to an acceleration of local hydrogen starvation. This explains why the development of fully starved region is still accelerated despite the temporary water accumulation effect (see Table VI).

Lastly, it shall be mentioned that the prediction in this section is based on a constant gas channel blockage among various simulation cases. In practice, the RH settings may have a non-negligible influence on the blockage length itself, which in turn accelerates or delays the local starvation. With a drier anode, the evaporation of liquid water is accelerated, yet the water flux from the cathode towards the anode is strongly increased. These effects and the potential dependency cannot be implemented in the current model, since multi-phase phenomena (or even phase change) are involved, which are beyond the scope of the current study. Nonetheless, the prediction in this section is of practical relevance, e.g. in the case where the operation conditions allow the liquid water blockage to stay nearly constant over the time scale observed, or if the starvation event is induced by blockages other than liquid water.

Sensitivity of cathode RH.—In this section, we study the sensitivity of cathode RH setting by varying it between 30% and 90%, while keeping the RH in the anode flow field constant at 90%. Figure 8a depicts the initial depletion time and corrosion amount after 1 s/2 s as benchmarking variables for the severity of the local hydrogen starvation event.

It is evident that a lower cathode RH leads to delayed initial depletion and milder corrosion issue, as opposite to the sensitivity study with RH in the anode flow field. This is not unexpected, since a lower cathode RH leads to lower net water transport towards the anode and less water accumulation within anode GDL. For additional clarity, Fig. 8b illustrates the profiles of gas partial pressures and the current density in the extreme case (No. 10, 30% cathode RH). The RH settings in this case represent the situation at anode outlet in an automotive PEMFC, where the local cathode is at its respective inlet (counter-flow) and is relatively dry. Although the H_2 partial pressure ought to be lower at anode outlet, it is kept at 1 bar throughout the sensitivity study for a better comparability.

Contrary to the previous case in Fig. 7b (dry anode/wet cathode), the present case (wet anode/dry cathode) shows prompt “water vapor drainage” at the early stage of blockage. As a result, the local total pressure drops rapidly, inducing very strong convection towards the blockage region. In fact, due to this “vacuum effect,” one observes local plateau of H_2 partial pressure in the blockage region even higher than in the anode gas channel. At the same time, the local dry-out of the CCM reduces the current density significantly over the whole blockage region. The combination of strong in-plane

Figure 8. Sensitivity analyses of cathode RH settings. (a) Initial depletion time and carbon loss after 1 s or 2 s in dependence on the RH setting on the cathode. All four cases run under same gas composition in the anode flow field (H_2 1 bar, 5% N_2 in H_2 , RH 90%). (b) Profile of hydrogen (p_{H_2}), nitrogen (p_{N_2}) and water vapor partial pressure (p_{H_2O}) as well as total pressure (p_{total}) and current density (i) on the anode MPL/CL interface in simulation case No. 10 (see Table V). (c) Total reversed current density and the current density of carbon corrosion reaction (COR) in the fully starved region as a function of the cathode RH. The right axis additionally shows the percentage of COR current with respect to the total reversed current. RH dependencies of the reaction kinetics and the oxygen crossover are taken into consideration in the modeling.

convective H_2 transport and reduced current density leads to significantly delayed H_2 depletion and a relatively slower development of the fully starved region thereafter.

Unlike the anode RH, the change of the cathode RH has additional influences on reversed current related phenomena within the fully starved region. As shown in Fig. 8c, the total reversed current and the COR current is reduced to around half ($\sim 55\%$) by reducing the cathode RH from 90% to 30%. This decrease serves as an additional mechanism towards lower carbon loss with a drier cathode (Fig. 8a).

In Table VII, we list some critical values related to electrochemistry of reversed current under the two different RHs. To explain the difference of reversed current quantitatively, one has to recall that the COR current during a local H_2 starvation event is controlled by the O_2 crossover towards the anode. Thus, it is directly linked with the oxygen permeability of the membrane, which is smaller with lower membrane water content (lower RH). Indeed, the effective diffusivity of O_2 in the membrane drops for 46%, when the cathode RH is reduced from 90% to 30%.

The RH dependency of COR kinetics, on the other hand, leads to a shift of cathode potential. Since COR reaction order is unity with respect to water (refer to Tables II and S3), the same cathode potential would only provide a third of the COR current at 30% RH compared to it at 90% RH. As the current density is reduced by 55% ($< \text{two thirds}$) at 30% RH, the cathode potential has to be slightly elevated (by 32 mV, see Table VII). In addition, the cell voltage is significantly lower with a drier cathode (current density in H_2 -rich region is set, lower proton conductivity within the CCM leads to lower cell voltage). As a result, the anode potential (cathode potential minus cell voltage) is considerably elevated (by 115 mV, see Table VII). This different anode potential, in turn, allows different levels of oxygen concentration within the ACL. In fact, the anode potential at 30% RH under reversed current is so high (868 mV vs RHE), that a significant O_2 level can be reached locally in the ACL (3.26 kPa). This reduces the O_2 concentration gradient across the CCM and further lowers O_2 crossover, explaining the discrepancy observed between change in reversed current ($\sim 55\%$) and change in O_2 permeability ($\sim 46\%$). In other words, the oxygen permeability plays the major role to determine the reversed current, while the COR kinetics only exerts minor influence on the reversed current via the O_2 level in the ACL, in case the anode potential is high enough. Hu et al.³⁰ suggested that at cell voltage > 0.5 V, the COR current is limited by oxygen crossover, whereas below, it is determined by COR kinetics. Yang et al.²⁴ obtained similar conclusions and suggested the ORR kinetics within the ACL as the limiting factor at a low cell voltage (0.5 V). These observations agree well with our results, where when the cell voltage lowers (here due to the reduced RH towards 0.5 V), the COR current is increasingly influenced by its "own kinetics," which is again closely linked with the O_2 level within the ACL.

Last but not least, it is worth mentioning that COR accounts for approximately 95% of the reversed current regardless of the RH setting (Fig. 8c), with the rest 5% being contributed by OER. This ratio agrees well with observations in the literature for a high surface area carbon.³⁶ The slight increasing ratio with increasing RH is due

to the small difference in COR/OER reaction order with respect to water vapor, namely unity³⁶ and 0.88.³⁴

Model validation.—In this section, we seek to validate the numerical model by means of dynamic current density distribution measurements using a current scan shunt (CSS) array. As already mentioned in the Experimental section, the results of the CSS, especially the absolute values of the measured current densities, are influenced by the in-plane current redistribution through GDL and metallic BPP. To allow a fair comparison between the numerical model and the experiments, this effect will also need to be represented by the model. As it will be shown in later discussions (Figs. 10, 11), the model prediction agrees, both qualitatively and quantitatively, reasonably well with the experimental observations under both tested RH conditions.

On the other hand, in order to prove that reversed current has taken place during the local starvation experiment (it could not be observed by the current density distribution (CDD) measurement as a consequence of the current redistribution effect), we have conducted localized performance evaluation at EOL as well as post-mortem thickness determination of the MEA. The localized performance and ECSA losses undoubtedly confirm the local degradation and occurrence of reversed current during the local starvation experiment.

Overall observations and the in-plane current redistribution.—

Figure 9 depicts the steady-state CDD of operating point I (20% N_2 , RH anode/cathode 30%/90%) after switching to the overall current density of 0.5 A cm^{-2} . It is apparent that the blockage (marked by orange frame in region A1 through E3) additionally induces strong starvation effects downstream (in region F1 through M3).

It can be observed from Fig. 9 that the minimum measured current density within the domain is around 0.15 A cm^{-2} , although a reversed current in the order of -1 mA cm^{-2} within the starved region shall be expected. This significant difference is largely related to the in-plane current redistribution,^{58–60} since the CSS senses the cell current density not directly at the CCM, but "outside the cell" after redistribution of current within the GDLs and the metallic BPP (refer to Fig. S15). As a result, in order to utilize the obtained CDD data for the model validation, the model needs to account for the in-plane redistribution effects as well. For this purpose, sub-model II, which was used to calculate the electron transport in the GDL, was extended to include the additional layers of GDLs, the BPP and the CSS. Details of this model extension are documented in the Supplementary Material (geometry can be found in Fig. S15). Table IX additionally summarizes major parameter adjustments of the model for its validation based on the experimental conditions. It shall be noted that instead of the semi-galvanostatic condition as applied in the previous modeling sections, an "overall" galvanostatic condition was applied here (control average current density over the entire domain) to match the experimental condition.

Current transient and comparison with modeling results.—

Figure 10 compares the dynamic CDD development predicted by the model with the experimentally obtained results from the CSS

Table VII. Sensitivity of reversed current and electrode potentials towards the cathode RH setting. Anode flow field composition is kept constant (5% N_2 , 90% RH).

Cathode RH	90%	30%	Difference 90% to 30%
Reversed current	1.81 mA cm^{-2}	0.827 mA cm^{-2}	-54.2%
Effective membrane O_2 diffusivity	$6.50 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$	$3.49 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$	-46.3%
COR kinetics	Reaction order unity		
Cathode potential	1.435 V vs RHE	1.467 V vs RHE	+32 mV
Cell voltage	0.681 V	0.598 V	-83 mV
Anode potential	0.754 V vs RHE	0.869 V vs RHE	+115 mV
O_2 accumulation within the ACL	0.16 kPa	3.26 kPa	+3.1 kPa

Figure 9. Steady-state current density distribution measured by the CSS superposed with the location matrix. Blockage within the channels is located in the orange-framed area (A1 through E3). Additionally, the orange crosses indicate that the hydrogen supply channels (region between the inlet manifold and the active area) were locally sealed to minimize H_2 flow to the blocked region via convection. Cell operates at 80°C with an average current density of 0.5 A cm^{-2} ; RH is 30% at the anode inlet and 90% at the cathode inlet.

Figure 10. Comparison of CDD (profile in across-the-channel direction) transient predicted by the model (sim) and obtained by the experiment via CSS (exp) at three physical times: 100, 500 and 1000 ms. Conditions of the experiment and model: cell temperature of 80°C , anode N_2 content of 20%, anode RH 30%, cathode RH 90%. Time zero in the experiment corresponds to the time where the cell current density was switched from OCV to 0.5 A cm^{-2} . The experimental profile was evaluated in region E (E1-E6, refer to the location matrix in Fig. 9). The blockage size is indicated by the dashed line (0–50 mm).

under the conditions of operating point I (30% anode RH and 90% cathode RH). Both profiles are shown in the direction perpendicular to the flow field (across-the-channel, same as the modeling geometry in Fig. 1). The experimental CDD was evaluated in region E (from E1 up to E6) of the location matrix. This region was chosen since part of it is still under the blockage and the region is expected to be the least influenced by possible effects of H_2 convection in the channel direction (which cannot be captured by the model).

It shall be mentioned that the steady state (profile shown in Fig. 9) was already reached after around 1000 ms starting from the time where the starvation event was triggered by applying a current density of 0.5 A cm^{-2} . Therefore, to represent the entire temporal development of the CDD during the starvation event, three physical times of 100, 500 and 1000 ms were chosen for comparison. Figure 10 reveals that the modeling results agree quantitatively

Figure 11. Modeled and experimentally obtained time development of average current density under the blockage under RH conditions of 30%/90% or 90%/30% (anode/cathode). Conditions of the experiment and model: cell temperature of 80°C , anode N_2 content of 20%. Time zero in the experiment corresponds to the time where the cell current density was switched from OCV to 0.5 A cm^{-2} . The experimental value was evaluated under the blockage of region E (i.e. E1, E2, and first half of E3).

reasonably well with the experimental data at all three physical times. It shall be emphasized that the profiles of the modeled results (solid lines) are the CDD profiles at the CSS (outside the BPP, see extended geometry in Fig. S15), not in the CCM. CCM and CSS profiles are significantly different from each other due to the in-plane current redistribution and a comparison is shown in Fig. S16.

Comparison of both RH conditions.—To shed more light on the temporal development of the CDD, the current density data in Fig. 10 (operating point I) was averaged in the blocked region (i.e. between 0 and 50 mm) and plotted against time in Fig. 11. The same procedure was repeated for operating point III with 90% RH on the anode and 30% RH on the cathode, allowing a comparison between different RH conditions.

In the modeling section (see sections “Sensitivity of anode RH” and “Sensitivity of cathode RH”), it was predicted that the combination of wet anode and dry cathode will lead to initial drop of current density within the blocked region, followed by overall

Table VIII. Test sequence of the validation experiment.

Point No.	Anode flow settings	RH anode/cathode	Holding time at 0.5 A cm ⁻²
I	1600 nccm H ₂ + 400 nccm N ₂	30%/90%	10 s
II	2000 nccm H ₂	30%/90%	150 s
III	1600 nccm H ₂ + 400 nccm N ₂	90%/30%	10 s
IV	2000 nccm H ₂	90%/30%	150 s
V	1600 nccm H ₂ + 400 nccm N ₂	30%/90%	90 min

delay in H₂ depletion (refer to Fig. 8b). The same effects are also evident in Fig. 11 for both experimental observations and simulative predictions, where the blue curves (RH 30% anode/90% cathode) are initially lower than their red counterparts (RH 90% anode/30% cathode), yet the latter drop more strongly at the beginning. It can be observed that starting from 0.2–0.3 s, current densities of the red curves stay higher than those of the blue curves for the entire course of the local starvation event (experimental as well as simulative data).

Some quantitative discrepancies between the model and the experiment have most likely resulted from three-dimensional effects within the experiment which cannot be represented by the 2D model. For instance, additional amount of H₂ may become available due to convective transport in the third dimension (along-the-channel direction), which may explain the delay of starvation event observed in the experiment. Current redistribution may also be present in the channel direction, which will lead to slightly different overall current density in region E1-E6 (compared to the target 0.5 A cm⁻²). Furthermore, the CSS measurement has limited resolution with regards to time (100 ms accuracy) and current density ($\pm$ several 10 mA cm⁻²). The gas compositions locally in region E are also expected to be slightly different from the values at anode inlet, based on which the modeling calculations were done.

Last, it may be noticed that the sensitivity to the RH condition is relatively weak both in the experimental and in the modeling case, which is primarily due to the presence of high N₂ content in the anode (20%, due to experimental constraints). As mentioned in the modeling section, both water vapor and N₂ influence the development of local starvation event by affecting the extent of H₂ convective transport within the anode GDL. Compared to the 5% N₂ condition during the previously discussed sensitivity study, 20% N₂ in the anode flow field will lead to significantly faster accumulation of N₂ under the blockage, whose effect is therefore also more dominant over the effect of water vapor. In the Supplementary Material, we additionally discuss the current transient observed at operating point II and IV (refer to Table VIII) with pure H₂ as anode gas, where it is demonstrated that the delaying effect of the RH conditions is considerably more dominant (Fig. S18).

Confirmation of reversed current conditions via post-mortem analysis.—Figure 12a depicts the localized MEA performance on segments K5 (reference), E2, H2 and K2. Evidently, the performance on segments E2, H2 and K2 is significantly reduced, indicating severe localized degradation. This agrees well with the cyclic voltammogram in Fig. 12b, where segments E2, H2 and K2 have lost nearly all H_{upd} features, demonstrating strong loss of Pt electrochemical active area. This was further confirmed by cross-sections where the local electrode thickness has decreased to 7.7 μ m (E2) and 5.3 μ m (K2), while the reference position K5 still shows the initial thickness of 10.5 μ m (see Fig. S21). These observations confirm the carbon corrosion and the associated degradation effects on the cathode, indicating the occurrence of reversed current during the experiment.

“Stability window”.—Based on the numerical model presented in the study, we are able to predict combinations of test conditions that would provide stability against local H₂ starvation under automotive conditions.

Figure 12. (a) Localized measurement of polarization curve on segments K5, E2, H2 and K2 (based on the location matrix). K5 is not affected by the blockage; E2 is located under the blockage; H2 and K2 are to the downstream side of the blockage. Conditions of the polarization curve measurement: 60 °C, 1000 nccm H₂/air, back pressure 1.5 bar and 79% RH on both anode and cathode sides. The measurement was dynamic using a scan rate of 25 mV s⁻¹ between 0.2 to 0.9 V cell voltage, where values in the plot are taken from the anodic scan. (b) Localized CV measurement on the same segments: 25 mV s⁻¹ scan between 0.075 and 0.8 V under 1000 nccm H₂/N₂. Temperature, RH, and pressure conditions remain the same as the polarization curve measurement.

Figure 13a illustrates which combination of the anode nitrogen content and blockage length is critical with regards to local starvation severity and irreversible degradation effects. The calculation was done under the base case condition (RH 70%/80%, 1 A cm⁻² in the normal region). Three operating regions are depicted. In the first region

Table IX. Major parameters adjusted to experimental conditions for the model validation.

Parameter	Symbol	Value	Unit	Notes, Source, Rationale
Size of the channel blockage	x_{Starve}	50	mm	Blockage size in the across-the-channel direction
Size of the computational domain	x_{Domain}	120	mm	Cell size in the across-the-channel direction
Current density (average in the whole domain)	i	0.5	A cm^{-2}	Experimental setting
(Dry) Nitrogen content in the anode flow field		20	%	Experimental setting
Total pressure	p_{total}	120	kPa	Experimental setting
Hydrogen partial pressure in the anode flow field	$p_{\text{H}_2,0}$	84.7 (30% RH) 62.6 (90% RH)	kPa	Calculated based on RH and N_2 content
Membrane thickness	d_{memb}	15	μm	MEA characteristics (Gore M 775.15)

Figure 13. “Stability window” during parametric study of two influential factors during the development of a local starvation event: N_2 content in the anode channel and the blockage size. Time marks in the graphs denote the time it takes for H_2 depletion to occur at the starvation center (first depletion time). Should H_2 depletion never take place under the given conditions, the percentage marks in parenthesis report the remaining current density at the starvation center (normalized to the operating current density 1 A cm^{-2}) after steady state is reached. Color codes (green/yellow/red) give rough indication on how safe the operation is under the given operation conditions with regards to local starvation severity. Both graphs were calculated under 1 bar of H_2 , a current density of 1 A cm^{-2} in the normal region, as well as (a) at 70% anode RH and 80% cathode RH; (b) at 90% anode RH and 30% cathode RH.

(green), combination of N_2 content and the length of the blockage (e.g. 5% N_2 content with a 5 mm size blockage) still allows a safe operation where no degradation can occur. The number in the parenthesis denotes the percentage of the remaining current density at the starvation center (normalized to the operating current density 1 A cm^{-2}) after steady state is reached. In the second region (yellow color), H_2 depletion and degradation eventually occurs, but not before at least 1 s has elapsed starting from the time the blockage was set (time marks given in the graph correspond to the time where the first depletion of H_2 occurs at the starvation center). This time delay would give some room for countermeasures e.g. related to liquid water removal from the anode channel. In the critical red region, on the other hand, irreversible degradation takes place almost instantaneously (sub-second) when the blockage is formed. From a local starvation point of view, it is therefore not recommended to operate the cell in this region. If the risk of large-size blockage (in this case, starting from $\sim 5 \text{ mm}$ size) cannot be avoided due to the operating conditions, one solution would be to operate the cell with as low of anode N_2 content as possible and reduce/avoid anode recirculation (in this case, with maximum of around 2% N_2).

One of the key messages from the present study is that a higher RH within the anode channel and a lower cathode RH lead to slight mitigation of the local starvation, provided that the size of the blockage stays the same. This can again be observed in Fig. 13b under the conditions of 90% anode RH and 30% cathode RH. Evidently, at high N_2 concentrations, the stability is not significantly influenced by the RHs, whereas with conditions of $<10\%$ N_2 , the cell may tolerate a much greater sizing of blockage under these changed RH conditions.

Conclusions

Local hydrogen starvation and related carbon corrosion can potentially cause severe performance degradation of state-of-the-art PEMFCs during their lifetime. Utilizing the numerical model developed in the present study, we first demonstrate the dominating effect of H_2 in-plane convective transport during such starvation events, as well as its suppression by the presence of other gas species. Through model sensitivity studies of RH settings, it is shown that the starvation severity is further linked with local water transport: where RH on the cathode side exceeds that of anode, blockage in the anode flow field leads to prompt accumulation of water vapor in the anode GDL and thus quicker development of starvation. The opposite effect takes place if the anode side is wetter than the cathode, where the starvation effect is weakened.

The model predictions, especially the predicted trend with regards to the RH settings, are validated by conducting dynamic CDD measurement on an automotive MEA with partially blocked anode flow field. The degradation effects during the starvation event are confirmed by means of localized performance evaluation and post-mortem analysis. For a quantitative comparison between the model and the experiment, it is noted that the presence of in-plane current redistribution in the experimental setup must be additionally accounted for in the model.

This study is the first of its kind to show that water transport through the CCM plays a crucial role during a local hydrogen starvation event. Additionally, the concept of “stability window” was introduced, where the risk of irreversible degradation can be assessed under various operating conditions using the present model. Overall, the findings in this study serve as valuable inputs for guiding future operational strategies towards starvation mitigation and better durability in FCEVs.

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