



Analyzing local degradation in an industrial PEMFC under EPA US06 drive cycle via 3D-CFD

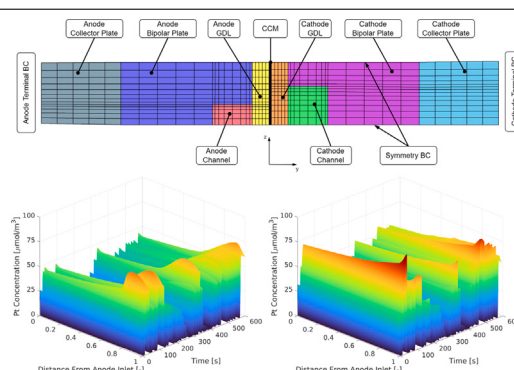
Maximilian Haslinger*, Thomas Lauer

Institute of Powertrains and Automotive Technology, Technische Universität Wien, Getreidemarkt 9, Vienna, 1060, Austria

HIGHLIGHTS

- Unsteady 3D-CFD Simulation of a large active area PEMFC.
- 600 s of EPA US06 drive cycle simulated.
- Comparison of local degradation phenomena at different humidity levels.
- Hydrogen peroxide concentration in ACL drops by 25 % at high air humidity.
- Low air humidity showed lower carbon corrosion and Pt dissolution in CCL.

GRAPHICAL ABSTRACT



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ABSTRACT

Considerable research efforts have been made to investigate the degradation mechanisms of various components of proton exchange membrane fuel cells (PEMFCs). However, understanding the degradation of large active area PEMFCs under automotive operating conditions remains an important research focus. In this study, an unsteady 3D computational fluid dynamics (CFD) model in combination with 1D models for carbon corrosion, platinum dissolution and hydrogen peroxide production provides detailed insights into the degradation potential of a PEMFC. Typical degradation phenomena in PEMFCs are influenced by local factors such as potential, temperature and humidity. These internal states cannot be easily captured with conventional measurement methods. The simulation of a driving cycle with high dynamic load at two humidification states of the intake air showed significant local variations. Although the hydrogen peroxide concentration in the anode catalyst layer decreases at high humidity by 25%, the Pt/C catalyst decomposition in the cathode catalyst layer increases. Low humidity conditions lead to strong temporal fluctuations of the water content in the membrane, which increases the risk of mechanical fatigue. Despite the increased Pt/C decomposition observed at high humidity, improved homogeneity of the local potentials within the catalyst layers and the water content of the membrane mitigates ionomer degradation.

1. Introduction

Hydrogen-powered fuel cells, particularly the polymer electrolyte membrane fuel cell (PEMFC), play a vital role in the field of transportation [1]. These fuel cells are especially well-suited for long-haul trucks,

off-road vehicles, and passenger cars, given their need for extensive driving ranges [2]. The PEMFC stands out as the optimal choice for such vehicles due to its high power density, rapid refueling capabilities, and overall efficiency. With these properties, PEMFCs powered by

* Corresponding author.

E-mail address: maximilian.haslinger@ifa.tuwien.ac.at (M. Haslinger).

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sustainable hydrogen represent a promising solution for the mobility sector, as they offer a fossil-free means of propulsion [3].

However, the lifetime and durability of PEMFCs are currently not as high as those of internal combustion engines or batteries. The targets of the U.S. Department of Energy (DOE) for the lifetime of a fuel cell stack for long-haul tractor-trailers in 2030 have been set at 25 000 h (ultimate 30 000 h) [4]. For automotive applications, the target lifetime of a fuel cell system was set to 5000 h (current 4130 h, ultimate 8000 h) in 2025. At the end of life (EOL), the voltage drop must not exceed 10% at rated power compared to begin of life (BOL) [5]. Therefore, a lot of research on degradation mechanisms is conducted to expand the lifetime of PEMFCs.

The operation of a fuel cell system for automotive applications in power-follow mode is very demanding. The fuel cell system takes over most of the requested power and the battery serves as a buffer for load peaks and recuperation [6]. A fluctuating load also means that internal conditions such as local humidity, water content, local potential, current density, and temperature are subject to rapid changes. These changes can lead to increased degradation of the catalyst layers and the ionomer material if unfavorable combinations of the mentioned internal conditions are present. Wallnöfer-Ogris et al. [7], Ren et al. [8] and Zhao and Li [9] give a comprehensive review of the degradation mechanisms present in a PEMFC in general and under automotive operating conditions.

The degradation of the catalyst layers (CLs) and the ionomer material of a PEMFC is triggered by typical operating conditions in automotive vehicles, such as highly dynamic loads and idling. Idle operation refers to the operation of the PEMFC near or at the open circuit voltage (OCV). The potential at the positive electrode reaches up to 1 V, which can trigger undesirable electrochemical reactions [8,10]. Platinum dissolution and carbon corrosion were identified as primary degradation processes in the CLs, as well as the secondary degradation processes triggered by them, such as Ostwald ripening, and particle detachment and agglomeration [7,11]. The consequences are a loss of support material in the CLs and a loss of electrochemical surface area (ECSA) as well as the detachment and agglomeration of Pt particles. In contrast to the cathode, the low local potential at the negative electrode promotes the formation of unwanted hydrogen peroxide H_2O_2 due to oxygen crossover [12–14]. Upon contact between hydrogen peroxide and metal ions, hydrogen peroxide radicals are formed. Metal ions can originate from impurities during assembly, the components of the fuel cell system, and the metal bipolar plates. These radicals then attack both the main and side chains of the ionomer [15–17]. This leads to the release of hydrogen fluoride and the decay of proton conductivity, and pinholes can form in very thin membranes [18].

High dynamic loads can lead to partial or complete fuel starvation because the pores are clogged with liquid water or the supply of fuel H_2 is insufficient. This leads to high potentials in the cathode catalyst layer (CCL) (local fuel starvation) or the anode catalyst layer (ACL) (complete fuel starvation) [19,20]. High potentials in the CLs trigger carbon corrosion and platinum dissolution. The dissolved water content in the membrane is subject to fluctuations under dynamic load, which is known as hygrothermal swelling and shrinking. Fuel cell stacks are usually held together by a clamping force that ensures the gas and liquid tightness of the system. Due to the constrained volume expansion, the area under the land where the bipolar plate comes into contact with the MEA is at the highest risk of mechanical fatigue of the membrane. Local mechanical stress peaks can trigger the formation of cracks and holes in the membrane, which cause an unrestricted crossover of fuel and oxidizing agent and lead to mixed potentials (= parasitic current) and hot spots in the fuel cell [21–24].

Due to the slow speed of the degradation mechanisms described above, accelerated stress tests (ASTs) (or dynamic stress tests (DSTs)) have been developed to investigate the degradation in a reasonable time [8,9,25]. Thiele et al. [25] provide a comprehensive review of the degradation mechanisms in automotive applications and their AST

methods. They present methods to capture the degradation of the active layers and the membrane by in-situ and ex-situ methods. Idling can be investigated by the application of a small current density during these tests to ensure high cathodic potentials of ≥ 0.9 V [26,27]. The crossover of oxygen can further be increased by a higher cathodic pressure or the supply of pure oxygen. The cycling of voltage, humidity, temperature, and pressure is used to mimic the high dynamic loads of fuel cells [8,25]. In-situ measurement methods include the quantification of CO_2 and HF emissions to quantify carbon corrosion and ionomer degradation [7,8]. The increase in ohmic losses is indicated by a change in the high-frequency response (HFR) [14]. Structural damage such as membrane thinning, pinholes, and cracks, as well as Pt surface loss and Pt particle growth, can be determined by ex-situ methods. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectrometer (XPS) are used for this purpose [28,29]. X-ray absorption spectroscopy (XAFS) allows the in-situ observation of ORR activity and oxidation states of the platinum particles [30].

The needed measurement equipment is expensive and hydrogen consumption of long-term degradation experiments is also a cost factor. The use of unsteady 3D-CFD methods allows the investigation of the internal states of a PEMFC with high temporal and spatial resolution and helps to reduce development costs and time [31,32]. These models provide the highest level of physical modeling and, therefore, an accurate description of the processes inside a PEMFC, which is especially important for phenomena that depend on local conditions, such as degradation. The simplifications of many dimension-reduced models lie in the description of the CLs by simplifying them to an interface [33–35]. In addition, the adsorption and desorption of water in the membrane are not modeled with the highest detail possible [35–37]. But the water uptake behavior of the membrane is one of the determining factors of voltage under- and overshoots after load steps [38–40]. In addition, the modeling of two-phase flow is more detailed than with physically and dimensionally reduced approaches [41,42]. However, the use of 3D-CFD models in combination with degradation models on large active area PEMFCs is computationally demanding [32]. But the use of single-channel models significantly reduces the computational cell count and enables the simulation of several 100 s in a reasonable time.

The simulation of large-scale PEMFCs with 3D-CFD simulation methods was done in the past [43–48]. For instance, Cheng et al. [45] investigated the non-uniformity of reactants and water content under different levels of hydrogen and air humidification. They found out that hydrogen humidification has a bigger impact on the membrane water content compared to increased air humidification. The use of 3D-CFD models in combination with degradation models is also present in the literature [44,49–53]. For example, Fink et al. [44] coupled a basic unsteady 3D-CFD model of a low-temperature PEMFC with unsteady degradation models for ionomer degradation, carbon corrosion, and platinum dissolution. It is possible to switch between steady-state mode and transient mode with feedback to performance, including the prediction of thickness reduction of the active layers and the membrane, particle agglomeration, ionomer properties change, and loss of ECSA. Huang et al. [52] combined a 3D-CFD model with a 1D degradation model to investigate the Pt degradation of a 100 cm^2 PEMFC. A quantitative assessment of two platinum loadings was carried out and compared. The results showed that the lower the platinum loading, the greater the drop in performance. Yang et al. [53] conducted research on the degradation of a 200 cm^2 PEMFC at constant load operation. They implemented the degradation models in ANSYS Fluent® but used a single-phase approach to reduce model complexity and computational effort. A PtCo alloy catalyst was used, and the long-term constant voltage operation was investigated. They witnessed a non-uniform distribution of ECSA loss due to significant gradients of current density over the active area.

The novelty of this work is the use of a high-detail and unsteady, single-channel 3D-CFD model of a large-active area PEMFC to simulate 600 s of an automotive drive cycle. Although the use of full-scale models is superior to single-channel models for investigating the internal distribution, the computational cost must be taken into account when using transient models [47]. However, the single-channel model used showed good agreement with the large-scale model in a previous work of the authors and is able to represent the conditions along a single channel with high accuracy [46]. The results of the basic 3D-CFD model feed 1D degradation models based on extended BVE approaches for carbon corrosion, platinum dissolution, and hydrogen peroxide production. Due to the high tortuous anode and cathode channels, the gradient of the internal conditions is high in the channel direction. The influence of air inlet humidity and temperature on the degradation is compared and discussed (Base Case and RHT Case). The power profile was taken from an experimental assessment of the 2016 Toyota Mirai at the Argonne National Laboratory by Lohse-Busch et al. [54]. The EPA US06 driving cycle with its demanding conditions was simulated due to the known higher degradation rate during demanding loads [55]. The power profile was applied to a real-time capable and validated quasi-3D model of a 120 kW industrial PEMFC stack to get boundary conditions for the 3D-CFD model. The simulation results of the 3D-CFD model showed that humidity, temperature, local potential, and dissolved water content in the active area are not uniform in the Base Case. In the inlet and outlet sections of the anode and cathode, large parts of the active area are not sufficiently humidified. A comparison of both simulated cases showed that the increase of intake air humidity decreased the hydrogen peroxide concentration in the ACL but slightly increased the production of CO₂ and Pt ion concentration during idling. The 3D-CFD model provides detailed access to the internal states that are not readily accessible with measurement methods or dimensionally reduced models. Thus, this study provides an extension of the knowledge of the degradation potential of a PEMFC under high dynamic loads and different humidification states. This knowledge can be used to reduce unfavorable conditions and help to develop more robust PEMFCs for automotive applications in the future.

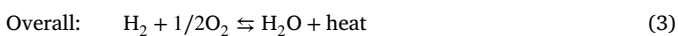
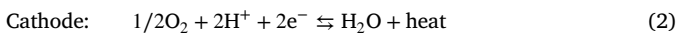
2. Materials and methods

2.1. 3D-CFD model

The 3D-CFD simulation model was set up using the commercially available software package AVL FIRE™ M (Version 2022R1). The full description of the base model is available in Fink et al. [44]. Based on the simulation results the production rates of carbon corrosion, platinum dissolution, and hydrogen peroxide H₂O₂ were determined. Using this methodology, the high spatial and temporal resolution of the simulated 3D-CFD data could be used to quantify the degradation rates.

2.1.1. Basic model

The most important features of the following analysis are presented in this section. The used PEM fuel cell model accounts for two-phase flow and multi-species flow and is non-isothermal. In a PEMFC, two spatially separated electrochemical reactions take place: the Hydrogen Oxidation Reaction (1) (HOR) and the Oxygen Reduction Reaction (2) (ORR) in the anode and cathode, respectively.



The membrane is an isolator against electrons but can conduct ions. The released hydrogen ions in the ACL travel through the membrane to the CCL whereas the electrons do useful electrical work and are conducted in an outer circuit to the CCL. The Butler-Volmer

Equation (BVE), Eq. (4) connects potential and reaction rate of an electrochemical system: [56]

$$J_{ec} = J_0 \left[\exp \left(\frac{2\beta_a F}{RT_s} \eta_{act} \right) - \exp \left(-\frac{2\beta_c F}{RT_s} \eta_{act} \right) \right] \quad (4)$$

$$\text{with } \eta_{act} = \phi_{elec} - \phi_{ion} - E_0 = U_{local} - E_0 \quad (5)$$

$$\text{and } \beta_a = \begin{cases} 1 - \beta \\ \beta \end{cases} \text{ and } \beta_c = \begin{cases} \beta \\ 1 - \beta \end{cases} \text{ at } \begin{cases} \text{cathode} \\ \text{anode} \end{cases} \quad (6)$$

The activation overpotential η_{act} indicates the overpotential, that is necessary to drive an electrochemical reaction. It is determined according to Eq. (5) [44]. The equivalent potential E_0 is per definition $E_{0,HOR} = 0$ V at the anode and $E_{0,ORR} = 1.23$ V at the cathode at standard state conditions. The transfer coefficients β_a and β_c apply to the anodic and cathodic half-reactions of the HOR (1) and ORR (2) [56,57]. In the CLs the macro-homogeneous model was used. Electric and ionic overpotentials are determined with the charge conservation Eq. (7). The source term on the right side is the produced current density from the electrochemical reaction and is only valid for the CLs. In the other porous and solid layers, the source term is 0.

$$\nabla \cdot (-\alpha_{elec/ionic} \sigma_{elec/ionic} \nabla \phi_{elec/ionic}) = \begin{cases} -J_{ec} & \text{elec} \\ +J_{ec} & \text{ionic} \end{cases} \quad (7)$$

In the ionomer, dissolved water, hydrogen, oxygen, and nitrogen are present. The dissolved water flux $\vec{n}_w$ in the ionomer is calculated with a Nernst-Planck equation, accounting for diffusion and electro-osmosis, Eq. (10). The dissolved water content C_w of the ionomer is determined with the PDE (8).

$$\frac{\partial}{\partial t} \left(\alpha_{ion} \frac{\rho_{ion}}{EW} C_w \right) + \nabla \cdot \vec{n}_{H_2O,ip} = S_{C_w} \quad (8)$$

$$S_{C_w} = k_{g,w} \frac{\rho_{ion}}{EW} (C_{w,eq} - C_w) + \begin{cases} -\frac{J_{ec}}{2F} \\ 0 \end{cases} \text{ at } \begin{cases} \text{cathode} \\ \text{anode} \end{cases} \quad (9)$$

$$\vec{n}_{H_2O,ip} = -C_{drag} \frac{\alpha_{ion} \sigma_{ion} \nabla \phi_{ion}}{F} - \alpha_{ion} \frac{\rho_{ion}}{EW} D_w \nabla C_w \quad (10)$$

The relationship derived by Springer et al. [58] for the equivalent water content $C_{w,eq}$ is used. The term $k_{g,w}$ indicated the interfacial resistance of the ionomer to water adsorption and desorption [22,59]. The surrounding gases in the CLs can dissolve in the ionomer phase and are transported by convection (due to the dissolved water flux $\vec{n}_w$) and by diffusion with the dissolved diffusion coefficient $D_{w,k}$ of species k , Eq. (12). According to Wong and Kjeang [60] diffusion is dominant compared to convection. Eq. (11) is the PDE to calculate the dissolved species mole fraction $x_{w,k}$ of species k . The subscript ip indicates values in the ionomer phase.

$$\frac{\partial}{\partial t} \left(\alpha_{ion} \frac{\rho_{ion}}{EW} C_w x_{k,ip} \right) + \nabla \cdot \vec{n}_{k,ip} = S_{k,ip} \quad (11)$$

$$\vec{n}_{k,ip} = \vec{n}_{H_2O,ip} x_{k,ip} - \alpha_{ion} \frac{\rho_{ion}}{EW_{ion}} C_w D_{k,ip} \nabla x_{k,ip} \quad (12)$$

with $k \in \{\text{H}_2, \text{O}_2, \text{N}_2\}$

The crossover hydrogen is assumed to be consumed by 100% at the Membrane/CCL interface resulting in a parasitic current density. The oxygen in the ACL forms water and hydrogen-peroxide (H₂O₂) according to the chemical Reaction (13). In contrast to the positive electrode, it is assumed that there is a small amount of oxygen left in the anode after these reactions. The remaining oxygen is flushed out in the anode gas channels [44]. The parasitic current densities on both electrodes introduce a mixed potential and thus contribute the biggest part of the voltage drop at OCV conditions between the theoretical fuel cell potential and the OCV.

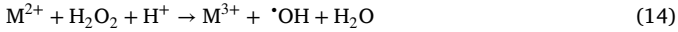
2.1.2. Degradation model

The following equations in this section were used to quantify the degradation potential of some selected degradation mechanisms during post-processing. These models are already implemented in proprietary software packages [44,61] and this was also the reason to use

them in this work, as they have proven their numerical stability and accuracy. The decay of material properties, e.g., ionic conductivity, equivalent weight, platinum ion diffusion, membrane/CL thickness, was not determined. The presented mechanisms depend on the local humidity, temperature, potential, water content, and O₂ concentration. In Section 2.1.1 the calculation of these quantities was discussed. The following degradation mechanisms are investigated in this work:

- Ionomer degradation in ACL
- Carbon corrosion in CCL
- Platinum dissolution in CCL

Ionomer degradation. The ionomer is attacked by hydrogen peroxide radicals (*OH, *OOH, *H) that are produced under certain conditions in both catalytic layers and the PEM. Hydrogen peroxide is formed by the two-electron ORR (13) at low local potentials in the CLs ($U_{local} < 0.695$ V) [60]. The produced H₂O₂ can diffuse into the membrane and with the presence of metal ions M²⁺, e.g., Fe²⁺ and Cu²⁺, hydroxyl radicals *OH according to Fenton's reaction mechanism (14) can be formed. Next to *OH other radicals such as *OOH or *H can occur but are not considered in this work as the *OH radical has the highest damage potential. Metal ions can be present due to cleanliness issues during the production and assembly of the fuel cell stack and/or metal bipolar plates. The presence of metal ions in fuel cell stacks with metallic bipolar plates is one of the main reasons for the poorer durability compared to graphite BPP [8,60]. The hydroxyl radical attacks the main and side chains of the ionomer and is responsible for the decrease of ionic conductivity, equivalent weight, and thickness of the membrane. The attack of the side chains releases hydrogen fluoride HF that can be detected at the outlets. Further information on the unzipping mechanism of the side chains can be found in [7,60]. The stability of the *OH radical is higher the lower the potential is. Therefore, the anode catalyst layer is more likely to be attacked by hydrogen peroxide radicals at idle load and low current densities [7,8,62].



The reaction rates of Reactions (13) and (14) are determined with separate BVE approaches, see Table A.1. These reaction rates are combined to a source for hydrogen peroxide in the ionomer phase of the ACL. The local concentration of H₂O₂ in the ionomer phase of the ACL is calculated according to Reaction (15).

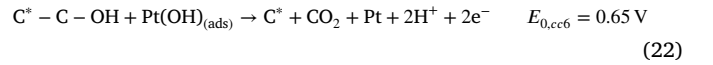
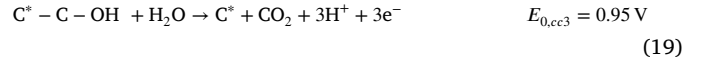
$$\frac{\partial}{\partial t} \left(\alpha_{ion} \frac{\rho_{ion}}{EW} C_w \frac{RT}{p} c_{H_2O_2,ip} \right) = S_{H_2O_2,ip} \quad (15)$$

$$S_{H_2O_2,ip} = \frac{j_{H_2O_2} a_{Pt}}{2F} - \dot{r}_{Fe} \alpha_{ion} \quad (16)$$

Carbon corrosion. Black carbon is used as a support material in catalyst layers of PEMFCs. The presence of platinum and a high local potential can trigger the oxidation of carbon, commonly referred to as carbon corrosion.

The carbon corrosion model is based on the assumption, that carbon oxidation happens only in the CCL. The model considers the effects of local humidity, load cycling, and local potentials. It was developed by Pandey et al. [63] and adapted by Fink et al. [44] and Kregar et al. [61]. The set of chemical reactions for carbon corrosion can be found in Eqs. (17)–(22) [63]. Each of these reactions is modeled with a Butler-Volmer approach, Eq. (4), to determine the production rates. The underlying assumption is, that there exist carbon defect sites C* that react with H₂O to unstable C-OH groups, Reaction (17). In Reaction (18), stable C=O groups are formed. The unstable C-OH groups can also be oxidized to CO₂ at higher potentials $U_{local} > 0.95$ V, Reaction (19). The equivalent potential in the ACL is per definition 0 V, thus, it is more likely that the CCL is subject to carbon corrosion. However, there are some internal states of the fuel cell that can trigger high

potentials in the ACL too, e.g., fuel starvation and start-up and shut-down. Reaction (19) also leaves a carbon defect site C* behind. The second path of carbon corrosion is via the oxidation of platinum and the formation of OH groups, Reactions (20)–(22). These mechanisms depend on the particle size of the CL. However, in this work the full set of BVE for the Reactions (17)–(22) was solved for only one particle size, see Table A.2. The surface coverage fractions of C, CO, COH, Pt, PtO, and PtOH are used to scale the corresponding half-reactions in the BVEs and are determined dynamically with ordinary differential equations, see Eqs. (A.1)–(A.6) and [61]. Reactions (19) and (22) can be combined to a source term for CO₂ production, see Eq. (A.13).



The particle size affects the equilibrium potential of Eqs. (20)–(22) due to the surface tension of the Platinum and its oxides (PtOH, PtO). This is accounted for by the Kelvin term that shifts the equilibrium potential from a flat surface to a curved one, see Eqs. (A.7)–(A.9).

Platinum dissolution. The dissolution of platinum can be described by three Reactions (23)–(25) [64]. It is mainly present in the CCL due to the high equilibrium potentials. The direct dissolution of platinum is possible at potentials higher than $E_{0,Pt,diss1}$ in an acidic environment [7]. According to Reaction (24) platinum oxides PtO can be formed at potentials higher than $E_{0,Pt,diss2} = 0.98$ V. Under decreasing potentials and available protons, the PtO can be dissolved to Pt²⁺, Reaction (25). Although Wallnöfer-Ogris et al. [7] stated that the equilibrium potential of Reaction (23) is likely to be never reached during normal fuel cell operation, Myers et al. [65] showed that it is the dominating mechanism. Therefore, Reaction (25) is not considered in the Pt dissolution source [61,66]. However, Reactions (24) and (25) are used in Eq. (A.5) for the buildup of platinum oxides. The Butler-Volmer equations for Reactions (23)–(25) can be found in Table A.3.



The production rate of Reaction (23) (j_{Pt1}) is used as a source term for Pt²⁺ ions. Eq. (26) determines the local concentration of Pt²⁺ [61]:

$$\alpha_{ion} \frac{dc_{Pt^{2+}}}{dt} = \sum_{p=1}^n \frac{4\pi r_{Pt,i}^2 N_{Pt,i}}{F} j_{Pt1,i} \quad (26)$$

where α_{ion} is the ionomer volume fraction in the CCL. The reaction rate $j_{Pt1,i}$ for each particle class i is summed up. The transport of platinum ions by diffusion is not considered in this work because it would require an additional transport equation for the Pt²⁺ ions. Therefore, the formation of a platinum band in the membrane due to the diffusion of Pt²⁺ ions into the membrane and Ostwald ripening was not considered.

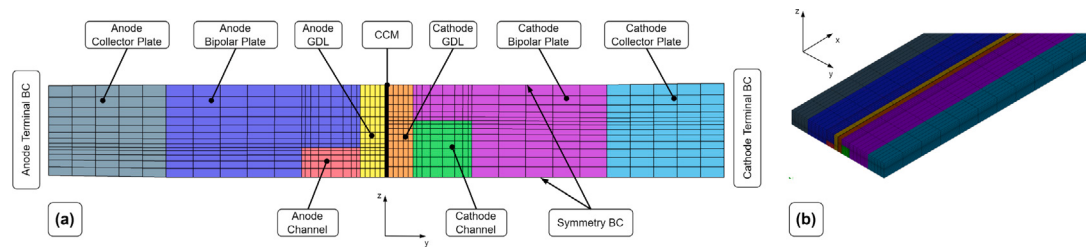


Fig. 1. Computational mesh of the single channel model.

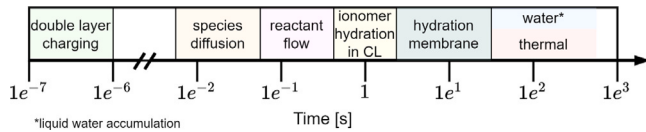


Fig. 2. Time scales of processes in a PEMFC. Based on [68,69].

2.1.3. Computational mesh

A single fuel cell of the investigated fuel cell stack was used to create a computational mesh. To keep the number of computational cells low, the geometry of the fuel cell is reduced to a single channel. The flow fields of the anode and cathode are of the parallel channel type, but the channels are highly tortuous between the inlet and outlet. The tortuosity factor of the flow field is ≈ 4.1 . Thus, the average stretched length of a channel is 1174 mm. Only half of the height of the stretched channel was modeled and symmetry boundary conditions were used. That helped to reduce the computational cell count significantly while keeping the accuracy in an acceptable range, see also Haslinger and Lauer [46]. Hexahedral cells were used for the discretization. The simulation results of a computational mesh with four times the number of cells showed similar results. Therefore, the coarser mesh was used for the following investigations. The created mesh is shown in Fig. 1.

The total number of computational cells is 887 120.

The boundary conditions for the 3D-CFD model were generated from the results of the quasi-3D model, see Section 2.2. Convection boundary conditions with a mean coolant temperature and a heat transfer coefficient at the terminal faces were used to reject the waste heat from the model.

2.1.4. Numerical settings

The unsteady 3D-CFD simulation was initialized with a steady state solution at the minimum current density of 0.025 A cm^{-2} after 5000 iterations. Ferreira et al. [51], Bednarek and Tsoitridis [67] and Edwards et al. [32] discussed the time-step size problem of such 3D-CFD PEMFC models. Typical time step values to achieve numerical stability and convergence would be 0.01 ms. For physical times as large as 600 s this would result in a total computational time that is not practical at all. Due to the numerical robustness of the 3D-CFD model used, larger time steps could be used while maintaining numerical stability and convergence. In Fig. 2 the time scales of the processes in a PEMFC are highlighted. The fastest processes are the electrochemical reactions with their double layer effect, which would require quite small time steps. However, the time dependence of the electrochemical reactions is not taken into account. Therefore, it is legitimate to use larger time steps that can sufficiently capture the effects of diffusion, mass transfer, and membrane hydration. In this study, dynamic time steps in the range of 25–100 ms were used depending on the gradient of the mass flows and the current. A maximum of 125 iterations per time step was set. The convergence conditions were set to 1×10^{-4} for each equation solved. With this time-stepping method, it was possible to simulate a driving cycle of 600 s physical time in an acceptable time.

2.2. Generation of boundary data with a Quasi-3D model

The investigated industrial PEMFC stack delivers 25 kW cont. (30 kW peak). It was set up at a system test bench to generate validation data for the parameterization of the basic fuel cell 3D-CFD and quasi-3D model [46,70]. No humidifier is installed in the cathode path, and the hydrogen is recirculated with a hydrogen pump at a constant speed. The compressed air is cooled down to constant 40°C in a charge air cooler before entering the fuel cell stack. The air inlet humidity has thus low levels of $\approx 40\%$. The anode and cathode flow fields are arranged in a counter-flow configuration with serpentine channels. The rejection of the waste heat is done by liquid cooling with cooling channels in the bipolar plates. The coolant inlet temperature is kept constant at 55°C . Anode stoichiometry is given by the recirculated hydrogen volume flow and is >1.5 . The inlet pressure of the anode gas is held constant to 1700 mbar. The gas humidity at the anode inlet is set to 99%. The cathode stoichiometry ranged between 1.5 and 2.

The real-time capable, electrochemical fuel cell model, implemented in the proprietary software package AVL CRUISE™ M (Version 2021R2), was used to generate boundary conditions for the more sophisticated 3D-CFD model implemented in AVL FIRE™ M. The electrochemical fuel cell model is a quasi-3D numerical model. The features and capabilities can be found in [71,72].

The experimental data of the load profile originate from measurements at the Argonne National Laboratories. Lohse-Busch et al. [73] performed a technology assessment on a dynamometer of the Toyota Mirai. The 2016 Toyota Mirai is equipped with a 114 kW PEM fuel cell system, a 1.6 kWh battery, and a 113 kW electric motor. Several different driving cycles were investigated with the Toyota Mirai on the dynamometer under different temperatures. For the investigations in this work, the EPA US06 driving cycle recorded at an ambient temperature of 40°C was chosen due to the shortest duration of all recorded cycles and its high dynamic and high load profile, see Fig. 3(a). It shows that the fuel cell system has a strongly load-controlled operating strategy. Although the EPA US06 drive cycle is a high load cycle, the fuel cell system is approx. 28% of the 600 s in idle. Since the battery has only a capacity of 1.6 kWh the fuel cell has to provide the major part of the requested power.

The rated power of the investigated fuel cell stack was not enough to deliver the requested power of the Toyota Mirai's fuel cell system. Thus, the number of fuel cells in the stack was multiplied by four in the quasi-3D model to reach a power rating of 100 kW cont. (120 kW peak). The electrical power, as requested in the Toyota Mirai dynamometer experiments, was used to prescribe the load of the PEMFC in the quasi-3D model. The anode, cathode and coolant inlet conditions were defined according to the above-mentioned settings of the investigated PEMFC stack. The simulated values of the quasi-3D model were scaled to one single-channel fuel cell of the investigated stack. The resulting current density was used as a boundary condition for the 3D-CFD model. In addition, anode and cathode gas inlet conditions (temperature, pressure, mole fractions) were also extracted from the quasi-3D model.

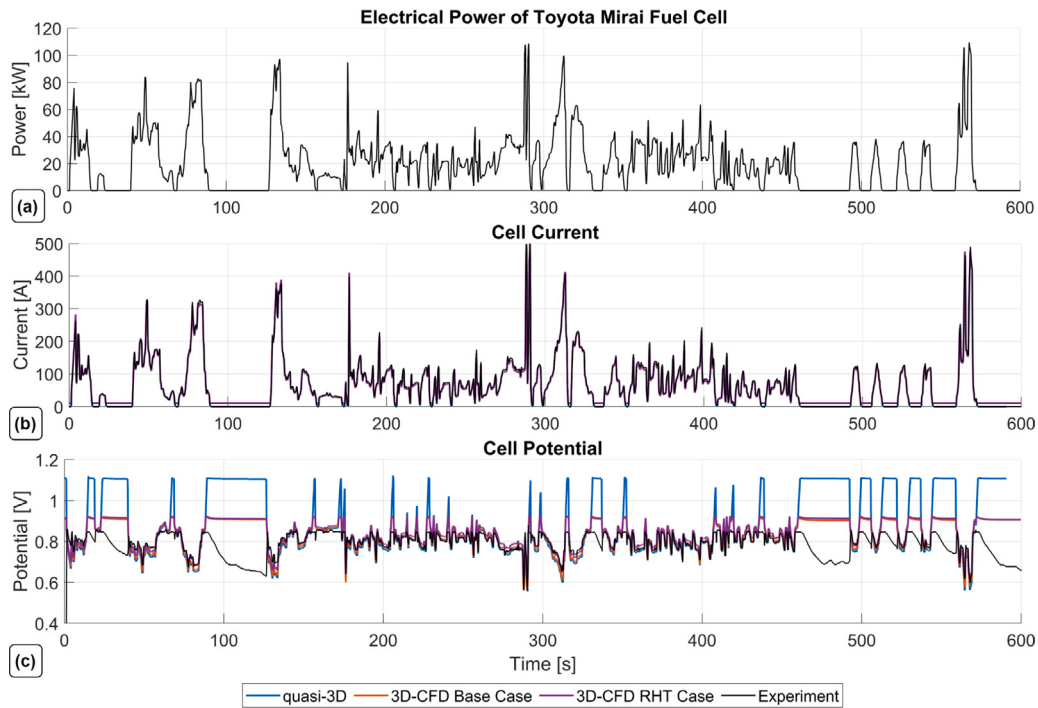


Fig. 3. (a) Electrical power drawn from Toyota Mirai's fuel cell during the experiment. Comparison of measured and simulated (b) Fuel cell stack current and (c) Potential of a single fuel cell of the stack. The open circuit voltage of the Toyota Mirai fuel cell stack ($U_{OCV,FC} = 0.85$ V) is lower than the OCV of the investigated FC stack.

3. Results and discussion

The results of the quasi-3D and 3D-CFD models are discussed in the following section. Two different levels of humidity and temperature of the cathode inlet gas stream were simulated to investigate the influence of an external humidifier in the cathode path. The levels were defined as follows and were constant at all times:

1. Base case: $\varphi_{Cat,In} = 0.4$, $T_{Cat,In} = 40^\circ\text{C}$
2. RHT case: $\varphi_{Cat,In} = 0.8$, $T_{Cat,In} = 55^\circ\text{C}$

3.1. Quasi-3D model

The quasi-3D model was parameterized with available experimental data from the institute's fuel cell system test bench. Material parameters such as protonic conductivity, reference exchange current density, porosities, etc. were fitted using numerical optimization methods. The use of numerical optimization methods with their high number of function evaluations was enabled by the real-time capability of the quasi-3D PEMFC model. The details and methodology of the parameterization can be found in [46,70].

The electrical power profile of Toyota Mirai's fuel cell system from the dynamometer experiments was used to prescribe the load of the investigated fuel cell stack, see Fig. 3. The simulated current and potential of one fuel cell are compared to the measured ones from the dynamometer. The voltage drops in the experiments during idle mode due to a stop of hydrogen flow. The Open Circuit Voltage (OCV) of the quasi-3D simulation is much higher than the OCV of the Toyota Mirai fuel cell stack. The quasi-3D simulation model is not able to account for the gas crossover and other losses at OCV. Thus, the OCV of the investigated fuel cell stack in the simulations is based on the theoretical OCV of ≈ 1.2 V per fuel cell at the operating temperature.

3.2. 3D-CFD model

The 3D-CFD model was parameterized based on the characteristics of the quasi-3D model, which has a similar physical behavior. The

main differences between these models lie in the description of the CLs and in the modeling of membrane hydration. By slightly adjusting the protonic conductivity and the reference exchange current density, the 3D-CFD model could be configured based on the specifications of the quasi-3D model. The methodology and a full list of material parameters can be found in Haslinger and Lauer [46]. The reference exchange current densities, transfer coefficients, reaction rate constants, etc. for the degradation models were taken from the original research articles [44,60,61,63,64] and are summarized in Appendix A. Five Pt particle classes to account for the higher degradation potential of smaller particles in the CCL are introduced with a mean radius of $r_{Pt,mean} = 3$ nm and a standard deviation of $\tau_{Pt} = 0.5$ nm. The particles are assumed to be normally distributed, and the five particle classes cover all particles in a range of $r_{Pt} \in r_{Pt,mean} \pm 3\tau_{Pt}$. The particle sizes were selected according to the measurements in Myers et al. [65].

Due to numerical stability reasons, a minimum current density of 0.025 A cm^{-2} is applied in idle mode. In addition, 10% of nitrogen is added to the hydrogen gas at the anode inlet to enhance the numerical stability of the 3D-CFD model. The EPA US06 drive cycle was simulated once for each case in full length and in high spatial and temporal resolution. The local states inside the fuel cell are investigated in the following. The simulation was carried out on the Vienna Scientific Cluster (VSC) on 128 cores.

In Fig. 3 the predicted voltage of the 3D-CFD model for the Base Case and RHT Case is shown. It can be seen, that the voltage at minimum current density is around 0.9 V. Due to the minimum current density restriction, the real OCV (≈ 0.95 V) cannot be reached, thus, influencing the production rates of the degradation mechanisms because the potential is higher (ACL) or lower (CCL). In addition, the mass flows in the anode and cathode were never completely stopped due to the minimum current density and the corresponding stoichiometric factor. Thus, no drop of voltage in idling can be observed. The higher relative humidity and temperature of the inlet air in the RHT Case lowers the losses in the fuel cell and increases the voltage to some extent during the dynamic current cycles, indicating a better-humidified membrane

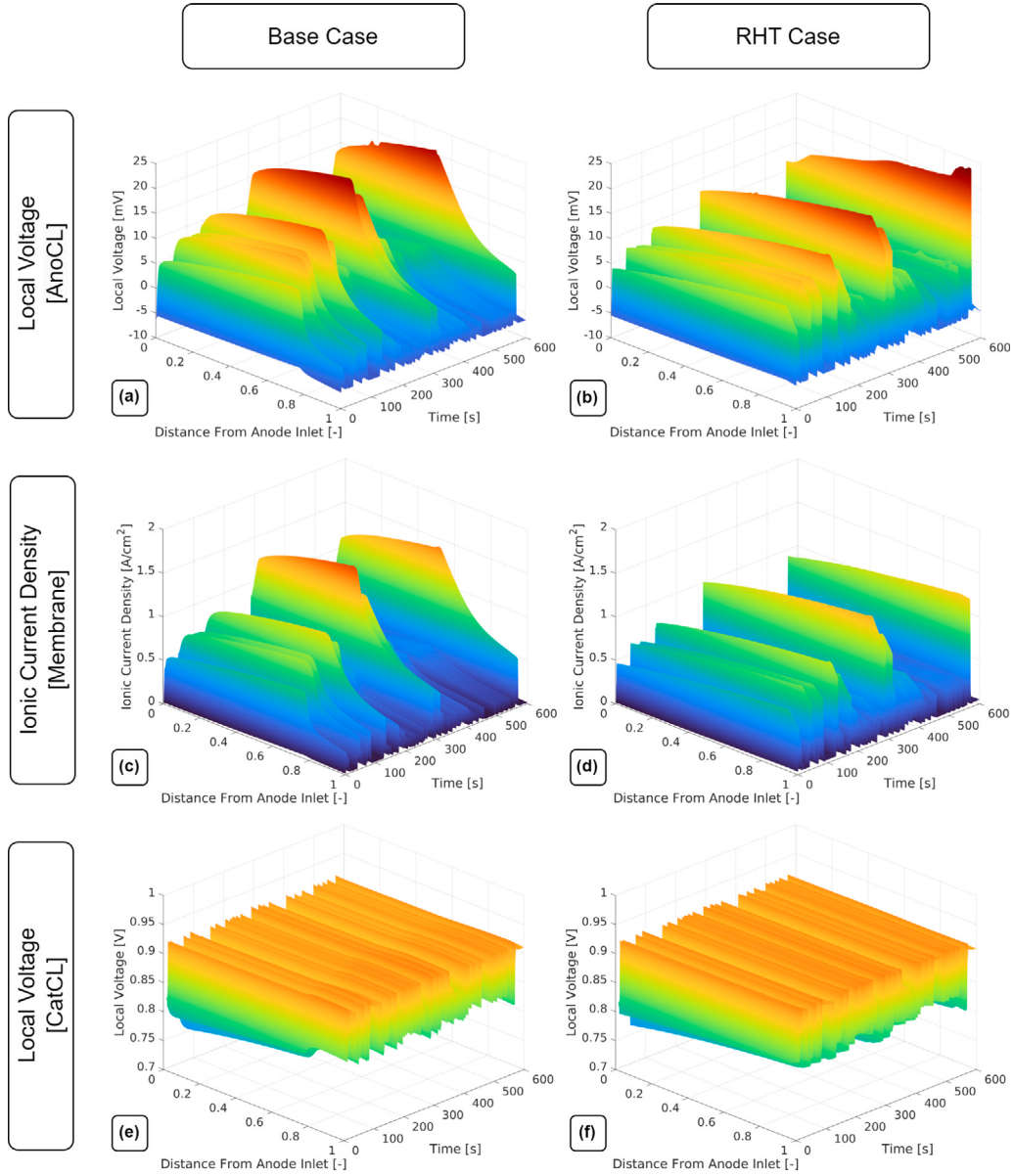


Fig. 4. (a)/(b) Local voltage in ACL, (c)/(d) Ionic current density in membrane, (e)/(f) Local voltage in CCL. (a),(c),(e) for the Base Case, (b),(d),(f) for the RHT Case. The distribution of ionic current density is more uniform in the RHT Case than in the Base Case. The reason for this is the higher humidification of the membrane over the entire length of the channel.

with higher ionic conductivity. The differences in idle are also reflected in a slightly higher cell potential.

In the following, the results with high spatial and temporal resolution will be discussed. Zones of the active area are identified in which degradation of the ionomer and catalyst layers take place.

Line plots and surface plots are shown. Line plots show spatially averaged data in x - and z -direction over time. The surface plots show spatially averaged data in z -direction over time. Thus, the distribution along the gas channel can be investigated. The spatial variable x is normalized and indicated with “Distance From Anode Inlet”. Due to the counter-flow configuration the cathode inlet is at $x = 1$.

3.2.1. Local potential and ionic current density

Fig. 4 shows the local potential in ACL and CCL, and the ionic current density in the membrane for both simulated cases. The local potential in the CLs is defined as the difference between the electrical potential ϕ_{elec} and the ionic potential ϕ_{ion} : $U_{local} = \phi_{elec} - \phi_{ion}$. It is an important variable for all electrochemical-triggered reactions.

The (ionic) current density, Fig. 4(c) and (d) does not only depend on the BVE kinetics but also depends on the conductivities of solid materials and the ionomer. The conductivity of the ionomer is the one with the higher influence because it strongly depends on the dissolved water content and the temperature and is one to three orders of magnitudes smaller than the electric conductivities of the surrounding solids [74]. In the CLs the ionic conductivity is further lowered due to the ionomer volume fraction α_{ion} in Eq. (7). As a result, areas with low humidification, such as the inlet areas of the gases, generate low local current densities. The heterogeneity of the current density in large-scale PEMFCs was also investigated by Cheng et al. [45]. Negative values of the local potential, e.g., in the ACL, indicate that the ionic potential is higher than the electronic potential and occurred during idling. In the Base Case a significant drop of the ionic current density near the air inlet can be observed and in the RHT Case not. The distribution of the ionic current density in Fig. 4(d) and, thus, the local potentials in ACL and CCL in Fig. 4(b) and (f) is more uniform in the RHT Case due to the more uniform humidification, see Fig. 8(c)

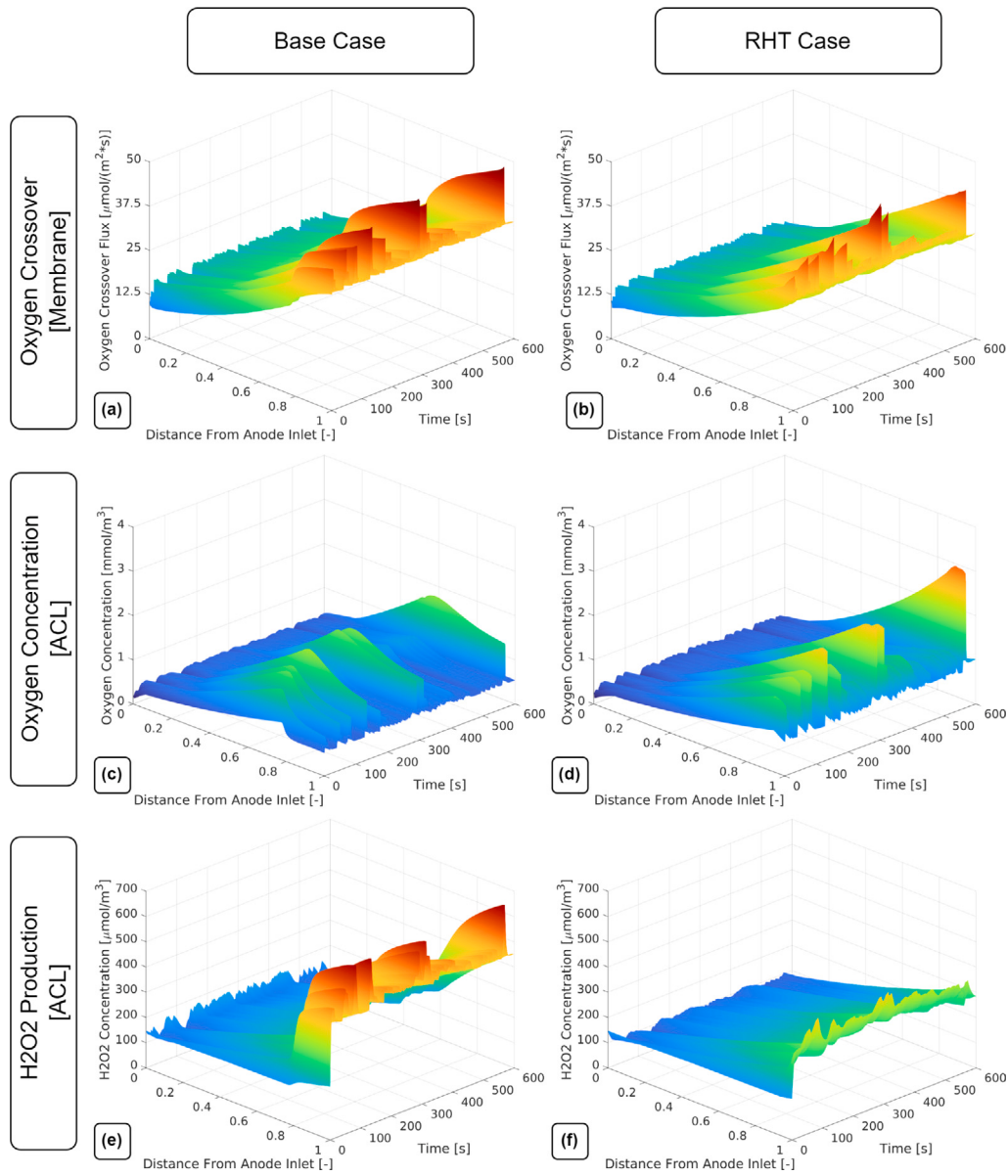


Fig. 5. (a)/(b) Oxygen flux in membrane, (b)/(d) Oxygen concentration in ACL, (e)/(f) H₂O₂ concentration in ACL. (a),(c),(e) for the Base Case, (b),(d),(f) for the RHT Case.

and (d). The local potential in the ACL remains at a higher level, while the local potential in the CCL near the air inlet $x = 1$ shows lower values than in the base case. The local potentials in ACL and CCL are drivers for electrochemical-induced degradation mechanisms such as hydrogen peroxide production, carbon corrosion, and platinum dissolution, which are discussed in the following.

3.2.2. Oxygen concentration and ionomer degradation in ACL

The crossover of oxygen through the membrane to the opposite electrode is an unwanted mechanism, see Fig. 5(a) and (b). Low local potentials in the ACL and the presence of oxygen triggers also Reaction (13). In the Base Case, the local potential in the ACL, Fig. 4(a), is lower near the air inlet than in the rest of the active area of the fuel cell. Thus, the hydrogen peroxide reaction rate is higher in the area near the air inlet indicated by a higher H₂O₂ concentration, Fig. 5(e). At $t = 0$ s the H₂O₂ concentration was set to 0.15 mmol m^{-3} . Due to the higher reaction rate, the oxygen concentration in the ACL drops in this section, too; see Fig. 5(c). Hydrogen peroxide alone is not responsible for the attack on the side chains of the ionomer, but its radicals $\cdot\text{OH}$ are. These radicals are formed with the presence of impurities, as mentioned

in Section 2.1.2. In order to avoid increased ionomer degradation in the area of the air inlet, it is important to improve the non-uniformity of the local potential in the ACL and to avoid contamination during the assembly of the fuel cell stack with unwanted metal ions.

In contrast to the Base Case, the distribution of local potential in the ACL in the RHT Case is more uniform, see Fig. 4(b). The H₂O₂ concentration, therefore, changes almost linearly along the gas channel with a peak value near the air inlet ($x = 1$), as shown in Fig. 5(f). The overall level of oxygen crossover flux does not change significantly, see Fig. 5(b). However, the oxygen concentration in the ACL, Fig. 5(d) is higher due to the lower consumption of O₂. Near the air inlet, the oxygen concentration hardly drops at all due to the lower reaction rate compared to the Base Case. In Fig. 7(c), the mean spatial values of the H₂O₂ concentration in the ACL at every time are shown. It can be observed, that the H₂O₂ concentration is on average 25.7% lower in the RHT Case due to the higher local potential in the ACL near the air inlet. Similar observations have been made by Zatoń et al. [14]. They stated, that with lower relative humidity, the ionomer degradation rate increases. However, they explained it with higher oxygen permeation through the membrane, which is not recognized here. Instead, the

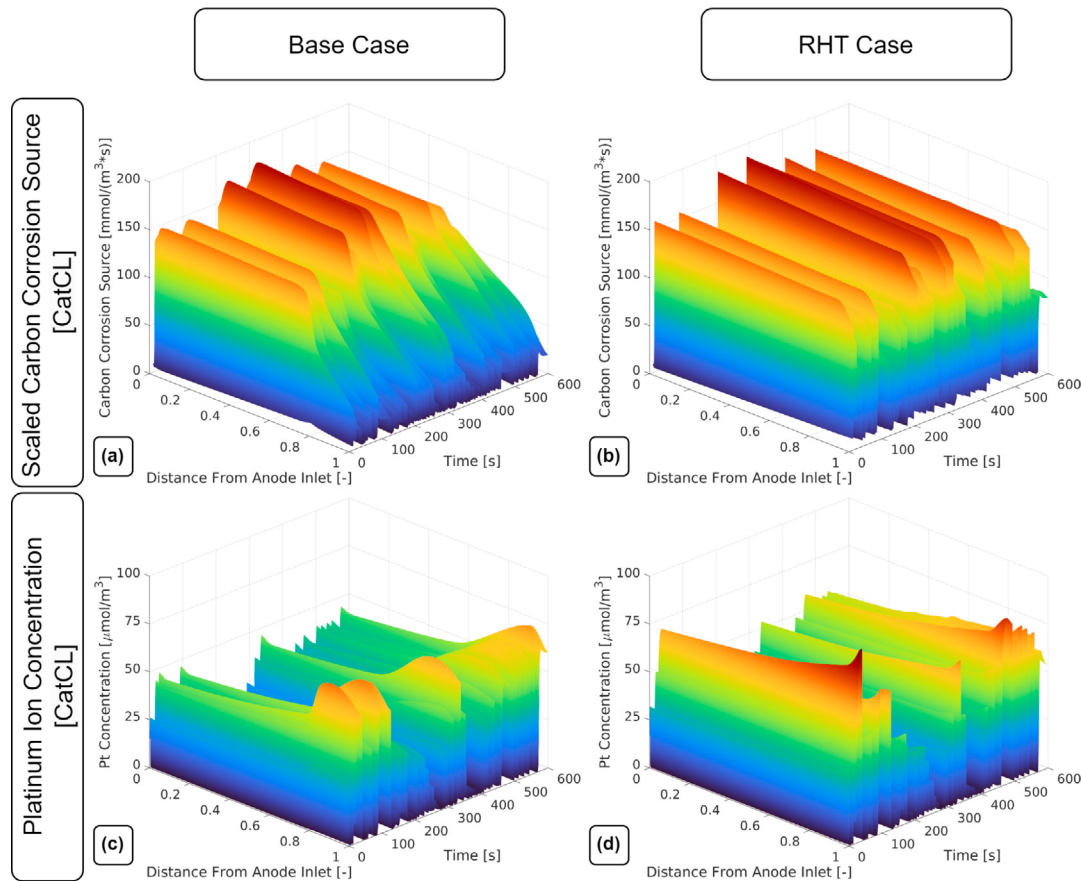


Fig. 6. (a)/(b) Carbon corrosion source in CCL over time and length of channel. (c)/(d) Pt^{2+} concentration in CCL over time and length of channel. (a),(b) for the Base Case, (c),(d) for the RHT Case. Although carbon corrosion and platinum dissolution reactions have a high equilibrium potential, they have different locations of their maximum value.

lower H_2O_2 production rate is a result of uniform and higher local potentials in the ACL. Chen et al. [75] recently investigated the chemical degradation of proton exchange membranes on a microscopic and mesoscopic scale. They concluded that the highest ionomer degradation is present at a relative humidity of 60%.

When high currents are drawn, a higher airflow of the compressor is requested, and the oxygen concentration in the CCL increases due to the higher pressure. The higher the oxygen concentration in the CCL, the higher the oxygen flux through the membrane. The highest oxygen crossover flux is near the air inlet, $x = 1$. According to [8,76,77] the oxygen crossover is the highest during idling. The reasons for this are the lack of O_2 consumption and the lack of water production by the ORR, which reduces the dissolved water content in the membrane. A lower water content increases membrane porosity and leads to higher gas permeation. In addition, the lower partial pressure of the water creates space for O_2 . In the simulations, however, the mean oxygen partial pressure in the CCL decreases during idling ($P_C \approx P_{Amb}$) because the back pressure in the cathode depends on a throttle valve with a fixed opening angle installed after the cathode outlet. This additional resistance in the cathode path creates different inlet and outlet pressures depending on the air mass flow. A lower (mean) pressure in the cathode system also lowered the oxygen concentration to a greater extent than the oxygen consumption by the ORR in load operation. In addition, the dissolved water content in the ionomer does not decrease at idle due to the minimum current density restriction, see Fig. 8(c).

The production of hydrogen peroxide is greatest near the air inlet, which was also observed by [44]. The formation of pinholes is also possible due to the degradation of the ionomer by hydroxyl radical attack, which falls in the category of mechanical failure of the membrane.

This fact must be taken into account, especially when using ultra-thin membranes. [7]

3.2.3. Carbon corrosion and platinum dissolution in CCL

As mentioned in Section 2.1.2, carbon corrosion and platinum dissolution depend on the particle size class. Due to the Kelvin shift, smaller particles have lower equivalent potentials and vice versa, see Eqs. (A.7)–(A.11). Since no validation data is available, the quantitative evaluation of the produced CO_2 and Pt^{2+} concentration is difficult. However, the reference exchange current densities for the solved BVEs were taken from validated models from the literature. The interaction of platinum dissolution and carbon corrosion was not modeled, but in reality, both mechanisms can be influenced by the other one as both lowers the ECSA of the CCL. The loss of carbon support by carbon corrosion leads to Pt particle detachment and free platinum particles and ions that can agglomerate to bigger ones or diffuse into the membrane and form a platinum band [7,8].

In Fig. 6(a) and (b) the CO_2 source for both simulated cases is shown. In the Base Case the carbon corrosion source is non-uniformly distributed over the active area. It decreased near the air inlet ($x \approx 0.75-1$) although the local potential is the highest in this area in the CCL as shown in Fig. 4(e). The reason for the decrease is the lower relative humidity in this section, because according to Reactions (17)–(22) the reaction rates scale with the presence of H_2O . In the RHT Case, the CO_2 source is at a more constant level due to the higher local humidity near the air inlet. However, the local potential has lower values near the air inlet compared to the Base Case, Fig. 4(f). The influence of the higher humidity outweighs the lower potential and leads to a higher carbon corrosion source overall. In Fig. 7(a) the simulated current density and potential of the investigated fuel cell are shown. Fig. 7(b) shows the

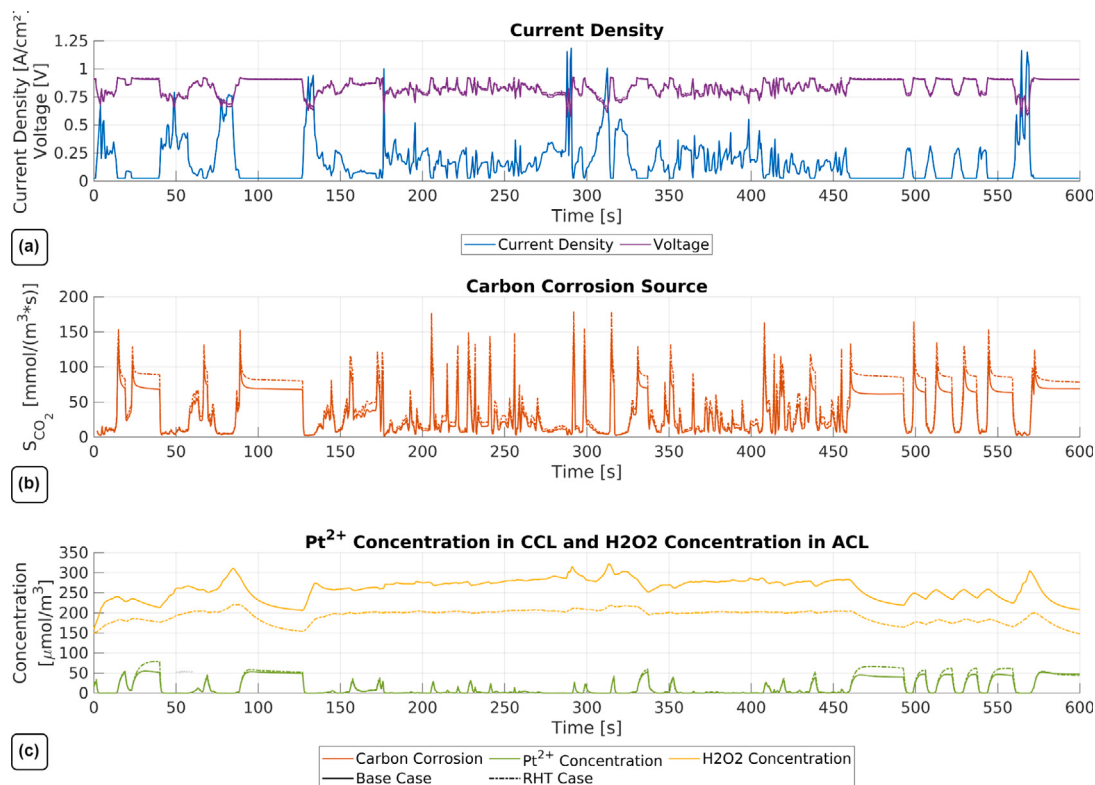


Fig. 7. (a) Simulated voltage and current density of the fuel cell with the 3D-CFD model. (b) Average CO₂ source in CCL. (c) Mean Pt²⁺ concentration in CCL and H₂O₂ concentration in ACL. The rate for carbon corrosion exhibited peaks when the current density drops to a low level (=operation voltage increases).

mean carbon corrosion source in the CCL over time for both simulated cases. It exhibited a strong peak when the current density gradient is negative and the current then reaches its minimum. Due to the voltage overshoot after the decrease of the load in a fuel cell, which can be seen in Fig. 7(a), the local potential in the CCL also reaches higher values. Higher local potentials increase the rate of carbon corrosion, see also [63,78,79]. It can also be observed, that the source is higher in the RHT Case. Similar observations were made by Lim et al. [80] and [81] where they investigated the influence of temperature and humidity on the CO₂ release of a PEMFC. The released amount of CO₂ increased with increasing humidity of the air.

The mean platinum ion concentration in the CCL over the length of the channel and all times is shown in Fig. 6(c) and (d) for both cases. The highest value of the Pt²⁺ concentration is near the air inlet, as the local potential in the CCL was highest. However, the distribution of Pt²⁺ ions is more uniform in the RHT Case compared to the Base Case. A higher platinum ion concentration lowers the crystalline platinum content in the CCL in this section which results in a decrease of ECSA.

The platinum ion concentration in the CCL can be seen in Fig. 7(c). At $t = 0$ s the Pt²⁺ concentration was set to $1 \times 10^{-5} \text{ mol m}^{-3}$ [64]. It increases during idling and decreases as soon as load is requested from the fuel cell. The Pt²⁺ concentration has similar values in both cases when current is drawn from the fuel cell. When idling, the RHT case shows higher concentrations due to the more uniform and overall higher concentration over the active area, see Fig. 6(d). Analogous investigations were made by Bi et al. [82]. Zhu et al. [66] showed that low humidity suppresses the Pt dissolution, which was also observed during the simulations.

Both the carbon corrosion and the Pt dissolution scale with the local potential in the CCL. In the RHT Case the potential of the fuel cell

is slightly higher in idle than in the Base Case. The OCV of Toyota Mirai's fuel cell is around 0.85 V, which helps to reduce the risk of high voltages in the CCL during idling. In addition, the voltage drops further when no power is requested due to a fuel and air cut-off, see Fig. 3 and Lohse-Busch et al. [73]. The investigated industrial fuel cell stack was primarily developed for stationary applications with little dynamic loads. It has a minimum current restriction, which was not applied in this study, that ensures lower potentials in the CCL during operation. Hence, the manufacturer minimizes the risk of degradation by their specified operating strategy.

In Fig. B.9 the surface coverage fractions of carbon and platinum are shown. It can be observed, that the high dynamic load cycle does not change the coverage of C and Pt oxides significantly. There is also almost no difference between the two simulated cases.

3.2.4. Liquid water saturation and dissolved water content fluctuations

Fig. 8 shows the liquid water saturation of the CCL and the dissolved water content of the membrane for both simulated cases. In the Base Case, the investigated fuel cell system has no external humidifier, thus, the incoming air needs to humidify itself by the counter-flow setup.

The local dissolved water content, which is significant for high ionic conductivity, is directly affected by the humidity of the incoming gas streams. The empirical correlation for the equilibrium water content developed by Springer et al. [58] is used. It depends on the relative humidity of the gases in the ACL and CCL and has a maximum value of ≈ 14 . The humidity situation in the fuel cell becomes worse during the load cycle, indicated by the change to lower levels of the dissolved water content in Fig. 8(c) in the Base Case. Due to the operating strategy, the (dry) air mass flow entering the fuel cell increases during phases

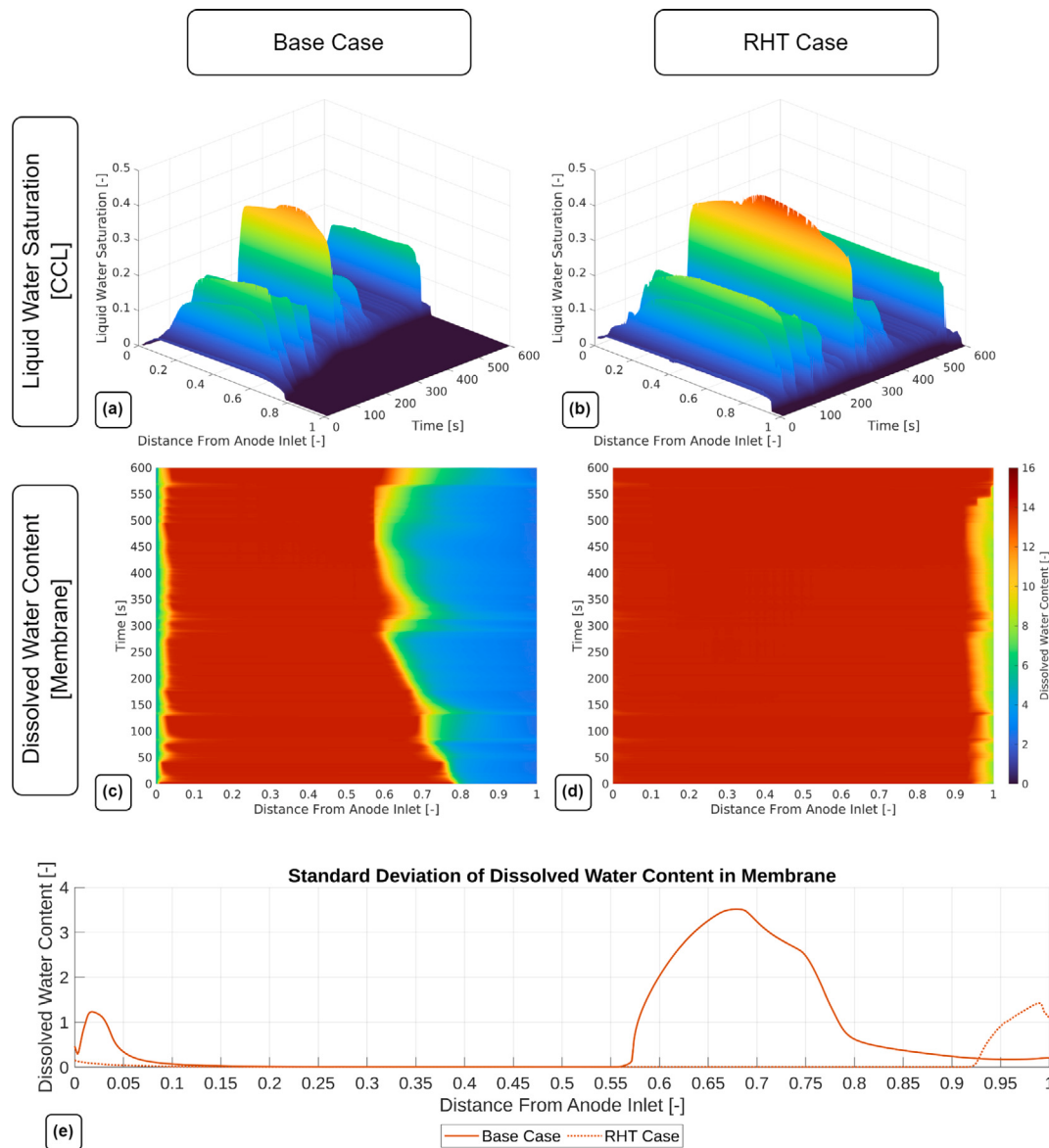


Fig. 8. (a)/(b) Liquid saturation in CCL, (c)/(d) Dissolved water content in membrane. (a),(c) for the Base Case, (b),(d) for the RHT Case. (e) Shows the standard deviation of the dissolved water content in the membrane over time and over the entire channel length.

when load is requested. More dry air mass needs more humidity for self-humidification, and thus, the relative humidity and the dissolved water content decrease. The produced water from the electrochemical reaction in the cathode did not deliver enough water to humidify the air mass sufficiently. During idling phases with the minimum current density of 0.025 A cm^{-2} and the lower (dry) air mass flow, the water content, and the relative humidity recover to a certain degree. Fig. 8(e) shows the standard deviation of the dissolved water content in the membrane for every spatial position. The temporal variations in the Base Case are high between $x = 0.55$ and 0.8 and pose a risk for mechanical fatigue of the membrane due to hygrothermal swelling. In the RHT Case only the section close to the air inlet shows higher temporal fluctuation due to the better overall humidification of the membrane. Sadeghi Alavijeh et al. [21] investigated the hygrothermal swelling and shrinking of PFSA membranes during humidity cycles. They stated that the observed shrinkage during humidity cycles would result in concerning high stresses in the membrane. Yang et al. [53] also showed the non-uniform distribution of water content in the

membrane of a large-active area fuel cell. The dissolved water was lowest near the cathode inlet and increased towards the cathode outlet. If the membrane is sufficiently humidified, the excess water from the electrochemical reaction condenses and increases the local liquid water saturation. The liquid water saturation s is a measure of how much space is left in the pores for the gas flow. It ranges between 0 to 1 and a value of 1 means that the pores are blocked with liquid water. The maximum local value in the CCL can be found in the RHT Case. The liquid water saturation reaches a maximum value of about 0.4 in the RHT Case. Thus no blockage of pores is witnessed. The operating strategy must be chosen wisely in order to ensure high and even humidification of the membrane on the one hand and to prevent the pores from clogging with liquid water on the other. Local changes in the dissolved water content in the base case can also trigger local stress peaks and lead to mechanical damage to the membrane.

4. Conclusions

In this work, the degradation potential of a large active area PEMFC under typical automotive drive cycle conditions is investigated. A validated single-channel PEMFC 3D-CFD model is used to theoretically investigate the ionomer degradation in the ACL and carbon corrosion and Pt dissolution in the CCL. The main findings are:

1. Water Management: At low humidity, the self-humidification strategy of the gas flows means that a large part of the active area is not available for high current densities. Due to the low humidification state of the membrane and the resulting low protonic conductivity, the current density in this area is also low. The liquid water saturation never exceeds values of approx. 0.4 after a load change, so no blockage of the diffusion paths for the gases could be observed. However, gas diffusion is considerably impaired by the liquid water. Although the liquid water distribution is more uniform in the case of high humidity, the liquid water saturation has the same maximum values as in the case of low humidity.
2. Ionomer Degradation: The hydrogen peroxide in the ACL shows the highest sensitivity on the inlet humidity of the air. The RHT Case shows on average 25.7% lower H_2O_2 concentrations in the ACL due to the more uniform distribution of local potential that ensures higher local potentials when current is drawn. The hydrogen peroxide concentration is especially higher near the air inlet in the Base Case. The H_2O_2 concentration drops during idling due to the lower oxygen crossover although the local potential is the lowest. The hygrothermal cycling of the membrane is also higher in the Base Case and shows that a considerable area of the membrane is exposed to a high risk of mechanical fatigue due to stress peaks in the material. A more uniform humidification of the membrane, as it is in the RHT Case, prevents it from high hygrothermal cycling loads.
3. CCL Degradation: Carbon corrosion and Pt dissolution show peaks after high negative gradients of the fuel cell current and overall high values during idling. The low humidity case shows heterogeneity of the internal conditions due to the self-humidifying strategy of the gas streams. Thus, the carbon corrosion source is lower near the air inlet due to the dependence on local relative humidity. In addition, the platinum dissolution is also highest during idling but decreases rapidly as soon as current is drawn. In contrast to the carbon corrosion source, the Pt concentration is higher near the air inlet due to the higher local potential in the CCL in the Base Case.

Due to the minimum current density requirement in the 3D-CFD model, the real OCV of the fuel cell could never be reached in the simulations during idling. Thus, the determined carbon corrosion source, Pt^{2+} concentration, and H_2O_2 production rate might be higher in the real fuel cell during idling. However, the results of this study extend the knowledge about the behavior of PEMFCs and their degradation potential under high dynamic load and high/low internal humidification. The use of a highly detailed and unsteady 3D-CFD model provides the internal states of a fuel cell that would not be readily accessible using measurement methods or physically and dimensionally reduced models.

Abbreviations

The following abbreviations are used in this manuscript:

ACL	Anode Catalyst Layer
AST	Accelerated Stress Test
BOL	Begin Of Life

BVE	Butler-Volmer Equation
CCL	Cathode Catalyst Layer
CCM	Catalyst Coated Membrane
CL	Catalyst Layer
DST	Dynamic Stress Test
ECSA	Electrochemical Active Surface Area
EOL	End Of Life
FC	Fuel Cell
GDL	Gas Diffusion Layer
HOR	Hydrogen Oxidation Reaction
MEA	Membrane Electrode Assembly
OCV	Open Circuit Voltage
ODE	Ordinary Differential Equation
ORR	Oxygen Reduction Reaction
PDE	Partial Differential Equation
PEM	Polymer Electrolyte Membrane
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PFSA	Perfluorosulphonic Acid

Glossary

The following symbols are used in this manuscript:

Greek symbol	Name	Unit	Value	Ref.
α_{ion}	Ionomer volume fraction in CLs	–	0.25	[70]
β	Transfer coefficient	–	–	–
Γ_C	Carbon oxidation surface density	A s m ⁻²	4.6	[83]
Γ_{Pt}	Pt oxidation surface density	A s m ⁻²	2.15	[84]
ε_{CCL}	CCL porosity	–	0.38	–
η	Overpotential	V	–	–
ρ_C	Density of carbon	kg m ⁻³	2000	[84]
ρ_{CO_2}	Density of carbon dioxide	kg m ⁻³	1980	–
ρ_{Pt}	Density of Pt	kg m ⁻³	21 090	[84]
ρ_{PtO}	Density of PtO	kg m ⁻³	14 100	[84]
ρ_{PtOH}	Density of PtOH	kg m ⁻³	14 170	[84]
σ_{Pt}	Surface tension of Pt	J m ⁻²	2.73	[84]
σ_{PtO}	Surface tension of PtO	J m ⁻²	1	[84]
σ_{PtOH}	Surface tension of PtOH	J m ⁻²	1.34	[84]
τ_{Pt}	Standard deviation of particle size	m	0.5×10^{-9}	[65]
φ	Relative humidity	–	–	–
ϕ	Potential	–	–	–

Symbol	Name	Unit	Value	Ref.
a_C	Carbon surface density	m ⁻¹	–	–
A_C	Specific carbon area	m ² kg ⁻¹	400 000	Assumed
a_{Pt}	Pt surface density	m ⁻¹	1×10^4	[60]
A_{active}	Active area of fuel cell	m ²	–	Geometry

C_w	Dissolved water content of ionomer	–	–	–
c	Concentration	mol m^{-3}	–	–
$c_{\text{Fe}^{2+}}$	Fe ion concentration	mol m^{-3}	0.21	[44]
$c_{\text{H}^+, \text{ref}}$	Reference H^+ concentration	mol m^{-3}	1167.4	[44]
c_{H^+}	Proton concentration	mol m^{-3}	–	[60]
$c_{\text{O}_2, \text{ref}}$	Reference O_2 concentration	mol m^{-3}	40.88	[44]
$c_{\text{Pt}^{2+}, \text{ref}}$	Reference Pt-ion concentration	mol m^{-3}	1000	[84]
$c_{\text{Pt}^{2+}}$	Platinum ion concentration	mol m^{-3}	–	–
d_{cc}	Carbon corrosion depth	nm	1	[61]
d_{CCL}	CCL thickness	m	10×10^{-6}	[70]
E	Equilibrium potential	V	–	–
$ECSA$	Electrochemical active surface area	$\text{m}^2 \text{kg}^{-1}$	55 000	[79]
F	Faraday constant	A s mol^{-1}	96 485.33	–
f_{C}	Surface coverage fraction of C	–	–	–
f_{CO}	Surface coverage fraction of C–O	–	–	–
f_{COH}	Surface coverage fraction of C–OH	–	–	–
f_{Pt}	Surface coverage fraction of Pt	–	–	–
f_{PtO}	Surface coverage fraction of Pt–O	–	–	–
f_{PtOH}	Surface coverage fraction of Pt–OH	–	–	–
j	Reaction current density	A m^{-2}	A m^{-3}	–
j_0	Reference exchange current density	A m^{-2}	A m^{-3}	–
k_{Fe}	Forward rate constant for Fentons reaction	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$	63×10^{-3}	[60]
k_{rev}	Reverse reaction deceleration	–	0.3	[64]
K_3	Equilibrium constant	–	–	[64]
M_{CO_2}	Molar mass of CO_2	kg mol^{-1}	44×10^{-3}	–
M_{Pt}	Molar mass of Pt	kg mol^{-1}	195×10^{-3}	[84]
m_{Pt}	Platinum loading	kg m^{-2}	4×10^{-3}	[44]
M_{PtO}	Molar mass of PtO	kg mol^{-1}	211×10^{-3}	[84]
M_{PtOH}	Molar mass of PtOH	kg mol^{-1}	212×10^{-3}	[84]
$N_{\text{Pt, tot}}$	Total number of platinum particles	m^{-3}	–	–

n	Particle classes	–	5	Assumed
p	Particle class	–	–	–
R	Gas constant	$\text{J mol}^{-1} \text{K}^{-1}$	8.314	–
$r_{\text{Pt, mean}}$	Mean particle radius	m	3×10^{-9}	[65]
$r_{\text{Pt, p}}$	Particle radius of particle class p	m	–	–
r_{ox}	Oxide interaction	kJ mol^{-1}	30	[84]
S_{CO_2}	CO_2 source term	$\text{mol m}^{-3} \text{s}^{-1}$	–	–
T	Temperature	K	–	–
V_{ion}	Ionomer volume in CCL	m^3	–	–

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Maximilian Haslinger: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Project administration, Methodology, Conceptualization. **Thomas Lauer:** Writing – review & editing, Supervision, Project administration, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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Appendix A. Solved equations for degradation mechanisms

A.1. Butler-Volmer equations

See Tables A.1–A.3.

Table A.1Solved Butler-Volmer equations for H_2O_2 production rate [44,60].

Reaction	Butler-Volmer equation	j_0 in A m^{-2}	β
(13)	$j_{\text{H}_2\text{O}_2} = -j_{0,\text{H}_2\text{O}_2} \frac{c_{\text{O}_2}}{c_{\text{H}^+} c_{\text{O}_2,ref}} \left(\frac{c_{\text{H}^+}}{c_{\text{H}^+,ref}} \right)^2 \exp \left(-\frac{2\beta_{\text{H}_2\text{O}_2} F}{RT_{CL}} \eta_{act,\text{H}_2\text{O}_2} \right)$	1×10^{-2}	0.25
(14)	$r_{\text{Fe}} = k_{\text{Fe}} c_{\text{H}_2\text{O}_2,p} c_{\text{Fe}^{2+},p}$	–	–

Table A.2

Solved Butler-Volmer equations for carbon corrosion [44,61,63].

Reaction	Butler-Volmer equation	j_0 in A m^{-2}	β
(17)	$j_{cc1,p} = j_{0,cc1} \left[\varphi_{\text{H}_2\text{O}} f_{\text{C},p} \exp \left(\frac{\beta_{cc1} F}{RT_{CL}} \eta_{act,cc1,p} \right) - f_{\text{COH},p} \exp \left(-\frac{(1-\beta_{cc1}) F}{RT_{CL}} \eta_{act,cc1,p} \right) \right]$	1.19×10^{-3}	0.5
(18)	$j_{cc2,p} = j_{0,cc2} \left[f_{\text{COH},p} \exp \left(\frac{\beta_{cc2} F}{RT_{CL}} \eta_{act,cc2,p} \right) - f_{\text{CO},p} \exp \left(-\frac{(1-\beta_{cc2}) F}{RT_{CL}} \eta_{act,cc2,p} \right) \right]$	6.14×10^{-3}	0.5
(19)	$j_{cc3,p} = j_{0,cc3} \varphi_{\text{H}_2\text{O}} f_{\text{COH},p} \exp \left(\frac{3\beta_{cc3} F}{RT_{CL}} \eta_{act,cc3,p} \right)$	3.687×10^{-6}	0.5
(20)	$j_{cc4,p} = j_{0,cc4} \left[\varphi_{\text{H}_2\text{O}} f_{\text{Pt},p} \exp \left(\frac{\beta_{cc4} F}{RT_{CL}} (\eta_{act,cc4,p} - r_{ox} (f_{\text{PtOH},p} + f_{\text{PtO},p})) \right) - k_{\text{Pt,rev}} f_{\text{PtOH},p} \exp \left(-\frac{(1-\beta_{cc4}) F}{RT_{CL}} \eta_{act,cc4,p} \right) \right]$	0.562	0.5
(21)	$j_{cc5,p} = j_{0,cc5} \left[f_{\text{PtOH},p} \exp \left(\frac{\beta_{cc5} F}{RT_{CL}} (\eta_{act,cc5,p} - r_{ox} (f_{\text{PtOH},p} + f_{\text{PtO},p})) \right) - k_{\text{Pt,rev}} f_{\text{PtO},p} \exp \left(-\frac{(1-\beta_{cc5}) F}{RT_{CL}} \eta_{act,cc5,p} \right) \right]$	0.562	0.5
(22)	$j_{cc6,p} = j_{0,cc6} f_{\text{PtOH},p} f_{\text{COH},p} \exp \left(\frac{2\beta_{cc6} F}{RT_{CL}} \eta_{act,cc6,p} \right)$	0.123	0.5

Table A.3

Solved Butler-Volmer equations for platinum dissolution [64].

Reaction	Butler-Volmer equation	j_0 in A m^{-2}	β
(23)	$j_{\text{Pt}1,p} = j_{0,\text{Pt}1} f_{\text{Pt},p} \left[\exp \left(\frac{2\beta_{\text{Pt}1} F}{RT_{CL}} \eta_{act,\text{Pt}1,p} \right) - \frac{c_{\text{Pt}^{2+}}}{c_{\text{Pt}^{2+},ref}} \exp \left(-\frac{2(1-\beta_{\text{Pt}1}) F}{RT_{CL}} \eta_{act,\text{Pt}1,p} \right) \right]$	8.77×10^{-5}	0.5
(24)	$j_{\text{Pt}2,p} = j_{0,\text{Pt}2} \left[\exp \left(-\frac{r_{ox} f_{\text{PtO},p}}{RT_{CL}} \right) \exp \left(\frac{2\beta_{\text{Pt}2} F}{RT_{CL}} \eta_{act,\text{Pt}2,p} \right) - f_{\text{PtO},p} \left(\frac{c_{\text{H}^+}}{c_{\text{H}^+,ref}} \right)^2 \exp \left(-\frac{2(1-\beta_{\text{Pt}2}) F}{RT_{CL}} \eta_{act,\text{Pt}2,p} \right) \right]$	1.31×10^{-2}	0.5
(25)	$j_{\text{Pt}3,p} = j_{0,\text{Pt}3} \left(f_{\text{PtO},p} c_{\text{H}^+}^2 - \frac{c_{\text{Pt}^{2+}}}{K_{3,p}} \right)$	3.09×10^{-15}	0.5
–	$K_{3,p} = \exp \left[\frac{2F}{RT_{CL}} (E_{\text{Pt}1} - E_{\text{Pt}2}) \right]$	–	–

A.2. Surface coverage fractions

The following ODEs for the surface coverage fractions were solved [61,63]:

$$\Gamma_{\text{C}} \frac{df_{\text{COH},p}}{dt} = j_{cc1,p} - j_{cc2,p} - j_{cc3,p} - j_{cc6,p} \quad (\text{A.1})$$

$$\Gamma_{\text{C}} \frac{df_{\text{CO},p}}{dt} = j_{cc2,p} \quad (\text{A.2})$$

$$f_{\text{C},p} = 1 - f_{\text{COH},p} - f_{\text{CO},p} \quad (\text{A.3})$$

$$\Gamma_{\text{Pt}} \frac{df_{\text{PtOH},p}}{dt} = j_{cc4,p} - j_{cc5,p} - \frac{d_{cc}}{r_{\text{Pt},p}} j_{cc6,p} \quad (\text{A.4})$$

$$\Gamma_{\text{Pt}} \frac{df_{\text{PtO},p}}{dt} = j_{cc5,p} + j_{\text{Pt}2,p} - j_{\text{Pt}3,p} \quad (\text{A.5})$$

$$f_{\text{Pt},p} = 1 - f_{\text{PtOH},p} - f_{\text{PtO},p} \quad (\text{A.6})$$

A.3. Equilibrium potentials

The equilibrium potentials of Reactions (20)–(22) are corrected by the Kelvin term [64,79].

$$E_{cc4,p} = E_{0,cc4} - \frac{1}{2F} \frac{\sigma_{\text{Pt}} M_{\text{Pt}}}{r_{\text{Pt},p}} \left(\frac{\sigma_{\text{PtOH}} M_{\text{PtOH}}}{\rho_{\text{Pt}}} - \frac{\sigma_{\text{PtOH}} M_{\text{PtOH}}}{\rho_{\text{PtOH}}} \right) \quad (\text{A.7})$$

$$E_{cc5,p} = E_{0,cc5} - \frac{1}{2F} \frac{\sigma_{\text{PtOH}} M_{\text{PtOH}}}{r_{\text{Pt},p}} \left(\frac{\sigma_{\text{PtOH}} M_{\text{PtOH}}}{\rho_{\text{PtOH}}} - \frac{\sigma_{\text{PtO}} M_{\text{PtO}}}{\rho_{\text{PtO}}} \right) \quad (\text{A.8})$$

$$E_{cc6,p} = E_{0,cc6} - \frac{1}{2F} \frac{\sigma_{\text{PtOH}} M_{\text{PtOH}}}{r_{\text{Pt},p}} \frac{\sigma_{\text{PtOH}} M_{\text{PtOH}}}{\rho_{\text{PtOH}}} \quad (\text{A.9})$$

$$E_{\text{Pt}1,p} = E_{0,\text{Pt}1} - \frac{1}{2F} \frac{\sigma_{\text{Pt}} M_{\text{Pt}}}{r_{\text{Pt},p}} \frac{\sigma_{\text{Pt}} M_{\text{Pt}}}{\rho_{\text{Pt}}} \quad (\text{A.10})$$

$$E_{\text{Pt}2,p} = E_{0,\text{Pt}2} - \frac{1}{2F} \frac{\sigma_{\text{Pt}} M_{\text{Pt}}}{r_{\text{Pt},p}} \left(\frac{\sigma_{\text{Pt}} M_{\text{Pt}}}{\rho_{\text{Pt}}} - \frac{\sigma_{\text{PtO}} M_{\text{PtO}}}{\rho_{\text{PtO}}} \right) \quad (\text{A.11})$$

A.4. Carbon corrosion source

The carbon corrosion source was determined with the following set of equations:

$$a_{\text{C},p} = A_{\text{C}} \rho_{\text{C}} f_{\text{C},p} \left(1 - \epsilon_{\text{CCL}} - \alpha_{\text{ion}} - \frac{m_{\text{Pt}}}{\rho_{\text{Pt}} d_{\text{CCL}}} \right) \frac{N_{\text{Pt},p}}{N_{\text{Pt},tot}} \quad (\text{A.12})$$

$$S_{\text{CO}_2} = \frac{M_{\text{CO}_2}}{F} \sum_{p=1}^n (a_{\text{C},p} j_{cc3,p} + 2\pi r_{\text{Pt},p} d_{cc} N_{\text{Pt},p} j_{cc6,p}) \quad (\text{A.13})$$

Appendix B. Surface coverage fractions

Fig. B.9 shows the calculated surface coverage fractions of carbon and platinum and their oxides.

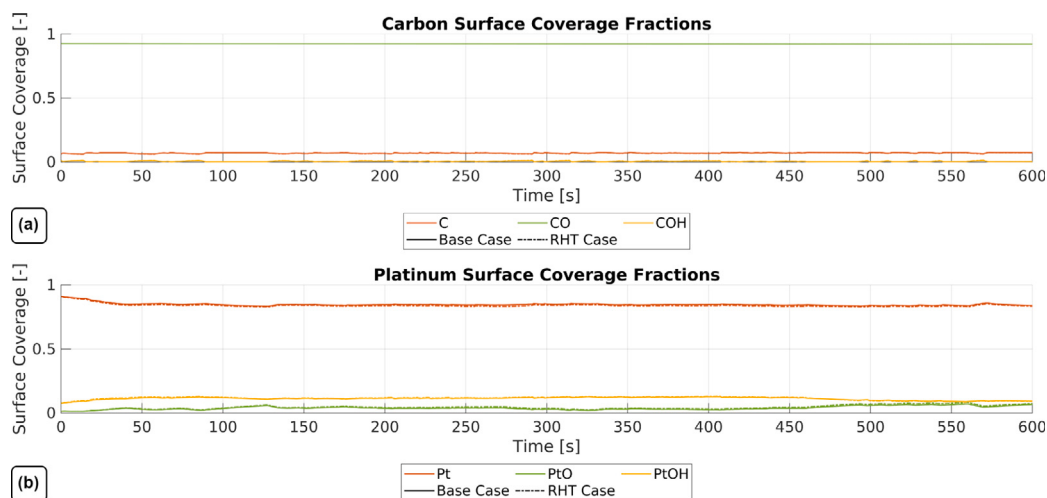


Fig. B.9. (a) Surface coverage fractions of carbon and its oxides for both simulated cases, (b) Surface coverage fractions of platinum and its oxides for both simulated cases.

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